Synthesis and characterization of novel periodic mesoporous organosilicas (PMOs) : versatile platforms for catalysis

Parijat Borah

2014

Parijat Borah. (2014). Synthesis and characterization of novel periodic mesoporous organosilicas (PMOs) : versatile platforms for catalysis. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/61844>

<https://doi.org/10.32657/10356/61844>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**SYNTHESIS AND CHARACTERIZATION OF NOVEL
PERIODIC MESOPOROUS ORGANOSILICAS (PMOs):
VERSATILE PLATFORMS FOR CATALYSIS**

PARIJAT BORAH

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2014

SYNTHESIS AND CHARACTERIZATION OF NOVEL PERIODIC
MESOPOROUS ORGANOSILICAS (PMOs): VERSATILE PLATFORMS
FOR CATALYSIS

PARIJAT BORAH

2014

**SYNTHESIS AND CHARACTERIZATION OF NOVEL
PERIODIC MESOPOROUS ORGANOSILICAS (PMOs):
VERSATILE PLATFORMS FOR CATALYSIS**

PARIJAT BORAH

PARIJAT BORAH

School of Physical and Mathematical Sciences

A thesis submitted to the Nanyang Technological University in partial
fulfillment of the requirement for the degree of Doctor of Philosophy

2014

*In dedication to my loving parents, brother and
sister-in-law: The wholesome reason for me to be
who I am.*

ACKNOWLEDGEMENT

It gives me immense pleasure and honor to express my deep sense of gratitude to my Ph.D. supervisor Nanyang Asst. Prof. Yanli Zhao for his meticulous supervision all throughout my research work at Nanyang Technological University (NTU). It is his constant encouragement, inspiration, wisdom and optimism which allow me not only to explore the scientific horizons but also help to grow as matured individual. Needless to say, I shall be highly obliged to him for all my life for being the best mentor any student can ask for.

I would like to express my gratitude to Head of the Division, Division of Chemistry and Biological Chemistry (CBC) for his constant efforts, encouragement and inspiration towards the betterment of graduate students as well as providing necessary facilities and infrastructure of the laboratory for carrying out the work during my stay at the CBC, NTU.

In this instance I would also like to extend my hearty gratitude:

- Ms Hum Wei Mei Celine, Ms Tan Wei Ting and Ms Heng-Choo Oi Keng Lynette for their whole hearted administrative support during my Ph.D. study.
- Special word of thanks to all technical support staffs especially Ms Goh Ee Ling, Mr Ong Yiren Derek, Ms Pui Pang Yi, Ms Zhu Wen Wei and Ms Seow Ai Hua for their unconditional help and support.
- A special token of gratitude to Prof. Richard Webster and his group for carrying out ICP analysis for my samples time to time.
- Very special thanks to all my colleagues from Prof. Zhao's group who have been constantly helping me since my day of joining as graduate student. Without their support and contribution my Ph.D. study never would have completed. Among them I

found some great mentors, great friends and great scientific collaborators. Very big thanks to each of you.

- I also want to express my love and appreciation to all my friends in Singapore who really helped me to maintain a social life in Singapore. I really appreciate your support and company for making my stay in Singapore so beautiful and eventful.
- Nanyang Technological University for all sort of financial assistance.

Last but not the least I am deeply and forever indebted to my family including my loving parents, elder brother and sister-in-law for their constant source of love, inspiration and blessings. I always appreciate their trust on me and allow me to follow my dreams without questioning on my abilities.

Parijat Borah

ABSTRACT

The primary focus of this research work has been made to design, synthesis and characterize novel periodic mesoporous organosilicas (PMOs) in order to utilize them as heterogeneous catalysts to perform various organic transformation with academic as well as industrial importance. With the help of these novel PMO based catalysts many existing disadvantages have been circumvented making the catalysis more environmentally benign and economically feasible. A variety of techniques of both materials and chemical science are used to fully characterize these PMOs as well as to monitor the catalysis.

TABLE OF CONTENTS

Acknowledgement	I
Abstract	III
Table Of Contents	IV
List Of Tables	VIII
List Of Figures	IX
List Of Schemes	XV
List Of Symbols	XVII
List Of Acronyms	XVIII
Chapter 1. Periodic mesoporous organosilica in heterogeneous catalysis: an overview	1
1.1. Research background of porous silica.....	1
1.1.1. Synthesis, structure and property of mesoporous silica	1
1.1.2. Introduction to PMO.....	4
1.1.3. Synthesis of PMO	5
1.2. Application of PMO in heterogeneous catalysis	8
1.2.1. PMO from one type of organic bridging organosilane precursor.....	8
1.2.2. Multi component PMO from more than one organosilane precursors	20
1.3. Research motivation and scientific contribution.....	28
1.4. References	30
Chapter 2. Synthesis of novel vanadyl complex grafted PMO as an efficient green catalyst for selective hydroxylation of benzene to phenol.....	37
2.1. Introduction	38
2.2. Results and discussion.....	40
2.2.1 Synthesis of organo alkoxysilane	40
2.2.2. Synthesis of PMOs	42
2.2.3. FT-IR study of PMOs	42
2.2.4. ^{13}C and ^{29}Si solid NMR study of PMOs	43
2.2.5. Textural and analytical studies of PMOs.....	45

2.2.6. XPS study of PMOs.....	46
2.2.7. Catalysts evaluation.....	48
2.3. Conclusions	52
2.4. Experimental	52
2.4.1. Synthesis of compound 3.....	53
2.4.2. Preparation of PMO by hydrothermal process	53
2.4.3. Catalytic test	54
2.4.4. Characterization.....	54
2.5. References	55
Chapter 3. β -Diketimine appended PMO: A novel scaffold for immobilization of palladium acetate towards efficient Wacker type reaction	60
3.1 Introduction	61
3.2 Results and Discussion.....	63
3.2.1. Synthesis of organo alkoxysilane	63
3.2.2. Characterization of β -diketiminato incorporated PMOs.....	64
3.2.2.1. FT-IR study of PMOs	64
3.2.2.2. ^{13}C and ^{29}Si solid NMR study of PMOs	65
3.2.2.3. Isothermal N_2 adsorption/desorption measurements of PMOs	67
3.2.2.4. Mesostructural morphology of PMOs	68
3.2.3. Synthesis and characterization of palladium loaded PMOs (Pd/PMOs)	69
3.2.3.1. TEM study of Pd/PMOs	70
3.2.3.2. Isothermal N_2 adsorption/desorption measurements of Pd/PMOs	70
3.2.3.3. FT-IR study of Pd/PMOs.....	72
3.2.3.1. XPS study of Pd/PMOs	72
3.2.4. Catalytic test.....	74
3.3. Conclusion.....	83
3.4. Experimental	84
3.4.1. Synthesis of β -diketimine (1)	84
3.4.2. Synthesis of β -diketiminato bis(4,1-phenylene) bis(3-triethoxysilylpropylcarbamate) (2)	85
3.4.3. Synthesis of PMO by hydrothermal process	85
3.4.4. Synthesis of PMOs containing Pd complex (Pd/PMO-n)	86

3.4.5. Catalytic tests.....	86
3.4.6. Characterization.....	87
3.5. References	88
Chapter 4. Synthesis of Urea Bridged PMO: A Heterogeneous Cooperative Organocatalyst for Henry Reaction (style is not consistent).....	91
4.1. Introduction	92
4.2. Results and Discussion.....	96
4.2.1. Synthesis of organo alkoxysilane	96
4.2.2. FT-IR study.....	97
4.2.3. ^{13}C and ^{29}Si solid NMR study of PMOs	98
4.2.4. Isothermal N_2 adsorption/desorption measurements of PMOs	100
4.2.5. Elemental analysis of PMOs.....	101
4.2.6. Mesosstructural morphology of PMOs	102
4.2.7. Catalytic evaluation of Urea/PMO	102
4.3. Conclusion.....	110
4.4. Experimental	110
4.4.1. Synthesis of bis-alkoxyorganosilane (3).....	111
4.4.2. Synthesis of PMO (Urea/PMO).....	111
4.4.3. Catalytic tests.....	112
4.4.4. Characterization.....	115
4.5. References	116
Chapter 5. Design, Synthesis and Application of Gated-Periodic Mesoporous Silica: An Efficient Protecting Scaffold for an Unsymmetrical NIR-Squaraine Dye.....	118
5.1 Introduction	119
5.2. Results and Discussion.....	124
5.2.1. Preparation of amino modified phenylene-PMO.....	124
5.2.2. FTIR Study of PMOs.....	125
5.2.3. ^{13}C and ^{29}Si solid NMR study of PMOs	126
5.2.4. UV/Vis study of azo@PMO	128
5.2.5. Loading of an unsymmetrical squaraine dye into azo@PMO.....	130
5.2.6. N_2 absorption measurements of PMOs	131
5.2.7. Morphological study of PMOs by TEM.....	132

5.2.8. Spectroscopic analysis of Sq-azo@PMO	133
5.2.9. Generation of $^1\text{O}_2$ by Sq-azo@PMO in aqueous medium	135
5.2.10. $^1\text{O}_2$ assisted oxidation of phenol in microreactor	136
5.3. Conclusion.....	142
5.4. Experimental	142
5.4.1. Preparation of Ph-PMO	143
5.4.2. Preparation of Ph-PMO- NO_2	143
5.4.3. Preparation of Ph-PMO- NH_2	143
5.4.4. Synthesis of 4-(4'-hydroxy-phenylazo)benzoic acid (3).....	144
5.4.5. Synthesis of 4-(4'-ethoxy-phenylazo)benzoic acid (4).....	144
5.4.6. Synthesis of squaraine dye (Sq).....	145
5.4.7. Preparation of azo@PMO.....	146
5.4.8. Preparation of Sq-azo@PMO	146
5.4.9. Microfluidic chip fabrication.....	147
5.4.10. Oxidation of phenol in microfluidic chip	147
5.4.11. Characterization.....	148
5.5. References	149
Chapter 6. Summary of the Research Work	153
Appendix.....	157
List of publications, Patent and conference	161

LIST OF TABLES

Table 1.1. Classification of porous materials	2
Table 1.2. Examples of few commonly used SDAs in the preparation of PMOs.	7
Table 2.1. Analytical, textural, and porosity data of different catalysts	45
Table 2.2. Catalytic activity of PMO-1 as functions of reaction time as well as benzene-to- H ₂ O ₂ (B:H) molar ratio	50
Table 3.1. BET surface area and BJH average pore diameter of PMOs	68
Table 3.2. Analytical, textural, and porosity data of different catalysts	71
Table 3.3. Catalytic activities of different catalysts in terms of styrene conversion and selectivity of different products	74
Table 4.1. Analytical, textural, and porosity data of different catalysts	101
Table 4.2. Catalytic activities in terms of yield of 2-nitro-1-(4-nitrophenyl)ethanol with different catalysts for the reaction in scheme 4.3. Reaction conditions: Aromatic aldehyde: Nitromethane=1:1.2 (mole ratio); reaction time: 12h; Solvent: Acetonitrile	105
Table 4.3. Catalytic activities of Urea/PMO for the reaction in scheme 4.5 as a function of various substituted benzaldehydes in terms of yield of corresponding β -nitro alcohols	108
Table 4.4. Catalytic activities of different catalysts for the reaction in scheme 5 as a function of mixture of substituted benzaldehydes in terms of yield of corresponding β -nitro alcohols...	109
Table 5.1. Textural and porosity data of different PMOs	132

LIST OF FIGURES

Figure 1.1. Few commonly used small hydrocarbon bridged silane molecules for the synthesis of PMO as silica source; such as (1) BTME, (2) BTEE, (3) BTESE, (4) BTEM, (5) BTMB and (6) BTEB.....	9
Figure 1.2. The bis-silylated organosilane precursors for the synthesis of chiral PMOs by condensation	20
Figure 1.3. The bis-silylated organosilane precursors for the synthesis of PMOs by condensation with TEOS or TMOS	24
Figure 1.4. The bis-silylated organosilane precursors for the synthesis of PMOs by condensation with TEOS or TMOS	27
Figure 2.1. FTIR spectra of (a) VO(acac) ₂ and (b) 3	41
Figure 2.2 FT-IR spectra of (a) PMO-1 and (b) PMO-2. Adapted and reproduced with permission from ref. 47; © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.	42
Figure 2.3. ¹³ C CP MAS NMR spectra (a) PMO-1 and (b) PMO-2. Adapted and reproduced with permission from ref. 47; © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.	43
Figure 2.4. ²⁹ Si CP MAS NMR spectra (a) PMO-1 and (b) PMO-2	44
Figure 2.5. HR-TEM images of (a) PMO-1 and (b) PMO-2. Adapted and reproduced with permission from ref. 47; © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.	46
Figure 2.6. High resolution XPS spectra at the V2p region for (a) VO(acac) ₂ , (b) compound 3 , (c) PMO-1, (d) PMO-2, and (e) PMO-1_Used. Adapted and reproduced with permission from ref. 47; © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.	46

Figure 2.6. XPS spectra with atomic percentages of (a) PMO-1, (b) PMO-2 and (c) PMO-1_Used.	47
Figure 2.8. Conversion and selectivity of benzene to phenol with different catalysts. Catalytic reaction conditions: $C_6H_6:H_2O_2 = 1:3$, $C_6H_6:catalyst = 200:1$, solvent: acetonitrile, temperature: 50 °C. [a] PMO-1 catalyst recovered from the first catalytic cycle and then reused, [b] PMO-1 catalyst recovered from the second catalytic cycle and then reused. Adapted and reproduced with permission from ref. 47; © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.....	49
Figure 3.1. FTIR spectra of (a) PMO-1 (b) PMO-2 and (c) PMO-3.....	64
Figure 3.2. ^{13}C CP MAS NMR spectra of (a) PMO-1, (b) PMO-2 and (c) PMO-3	65
Figure 3.3. ^{29}Si CP MAS NMR spectra of (a) PMO-1, (b) PMO-2 and (c) PMO-3.....	66
Figure 3.4. Isothermal N_2 adsorption/desorption plot of (a) PMO-1, (b) PMO-2 and (c) PMO-3 along with respective BJH pore size distribution plot in the inset.....	67
Figure 3.5. TEM images of (a) PMO-1 (b) PMO-2 (c) PMO-3 (d) Pd/PMO-1 (e) Pd/PMO-2 and (f) Pd/PMO-3	68
Figure 3.6. Isothermal N_2 adsorption/desorption plot of (a) Pd/PMO-1, (b) Pd/PMO-2 and (c) Pd/PMO-3 along with respective BJH pore size distribution plot in the inset	71
Figure 3.7. FTIR spectra of (a) Pd/PMO-1 (b) Pd/PMO-2, (c) Pd/PMO-3 and (d) $Pd(CH_3COO)_2$	72
Figure 3.8. High-resolution XPS spectra at the 3d region for (a) Pd/PMO-1 (b) Pd/PMO-2, (c) Pd/PMO-3 and (d) $Pd(OAc)_2$	73

Figure 3.9. Catalytic activities of Pd/PMO-1, Pd/PMO-2 and Pd/PMO-3 in terms of TOF for acetophenone as a function of solvent volume. Reaction conditions: Styrene/H ₂ O ₂ = 1:3 (mole ratio), Styrene/catalyst = 200:1 (mole ratio), acetonitrile as solvent at 60 °C.....	75
Figure 3.10. Catalytic activities of Pd/PMO-3 in terms of styrene conversion and selectivity of different products as a function of reaction time. Reaction conditions: Styrene/H ₂ O ₂ = 1:3 (mole ratio), Styrene/catalyst = 200:1 (mole ratio), acetonitrile as solvent at 60 °C.....	76
Figure 3.11. Catalytic activities of Pd/PMO-3 in terms of TOF for acetophenone as a function of H ₂ O ₂ :styrene ratios	79
Figure 3.12. Catalytic activities of Pd/PMO-3 in terms of styrene conversion and selectivity of different products as a function of H ₂ O ₂ :styrene ratios. Reaction conditions: Styrene/catalyst = 200:1 (mole ratio), 30 ml of acetonitrile as solvent at 60 °C	80
Figure 3.13. TEM image of Pd/PMO-3 (a) before catalysis; (b) after the 5 th cycle of catalysis with 5 h of reaction time; (d) after catalysis done by adding H ₂ O ₂ in a single addition with a H:S of 5:1; (f) after the 2 nd cycle of catalysis with 10 h of reaction time; (g) after the 4 th cycle of catalysis with 10 h of reaction time. (c), (e) and (h) are respective XPS spectra of b, d and g.....	81
Figure 3.14. Catalytic recycling experiments of Pd/PMO-3 by maintaining reaction time of 5 h in each cycle. Reaction conditions: Styrene/H ₂ O ₂ = 1:3 (mole ratio) with a slow addition of oxidant, Styrene/catalyst = 200:1 (mole ratio), 30 ml of acetonitrile as solvent at 60 °C	82
Figure 3.15. Catalytic recycling experiments of Pd/PMO-3 by maintaining reaction time of 10 h in each cycle. Reaction conditions: Styrene/H ₂ O ₂ = 1:3 (mole ratio) with a slow addition of oxidant, Styrene/catalyst = 200:1 (mole ratio), 30 ml of acetonitrile as solvent at 60 °C	83

Figure 4.1. FT-IR spectra of (a) compound 3 and (b) Urea/PMO	97
Figure 4.2. ^{13}C CP MAS solid state NMR of (a) Urea/PMO and (b) Urea/PMO_U ^a	98
Figure 4.3. ^{29}Si CP MAS NMR spectra of (a) Urea/PMO and (b) Urea/PMO_U	100
Figure 4.4. Isothermal N_2 adsorption/desorption plot of Urea/PMO (black) and Urea/PMO_U (red) along with respective BJH pore size distribution plot in the inset	100
Figure 4.5. TEM images (a) Urea/PMO and (b) Urea/PMO_U	102
Figure 4.6. Catalytic activities of Urea/PMO in terms of yield of 2-nitro-1-(4-nitrophenyl)ethanol as a function of catalyst loading for the reaction in scheme 4.3. Reaction conditions: Aromatic aldehyde: Nitromethane=1:1.2 (mole ratio); reaction time: 6h; Solvent: Acetonitrile	103
Figure 4.7. Catalytic activities of Urea/PMO in terms of yield of 2-nitro-1-(4-nitrophenyl)ethanol as a function of reaction time for the reaction in scheme 4.3. Reaction conditions: Aromatic aldehyde: Nitromethane=1:1.2 (mole ratio); reaction time: 6h; Solvent: Acetonitrile	104
Figure 4.8. Catalytic recycling experiments of Urea/PMO for the reaction in scheme 4.3. Reaction conditions: Aromatic aldehyde: Nitromethane=1:1.2 (mole ratio); catalyst loading: 10 mol%; reaction time: 12h; Solvent: Acetonitrile, room temperature	107
Figure 5.1. FT-IR spectra of (a) Ph-PMO, (b) Ph-PMO- NO_2 , (c) Ph-PMO- NH_2 and (d) azo@PMO	125
Figure 5.2. ^{13}C CP MAS solid state NMR of (a) Ph-PMO, (b) Ph-PMO- NH_2 and (d) azo@PMO	126
Figure 5.3. ^{29}Si CP MAS solid state NMR of (a) Ph-PMO- NH_2 and (d) azo@PMO	127

Figure 5.4. UV/Vis absorption spectrum of (a) Ph-PMO-NH ₂ and (b) azo(<i>trans</i>)@PMO (both 1.5 mg mL ⁻¹ in aqueous solution). (c) Changes in the UV/Vis absorption spectrum azo(<i>cis</i>)@PMO (1.5 mg mL ⁻¹) after irradiation for 20 minutes with 383 nm UV light. Inset: the change in absorbance at 383 nm of azo@PMO as a function of cycles upon either alternating UV irradiation or heating at 55 °C.....	128
Figure 5.5. (i) Isothermal N ₂ adsorption/desorption plot of (a) Ph-PMO, (b) Ph-PMO-NH ₂ , (c) azo@PMO and (d) Sq-azo@PMO. Along with BJH pore size distribution plots of (ii) Ph-PMO, (iii) Ph-PMO-NH ₂ , (iv) azo@PMO and (v) Sq-azo@PMO	131
Figure 5.6. TEM images (a) Ph-PMO, (b) Ph-PMO-NH ₂ , (c) azo@PMO and (d) Sq-azo@PMO.....	133
Figure 5.7. (i) UV/Vis absorption spectrum of (a) Sq-Dye in DCM (b) azo@PMO in water and (c) Sq-azo@PMO in water. (ii) Emission spectra of (a) Sq-dye in DCM and (b) Sq-azo@PMO in water.....	134
Figure 5.8. UV/Vis absorption spectra of (a) Sq-azo@PMO in water and (b) Sq-azo@PMO in water after irradiation of UV light with 383 nm for 60 min	135
Figure 5.9. UV/Vis absorption spectra UV–vis absorption changes between 340 and 420 nm corresponding to the absorption of ADMA upon the irradiation of 664 nm light to an aqueous solution of ADMA along with (a) Sq-azo@PMO and (b) azo@PMO	135
Figure 5.10. (a) Visualization of microfluidic channels by using a red dye; (b) loading of Sq-azo@PMO in the cavity and (c) schematic representation of the cross sectional view of the prepared microreactor	137
Figure 5.11. Operational mode of the Sq-azo@PMO loaded microreactor under the irradiation of 664 nm light	138

Figure 5.12. Production of BQ as a function of time under above mentioned conditions.....	139
Figure 5.13. Oxidation of phenol inside the microfluidic channel (a) as a function of cycles upon alternating irradiation of 664 nm light and (b) continuous irradiation of 664 nm light.....	141
Figure 5.14. UV/Vis absorption spectra of Sq-azo@PMO in water (a) before reaction and (b) recovered after the prolong reaction	141

LIST OF SCHEMES

Scheme 1.1. General synthetic pathway to PMOs from bissilylated organic bridging units. R=organic bridge. Adapted and reproduced with permission from ref. 5; © 2011, RSC.....	6
Scheme 1.2. Various applications of PMOs in catalysis	30
Scheme 2.1. Schematic synthesis pathway for preparations of 3 and PMOs	40
Scheme 2.2. Schematic representation of the catalytic cycle of V^{4+} during selective oxidation of benzene to phenol using H_2O_2 as an oxidant. Adapted and reproduced with permission from ref. 47; © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim	51
Scheme 3.1. Schematic representation of the synthesis for compounds 1 and 2	63
Scheme 3.2. Schematic representation for the incorporation of $Pd(OAc)_2$ into the PMOs	69
Scheme 3.3. Possible catalytic products from the oxidation of styrene	77
Scheme 3.4. Proposed catalytic mechanism of using Pd/PMO catalysts for selective oxidation of styrene to acetophenone with H_2O_2 as oxidant.....	78
Scheme 4.1. Self-quenching of urea unit due to the dimerization with neighboring units after post grafting methods.....	94
Scheme 4.2. Schematic representation of the synthetic route for the organic silane precursor (3).....	96
Scheme 4.3. Henry condensation reaction used a test reaction for the evaluation of Urea/PMO at R.T. using acetonitrile as solvent	102

Scheme 4.4. Schematic presentation of proposed mechanism involved during in the surface catalysis.....	106
Scheme 5.1. Two steps direct amination of phenylene-bridged PMO	119
Scheme 5.2. Synthetic routes to prepare compound 4	124
Scheme 5.3. External stimuli responsive reversible isomerization of azo@PMO	129
Scheme 5.4. A schematic representation of Sq loading into azo@PMO	130
Scheme 5.5. Synthesis of Sq . Reagents and conditions: i) (1:1 butanol/benzene azeotropic mixture), 90°C, 10 h.....	145

LIST OF SYMBOLS

<u>Symbol</u>	<u>Definition</u>
μs	Micro second
μm	Micro meter
ε	Molar absorptivity
$^{\circ}\text{C}$	Degree celsius
cm	Centimeter
g	Gram
mL	mililiter
h	Hour
kcal	Kilocalorie
MHz	Megahertz
mmol	Millimole
mol	Mole
nm	Nano meter
ppm	Parts per million
V	Volt
D	Day

LIST OF ACRONYMS

2D/ 3D	Two Dimensional/ Three Dimensional
acac	Acetylacetonate
ADMA	9,10-anthracenediyl-bis- (methylene)dimalonic acid
APTES	(3-aminopropyl)triethoxysilane
APTMS	(3-aminopropyl)trimethoxysilane
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BTEB	1,4-Bis(triethoxysilyl)benzene
BTEE	1,2-Bis(triethoxysilyl)ethane
BTESE, BTSE	1,2-Bis(triethoxysilyl)ethene
BTEM	1,2-Bis(triethoxysilyl)methane
BTME	1,2-Bis(triethoxysilyl)methane
CP–MAS NMR	cross-polarization magic angle spinning nuclear magnetic resonance
CTAB	Cetyltrimethylammonium bromide
DCM	Dichloromethane
DMF	Dimethylformamide
EA	Elemental Analysis
EtOH	Ethanol
FT-IR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
GC-MS	Gas Chromatography–Mass Spectrometry
GNP	Gold Nano-Particle

HBD	Hydrogen Bond Donation
HR-TEM	High Resolution Transmission Electron Microscopy
ICP	Inductively Coupled Plasma
IUPAC	International Union of Pure and Applied Chemistry
MOF	Metal Organic Framework
MPTMS	(3-Mercaptopropyl)trimethoxysilane
MS	Mass Spectrometry
NMR	Nuclear magnetic resonance
PDMS	Poly(dimethylsiloxane)
POP	Porous Organic Polymers
RT	Room Temperature
SDA	Structure Directing Agent
TBHP	<i>tert</i> -Butyl hydroperoxide
TEM	Transmission Electron Microscopy
TEOS	Tetraethyl Orthosilicate
THF	Tetrahydrofuran
TOF	Turn Over Frequency
TON	Turn Over Number
UV/Vis	Ultra Violet/Visible
VO(acac) ₂	Vanadyl (IV) Acetylacetonate
XPS	X-Ray Photoelectron Spectroscopy
TLC	Thin layer chromatography

Chapter 1: Periodic Mesoporous Organosilica in

Heterogeneous Catalysis: An Overview

Ever since the discovery of mesoporous silica, researchers have been showing great interest to develop new materials by capitalizing its mesostructure and high surface area. The quest to explore mesoporous silica materials ultimately leads to the development of various silica-organic based hybrid materials and the development is still growing exponentially. The latest development of functionalized hybrid mesoporous silica is the discovery of Periodic Mesoporous Organic Silica in short 'PMO'. In the first part, a general introduction to the chronological progress of mesoporous silica to PMO is given, covering basic knowledge of PMO including synthetic and chemical functionalization aspects and related applications with special emphasis on catalysis are provided. Further, based on the current research progress of PMO, a focus on its catalytic applications, several novel design strategies were discussed which would be illustrated in the part of the research motivation.

1.1. Research background of porous silica

1.1.1. Synthesis, Structure and Property of Mesoporous Silica

Porous materials are of great utilities which have been offering huge contribution to the development of human civilization especially since the time of industrialization. These materials, obtained either from natural abundance or created by synthetic routes, have been appeared as vital thrust for us in various scientific and industrial aspects. According to the

definition by IUPAC different kind of porous materials can be classified into three significant categories.

Table 1.1: Classification of porous materials

S. No	Class of material	Pore size in diameter (nm)
1	Microporous	< 2
2	Mesoporous	2-50
3	Macroporous	>50

Apart from chemical, thermal and mechanical stability, high surface area and large pore volumes, an ideal porous material demands a narrow pore size distribution which qualifies the material for various size-specific applications among which catalysis and gas adsorption/separation are vital ones.¹ Among all porous materials zeolites, class of microporous crystalline aluminosilicates, have been extensively explored and widely applied many industrial applications. Zeolites became more favorable owing to its highly crystalline network structure and the extremely narrow as well as uniform pore size distribution. Unfortunately this wonderful class of porous materials exhibit limited micropores (> 1.5 nm) for which they cannot meet the elementary eligibility criteria for many size specific processes involving large molecules.

In order to circumvent all the drawbacks from zeolites, attempts have been made to develop zeolite type material within mesoporous range although initial success rate was very limited.² Continuous attempts were made to achieve mesoporous materials made of silica-alumina, titanium or zirconium phosphates or clays with a narrow pore size distribution. But narrow pore size distribution as well as crystallinity remains as a bottle neck.² In the following years a new class of mesoporous silica and aluminosilicate designated as M41S with narrow

mesopores distribution was developed.³ Subsequently M41S type materials were proven to be pioneering in material chemistry and related fields due to the introduction of supramolecular assemblies through micellar formation by using SDAs for the first time in the preparation of mesoporous materials. Finally in 1992, scientists from Mobil Corporation successfully developed MCM-41 (Mobil Composition of Matter No. 41), a silica material having hexagonal array of unidimensional cylindrical uniform pores within the mesoporous range through surfactant-directed self-assembly process although the material was found to be amorphous.^{3,4} Surprisingly synthesis of similar kind of mesoporous material was reported in a patent filed in 1969 but it failed to gain attention due to inadequate level of analytical techniques during that time to perform extensive characterization of the material. Nevertheless, MCM-41 came up as a major breakthrough during early 90s of last century which opened up a new dimension in the field of mesoporous materials. These mesoporous materials were able to circumvent many limitations associated with classical zeolites such as pore dimensions as well as large specific surface area. Unfortunately the presence of silanol groups on the surface eventually makes these mesoporous silica materials very hydrophilic making the surface unfavorable for adsorption of various hydrophobic organic molecules. With the initial purpose of controlling the hydrophilicity/ hydrophobicity of the internal MCM-41 surface, silylation procedures in which an aliphatic alkyl group was covalently attached to the silica surface became widely used.⁴

The condensation of the silica precursors at the interface of the micelles is not a complete process which results the formation of free -Si-OH (silanol) groups on the silica surface with a typical density of about 2–3 silanol groups per nm^2 .⁵ Fortunately these free silanol groups with their abstract able protons have the ability to undergo further condensation reactions

with various condensation reagents such as chloroorganosilanes, silazanes (silylamines), alkoxyorganosilanes and so on. There are two widely established approaches to decorate the surface of mesoporous silica materials namely:

- 1 Grafting method (post-synthetic functionalisation)
- 2 Co-condensation approach (one-pot synthesis)

The major advantage of the above mentioned approaches is the retention of the mesostructure of the starting silica phase even after applying either of the modifications. Moreover in case of grafting method it is very difficult to control the distribution of functionalized groups in a homogeneous fashion on the surface. On the contrary, the co-condensation approach facilitates homogeneous distribution of organic molecules on the surface. But in many instances pore-blocking effect by the functionalized molecule can be observed in both the cases. Higher loading of functionalization in co-condensation approach always leads to the decrease of the degree of mesoscopic order of the silica materials. In this context it is necessary to highlight that surface modifications achieved by these two approaches, the functionalized molecules remain hanging into the pore channels. This results the reduction of pore diameter as well as in some extreme cases (e.g., with very bulky grafting species), this can lead to a complete closure of the pores ('pore-blocking effect'). Moreover, the grafted molecules obstruct the diffusion of substrate molecules into the center of the pores during the subsequent applications.

1.1.2. Introduction to PMO

In 1999, as an answer to all the demerits encountered by functionalized mesoporous materials, Stein,⁶ Ozin⁷ and Inagaki⁸ have reported separately a novel concept to prepare

mesoporous materials in which an organosilane containing at least two terminal trialkoxysilane groups was used as silicon source and terminal silane groups were allowed to condense to form a hybrid polymeric material in presence of some surfactant as SDA. The resulting hybrid organic/inorganic material was termed as periodic mesoporous organosilica (PMO). The presence of organic functionality within the inorganic silica framework not only provides the robustness to the structure but also makes potentially useful for various applications. Unlike those previously mentioned two surface-functionalization approaches where the functionalized molecule mainly locate at the surfaces and the pore channels,⁹⁻¹² the current approach provides an unique way of surface decoration where the modified centers are homogeneously distributed at a molecular level as an integral part of the silica framework on the pore walls leaving the pore voids completely accessible for further applications.

1.1.3. Synthesis of PMO

The typical synthesis of PMO is similar to any other SDA-assisted synthetic processes used to obtain mesoporous silica materials such as MCM-41, SBA-15 etc. In order to achieve PMOs having different morphology with various pore sizes, variety of surfactants have been adopted under all probable reaction conditions such as acidic, neutral or basic (Scheme 1.1). Hydrothermal and Evaporation-Induced Self-Assembly (EISA) are two primary synthetic processes which have been adopted extensively for the synthesis of various PMOs. But based on the source of silica used to prepare polysiloxane network, the synthesis process of different PMOs can be categorized into two major approaches:

- a) Polycondensation of one type of organic bridging organosilane precursor.

In this approach single species of suitable organic bridge with terminal trialkoxysilane precursor ($R[Si(OR')_3]_n$; $n \geq 2$) can be used as silica source to undergo polycondensation in presence of some surfactant as SDA to form mesoporous silica network. PMOs obtained through this method were found to be highly influenced by the molecular design of the bridged organosilane precursors towards their structural morphology due to the dense packing of organic species within the framework.

- b) Co-condensation of one or more bridging organosilane precursors along with conventional silica precursors.

This approach is often used to graft different functional organosilanes into the mesoporous framework at molecular level making the hybrid material potentially useful for various applications. One crucial point in this method to design a bridged alkoxy silane precursor ($R[Si(OR')_3]_n$; $n \geq 2$) with an appropriate molecular size and complexity.

Scheme 1.1: General synthetic pathway to PMOs from bisilylated organic bridging units. R =organic bridge. Adapted and reproduced with permission from ref. 5; © 2011, The Royal Society of Chemistry.

In order to generate ordered mesoporous material, the most widely used method is the template-assisted approach developed by Mobil Corp. where SDAs were used as template. So far many PMOs have been prepared with various pore diameters just using different surfactants as SDA including anionic, cationic and neutral ones. Few important surfactants that play role as SDAs in the preparation of PMOs are listed below.

Table 1.2: Examples of few commonly used SDAs in the preparation of PMOs.

S. No	Surfactant	Chemical structure
1	CTAB
2	P123
3	Brij 56
4	Brij 76

PMOs are nothing but mesoporous organic–inorganic hybrid materials organic parts were homogeneously distributed in the silica network at molecular level. The inorganic silica network renders tremendous structural stability whereas the grafted organic groups make them versatile tool for various applications including catalysis, stationary phases in high-performance liquid chromatography, enzyme immobilization and biocatalysis, light harvesting and LEDs, low-*k* materials, magnetic hollow nanoparticles, pollutant removal, refolding of proteins, sensors, drug delivery etc. Few review articles give a vivid overview of the various utilities of PMOs proving their excellent versatility.^{5,13-15}

1.2. Application of PMO in Heterogeneous Catalysis

In the field of heterogeneous catalysts, various mesoporous silica phases were extensively used as the support to prepare catalysts.^{2,16} Thanks to the reactive surface silanol groups which have made the grafting of metal–organic compounds on the surface of mesoporous silica possible. Based upon this privilege offered by mesoporous silica many solid catalysts were designed to investigate various catalytic reactions. Keeping the current exponential growth of this area of research in mind Prof. Jean-Marie Basset referred this area as ‘surface organometallic chemistry’ (SOMC).¹⁷ In the recent years PMO-based materials have emerged as a new potential hybrid material in addition to other conventional mesoporous silica based heterogeneous catalysts. In many instances PMO-based catalysts offer various advantages over the post modified mesoporous silica counterparts because of the intelligent designs of PMO precursors. Apart from that PMOs also capable to offer all advantages of mesoporous silica including high surface area with tunable and uniform mesopores and high pore volume helping to achieve a high density of catalytically active sites. However, the PMOs are entitled of many indigenous benefits attributed by the organic groups in the pore wall, such as easily modified surface hydrophilic/hydrophobic properties, increased mechanical/hydrothermal stabilities compared with mesoporous silica, and tunable chemical/physical properties.

1.2.1. PMO from one type of organic bridging organosilane precursor

The development of PMOs was initiated by the concept of polycondensation of silane molecules containing hydrocarbon units with relatively small molecular sizes among which bridges like ethylene ($-\text{C}_2\text{H}_4-$) [Figure 1.1 (3)], ethenylene ($-\text{C}_2\text{H}_2-$), methylene ($-\text{CH}_2-$)

[Figure 1.1 (4)] and phenylene ($-\text{C}_6\text{H}_4-$) [Figure 1.1 (5, 6)] are most commonly and widely used precursors.^{6-8,18,19} Latter on organic bridges with higher functionalities and molecular sizes such as biphenyl,²⁰ divinylbenzene²¹ and acridone²² were also brought into practice for the preparation of various potential PMOs. As the complexity of the organic bridges increases, new hydrolytic based synthetic procedures were developed helping PMOs to evolve from simple lamellar and 2D hexagonal morphology to 3D cage-like phases. Concurrently, well-defined mesopores of PMOs with pore diameter up to 30 nm has been achieved by the appropriate selection and well-controlled utilization of various SDAs and additives.^{23,24} These novel PMOs were proven to be potential candidates for many applications among which catalysis is inevitable. The physiological abilities inherited from the mesopores and the relatively hydrophobic surface due the presence of the hydrocarbon bridges reinforces the catalytic activities of PMOs towards various organic reactions.

Figure 1.1: Few commonly used hydrocarbon containing silane molecules for the synthesis of PMO as silica source; such as (1) BTME, (2) BTEE, (3) BTESE, (4) BTEM, (5) BTMB and (6) BTEB.

There is always a scope for the chemical post modification of the organic bridges in PMOs which has been proven as a smart approach to create an effective chemical environment inside the pores to perform catalysis. Inagaki *et.al.* demonstrated the successful post modification of mesoporous benzenesilica through sulfonation for the first time without

destroying the mesoporous framework although the catalytic evaluation of the sulfonated PMO was not performed.¹⁹ High order of functionalization of sulfuric acid on the surface as well as the increased hydrophobicity around the active sulfonic acid sites are the major traits to establish sulfonated PMO materials as potential solid acid catalysts for many important catalytic reactions such as Friedel–Crafts reactions, esterification, hydration, and hydrolysis. Besides the incorporation of sulfonic acid groups in the mesopore of PMOs could also be achieved by either co-condensation or grafting method. In these processes thiol functionalized PMOs were synthesized followed by oxidative transformation of the thiol-functionalized organosilicas using HNO_3 as an oxidant.²⁵ The acid exchange capacity of the sulfuric acid-grafted PMOs is in the range of 0.14 to 0.70 mmol of proton (H^+) per gram of material (in short $\text{mmol g}^{-1} \text{H}^+$). In a separate study the authors observed that the materials exhibited comparable catalytic activity to commercial Nafion-H for the esterification of acetic acid with ethanol.²⁶ In another instance the sulfonic acid-functionalized PMOs was synthesized directly by co-condensation of $(\text{R}'\text{O})_3\text{Si}-\text{R}-\text{Si}(\text{OR}')_3$ where $\text{R} = -\text{CH}_2\text{CH}_2-$ and $-\text{C}_6\text{H}_4-$ with MPTMS using nonionic oligomeric surfactant Brij-76 in acidic medium in the presence of H_2O_2 .²⁷ The purpose of using H_2O_2 is to generate sulfonic acid functionalities by in situ oxidation of the propylthiol during the synthesis of PMO. The sulfonated PMO with ethansilicas showed the highest acid-exchange capacity of $1.72 \text{ mmol g}^{-1} \text{H}^+$. The catalytic properties of the PMOs were evaluated for the liquid-phase synthesis of Bisphenol A through the condensation of phenol with acetone. PMO consists of ethanesilicas offered higher catalytic activity over benzenesilicas. But surprisingly the sulfonated etanesilica based PMO prepared by post grafting method showed better TOF for the reaction than those prepared by in situ co-condensation process. The observation was attributed to the irregular distribution of active sites of the grafted materials where the active sites were believed to be on the surface

and near the pore mouth thereby being more accessible for the reactants. The improved catalytic ability by sulfonated ethane based PMO was further investigated using acid catalyzed esterification of ethanol with acetic acid as probe reaction.²⁸ The catalytic results demonstrated that the hydrophobicity of the PMO contributed by ethane moieties has profound influence on the catalytic ability.

In a separate study by Molar *et al.*, preparation and characterization of PMOs using BTEB with anchored benzenesulfonic and propanesulfonic acid groups were reported. It has been found that the sulfonated PMO where sulfuric acid unit anchored to the organic bridges e.g. benzenesulfonic acid showed a better catalytic activity over those prepared by co-condensation method towards the dimerization of 2 phenylpropene and the rearrangement–aromatization of ketoisophorone.²⁹ The difference of surface hydrophilicity/hydrophobicity rendered by propyl- and arene-sulfonic-acid modified PMOs prepared by BTME has been carefully correlated with their catalytic properties for the acetalization of heptanal by 1-butanol.³⁰ The incorporation of a hydrophobic ethane moiety within the frameworks of propyl- and arene-SO₃H-modified PMOs have shown enhanced catalytic activities than those of HY zeolite and Amberlyst-15. Besides, the catalytic efficacy of arene-SO₃H groups was found to be higher than propyl-SO₃H acid sites due to the hydrophobic environment near the arene-sulfonic acid sites. These type of PMO-based hydrophobic acid catalysts are very effective mainly those reactions where water is produced by the reaction and deactivates the acid sites.

Phenylene-bridged PMOs prepared from BTEB as a single silica source using Brij 76 as SDA were found to undergo structural and surface changes led by the C–Si bond cleavage upon calcination at 400 °C under humid conditions and/or oxidizing atmosphere whereas

PMOs are thermally stable under N₂ atmosphere.³¹ The cleavage of C-Si bond caused to generate many oxidized groups such as phenolic and carbonyl type on the surface. Subsequent sulfonation of these oxidized materials by reacting with chlorosulfonic acid yielded a higher extent of sulfonated surface than those calcined under nitrogen along with the preservation of structural and surface properties in all cases. These sulfonated PMOs served as active as catalysts for the esterification of acetic acid with ethanol, particularly those calcined in the air. Moreover these modified sulfonated PMOs were more active than Amberlyst-15 particularly in aqueous medium. PMO can also be used as acid catalyst as well as base catalyst together in a cooperative manner. Sankaranarayanapillai Shylesh *et al.* demonstrated the synthesis of PMO with acidic frameworks along with basic sites in the pores.³² They achieved such PMO through the co-condensation of BTEB and APTMS in presence of CTAB. Sulfonation at the bridging phenylene units was carried out with the help of chlorosulfonic acid. A well separated arrangement of these catalytically active sulfonic acid groups i.e. acid sites and the propylamine groups i.e. basic sites were achieved with the help of the difference of hydrophobic phenylene layers giving rise to a bi-functional organosilica containing two antagonistic functionalities. The cooperative catalytic activity of the PMO was evaluated for the catalytic conversion of benzaldehyde dimethyl acetal into 2-nitrovinyl benzene. This tandem catalytic reaction involves two key steps: an acid-catalyzed deprotection to give the intermediate benzaldehyde and the subsequent base-catalyzed nitroaldol (Henry) reaction to yield 2-nitrovinyl benzene. Due to the advanced structural engineering of PMO provided the well separated homogeneous distribution of both acidic and basic catalytic sites, a profound cooperative behavior of this bifunctionalized catalyst was observed with a high final product yield. Asim Bhaumik *e. al.* proposed an alternative route to prepare a propylsulfonic acid-modified ethane bridged PMO through a postsynthetic

method.³³ At first they prepared ethylene bridged PMOs with various pore sizes by using BTSE as silica source in presence of various surfactants such as P123, Brij 76 and Brij 56 under acidic condition. The ethylene units present in the PMOs were subjected to undergo epoxidation by using TBHP. The surface bound epoxides were further transformed into sulfonic acid by treating with a mixture of NaHSO_3 and Na_2SO_3 followed by ion exchange with HCl. Unlike the other well-known protocols which involve either oxidation of mercaptol using H_2O_2 or treatment of harsh concentrated H_2SO_4 , this process can be carried out under mild conditions. This sulfonic acid functionalized PMO displayed excellent catalytic activity in the esterification of acetic acid with ethanol under liquid-phase reaction conditions. Prof Dumesic *et al.* reported propylsulfonic acid-modified ethane bridged PMOs with SBA-15 type structures, prepared by co-condensation of BTME and MPTMS with various mole ratios in presence of P123 under acidic condition, followed by in situ oxidation of thiol by H_2O_2 .³⁴ The activity, selectivity, and stability of the PMO-based catalysts were evaluated in a packed-bed, continuous reactors to produce 5-hydroxymethylfurfural (HMF) continuously from fructose dissolved in a single-phase solution of THF and H_2O (4:1 w/w), operated at 130 °C for extended periods, up to 190 h. As compared to other propylsulfonic acid-modified silicas such as available nonordered porous silica and SBA-15-type ordered porous silica, the PMO catalysts were found to be more hydrothermally stable and maintained a longer steady catalytic activity.

Like many other mesoporous materials including other mesoporous silica phases e.g. MCM series, SBA series etc., PMO can also be exploited as a suitable support for various transition metal catalysts. Apart from the possibility to achieve a high density of catalytically active metal sites due to their high inner surface areas, single component PMOs also provide high

degree of surface hydrophobicity. In many instances this surface hydrophobicity inherited by the organic bridges plays crucial role in catalytic organic transformation especially aqueous phase reactions. A handful amount of examples have been reported where PMOs made from single component silane were used as a support for the immobilization of various catalytically active transition metals.

Chromium-containing ethane-bridged hybrid mesoporous materials (Cr-PMO) were synthesized by using BTEE as one component silica source and alkyltrimethyl ammonium salts (ATMA) as SDA.³⁵ Chromium present in this PMO was mainly in the form of dichromate whereas nano-sized Cr_2O_3 species was found in case of PMO prepared by the co-condensation of TEOS-BTEE. The Cr-PMO materials showed high catalytic activity in the oxidation reaction of cyclohexane and a high selectivity to cyclohexanone, especially under TBHP as oxidant, than the traditional Cr-MCM-41 catalyst. Benzene bridged PMO was also synthesized by using BTEB as one component silica source through Brij-76 template-assisted hydrothermal method which was successfully used as an excellent support for PdCl_2 .³⁶ This palladium-supported Ph-PMO catalyst exhibited much better catalytic efficacy than MCM-41 based catalysts towards the Ullmann coupling reaction of iodobenzene and bromobenzene in water. High adsorption affinity of the hydrophobic surface Ph-PMO is responsible for the high catalytic performance towards the hydrophobic organic molecules in aqueous environment. Another ethane bridged PMO was developed by the self-assembly assisted co-condensation of BTEE and APTMS using P123 as template under acidic condition.³⁷ The amine-ligand anchored on the surface of ethyl-bridged PMO was made use to coordinate with palladium from $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$. The prepared PMO-based mesoporous Pd(II) organometallic catalyst was used to perform Barbier reaction in water as an environmentally friendly

medium with comparable catalytic activity and selectivity with the corresponding homogeneous Pd(II) catalyst. Similar strategy was adopted to develop another ethane bridged PMO where diphenylphosphino (PPh_2) ligand was used to coordinate with $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ instead of amine ligand as described in the previous case.³⁸ In this case, however, EISA process using P123 as SDA was adopted to obtain the PMO materials via co-condensation of DPPEs and BTEE. The resultant Pd(II) loaded PMO catalyst exhibited high catalytic activity for carbon–carbon coupling reactions in water-medium with a high catalyst recyclability presumably as a result of favorable hydrophobic micro-environment. They have also extended this concept by preparing benzene bridged PMO grafted with diphenylphosphino (PPh_2) ligand to coordinate with $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$.³⁹ The resulting heterogeneous catalyst displayed an efficient recyclable catalytic activity towards water-medium Sonogashira coupling reaction with a similar catalytic efficiency of corresponding homogeneous $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ catalyst. In this instance also it was the enhanced surface hydrophobicity of benzene bridged PMO, which facilitated the adsorption for organic reactant molecules in aqueous medium. Sebastian Polarz *et al.* synthesized and characterized a bi-functional PMO using aniline and benzoic acid as building blocks.⁴⁰ Furthermore, the carboxy function from the surface embedded benzoic acid was utilized to coordinate the vanadyl cation $[\text{VO}]^{2+}$. In order to show the cooperative effect of the bifunctional PMO, a two-step chemical transformation was studied where they have successfully demonstrated cleavage of an acetal catalyzed by vanadyl group embedded on PMO followed by Knoevenagel condensation.

PMO also plays role as 3D nano cage to support many homogeneous catalysts. In order to illustrate this property ethane bridged PMO was synthesized using BTME as silica source and P123 as surfactant under acidic condition followed by the silylation of the free silanol

groups present on the surface with a suitable organosilane.⁴¹ These PMO-based mesostructured channels were efficient enough to accommodate series of dimeric manganese–salen complexes. The heterogeneous PMO-caged dimeric manganese–salen complexes showed high catalytic activity with a high recyclability towards the epoxidation of alkenes (styrene, cyclohexene, and 1-phenylcyclohexene) in presence of NaClO as an oxygen source. Investigations revealed that the advanced textural and morphological properties PMO catalysts loaded with dimeric Mn(salen) complexes made them better catalysts in comparisons to homogeneous manganese–salen complexes.

PMOs are also proven to be suitable platform to accommodate nanoparticles as well. Qi Wei *et al.* prepared a PMO from BTEE using P123 as the SDA through a hydrothermal process which showed excellent potential in the application of host-guest inclusion by confining gold nanoparticles in the pore channels.⁴² They adopted a modified external passivation route to prevent the formation of large aggregated gold particles on the exterior surface. They performed this route by functionalizing the external surface with n-octadecyltrimethoxysilane (C₁₈TMS), followed by the modification of the internal surface by APTMS to promote the selective adsorption of HAuCl₄ complex on the internal surface of mesostructures. The surface adsorbed gold complexes were reduced under H₂ atmosphere to yield GNPs. The confined GNPs in PMOs exhibit good catalytic properties in the reduction of methylene blue (MB) dye with sodium boron hydride (NaBH₄) as reducing agent. Another report by Babak Karimi *et al.* where ethane and phenyl bridged bifunctional PMO was used to incorporate GNP into the mesostructured.⁴³ In this case the bi functional PMO was initially impregnated with sodium tetra chloroaurate(III) (NaAuCl₄) as the gold source in water followed by reduction of Au (III) to GNP by NaBH₄ (0.1 M) at room temperature. The novel GNP

supported on bifunctional PMO was found to be very effective and reusable heterogeneous catalyst for the Ullmann coupling of aryl iodides. Recently a new PMO base bifunctional GNP-acid catalyst was reported.⁴⁴ Initially they synthesized a thiol functionalized ethane bridged PMO [HS-PMO(Et)] by co-condensation of MPTMS and BTEE using P123 as SDA under acidic condition. With the help of HS-PMO(Et) as support, authors had reported a straight forward process to synthesize the final GNP decorated acidic PMO catalyst. The process included three sequential steps viz reduction of Au^{3+} to GNP, oxidation of HS to SO_3H , and coordination of the GNPs with the unreacted HS ligand which prevented GNPs from unwanted aggregation. The hybrid mesostructured catalyst performed effectively towards water-medium alkyne hydration, intramolecular hydroamination, styrene oxidation, and three-component coupling reactions and even the solvent-free alkyne hydration process. This PMO-based catalyst was found to be better than various homogeneous catalysts in terms of product yield as well as its tremendous catalyst recyclability. Apart from GNP, PMO also acts as support for Pd nanoparticle as well. A Si-H functionalized phenyl-bridged PMO [H-PMO(Ph)] was reported by He Xing Li *et al.* which was synthesized by the co-condensation of BTEB and triethoxysilane with Brij-76 as SDA.⁴⁵ Then PdCl_2 was impregnated to the PMO followed by in situ reduction of Pd(II) to Pd(0) by Si-H present on the PMO surface resulting the formation of highly dispersed Pd nanoparticles inside the channels of PMO. The catalyst also showed excellent catalytic activity, selectivity and high recyclability towards the Ullmann reactions in aqueous medium. Such a high catalytic performance was attributed to synergetic effects derived from the highly dispersed catalytic species and the hydrophobic microenvironments.

PMO-based materials are also used for photocatalysis. In order to realize this potentiality, a benzene bridged PMO was synthesized where meso-tetra(4-carboxyphenyl) porphyrin was introduced to the silica matrix by adding during the preparation of PMO.⁴⁶ It has been believed that the porphyrin was embedded in to the close proximity of polysiloxane network. This porphyrin - PMO material can selectively bind to trinitrotoluene (TNT) over structurally similar compounds such as *p*-nitrophenol. Upon the illumination of sunlight this porphyrin embedded PMO hybrid promoted the photo-degradation of nitroaromatics present in aqueous medium.

Sebastian Polarz *et al.* synthesized a optically active chiral bis-alkoxysilane [(-)-1-(3,5-Bis-tri-isopropoxysilylphenyl)-ethanol] to construct a novel PMO with mesostructured walls exclusively made of a chiral organic bridges.⁴⁷ They also engineered to attach Al(III) as a Lewis acid center to the chiral group to achieve a Lewis acid based heterogeneous catalyst for asymmetric catalysis. The catalytic evaluation of this catalyst for asymmetric carbonyl-ene reaction displayed that the enantioselectivity of the chiral PMO catalyst was much higher than that of analogue of the homogeneous catalyst. This is one of the few examples of heterogeneous catalysis where enhanced enantioselective has been observed even after the heterogenization.

Hollow structured PMO sphere were also prepared using α -Fe₂O₃ as a hard template. In order to prepare silica shell around α -Fe₂O₃, BTEB was used as silica sources and CTAB as template-SDA to construct meso structure.⁴⁸ Furthermore, these hollow-structured PMO could be easily functionalized with the MacMillan catalyst through a co-condensation process and post-modification via click chemistry. Catalytic evaluation exhibited high catalytic activities in terms of conversion (up to 98%) and enantiomeric excess (81% ee for

endo) in asymmetric Diels–Alder reactions in water as solvent. The catalyst could also be reused for at least seven runs without a significant loss of catalytic activity. Moreover it was observed that hollow structured PMO spheres exhibit higher catalytic efficiency than solid (nonhollow) PMO spheres. Another example for the synthesis of advanced structured PMO is construction of PMO-based yolk–shell nanoparticles (YSNs). The reported YSN consisted of a core of silica sphere and a PMO-based outer shell with perpendicularly aligned mesoporous channels. In order to synthesize this type of PMO-based YSN at first the vesicles formed in aqueous solution by a fluorocarbon surfactant $[\text{C}_3\text{F}_7\text{O}(\text{CF}_2\text{CF}_3\text{CF}_2\text{O})_2\text{CF}_2\text{CF}_3\text{CONH}(\text{CH}_2)_3\text{N}^+(\text{C}_2\text{H}_5)_2\text{CH}_3\text{I}^-]$ (FC_4) around the silica core which ultimately generate the void space between the core and the shell. The PMO shell was achieved by hybrid organosilane-surfactant micellar aggregation process where BTME was used as organosilane and CTAB as surfactant which role was mainly as SDA. By altering the synthesis parameters, it is also possible to adjust the dimension of the hollow space (4~52 nm), and the shell thickness (16~34 nm). They also demonstrated the utilization of the mesopores and void space between the core and the shell to encapsulate Pd nanoparticles by the impregnation and reduction of Pd precursors. These Pd nanoparticles loaded PMO-based YSNs acted as an efficient nanoreactors for the aqueous medium selective oxidation alcohols to their corresponding aldehydes with high conversion (up to 100%) and selectivity (up to 99%) using molecular O_2 as oxidant.

PMO consisting zwitterionic species were reported by synthesizing via template-directed (P123) hydrolysis–polycondensation of various alkoxysilanes derived from zwitterionic ammonium sulfonate precursors.⁴⁹ Particularly in this case precursor-template interactions play a crucial role for the construction of mesostructured PMO phases. This zwitterionic

PMO was found to be highly efficient catalyst for the Biginelli reaction to the formation of 3,4-dihydropyrimidinones with a solid recyclability. The scope of this type of PMO containing ionic substructures in heterogeneous catalysis was further explored elaborately for various organic reactions such as Knoevenagel condensation, Henry reactions and Monoglyceride synthesis by ring opening of glycidol.⁵⁰

1.2.2. Multi component PMO from more than one organosilane precursors

It has already been mentioned before that multi functionalized PMOs can be prepared through the co-condensation of more than one organosilane precursors. Since precursors were premixed homogeneously and allow them to self-assemble before the process of poly condensation to form siloxane network, it can be assumed the distribution of different organic building blocks in the final PMO is more homogeneous at molecular level.

Figure 1.2: The bis-silylated organosilane precursors for the synthesis of chiral PMOs by condensation.

A Rh(I) organometallicsilane [Fig. 1.2(7)] was synthesized simply through the complexation between 2-(diphenylphosphino)- ethyltriethoxysilane [$\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3$] and Rh-(COD) Cl_2 under complete dry condition.⁵¹ The synthesized **7** was further used in a surfactant-directed co-condensation with BTEB to prepare phenyl and Rh(I) organometal bridged PMO. The prepared Rh containing PMO exhibited high catalytic activity for the water-medium reaction between phenylboronic acid and butyl acrylate or the 1,4-conjugate addition reaction between phenylboronic acid and N,N-dimethylacrylamide, owing to the high dispersion of Rh(I) within the ordered mesoporous channels and the strong surface hydrophobicity rendered by phenyl fragments of the silica walls facilitating the adsorption of organic molecules onto the catalyst in aqueous solution.

In another example of SBA-15 type PMO was developed by co-condensation of BTEE and a chiral organosilane [Fig. 1.2(8)]. The organosilane used in this case was bis-silylated tartramide, **8** which was synthesized through an in-situ transamidation reaction between (N-methylaminopropyl)trimethoxysilane and protected dimethyltartrate (DMT) during the preparation of the PMO.⁵² The chiral PMOs were synthesized with BTEE:DMT molar ratio as high as 1:1 without disturbing the ordered mesoporous morphology. The catalytic efficacy of this heterogeneous chiral PMO was evaluated for the asymmetric oxidation of thioanisole and was able to afford successfully an enantiomeric excess (ee) and yield to sulfoxide up to 30% and 71%, respectively.

The chiral bis(cyclohexyldiamine) grafted phenylbridged PMO was prepared by co-condensation of BTEB and (1R,2R)-cyclohexyldiamine-derived organosilica [Fig. 1.2(9)] using P123 as template for mesopores.⁵³ The optically active (1R,2R)-cyclohexyldiamine unit, **9** on the PMO surface was used to immobilize Ni(ii) through the complexation with **9**.

The prepared phenyl bridged PMO incorporated with the well-defined single-site chiral bis(cyclohexyldiamine)-based nickel(II) active centers exhibited as an active heterogeneous chiral catalyst with high catalytic activity and excellent enantioselectivity in asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes (more than 92% conversions and up to 99% ee). Besides, this heterogeneous catalyst also showed remarkable catalytic recyclability without affecting its ee value. The same group has also demonstrated that same catalytic phase also offered a high catalytic activity and excellent enantioselectivity towards the asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes, comparable to those with homogeneous catalysts.⁵⁴

A novel ethane bridged PMO embedded with a N-heterocyclic carbene was also developed by the co-condensation route using BTEE and bis silylated-*N,N'*-bis(2,6 dimethylphenyl)imidazol-2-ylidene [Fig 1.2(**10**)] in the presence of P123 as SDA.⁵⁵ Surface bound N-heterocyclic carbene, **10** further used as binding site to immobilize Pd(OAc)₂ through coordination. These Pd(OAc)₂ immobilized PMO acted as an active solid catalyst for Suzuki-Miyaura couplings of challenging aryl chlorides with higher activity than mesoporous silica-based catalyst and commercial Pd/C catalyst. Apart from this the same solid catalyst exhibited efficacy towards the couplings of benzyl chloride and arylboronic acids as well.

A phenyl-ethane bridged PMO was synthesized by the co-condensation of BTEB and BTEE with the help of P123 under acidic condition.⁵⁶ The hydrophobic nano channels of this bifunctionalized PMO acted as an excellent matrix in order to stabilize gold nanoclusters. This GNP immobilized PMO was found to be a highly efficient catalyst for the aerobic oxidation of various types of alcohol into their corresponding aldehydes and ketones at room temperature. This novel heterogeneous PMO-based gold catalyst exhibited superior activity

especially in the case of aerial oxidation of primary aliphatic alcohols to the corresponding aldehydes at room temperature.

Recently series of bistrithoxysilyl-BINAP with various number of carbon in the terminal alkoxysilane were prepared and co-condensed with BTEB in the presence of Brij 76 as surfactant templates under acidic condition to give respective PMOs functionalized with BINAP [Fig. 1.2(**11**)].⁵⁷ Later immobilization of ruthenium (Ru) in these PMOs was achieved through the complexation with BINAP moieties, **11** embedded on the PMO walls. With the help of the chirality inherited from BINAP units, **11**, these PMOs were evaluated for the asymmetric catalytic hydrogenation and asymmetric transfer hydrogenation. The catalysts demonstrated very high levels of activity with 99% of product yield and 99% of ee for each type of catalytic reaction.

PMO can also be synthesized through co-condensation method where TEOS or TMOS play one of the sources for silica. The organic silanes can be mixed with TEOS or TMOS with appropriate molar ratio to achieve highly ordered mesoporous structure. Various catalytically active organosilanes were prepared to develop PMO-based catalysts by co-condensing with either TEOS or TMOS.

Hermenegildo Garcia and Avelino Corma *et al.* reported the synthesis of a series of chiral vanadyl salen complexes [Fig. 1.3(**12,13**)] with two terminal trimethoxysilyl groups which further co-condensed with TEOS using CTAB as surfactant to achieve MCM-41 type chiral PMOs.^{58,59} The catalytic activity of these PMOs was explored for the cyanosilylation of various carbonyls. Evaluation revealed that the catalyst can give enantioselectivity upto 30 % for those reactions. The same group also developed a carbapalladacycle complex [Fig. 1.3(**14**)] having two peripheral trimethoxysilyl groups.⁶⁰ With the help of this organometallic

silane, **14**, series of PMO were developed by varying TEOS: carbapalladacycle complex ratio in the presence of CTAB as surfactant under basic condition. The novel PMO catalysts exhibited significantly higher activity for the Suzuki cross-coupling of phenylboronic acid with bromobenzoic acid and bromoacetophenone than that of a related amorphous silica catalyst containing the carbapalladacycle complex. Due to lack of metal leaching the PMO catalysts showed high catalytic recyclability as well.

Figure 1.3: The bis-silylated organosilane precursors for the synthesis of PMOs by condensation with TEOS or TMOS.

Can Li *et al.* synthesized a N,N-bis[4-(trimethoxysilyl)benzyl]-(-)-(1R,2R)-diaminocyclohexane which further co-condensed with TEOS to developed a MCM-41 type PMO.⁶¹ The *trans*-(1R,2R)-diaminocyclohexane moieties incorporated into the framework of mesoporous silica were further utilized to co-ordinate with [Rh(cod)Cl]₂. The resulted Rh(II)

loaded PMO showed tremendous catalytic activities towards the asymmetric transfer hydrogenation of various ketones. Particularly, in the hydrogenation of acetophenone, the catalyst offered a TOF up to $\sim 414 \text{ h}^{-1}$ with 30% ee.

A bis silylated organosilane integrated with a chiral modified tartrate (Sharpless and Kagan ligand) [Fig. 2(8)] was also synthesized to co-condense with TEOS in order to develop a chiral MCM-41 type PMO. The synthesized chiral PMO was found to be an effective catalyst for the asymmetric oxidation of thioanisole with good sulfoxide yield and moderate enantioselectivity.⁶²

A silsesquioxane derivate of tetrakis (4-carboxyphenyl)porphyrin(TCPP) was synthesized to prepare PMO through co-condensation method using microwave with the TEOS using P123 as surfactant under acidic condition.⁶³ The prepared TCPP-PMOs displayed good organocatalytic activity for the hydrogen transfer reactions of various ketones such as acetophenone, cyclohexanone and pinacolone. The same catalyst also showed photocatalytic activity for the degradation of methylene blue (MB). After incorporation of metal (Fe) into the surface embedded TCPP by ion exchange method, the PMO exhibited excellent catalytic activity in the oxidation of cyclohexene in presence of H_2O_2 as oxidant. Extended investigation of this TCPP-PMO was carried out by loading other metals such as Fe, Cu and Sn.⁶⁴ The catalytic activity of these metal incorporated PMO was evaluated for Baeyer-Villiger oxidation of ketones to corresponding esters using molecular oxygen as an oxidant. The results showed that Fe-TCPP-PMO exhibited higher catalytic activity than Cu-TCPP-PMO and Sn-TCPP-PMO due to the high-valent Fe-porphyrin on the wall of mesoporous silica along with cyclohexanone leading to the successful completion of the oxygen transfer step and generation of ϵ -caprolactone.

Co-condensation method was also employed to synthesize an ionic liquid based PMO which was successfully utilized to support and stabilized Pd nanoparticles.⁶⁵ A 1,3-bis(trimethoxysilylpropyl) imidazolium chloride was prepared as an organosilane precursor to perform co-condenses with TMOS in presence of P123 to achieve final PMO. It was found that the ionic liquid unit can prevent the Pd nanoparticles from unwanted agglomeration as well as facilitate releasing and recapturing of Pd nanoparticles during the catalytic reaction. The catalyst was demonstrated as an efficient and reusable catalyst for the Suzuki–Miyaura coupling reaction of various types of iodo-, bromo-, and even deactivated aryl chlorides in water. Catalytic activity of this catalyst was further investigated for the aerobic oxidation of various primary and secondary alcohols under molecular oxygen and air atmospheres.⁶⁶ The catalyst was found to be effective enough under such catalytic reaction conditions up to several catalytic cycles without any significant decrease in activity and selectivity. Very recently Pd loaded imidazolium grafted PMO was also reported as an efficient and reusable catalyst for the heck reaction with various aryl iodides, aryl bromides, and activated aryl chlorides, which gave the corresponding coupling products in excellent yields and with excellent E-selectivity.⁶⁷ In another instance they have demonstrated that the PMO with 10% imidazolium content can host effectively for the immobilization of perruthenate species through simple ion-exchange process.⁶⁸ This resulting ruthenium loaded PMO is also capable of acting as a recyclable catalyst in the aerobic oxidation of various types of alcohols with high efficacy. This versatile alkylimidazolium embedded PMO phase has been further utilized to support GNPs. In this instance also the imidazolium units provide a means of generating and stabilizing active catalytic AuNPs species while imidazolium chloride was subjected to undergo ion exchange with AuCl_4^- .⁶⁹ The resultant GNP supported PMO was

found to be highly active and recyclable catalyst for three component coupling reaction of aldehyde, alkyne and amine to give the corresponding propargylamine.

In another example by Can Li *et al.*, a chiral BINAP bridged PMO with highly ordered 2-D hexagonal structure was synthesized by co-condensation of (R)-5,50-bis(3-triethoxysilylpropyl-1-ureyl)-2,20-bis(diphenylphosphinooxide)-1,10-binaphthyl [Fig. 1.4(**15**)] with TEOS in the presence of block copolymer P123 as template under weakly acidic conditions followed by the reduction of embedded BINAPO using trichlorosilane.⁷⁰ The chiral **15** grafted on the PMO can coordinate effectively with $[\text{RuCl}_2(\text{benzene})_2]$ and the resulted metal loaded PMO was found to be an efficient solid catalyst for the asymmetric hydrogenation of β -keto esters with ee as high as 99%.

Figure 1.4: The bis-silylated organosilane precursors for the synthesis of PMOs by condensation with TEOS or TMOS.

A novel organosilane precursor [Fig. 1.4(**16**)], designed via Vilsmeier–Haack formylation of phloroglucinol followed by its Schiff base condensation with APTES, was used to co-condense with TEOS in presence of cetylpyridinium chloride as surfactant and Brij-35 as co-surfactant to form a new PMO.⁷¹ The phenolic-OH and imine-N donor sites from **16** present on the walls of PMO material were further utilized to immobilize Pd(II) species through

strong coordination. The Pd-anchored PMO showed excellent catalytic activity in Heck type coupling reaction with trans-selectivity for the synthesis of many value-added aromatic and aliphatic olefins. Moreover, Pd coordinated PMO catalyst also found to be effective in terms of product yields and catalyst recyclability for various other important organic reactions such as fluoride-free Hiyama cross-coupling reactions in water at alkaline pH conditions, Sonogashira cross-couplings between terminal alkynes and aryl halides in water without any Cu based co-catalyst and cyanation reactions of aryl halides.⁷²

Very recently series of sulfonic acid functionalized active PMO-based acid catalysts were developed and their catalytic activities were evaluated for esterification reactions.⁷³ The reported PMOs were synthesized by co-condensation between bis[3-(triethoxysilyl)propyl]tetrasulfide and either TEOS or BTEB under acidic conditions in the presence of Brij-76 as a structure-directing agent followed by the post-modification via oxidative cleavage of tetrasulfide bridges by using H₂O₂ to generate sulfuric groups. Catalysis results showed that these PMOs exhibited a comparable activity to that of Amberlyst-15 and. However, it was also observed that the PMOs synthesized from TEOS were more active than those prepared by co-condensation with BTEB.

1.3. Research Motivation and Scientific Contribution

Ever since the discovery of PMO, numerous scientific reports based on their applications including in the field of heterogeneous catalysis have been published. Few excellent review articles summarized the current trend of PMO as potential candidate in heterogeneous catalysis.⁷⁴⁻⁸⁰ Very recently number of publications in this field has been increased exponentially which reflects the growing interest for the quest of new PMO materials in

order to achieve efficient catalytic systems. Therefore we have attempted to exploit the great potential of PMO to address various issues often encountered in the liquid phase catalysis. Immobilization of various homogeneous catalysts for liquid phase reactions without curtailing their activity is always important yet challenging from both academic and industrial points of view. Based on the previous research background of PMO, this research work brought up several PMO-based catalysts which were proven to be very effective for various liquid phase hydrocarbon oxidation reactions. The enhanced catalytic activity of these heterogeneous catalysts was engineered by new designing of organic bridges (Scheme 1.2, chapter 2&3). Emphasis was also given to detail characterization of these novel PMOs in order to understand the surface chemistry of these novel materials. During this research we have managed to design new type of PMO-based HBD organocatalyst (Scheme 1.2, chapter 4). With the help of an advanced design of PMO, we have also able to achieve not only the HBD based catalytic activity but also cooperative catalytic reinforcement by our PMO. The internal hydrophobicity of PMO inside the pore channels as well as the scope to functionalize the organic bridges helped to develop catalyst with advanced ability. With the help of such PMO with advanced structural morphology we successfully encapsulate Squaraine dye preventing them from unwanted aggregation in water medium availing its immense activity towards catalysis (Scheme 1.2, chapter 5). Undoubtedly, PMO is relatively new addition to the area of porous silica; researchers are still actively pursuing novel architectures, functionalities and applications of such materials. We recognized the potential importance of PMOs, and though our investigations were intended to insight to enhance their industrial applicability in the field of catalysis.

Scheme 1.2: Various applications of PMOs in catalysis.

1.4. References

- (1) Behrens, P. *Adv. Mater.* **1993**, 5, 127.
- (2) Corma, A. *Chem. Rev.* **1997**, 97, 2373.
- (3) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, 359, 710.
- (4) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W. *J. Am. Chem. Soc.* **1992**, 114, 10834.
- (5) Hoffmann, F.; Froba, M. *Chem. Soc. Rev.* **2011**, 40, 608.

- (6) Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1999**, *11*, 3302.
- (7) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *402*, 867.
- (8) Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611.
- (9) Feng, X.; Fryxell, G. E.; Wang, L.-Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science* **1997**, *276*, 923.
- (10) Lim, M. H.; Blanford, C. F.; Stein, A. *J. Am. Chem. Soc.* **1997**, *119*, 4090.
- (11) Kidder, M. K.; Britt, P. F.; Zhang, Z.; Dai, S.; Hagaman, E. W.; Chaffee, A. L.; Buchanan, A. C., III *J. Am. Chem. Soc.* **2005**, *127*, 6353.
- (12) Bek, D.; Balcar, H.; Zilkova, N.; Zukal, A.; Horacek, M.; Cejka, J. *ACS Catal.* **2011**, *1*, 709.
- (13) Mizoshita, N.; Tani, T.; Inagaki, S. *Chem. Soc. Rev.* **2011**, *40*, 789.
- (14) Wang, W.; Lofgreen, J. E.; Ozin, G. A. *Small* **2010**, *6*, 2634.
- (15) Van Der Voort, P.; Esquivel, D.; De Canck, E.; Goethals, F.; Van Driessche, I.; Romero-Salguero, F. J. *Chem. Soc. Rev.* **2013**, *42*, 3913.
- (16) Corma, A.; Garcia, H. *Adv. Syn. Catal.* **2006**, *348*, 1391.
- (17) Basset, J. M.; Ugo, R. In *Modern Surface Organometallic Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: 2009, p 1.

- (18) Yoshina-Ishii, C.; Asefa, T.; Coombs, N.; J. MacLachlan, M.; A. Ozin, G. *Chem. Commun.* **1999**, 2539.
- (19) Inagaki, S.; Guan, S.; Ohsuna, T.; Terasaki, O. *Nature* **2002**, 416, 304.
- (20) Kapoor, M. P.; Yang, Q.; Inagaki, S. *J. Am. Chem. Soc.* **2002**, 124, 15176.
- (21) Sayari, A.; Wang, W. *J. Am. Chem. Soc.* **2005**, 127, 12194.
- (22) Takeda, H.; Goto, Y.; Maegawa, Y.; Ohsuna, T.; Tani, T.; Matsumoto, K.; Shimada, T.; Inagaki, S. *Chem. Commun.* **2009**, 6032.
- (23) Hoffmann, F.; Cornelius, M.; Morell, J.; Fröba, M. *Angew. Chem. Int. Ed.* **2006**, 45, 3216.
- (24) Fujita, S.; Inagaki, S. *Chem. Mater.* **2008**, 20, 891.
- (25) Yang, Q.; Kapoor, M. P.; Inagaki, S. *J. Am. Chem. Soc.* **2002**, 124, 9694.
- (26) Yang, Q.; Kapoor, M. P.; Inagaki, S.; Shirokura, N.; Kondo, J. N.; Domen, K. *J. Mol. Catal. A Chem.* **2005**, 230, 85.
- (27) Yang, Q.; Liu, J.; Yang, J.; Kapoor, M. P.; Inagaki, S.; Li, C. *J. Catal.* **2004**, 228, 265.
- (28) Liu, J.; Yang, Q.; Kapoor, M. P.; Setoyama, N.; Inagaki, S.; Yang, J.; Zhang, L. *J. Phys. Chem. B* **2005**, 109, 12250.
- (29) Rác, B.; Hegyes, P.; Forgo, P.; Molnár, Á. *App. Catal. A, Gen.* **2006**, 299, 193.
- (30) Rat, M.; Zahedi-Niaki, M. H.; Kaliaguine, S.; Do, T. O. *Microporous Mesoporous Mater.* **2008**, 112, 26.
-

- (31) Esquivel, D.; Jimenez-Sanchidrian, C.; Romero-Salguero, F. J. *J. Mater. Chem.* **2011**, *21*, 724.
- (32) Shylesh, S.; Wagener, A.; Seifert, A.; Ernst, S.; Thiel, W. R. *Angew. Chem. Int. Ed.* **2010**, *49*, 184.
- (33) Sasidharan, M.; Bhaumik, A. *ACS App. Mater. Interfaces* **2013**, *5*, 2618.
- (34) Tucker, M. H.; Crisci, A. J.; Wigington, B. N.; Phadke, N.; Alamillo, R.; Zhang, J.; Scott, S. L.; Dumesic, J. A. *ACS Catal.* **2012**, *2*, 1865.
- (35) Shylesh, S.; Srilakshmi, C.; Singh, A. P.; Anderson, B. G. *Microporous Mesoporous Mater.* **2007**, *99*, 334.
- (36) Wan, Y.; Zhang, D.; Zhai, Y.; Feng, C.; Chen, J.; Li, H. *Chem. Asian J.* **2007**, *2*, 875.
- (37) Li, H.; Xiong, M.; Zhang, F.; Huang, J.; Chai, W. *J. Phys. Chem. C* **2008**, *112*, 6366.
- (38) Kang, C.; Huang, J.; He, W.; Zhang, F. *J. Organomet. Chem.* **2010**, 695, 120.
- (39) Yin, J.; Chai, W.; Zhang, F.; Li, H. *App. Organomet. Chem.* **2013**, DOI 10.1002/aoc.3017.
- (40) Kuschel, A.; Drescher, M.; Kuschel, T.; Polarz, S. *Chem. Mater.* **2010**, *22*, 1472.
- (41) Hu, J.; Wu, Q.; Li, W.; Ma, L.; Su, F.; Guo, Y.; Qiu, Y. *ChemSusChem* **2011**, *4*, 1813.

- (42) Wei, Q.; Zhong, Z.-X.; Nie, Z.-R.; Li, J.-L.; Wang, F.; Li, Q.-Y. *Microporous Mesoporous Mater.* **2009**, *117*, 98.
- (43) Karimi, B.; Kabiri Esfahani, F. *Chem. Commun.* **2011**, *47*, 10452.
- (44) Zhu, F.-X.; Wang, W.; Li, H.-X. *J. Am. Chem. Soc.* **2011**, *133*, 11632.
- (45) Zhang, F.; Yin, J.; Chai, W.; Li, H. *ChemSusChem* **2010**, *3*, 724.
- (46) Johnson-White, B.; Zeinali, M.; Malanoski, A. P.; Dinderman, M. A. *Catal. Commun.* **2007**, *8*, 1052.
- (47) Kuschel, A.; Polarz, S. *J. Am. Chem. Soc.* **2010**, *132*, 6558.
- (48) Shi, J. Y.; Wang, C. A.; Li, Z. J.; Wang, Q.; Zhang, Y.; Wang, W. *Chem. Eur. J.* **2011**, *17*, 6206.
- (49) Hankari, S. E.; Motos-Perez, B.; Hesemann, P.; Bouhaouss, A.; Moreau, J. J. E. *Chem. Commun.* **2011**, *47*, 6704.
- (50) El Hankari, S.; Motos-Perez, B.; Hesemann, P.; Bouhaouss, A.; Moreau, J. J. E. *J. Mater. Chem.* **2011**, *21*, 6948.
- (51) Yang, X.; Zhu, F.; Huang, J.; Zhang, F.; Li, H. *Chem. Mater.* **2009**, *21*, 4925.
- (52) Garcia, R. A.; Grieken, R. v.; Iglesias, J.; Morales, V.; Villajos, N. *J. Catal.* **2010**, *274*, 221.
- (53) Jin, R.; Liu, K.; Xia, D.; Qian, Q.; Liu, G.; Li, H. *Adv. Syn. Catal.* **2012**, *354*, 3265.
- (54) Liu, K.; Jin, R.; Cheng, T.; Xu, X.; Gao, F.; Liu, G.; Li, H. *Chem. Eur. J.* **2012**, *18*, 15546.
-

- (55) Yang, H.; Han, X.; Li, G.; Ma, Z.; Hao, Y. *J. Phys. Chem. C* **2010**, *114*, 22221.
- (56) Karimi, B.; Esfahani, F. K. *Adv. Syn. Catal.* **2012**, *354*, 1319.
- (57) Seki, T.; McEleney, K.; Crudden, C. M. *Chem. Commun.* **2012**, *48*, 6369.
- (58) Baleizao, C.; Gigante, B.; Das, D.; Alvaro, M.; Garcia, H.; Corma, A. *Chem. Commun.* **2003**, 1860.
- (59) Baleizão, C.; Gigante, B.; Das, D.; Álvaro, M.; Garcia, H.; Corma, A. *J. Catal.* **2004**, *223*, 106.
- (60) Corma, A.; Das, D.; García, H.; Leyva, A. *J. Catal.* **2005**, *229*, 322.
- (61) Jiang, D.; Yang, Q.; Wang, H.; Zhu, G.; Yang, J.; Li, C. *J. Catal.* **2006**, *239*, 65.
- (62) García, R. A.; van Grieken, R.; Iglesias, J.; Morales, V.; Gordillo, D. *Chem. Mater.* **2008**, *20*, 2964.
- (63) Jeong, E.-Y.; Burri, A.; Lee, S.-Y.; Park, S.-E. *J. Mater. Chem.* **2010**, *20*, 10869.
- (64) Jeong, E.-Y.; Ansari, M. B.; Park, S.-E. *ACS Catal.* **2011**, *1*, 855.
- (65) Karimi, B.; Elhamifar, D.; Clark, J. H.; Hunt, A. J. *Chem. Eur. J.* **2010**, *16*, 8047.
- (66) Karimi, B.; Elhamifar, D.; Clark, J. H.; Hunt, A. J. *Org. Biomol. Chem.* **2011**, *9*, 7420.
- (67) Elhamifar, D.; Karimi, B.; Banakar, M. H. *ChemCatChem* **2013**, *5*, 2418.

- (68) Karimi, B.; Elhamifar, D.; Yari, O.; Khorasani, M.; Vali, H.; Clark, J. H.; Hunt, A. J. *Chem. Eur. J.* **2012**, *18*, 13520.
- (69) Karimi, B.; Gholinejad, M.; Khorasani, M. *Chem. Commun.* **2012**, *48*, 8961.
- (70) Wang, P.; Liu, X.; Yang, J.; Yang, Y.; Zhang, L.; Yang, Q.; Li, C. *J. Mater. Chem.* **2009**, *19*, 8009.
- (71) Modak, A.; Mondal, J.; Aswal, V. K.; Bhaumik, A. *J. Mater. Chem.* **2010**, *20*, 8099.
- (72) Modak, A.; Mondal, J.; Bhaumik, A. *Green Chem.* **2012**, *14*, 2840.
- (73) López, M. I.; Esquivel, D.; Jiménez-Sanchidrián, C.; Romero-Salguero, F. J. *ChemCatChem* **2013**, *5*, 1002.
- (74) Rosenholm, J. M.; Sahlgren, C.; Linden, M. *Nanoscale* **2010**, *2*, 1870.
- (75) Tang, F. Q.; Li, L. L.; Chen, D. *Adv. Mater.* **2012**, *24*, 1504.
- (76) Zhao, Y. N.; Vivero-Escoto, J. L.; Slowing, II; Trewyn, B. C.; Lin, V. S. Y. *Expert Opin. Drug Deliv.* **2010**, *7*, 1013.
- (77) Pasqua, L.; Cundari, S.; Ceresa, C.; Cavaletti, G. *Curr. Med. Chem.* **2009**, *16*, 3054.
- (78) Yang, P. P.; Gai, S. L.; Lin, J. *Chem. Soc. Rev.* **2012**, *41*, 3679.
- (79) Manzano, M.; Vallet-Regi, M. *J. Mater. Chem.* **2010**, *20*, 5593.
- (80) Papat, A.; Hartono, S. B.; Stahr, F.; Liu, J.; Qiao, S. Z.; Lu, G. Q. *Nanoscale* **2011**, *3*, 2801.

Chapter 2: Synthesis of Novel Vanadyl Complex

Grafted PMO as an Efficient Green Catalyst for Selective Hydroxylation of Benzene to Phenol

Abstract

Heterogenization of Vanadyl acetylacetonate [VO(acac)₂] has been achieved by appending it into a PMO. In order to prepare PMO a vanadyl complex with bis-terminal alkoxysilane was synthesized through the Schiff-base condensation between the amino group of APTES and the carbonyl unit of VO(acac)₂. Prepared PMOs with different vanadyl grafting were characterized by FTIR, CP-MAS Solid NMR, TEM, XPS, N₂ adsorption measurements and ICP analysis and it was shown that the integrity of the vanadyl complex was preserved in the mesostructural channels of PMOs. These PMOs have been shown to be active catalysts for the direct hydroxylation of benzene preferentially to phenol using H₂O₂ as oxidant in liquid phase catalysis. The highest benzene conversion of 27% to phenol with 100% selectivity towards phenol production was obtained using a PMO catalyst in acetonitrile media. Moreover, the catalysts offered a robust recyclability without any significant catalytic deactivation.

2.1. Introduction

Selective hydroxylation of benzene to phenol is a fundamental catalytic organic reaction with great academic and commercial importance.¹⁻³ So far, many potential attempts have been made for direct hydroxylation of benzene to phenol^{4,5} using different green oxidants such as O₂,^{6,7} H₂O₂,⁸⁻¹⁴ and N₂O¹⁵⁻²⁰ through a single-step process instead of a three-step cumene process reported by Hock and Lang in 1944 which is still employed widely as a commercial process for the production of phenol.³ Although the direct hydroxylation of benzene in gas phase has been explored extensively, the process is associated with a major limitation of the rapid deactivation of catalysts on account of the coke formation.²¹⁻²⁴ Among the reported processes, the direct hydroxylation of benzene to phenol with H₂O₂ in liquid phase has been investigated as an environmentally friendly process.²⁵ Such process, however, is often affected by poor selectivity, i.e., a substantial over-oxidation of phenol exists, forming various by-products such as catechol, hydroquinone, and benzoquinone.¹ Titanium silicalite (TS-1) is a well-known catalyst for the hydroxylation of benzene to phenol in the presence of H₂O₂, offering a conversion (X) of 31% and a selectivity (S) of 95%.²⁶ Modified titanium silicalite catalyst, TS-1B, affords a low efficiency (X = 4.6%, S = 43%) for the hydroxylation.²⁷ Other catalysts such as Fe-impregnated carbon (X = 50 %, S = 40%),²⁸ Cu-containing ternary hydrotalcite (X = 1.6%, S = <100%),²⁹ and Fe(DDS)₃-based microemulsions (X = 56.1%, S = 50.5%)³⁰ have also been reported. In order to increase the selectivity from benzene to phenol, Bianchi *et al.* have developed a water-acetonitrile biphasic reaction method in which phenol is extracted into acetonitrile and the catalyst (FeSO₄) is soluble in the aqueous medium along with H₂O₂.⁴ By employing this method, a significant selectivity enhancement from benzene to phenol (X = 97%) was observed,

although the benzene conversion was found to be only 8.6%. In another study by Zhang *et al.*, keggins type molybdovanadophosphoric heteropoly acids were found to be very effective homogeneous catalysts for the same reaction with hydrogen peroxide as oxidant in a mixed solvent of glacial acetic acid and acetonitrile.³¹ They have achieved maximum benzene conversion of 34.5% with 100% selectivity towards phenol although the recyclability of catalysts and the product separation are the major issues in this system. Vanadyl complexes are another important class of catalysts for their intrinsic ability towards hydrocarbon oxidation including direct hydroxylation of benzene with H_2O_2 .³² Thus far different vanadyl based complexes have been evaluated for the catalysis in both ways – (a) homogeneous VO-catalysts³³⁻³⁵ and (b) VO-catalysts immobilized on different solid supports.³⁶⁻⁴⁰ Many attempts have therefore been made with vanadium containing catalysts such as V / MCM-41 (X = 13 % , S = 48 %),⁴¹ clay supported vanadium oxide (X = 14 % , S = 94 %),³⁷ (VOx)/ MCM-41 (X = 8.8 % , S = 67 %),³⁸ (VOx)/ AMM (X = 8.8 % , S = 67 %),³⁸ sodium vanadate (X = 13.5 % , S = 94 %),³⁹ polymer bound VO(acac)₂ (Y = 10 %),⁴⁰ V-HMS (X= ~80%, S= ~8%)⁴². However despite several efforts the direct hydroxylation of benzene to phenol with both good conversion and high selectivity has not been achieved.

Herein, we report (a) the synthesis of a new type of PMO grafted with catalytically active vanadyl(IV) centers and (b) its application as an efficient green catalyst for selective hydroxylation of benzene to phenol.⁴³ VO(acac)₂ is an important homogeneous catalyst widely used for various organic transformations.^{44,45} The immobilization of the VO(acac)₂ onto silica gels, mesoporous silicas, and alumina has been achieved through a wet impregnation process followed by calcination.⁴⁶⁻⁴⁸ It has also been anchored onto activated carbon materials, silica materials, and clay materials by the reaction between the carbonyl group of the acac ligand and the amino group pre-grafted onto the material surfaces.^{49,50} As

compared with previous reports wherein either the hydroxylation selectivity from benzene to phenol or the recyclability of catalyst has always been a challenge, our VO(acac)₂-grafted PMO catalyst showed consistently a selectivity of 100% towards the phenol formation with a benzene conversion of over 27%. The catalyst presents a high recyclability and can be used for many cycles. In addition, the benzene hydroxylation by the VO(acac)₂-grafted PMO catalyst is a green catalytic process in terms of the selectivity and recyclability.

2.2. Results and Discussions

2.2.1. Synthesis of organo alkoxy silane

Scheme 2.1: Schematic synthesis pathway for preparations of **3** and PMOs.

Figure 2.1: FTIR spectra of (a) VO(acac)₂ and (b) **3**.

In order to prepare a PMO for catalytic applications, it is desirable to have a high degree of functionality within PMO by choosing an organic precursor with suitable complexity and molecular size. Another crucial requirement associated with the preparation of a PMO is to synthesize an organic precursor with at least two terminal alkoxy silanes.⁵¹⁻⁵³ In the current work, an essential organic precursor (**3**) was synthesized (Scheme 2.1) through the Schiff-base condensation between the amino group of **2** and the carbonyl unit of **1**. **3** was confirmed by mass spectrum, EA, XPS and FT-IR. As compared with the FT-IR spectrum (Figure 2.1) of VO(acac)₂ (**1**), the FT-IR spectrum of **3** shows (a) the appearances of new bands centered at 1608 and 1579 cm⁻¹, respectively, due to the combinational vibration of newly formed C=N bonds, and (b) a complete disappearance of the band at 1556 cm⁻¹ which is assigned to the initial C=O bonds in **1**.⁵⁴ The observations provide evidence for the formation of **3** by the Schiff-base condensation between **1** and **2**.

2.2.2. Synthesis of PMOs

A reported procedure was adopted⁵⁵ to synthesize the novel PMO through co-condensation of **3** and **4** or TEOS using CTAB (**5**) as the structure-directing template. Since the phase separation and the self-condensation of organosilica precursors are two major disadvantages for the preparation of PMOs, an optimum reaction condition is needed in order to obtain a periodic mesoporous structure grafted covalently with the organic functionality. For the optimization of the synthetic condition, a series of PMOs were prepared by using **4** or TEOS and **3** with different molar ratios ranging from 80:20 to 95:5. Although we were able to synthesize mesoporous materials with all the molar ratios, ICP analysis results showed very low vanadium contents for most of the prepared PMO samples other than two PMO samples prepared with molar ratios of 80:20 and 85:15 (denoted as PMO-1 and PMO-2 respectively). Therefore, we limit our scope of discussions within PMO-1 and PMO-2.

2.2.3. FT-IR study of PMOs

Figure 2.2. FT-IR spectra of (a) PMO-1 and (b) PMO-2. Adapted and reproduced with permission from ref. 47; © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

The FT-IR spectra (Figure 2.2) of PMO-1 and PMO-2 show the characteristic peaks of MCM-41 type materials,^{56,57} indicating the formation of polycondensation of silica. Peaks in the range of 1550 to 1400 cm^{-1} assigned to the **3** unit can be observed in both the FT-IR spectra, providing clear evidence of grafting the **3** unit onto the organosilica framework. The predominant band of physisorbed water centered at 1630 cm^{-1} overlaps completely with the peak of the C=N bonds. A broad band around 3426 cm^{-1} is attributed to the O–H stretching vibration of hydrogen bonded silanols on PMOs.⁵⁸

2.2.4. ^{13}C and ^{29}Si solid NMR study of PMOs

Figure 2.3: ^{13}C CP MAS NMR spectra (a) PMO-1 and (b) PMO-2. Adapted and reproduced with permission from ref. 47; © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

The ^{13}C CP MAS NMR spectra of PMO-1 and PMO-2 (Figure 2.3) exhibit strong signals at 9.1, 22.0, 30.0, 42.6 and 63.4 ppm which can be attributed to different aliphatic primary and

secondary carbon atoms as marked in the inset of Figure 2.3. In addition to these signals two minor peaks at ~162 and 185 ppm are assigned to the carbons from -imine and -enol groups

Figure 2.4: ^{29}Si CP MAS NMR spectra (a) PMO-1 and (b) PMO-2.

of the incorporated **3**. This result indicates that the structure of grafted **3** was intact inside the silica framework. The NMR data provide a solid support towards the successful incorporation of compound **2** into the silica framework in both synthesized PMOs. ^{29}Si CP-MAS NMR analysis was also carried out for all the three PMOs to realize the covalent incorporation of the organic bridging units into the inorganic siloxane network. ^{29}Si NMR spectra of PMO-1 and PMO-2 (Figure 2.4) show signals with major intensities centered at -110 and -100 ppm with a small shoulder at -90 ppm which can be attributed to Q^4

$[(\equiv\text{SiO})_4\text{Si}]$, $\text{Q}^3 [(\equiv\text{SiO})_3\text{Si}(\text{OR})]$ and $\text{Q}^2 [(\equiv\text{SiO})_3\text{Si}(\text{OR})_2]$ respectively, where $\text{R} = \text{Et}$ or H . Along with these signals all the PMOs also displayed one more peak at -64.3 ppm which is corresponding to T^3 resonance from silicon species attached to the organic group $[-\text{CH}_2-\text{Si}(\text{OSi}\equiv)_3]$. Apart from T^3 signal all the spectra don't display any other signals corresponding to T^0 , T^1 and T^2 . This is solid evidence in support of complete grafting of organic precursors in to the silica framework through the hydrolysis of terminal alkoxysilanes.

2.2.5. Textural and analytical studies of PMOs

Table 2.1. Analytical, textural, and porosity data of different catalysts.

No	Catalyst	V content from ICP (mmol g ⁻¹)	Atomic content from XPS (%)		BET surface area (m ² g ⁻¹)	Pore diameter (nm)	Total pore volume (cm ³ g ⁻¹)
			N	V			
1	PMO-1	0.066	2.7	1.3	455	4.5	0.5
2 ^[a]	PMO-1_Used	0.064	2.4	1.3	-	-	-
3	PMO-2	0.058	2.5	1.1	591	4.1	0.6

[a] PMO-1 recovered after 3 catalytic cycles. Adapted and reproduced with permission from ref. 47; © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

The isothermal N_2 adsorption/desorption measurement indicates the sizes of mesopores in both PMO-1 and PMO-2 are 4.5 and 4.1 nm in diameter, respectively. From the adsorption isotherm under the lowest pressure, the BET surface areas of PMO-1 and PMO-2 were measured to be 455 and 591 m² g⁻¹, respectively (Figures A1 to A4 in the Appendix). The increase in the surface area of PMO-2 over PMO-1 is due to bigger total pore volume of PMO-2 (Table 2.1). Results from the ICP analysis in Table 2.1 also confirm the vanadium contents in PMO-1 and PMO-2 quantitatively, which are 0.066 and 0.058 mmol g⁻¹, respectively. The HR-TEM analysis (Figure 2.5) shows nice mesostructural morphologies for

both PMO-1 and PMO-2. It can be clearly seen that both PMO-1 and PMO-2 present periodic mesopore channels. The mesopore diameters measured from the TEM images are well consistent with those obtained from the N_2 adsorption/desorption analysis.

Figure 2.5: HR-TEM images of (a) PMO-1 and (b) PMO-2. Adapted and reproduced with permission from ref. 47; © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.2.6. XPS study of PMOs

Figure 2.6: High resolution XPS spectra at the V2p region for (a) $VO(acac)_2$, (b) compound **3**, (c) PMO-1, (d) PMO-2, and (e) PMO-1_Used. Adapted and reproduced with permission from ref. 47; © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

XPS spectra of PMO-1 and PMO-2 [Figure 2.7 (a) and (b)] demonstrate the presences of carbon, nitrogen, and vanadium atoms in the PMO materials, in addition to the silica and oxygen atoms that are obviously present in all silica-based materials. The XPS atomic percentages (Table 2.1) show that atomic ratio of nitrogen to vanadium is about 2 in PMOs, proving that one grafted vanadium atom coordinates with two nitrogen atoms in all the phases. The XPS spectrum of compound **3** in the V2p region (Figure 2.6) shows the characteristic V2p_{3/2} peak with a binding energy (B.E.) of 516 eV, which is essentially similar to the V2p band profile of VO(acac)₂. The observations indicate that the integrity of the vanadyl(IV) unit in **3** was remained after the modification reaction. The V2p band was also observed in the cases of PMO-1 and PMO-2 (Figure 2.6), confirming the presence of the

Figure 2.7: XPS spectra with atomic percentages of (a) PMO-1, (b) PMO-2 and (c) PMO-1_Used.

vanadyl(IV) unit in PMOs. As compared with the V2p band of compound **3**, the slight band shift to low binding energy in PMO-1 and PMO-2 is attributed to a new chemical environment around the vanadyl complex in PMOs. A similar V2p band profile can be observed after PMO-1 is used for three catalytic cycles (denoted as PMO-1_Used), which confirms the strong stability of the vanadyl complex within the silica framework during the catalytic process.

2.2.7. Catalysts evaluation

The catalytic activity of PMOs for selective hydroxylation of benzene to phenol was evaluated at 50 °C using acetonitrile as a solvent and H₂O₂ as an oxidant. The catalytic results (Figure 2.8) show that both PMO-1 and PMO-2 afford a selectivity of 100% towards the phenol formation with a benzene conversion of ca. 27% under a catalyst-to-benzene molar ratio of 1:200 and a benzene-to-H₂O₂ molar ratio of 1:3. It is also clear from the turn over number (TON_V) and H₂O₂ efficiency data that the immobilized vanadyl group in PMOs are more catalytically active than VO(acac)₂. The VO(acac)₂ complex, a homogeneous catalyst, presents a poor selectivity of only 76.9% under the same experiment conditions. Much better selectivity towards the phenol formation offered by the PMO-based catalysts can be attributed to the presence of the silanol groups on PMOs. According to the information obtained by the FT-IR analysis, the framework of PMOs is weakly acidic on account of the hydrogen bonded silanol groups acting as brönsted acidic sites.⁵⁹ Based upon this fact, we can rationally assume that the weakly basic benzene can be easily adsorbed onto the acidic framework of the PMO catalysts through electrostatic interactions. Once benzene is converted to phenol, an acidic molecule, on the framework, acidic phenol is desorbed immediately from the acidic framework, thus preventing further formation of over-oxidized

products. Moreover, higher benzene conversion of PMO-1 than that of PMO-2 is obvious, since the latter contains less amount of the vanadium complex.

Figure 2.8: Conversion and selectivity of benzene to phenol with different catalysts. Catalytic reaction conditions: C₆H₆:H₂O₂ = 1:3, C₆H₆:catalyst = 200:1, solvent: acetonitrile, temperature: 50 °C, reaction time= 8h. [a] PMO-1 catalyst recovered from the first catalytic cycle and then reused, [b] PMO-1 catalyst recovered from the second catalytic cycle and then reused. Adapted and reproduced with permission from ref. 47; © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

A series of catalytic experiments using PMOs were carried out in order to understand the variation of the benzene-to-phenol conversion as a function of reaction time (Table 2.2). The results show an increasing trend in the benzene-to-phenol conversion and a remarkable decrease in the selectivity as well as in the TON_v upon increasing the reaction time. A similar variation of the benzene-to-phenol conversion as a function of the benzene-to-H₂O₂ molar ratio was also examined. A selectivity of 100% for the phenol formation was observed when the benzene-to-H₂O₂ molar ratio is 1:2 or 1:3, while the conversion rate (27.4%) of using the 1:3 molar ratio is much higher. A significant increase of the benzene conversion

(32.6%) was obtained when the benzene-to-H₂O₂ molar ratio increases from 1:3 to 1:5, but the selectivity decreases a lot from 100% to 79.3%. Upon the increase of reaction time shows another decreasing trend for H₂O₂ efficiency which can be mainly due to the self-decomposition of H₂O₂.

Table 2.2: Catalytic activity of PMO-1 as functions of reaction time as well as benzene-to-H₂O₂ (B:H) molar ratio.

No	Catalyst	B:H ^[a]	Reaction time (h)	Conversion of benzene (%)	Selectivity of phenol (%)
1	PMO-1	1:3	8	27.4	100
2	PMO-1	1:3	16	32.6	76.9
3	PMO-1	1:3	24	38.2	64
4	PMO-1	1:2	8	12.6	100
5	PMO-1	1:5	8	32.6	79.3

[a] Catalytic reaction conditions: C₆H₆:catalyst = 200:1, solvent: acetonitrile, temperature: 50 °C.

X_B: Conversion of benzene based upon the FID-GC results

S_P: Selectivity of phenol calculated as total moles of phenol formed/ total moles of benzene converted.

TON_V: Turnover number calculated as moles of phenol formed on one mole of V in catalyst

E_O: H₂O₂ Efficiency calculated as 100 X products (mol of phenol)/total mol of H₂O₂ added.

Adapted and reproduced with permission from ref. 47; © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

During the catalytic evaluation of different catalysts, we have observed that under few reaction conditions the selectivity of phenol production has been decreased. From the qualitative analysis of the product mixture done by the GC-MS revealed that poor selectivity is due to the formation of over oxidized products namely hydroquinone and benzoquinone. Besides that polymerization of phenol was also observed when the catalytic oxidation was extended up to 16 h and 24 h.

It has been well demonstrated that the peroxo vanadyl complex can catalyze heterolytic oxygen transfer.⁶⁰ Based upon this knowledge, we propose a reversible V^{4+}/V^{5+} redox mechanism (Scheme 2.2) for the catalytic cycle of the vanadyl(IV) complex grafted PMOs in the hydroxylation of benzene to phenol. In another study, Mimoun *et al.* has reported a mechanistic study regarding catalytic properties of V^{5+} peroxo complexes where they argued that the peroxo group is active for the benzene hydroxylation.¹² Congruent with those studies we assume that H_2O_2 oxidizes V^{4+} to a peroxo vanadyl radical ($V^{5+}-O-O^{\bullet}$) followed by the insertion of oxygen in the C-H bond of benzene and the regeneration of V^{4+} species. Thus, an efficient regeneration of V^{4+} is essential for the recycling use of the catalyst.

Scheme 2.2: Schematic representation of the catalytic cycle of V^{4+} during selective oxidation of benzene to phenol using H_2O_2 as an oxidant. Adapted and reproduced with permission from ref. 47; © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

The efficacy of a heterogeneous catalyst is also evaluated from its recyclability and stability (e.g., no metal leaching). PMO-1 presents a tremendous recyclability towards the phenol formation with a consistent 100% selectivity over 3 catalytic cycles. The excellent recyclability of PMO-1 can be ascribed to the absence of the metal leaching, which was confirmed by the ICP analysis of the used catalysts. ICP results indicate the vanadium content in PMO-1 remained 0.066 mmol/g up to 3 catalytic cycles. Since the PMO catalyst

possesses such a nice recyclability, the benzene conversion rate can be even enhanced after several catalytic cycles. No metal leaching and the consistent integrity of catalytic metal centers make the present PMO a remarkable catalyst for selective hydroxylation of benzene to phenol.

2.3. Conclusion

In conclusion, a novel type of PMO embedded with the $\text{VO}(\text{acac})_2$ complex has been successfully synthesized for selective hydroxylation of benzene to phenol. As compared with earlier reports wherein the hydroxylation selectivity from benzene to phenol has always been a challenge, our $\text{VO}(\text{acac})_2$ -grafted PMO catalyst showed consistently a selectivity of 100% towards the phenol formation with a benzene conversion of over 27%. In addition, the benzene hydroxylation by the $\text{VO}(\text{acac})_2$ -grafted PMO catalyst is a green catalytic process, since the incorporation of the homogeneous catalyst $\text{VO}(\text{acac})_2$ onto PMO improves not only the selectivity towards the phenol production, but also presents a robust recyclability, making the catalytic process more benign from environmental and commercial point of view. This method may therefore provide a promising alternate route for the synthesis of phenol instead of the current three step cumene process.

2.4. Experimental

All starting materials used in the synthesis and catalysis were purchased from Sigma Aldrich or Alfa Aesar and used without further purification.

2.4.1. Synthesis of compound **3**

Vanadyl acetylacetonate (1.0 g, 3.7 mmol, from Sigma-Aldrich) was dissolved in dry EtOH (50 mL) under N₂ in a two-necked round-bottom flask equipped with a condenser. APTES (1.7 g, 7.4 mmol, from Alfa Aesar) was then added dropwise to the solution over 30 min. The reaction mixture was allowed to reflux for overnight. After the reaction, the reaction mixture was cooled down to room temperature. EtOH solvent was removed in vacuo, leaving a highly viscous liquid. Hexane was added to the viscous liquid and the precipitates were formed. The dark brown solid **3** was isolated by filtration in vacuo and stored in a screw-capped vial. ¹H NMR (CDCl₃, 400 MHz) δ 4.92 (2H, s, H), 3.85 (12H, q, OCH₂), 3.18 (4H, t, NCH₂), 1.83 (6H, s, CH₃C-O), 1.78 (6H, s, CH₃C=N), 1.6 (4H, quint, CH₂), 1.23 [18H, t, CH₃(OEt)], 0.66 (4H, t, SiCH₂). ¹³C NMR (100 MHz, CDCl₃) δ ppm= 182, 165, 81, 59, 40, 30, 24, 22, 18, 10. MS: calcd for C₂₈H₅₆N₂O₉Si₂V m/z = 672, found: m/z = 673 [M+H]⁺; Elemental analysis: calcd %: C 50.05, H 8.40, N 4.17, found %: C 49.44, H 8.19, N 4.37.

2.4.2. Preparation of PMO by Hydrothermal Process

PMO was prepared according to a reported method with little modifications.⁵⁵ Compound **3** and TEOS were used as silica sources and CTAB was used as the structure-directing agent. A gel was formed with a particular molar ratio of Si : CTAB : NH₃ (20%) : H₂O : EtOH = 1.0 : 0.12 : 8.0 : 114 : 10. Several TEOS to **3** molar ratios ranging from 80:20 to 95:5 were tested. In a typical synthesis of PMO, CTAB (1.5 g, 4.1 mmol) was dissolved in H₂O (70 mL) and then NH₃ solution (20 mL, 25%) was added to the above solution. The mixture solution was stirred at 20 °C for 30 min. A premixed solution of **3** (2.35 g, 3.5 mmol) and TEOS (5.8g, 28.0 mmol) in EtOH (18 mL) was added dropwise to the mixture solution under vigorous stirring within 0.5 h. After the reaction for 2 h, the resulting gel was transferred to a

polyethylene container and heated to 90 °C for 4 days. The solid obtained was washed with H₂O and dried in air at 60 °C. The structure-directing agent was finally removed by extraction of the solid with dilute ethanolic HCl solution (20 mL of 0.5 M ethanolic HCl for 0.5 g of solid) at 40 °C for 2 h. PMO was obtained by filtration and dried in vacuo.

2.4.3. Catalytic Tests

The catalytic tests were carried out in a two-necked round bottom flask. In a typical experiment, benzene (0.36 mL, 4 mmol) was added to an acetonitrile solution (10 mL) containing PMO-1 (0.3 g) as catalyst. In order to avoid immediate decomposition of H₂O₂ and strong effervescence, H₂O₂ (1.36 mL, 30%) was added slowly to the mixture solution over a period of 1 h. The resulting mixture was stirred under 250 rpm at 50 °C for 8 h. The reaction mixture was first analyzed by Quadrupole ion trap Mass Spectrometer equipped with Thermo Accela LC for identification of the reactants and products. The products were then quantified using an Agilent 6890 GC system equipped with a flame ionization detector after determining the response factors for the reactants and products individually.

In order to check the catalyst recyclability, catalyst from the reaction mixture was recovered by centrifugation followed by washing with acetonitrile for several times. The recovered catalysts were kept under vacuum oven for complete dryness before using for the subsequent catalysis or various characterizations.

2.4.4. Characterization

¹H and ¹³C NMR spectra were recorded on a Bruker spectrometer operating at 400 MHz. The solid-state spectra were collected on an ECA400 NMR spectrometer (JEOL, 400 MHz) using a 4 mm CP/MAS probe at room temperature. TEM images

were collected on a JEOL JEM-1400 instrument operated at 100 kV. FT-IR spectra were recorded as KBr pellets on a SHIMADZU IRPrestige-21 spectrometer with the sample powder diluted in KBr (1%). N₂ adsorption/desorption measurements for BET and BJH calculations were obtained using an autosorp-IQ instrument from Quantachrome Instruments Corporation. The BET method was utilized to calculate the specific surface areas of the materials whereas the BJH model derived from desorption branches of isotherms was adopted for the pore-size distributions of the PMOs. Prior to isothermal N₂ adsorption/desorption measurements, the samples were pretreat under 10⁻⁶ bar pressure at 120°C with 10°C/min ramping. EA were obtained from EuroVector Euro EA Elemental Analyzer. Thermo Fischer iCAP 6000 series ICP-OES was used for performing trace metal analysis. XPS analysis was done by a SPECS HSA3500 plus spectrometer using Mg X-ray source. Quadrupole ion trap Mass Spectrometer equipped with Thermo Accela LC and Agilent 6890 GC system equipped with a flame ionization detector were used for analysis of catalytic reactions.

2.5. References

- (1) Centi, G.; Perathoner, S. *Catal. Today* **2009**, *143*, 145.
- (2) Lee, B.; Naito, H.; Hibino, T. *Angew. Chem. Int. Ed.* **2012**, *51*, 440.
- (3) Hock, H. *Ber. Desch. Chem. Ges.* **1944**, *B77*, 257.
- (4) Bianchi, D.; Bortolo, R.; Tassinari, R.; Ricci, M.; Vignola, R. *Angew. Chem. Int. Ed.* **2000**, *39*, 4321.
- (5) Itoh, N.; Niwa, S.; Mizukami, F.; Inoue, T.; Igarashi, A.; Namba, T. *Catal. Commun.* **2003**, *4*, 243.
- (6) Herron, N.; Tolman, C. A. *J. Am. Chem. Soc.* **1987**, *109*, 2837.

-
- (7) Kitano, T.; Kuroda, Y.; Mori, M.; Ito, S.; Sasaki, K.; Nitta, M. *J. Chem. Soc., Perkin Trans. 2* **1993**, 981.
- (8) Walling, C.; Johnson, R. A. *J. Am. Chem. Soc.* **1975**, 97, 363.
- (9) Walling, C. *Acc. Chem. Res.* **1975**, 8, 125.
- (10) Smith, J. R. L.; Norman, R. O. C. *J. Chem. Soc. (Resumed)* **1963**, 2897.
- (11) Milas, N. A. *J. Am. Chem. Soc.* **1937**, 59, 2342.
- (12) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, 105, 3101.
- (13) Nomiya, K.; Yanagibayashi, H.; Nozaki, C.; Kondoh, K.; Hiramatsu, E.; Shimizu, Y. *J. Mol. Catal. A* **1996**, 114, 181.
- (14) Lee, C. W.; Lee, W. J.; Park, Y. K.; Park, S.-E. *Catalysis Today* **2000**, 61, 137.
- (15) Iwamoto, M.; Hirata, J.; Matsukami, K.; Kagawa, S. *J. Phys. Chem.* **1983**, 87, 903.
- (16) Burch, R.; Howitt, C. *Appl. Catal. A* **1992**, 86, 139.
- (17) Burch, R.; Howitt, C. *Appl. Catal. A* **1993**, 103, 135.
- (18) Panov, G. I.; Sheveleva, G. A.; Kharitonov, A. S.; Romannikov, V. N.; Vostrikova, L. A. *Appl. Catal. A* **1992**, 82, 31.
- (19) Sobolev, V. I.; Dubkov, K. A.; Paukshtis, E. A.; Pirutko, L. V.; Rodkin, M. A.; Kharitonov, A. S.; Panov, G. I. *Appl. Catal. A* **1996**, 141, 185.
- (20) Liptáková, B.; Hronec, M.; Cvengrošová, Z. *Catal. Today* **2000**, 61, 143.
- (21) Panov, G. I.; Kharitonov, A. S.; Sobolev, V. I. *Appl. Catal. A* **1993**, 98, 1.
- (22) Hensen, E. J. M.; Zhu, Q.; van Santen, R. A. *J. Catal.* **2003**, 220, 260.
-

-
- (23) Ribera, A.; Arends, I. W. C. E.; de Vries, S.; Pérez-Ramírez, J.; Sheldon, R. *A. J. Catal.* **2000**, *195*, 287.
- (24) Kubánek, P.; Wichterlová, B.; Sobalí; amp; x; k, Z. *J. Catal.* **2002**, *211*, 109.
- (25) Podgoršek, A.; Zupan, M.; Iskra, J. *Angew. Chem. Int. Ed.* **2009**, *48*, 8424.
- (26) Tanev, P. T.; Chibwe, M.; Pinnavaia, T. J. *Nature* **1994**, *368*, 321.
- (27) Balducci, L.; Bianchi, D.; Bortolo, R.; D'Aloisio, R.; Ricci, M.; Tassinari, R.; Ungarelli, R. *Angew. Chem. Int. Ed.* **2003**, *42*, 4937.
- (28) Choi, J.-S.; Kim, T.-H.; Choo, K.-Y.; Sung, J.-S.; Saidutta, M. B.; Ryu, S.-O.; Song, S.-D.; Ramachandra, B.; Rhee, Y.-W. *Appl. Catal. A* **2005**, *290*, 1.
- (29) Dubey, A.; Kannan, S. *Catal. Commun.* **2005**, *6*, 394.
- (30) Liu, H.; Fu, Z.; Yin, D.; Yin, D.; Liao, H. *Catal. Commun.* **2005**, *6*, 638.
- (31) Zhang, F.; Guo, M.; Ge, H.; Wang, J. *Chinese Journal of Chemical Engineering* **2007**, *15*, 895.
- (32) da Silva, J. A. L.; da Silva, J. J. R. F.; Pombeiro, A. J. L. *Coord. Chem. Rev.* **2011**, *255*, 2232.
- (33) Maurya, M. R.; Agarwal, S.; Bader, C.; Ebel, M.; Rehder, D. *Dalton Trans.* **2005**, 537.
- (34) Fernández, T. L.; Souza, E. T.; Visentin, L. C.; Santos, J. V.; Mangrich, A. S.; Faria, R. B.; Antunes, O. A. C.; Scarpellini, M. *J. Inorg. Biochem.* **2009**, *103*, 474.
- (35) Reis, P. M.; Armando, J.; Silva, L.; da Silva, J. J. R. F.; Pombeiro, A. J. L. *Chem. Commun.* **2000**, 1845.
- (36) Shul'pin, G. B.; Mishra, G. S.; Shul'pina, L. S.; Strelkova, T. V.; Pombeiro, A. J. L. *Catal. Commun.* **2007**, *8*, 1516.
- (37) Gao, X.; Xu, J. *Appl. Clay Science* **2006**, *33*, 1.
-

-
- (38) Lemke, K.; Ehrich, H.; Lohse, U.; Berndt, H.; Jähnisch, K. *Appl. Catal. A* **2003**, *243*, 41.
- (39) Jian, M.; Zhu, L.; Wang, J.; Zhang, J.; Li, G.; Hu, C. *J. Mol. Catal. A* **2006**, *253*, 1.
- (40) Kumar, J. A.; Das, S. K.; Kumar, A. *J. Catal.* **1997**, *166*, 108.
- (41) Chen, Y.-W.; Lu, Y.-H. *Industrial & Engineering Chemistry Research* **1999**, *38*, 1893.
- (42) Feng, S.; Pei, S.; Yue, B.; Ye, L.; Qian, L.; He, H. *Catal Lett* **2009**, *131*, 458.
- (43) Borah, P.; Ma, X.; Nguyen, K. T.; Zhao, Y. *Angew. Chem. Int. Ed.* **2012**, *51*, 7756.
- (44) Ligtenbarg, A. G. J.; Hage, R.; Feringa, B. L. *Coord. Chem. Rev.* **2003**, *237*, 89.
- (45) Chong, A. O.; Sharpless, K. B. *J. Org. Chem.* **1977**, *42*, 1587.
- (46) Shylesh, S.; Singh, A. P. *J. Catal.* **2006**, *244*, 52.
- (47) Hanu, A.-M.; Liu, S.; Meynen, V.; Cool, P.; Popovici, E.; Vansant, E. F. *Microporous Mesoporous Mater.* **2006**, *95*, 31.
- (48) Baltes, M.; Collart, O.; Van Der Voort, P.; Vansant, E. F. *Langmuir* **1999**, *15*, 5841.
- (49) Jarrais, B.; Silva, A. R.; Freire, C. *Eur. J. Inorg. Chem.* **2005**, *2005*, 4582.
- (50) Lattanzi, A. *Org. Lett.* **2002**, *4*, 1519.
- (51) Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611.
- (52) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *402*, 867.
-

- (53) Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1999**, *11*, 3302.
- (54) Pereira, C.; Silva, A. R.; Carvalho, A. P.; Pires, J.; Freire, C. *J. Mol. Catal. A* **2008**, *283*, 5.
- (55) Baleizão, C.; Gigante, B.; Das, D.; Álvaro, M.; Garcia, H.; Corma, A. *J. Catal.* **2004**, *223*, 106.
- (56) Silva, A. R.; Wilson, K.; Whitwood, A. C.; Clark, J. H.; Freire, C. *Eur. J. Inorg. Chem.* **2006**, 1275.
- (57) Jarrais, B.; Pereira, C.; Silva, A. R.; Carvalho, A. P.; Pires, J.; Freire, C. *Polyhedron* **2009**, *28*, 994.
- (58) Chakraborty, B.; Viswanathan, B. *Catal. Today* **1999**, *49*, 253.
- (59) Jentys, A.; Kleestorfer, K.; Vinek, H. *Microporous Mesoporous Mater.* **1999**, *27*, 321.
- (60) Pillai, U. R.; Sahle-Demessie, E. *Chem. Commun.* **2002**, 2142.

Chapter 3: β -Diketimine Appended PMO: A Novel Scaffold for Immobilization of Palladium Acetate towards Efficient Wacker Type Reaction

Abstract

A series of novel β -diketimine appended periodic mesoporous organosilicas (PMOs) were prepared and characterized. These PMOs were found to be excellent scaffold for the immobilization of palladium acetate ($\text{Pd}(\text{OAc})_2$) through the complexation between iminic nitrogen atoms of β -diketiminates and $\text{Pd}(\text{OAc})_2$, leading to resulting in efficient heterogeneous catalysts (Pd/PMO) for the oxidation of styrene. Catalytic evaluations showed that, in liquid phase using H_2O_2 as oxidant, Pd/PMO promotes styrene to undergo Wacker type reaction with a high selectivity of up to 100% towards the formation of acetophenone, a useful chemical with high demand in the global market. The novel solid catalyst offers a tremendous catalytic recyclability with consistently high catalytic activity. In addition, it was experimentally demonstrated that H_2O_2 plays an important role to prevent unwanted catalyst deactivation. The current work presents a convenient approach for the direct production of acetophenone from styrene.

3.1. Introduction

In the area of catalysis, one of important research directions has been oriented towards the direct and selective oxidation of various hydrocarbons on account of their industrial as well as academic significance. Amongst various commercially imperative oxidation processes, Wacker reaction is always a popular topic especially in the functionalization of terminal olefins.¹⁻³ An excellent representation of Wacker reaction is the selective oxidation of styrene to acetophenone, a raw material in pharmaceuticals, resin and fragrance industries as well as other carbonyl-related products.⁴ The most common industrial process for the production of acetophenone is the acetylation of benzene using acetyl chloride/acetic anhydride, which is considered as an inefficient process.⁵ On the contrary, Pd catalyzed Wacker reaction is a clean process to produce acetophenone as compared to the Friedel–Crafts route. However, Wacker reaction for the styrene oxidation is often associated with various problems such as low selectivity towards acetophenone production, difficulties in the product separation, necessities of acetic acid and CuCl_2 to promote the re-oxidation of $\text{Pd}(0)$ into highly active $\text{Pd}(\text{II})$ resulting in the corrosion hazards of the reactor, and large amounts of toxic and corrosive wastes generated. In order to circumvent all the major drawbacks associated with the Wacker process, many catalytic systems have been investigated for the selective oxidation of styrene to acetophenone owing to abovementioned highly commercial importance. Hitherto, the improved efficiency of the catalytic systems has been attempted by avoiding copper(II) salts,⁶ using supported catalysts,⁷⁻⁹ surfactants,¹⁰ cyclodextrins,¹¹ and calixarenes.¹¹ In addition, making use of various alternative solvents such as fluorous phases,¹² polyethylene glycols,¹³ supercritical CO_2 ^{7,14} and ionic liquids^{5,15} have been adopted to reduce the main drawbacks of

the Wacker oxidation process. However, the development of a simple, efficient and environmentally benign method for selective synthesis of styrene to acetophenone is still of great challenge.

In order to address the challenge, herein, we developed a novel strategy to immobilize $\text{Pd}(\text{OAc})_2$ onto the PMO frameworks via the formation of β -diketiminato-acetate Pd^{2+} complex. With that purpose we synthesized a new type of PMO grafted with β -diketimine moiety bound onto the walls through a homogeneous molecular distribution. β -Diketimine has gained a lot of attention as a versatile ligand for the formations of various transition metal complexes that have been proven to be useful in catalysis, metallo-organic chemical vapor deposition, and so on.¹⁶⁻²⁰ For instance, Jin et. al. have reported air and moisture stable β -diketiminato-phosphane Pd complex for catalytic C-C coupling reactions.¹⁸⁻²⁰ We capitalized the embedded β -diketiminate centers in PMO to immobilize $\text{Pd}(\text{OAc})_2$, leading to a heterogeneous architecture consisting of stable PMO grafted with β -diketiminato-acetate Pd^{2+} complex for carrying out oxidation of styrene. Heterogeneous catalysis of styrene oxidation in liquid phase using PMO based catalysts have been studied in few instances where epoxide and benzaldehyde were formed as selective products.²¹⁻²⁴ To our best knowledge, this is the first demonstration of employing novel PMO based catalytic system for selective oxidation of styrene to acetophenone through Wacker reaction using H_2O_2 as oxidant. Various controlled catalytic reactions were carried out in order to establish a green catalytic process in terms of high selectivity as well as catalyst reusability.

3.2. Results and discussion

3.2.1. Synthesis of organo alkoxysilane

PMO is a unique hybrid material with a uniform molecular distribution of organic bridging units within inorganic silica network. In this context, it is important to mention that an appropriate organic bridging unit should comprise suitable complexity and molecular size along with at least two terminal alkoxysilanes. In the current work, an essential organic precursor, compound **4**, was synthesized through two-step reactions (Scheme 3.1). Throughout the synthesis, for the isolation and storage of compound **4**, moisture free and inert conditions were adopted in order to avoid unwanted polymerization of silane.

Scheme 3.1: Schematic representation of the synthesis for compounds 3 and 4.

3.2.2. Characterization of β -diketiminate incorporated PMOs

3.2.2.1. FT-IR study of PMOs

Figure 3.1: FTIR spectra of (a) PMO-1 (b) PMO-2 and (c) PMO-3.

The FT-IR spectra (Figure 3.1) of PMO-1, PMO-2 and PMO-3 (for the explanation of denotations please see Section 3.4.3) show all the characteristic peaks of typical siloxane network of mesoporous silica materials.^{25,26} Peaks in the range from 1550 to 1400 cm^{-1} (inset in Figure 3.1) are assigned to the organic unit in **4**, which can be observed in all the three FT-IR spectra, providing clear evidence of grafting compound **4** into the organosilica framework. It can also be seen from the spectra that the intensities of those peaks attributed by **4** were increased gradually upon the content increase of loading **4**. The predominant band of physisorbed water centered at 1630 cm^{-1} overlaps completely with the peaks of the C=O and C=N bonds. A broad band

around 3426 cm^{-1} is attributed to the O–H stretching vibration of hydrogen bonded silanols on PMOs.²⁷

3.2.2.2. ^{13}C and ^{29}Si solid NMR study of PMOs

Figure 3.2: ^{13}C CP MAS NMR spectra of (a) PMO-1, (b) PMO-2 and (c) PMO-3.

The ^{13}C CP–MAS NMR spectra of PMO-1, PMO-2 and PMO-3 (Figure 3.2) exhibit strong signals ranging from 9 to 42 ppm, which can be attributed to different aliphatic primary as well as secondary carbon atoms from the organic bridging unit. Strong signals from aromatic carbons on the phenyl ring can be identified at ~ 105 ppm as well as in the range from 140 to 150 ppm. In addition to these signals, two significant peaks at ~ 151 and 157 ppm are assigned to the carbons from carbamate and imine groups of the incorporated organic bridging unit, respectively. The NMR data provide a solid

Figure 3.3: ^{29}Si CP-MAS NMR spectra of (a) PMO-1, (b) PMO-2 and (c) PMO-3.

support towards the successful incorporation of compound 2 into the silica framework in all three synthesized PMOs. ^{29}Si CP-MAS NMR analysis was also carried out for all the three PMOs to realize the covalent incorporation of the organic bridging units into the inorganic siloxane network. ^{29}Si solid NMR spectra of PMO-1, PMO-2 and PMO-3 (Figure 3.3) show signals with major intensities centered at -110 and -100 ppm with a small shoulder at -90 ppm which can be attributed to Q^4 [$(\equiv\text{SiO})_4\text{Si}$], Q^3 [$(\equiv\text{SiO})_3\text{Si}(\text{OR})$] and Q^2 [$(\equiv\text{SiO})_3\text{Si}(\text{OR})_2$] respectively, where $\text{R} = \text{Et}$ or H . Along with these signals all the PMOs also displayed one more peak at -67 ppm which is corresponding to T^3 resonance from silicon species attached to the organic group [$-\text{CH}_2-\text{Si}(\text{OSi}\equiv)_3$]. Apart from T^3 signal all the spectra don't display any other signals corresponding to T^0 , T^1 and T^2 . This is solid evidence in support of complete grafting of

organic precursors in to the silica framework through the hydrolysis of terminal alkoxysilanes.

3.2.2.3. Isothermal N₂ adsorption/desorption measurements of PMOs

Figure 3.4: Isothermal N₂ adsorption/desorption plot of (a) PMO-1, (b) PMO-2 and (c) PMO-3 along with respective BJH pore size distribution plot in the inset.

The isothermal N₂ adsorption/desorption measurements were carried out for all three PMOs to determine the surface areas and pore size distributions (Figure 3.4). From the N₂ adsorption isotherm under the lowest pressure, the BET surface areas of PMO-1, PMO-2 and PMO-3 were measured to be 720 m²g⁻¹, 676 m²g⁻¹ and 712 m²g⁻¹, respectively (Table 3.1). BJH model for the pore-size distribution indicates the presence of

mesopores in all PMOs and the average pore diameter for PMO-1, PMO-2 and PMO-3 were found to be 2.7, 2.8 and 3.5 nm respectively (Table 3.1). A profound effect was observed between the loading percentages of compound **4** and the mesopore size, which can be attributed to the swelling of the pore channels caused by the addition of organic bridging molecule with high degree of complexity.

Table 3.1: BET surface area and BJH average pore diameter of PMOs

S No	Materials	BET surface area (m^2g^{-1})	BJH average pore diameter (nm)
1	PMO-1	720	2.7
2	PMO-2	676	2.8
3	PMO-3	713	3.5

3.2.2.4. Mesosstructural morphology of PMOs

Figure 3.5. TEM images of (a) PMO-1 (b) PMO-2 (c) PMO-3 (d) Pd/PMO-1 (e) Pd/PMO-2 and (f) Pd/PMO-3.

TEM analysis (Figure 3.5a, 3.5b and 3.5c) shows nice mesostructural morphologies for PMO-1, PMO-2 and PMO-3. The periodicity of mesoporous channels gradually declines upon increasing the loading percentage of organic unit in the PMO materials.

3.2.3. Synthesis and characterization of palladium loaded PMOs (Pd/PMO)

Scheme 3.2: Schematic representation for the incorporation of $\text{Pd}(\text{OAc})_2$ into the PMOs.

The incorporation of $\text{Pd}(\text{OAc})_2$ into PMOs was achieved by generating β -diketiminato-acetate Pd^{2+} complex through a method mentioning in the experimental section (Scheme 3.2). The Soxhlet extraction method was adopted to ensure the removal of free Pd^{2+} from the materials, leaving behind only the Pd^{2+} immobilized PMOs. Successful incorporation of Pd^{2+} was confirmed quantitatively through Inductively Coupled Plasma (ICP) analysis for each Pd/PMO, and the obtained results show that the Pd contents in Pd/PMO-1, Pd/PMO-2 and Pd/PMO-3 (for the explanation of denotations please see Section 3.4.4) are ~ 0.13 , 0.16 and 0.24 mmol g^{-1} respectively (Table 3.2). From EA analysis, it was found that the amount of β -diketiminato unit

present in each Pd/PMO is almost equal to the Pd content in the PMO indicating the 1:1 coordination between them (Table 3.2).

3.2.3.1. TEM study of Pd/PMOs

The TEM images (Figure 3.5) show the retention of the mesostructural morphologies for Pd/PMO-1, Pd/PMO-2 and Pd/PMO-3, which are apparently similar to that of PMO-1, PMO-2 and PMO-3. The observations indicate that the synthesized PMOs possess enough structural stability in order to maintain their morphological integrity even after the metal incorporation. In many previous reports where $\text{Pd}(\text{OAc})_2$ was attempted to load into porous materials, the black dots were observed in the TEM images of obtained materials, which may be attributed to the formation of Pd(0) nanoparticles.²⁸⁻³¹ The formation of the nanoparticles has been described as an outcome of electron-beam induced reduction of original Pd(II) species during the TEM measurements.³¹ In our Pd-loaded PMOs, however, there was no evidence for the formation of Pd nanoparticles on PMOs, which endorses the homogeneous distribution of β -diketiminato-acetate Pd^{2+} complex into PMOs.

3.2.3.2. Isothermal N_2 adsorption/desorption measurements of Pd/PMOs

A significant reduction in BET surface area was observed for all PMOs upon the incorporation of $\text{Pd}(\text{OAc})_2$ (Table 3.2 and Figure 3.6). This change can be ascribed to the fact that incorporated $\text{Pd}(\text{OAc})_2$ occupies certain amount of space inside the pores, resulting in a contraction in the pore diameter. The decrease in the average pore diameter of PMOs after the introduction of Pd^{2+} is also evidenced from the BJH average pore size distribution (Table 3.2).

Table 3.2: Analytical, textural, and porosity data of different catalysts

No	Catalyst	EA (Wt %)			Amount of β -diketiminato (mmol g^{-1})	Pd content from ICP (mmol g^{-1})		N ₂ adsorption/desorption measurements	
		C	N	H		Before catalysis	After catalysis	BET surface area ($\text{m}^2 \text{g}^{-1}$)	BJH average pore diameter (nm)
1	Pd/PMO-1	3.7	0.9	3.0	0.159	0.133	0.131 ^a	655	2.5
2	Pd/PMO-2	5.8	1.0	2.5	0.179	0.159	0.157 ^a	625	2.7
3	Pd/PMO-3	6.7	1.4	3.2	0.25	0.238	0.232 ^b	570	3.0

^aCatalyst recovered from single catalytic cycle. ^bCatalyst recovered from the 5th catalytic cycle.

Figure 3.6: Isothermal N₂ adsorption/desorption plot of (a) Pd/PMO-1, (b) Pd/PMO-2 and (c) Pd/PMO-3 along with respective BJH pore size distribution plot in the inset.

3.2.3.3. FT-IR study of Pd/PMOs

The FT-IR spectra (Figure 3.7) of Pd/PMO-1, Pd/PMO-2 and Pd/PMO-3 show all the characteristic peaks of PMOs as well as peaks of acetate groups from $\text{Pd}(\text{OAc})_2$. These IR signals provide solid evidence in support of the formation of β -diketiminato-acetate Pd^{2+} complex within PMOs. The intensities of peaks contributed by the acetate group, increases as direct function of the loading amount of compound **4** in PMOs. This is an obvious phenomenon, since the more β -diketimine units are incorporated within PMOs, the more β -diketiminato-acetate Pd^{2+} complex is formed.

Figure 3.7: FTIR spectra of (a) Pd/PMO-1 (b) Pd/PMO-2, (c) Pd/PMO-3 and (d) $\text{Pd}(\text{CH}_3\text{COO})_2$.

3.2.3.4. XPS study of Pd/PMOs

The incorporation of Pd^{2+} into PMOs through the complexation with the iminic nitrogen atoms of the β -diketiminato moiety was further investigated by high resolution

XPS. The XPS spectra of Pd/PMO-1, Pd/PMO-2 and Pd/PMO-3 are presented in the Appendix (Figures A1-A3). The high resolution XPS spectra of Pd/PMO-1, Pd/PMO-2 and Pd/PMO-3 (Figure 3.8) exhibit characteristic $3d_{5/2}$ peak with the binding energy (BE) of 337.8 eV, indicating the presence of Pd^{2+} in PMOs.³² However, the BE of $\text{Pd}_{3d_{5/2}}$ peak in the cases of Pd/PMOs shows a significant decline as compared to that (338.7 eV) of $\text{Pd}(\text{OAc})_2$. This negative shift in the BE of $\text{Pd}_{3d_{5/2}}$ peak can be attributed to the strong coordination of $\text{Pd}(\text{OAc})_2$ with the iminic nitrogen of the β -diketiminato moiety, which eventually makes the Pd^{2+} species less electron deficient. On account of this observation, a rational conclusion regarding the successful immobilization of β -diketiminato-acetate Pd^{2+} complex within PMOs can be reached.

Figure 3.8. High-resolution XPS spectra at the 3d region for (a) Pd/PMO-1 (b) Pd/PMO-2, (c) Pd/PMO-3 and (d) $\text{Pd}(\text{OAc})_2$.

3.2.4. Catalytic tests

Table 3.3: Catalytic activities of different catalysts in terms of styrene conversion and selectivity of different products.^a

No	Catalyst	Reaction time (h)	Conversion of styrene (mol%)	Selectivity of products (mol %)			TOF ^b (h ⁻¹)
				Acetophenone	Benzaldehyde	Benzoic acid	
1	---	10	3	---	65	35	0
2	Pd/PMO-1	5	51	>99	Trace	---	20.2
3	Pd/PMO-2	5	66	>99	Trace	---	26.1
4	Pd/PMO-3	5	75	>99	Trace	---	29.7

^a Reaction conditions: Styrene/H₂O₂ = 1:3 (mole ratio), Styrene/catalyst = 200:1 (mole ratio), acetonitrile as solvent at 60 °C. ^b TOF: Turn over frequency i.e. moles of substrate converted per mole of active catalytic centre per hour.

Catalytic activity of different Pd/PMO catalysts for the oxidation of styrene was evaluated at 60 °C using acetonitrile as solvent and H₂O₂ as oxidant. From the results (Table 3.3), it is evident that all the Pd/PMOs offer nearly 100% selectivity towards the production of acetophenone (SA), which is in contrast to many other reports where benzaldehyde was the predominant product by using Pd²⁺ as catalyst without co-catalyst.⁸ Amongst three Pd/PMO catalysts, Pd/PMO-3 demonstrated the highest catalytic activity (Table 3.3, entry 4) under the given reaction conditions. Due to the low Pd loading in Pd/PMO-1 and Pd/PMO-2, the required amount of solid catalysts is much high which made the catalyst suspended reaction mixture very dense. Consequently the mobility of substrate containing solvent reduces markedly making it becomes difficult for the substrate to diffuse effectively into the pore channel. Moreover, most of the substrate got absorbed on the surface of PMO and remained unreacted due to low density of catalytic site on the surface of PMO. These are the primary reasons responsible for the low conversion and TOF observed in case of Pd/PMO-1 and Pd/PMO-2.

Series of reactions were carried out by varying the solvent volume and a profound effect has been observed (Figure 3.9). Poor catalytic activity for each was observed when volume of solvent was as low as 20 ml which can be improved by increasing the same. However a slight decrease of activity in case of Pd/PMO-3 was also observed upon the increase of solvent volume mainly due to the high dilution effect. On the other hand, severely poor conversion of styrene was observed in the absence of any Pd/PMO catalyst even after 12 h of reaction, resulting in preferential production of benzaldehyde and benzoic acid (Table 3.3, entry 1).

Figure 3.9: Catalytic activities of Pd/PMO-1, Pd/PMO-2 and Pd/PMO-3 in terms of TOF for acetophenone as a function of solvent volume. Reaction conditions: Styrene/H₂O₂ = 1:3 (mole ratio), Styrene/catalyst = 200:1 (mole ratio), acetonitrile as solvent at 60 °C.

A series of catalytic experiments using the best catalyst, i.e. Pd/PMO-3, were carried out in order to understand the variation from styrene to acetophenone as a function of reaction time (Figure 3.10). The results indicate that the conversion rate increases quite remarkably upon increasing the time of the reaction, along with the conversion enhancement from 40% for 3 h of reaction to 100% for 10 h of reaction. But the highest TOF for the catalyst under given re-

action conditions was observed at 5 h and it was recorded as 29.7 h^{-1} . Apparent decrease of TOF upon increasing the reaction time is due to the formation of benzaldehyde and benzoic acid, which were observed in the absence of the catalysts. When the reaction continued up to 12 h, the SA was further decreased to 92%, giving rise to few other byproducts.

Figure 3.10: Catalytic activities of Pd/PMO-3 in terms of styrene conversion and selectivity of different products as a function of reaction time. Reaction conditions: Styrene/ H_2O_2 = 1:3 (mole ratio), Styrene/catalyst = 200:1 (mole ratio), acetonitrile as solvent at 60°C .

It has been well-known that catalytic oxidation of styrene using H_2O_2 as oxidant can undergo different pathways to afford various possible oxidized products, such as styrene oxide, benzaldehyde, benzoic acid, 1-phenylethane-1,2-diol, and phenylacetaldehyde primarily via Path 1 as well as acetophenone and 1,3-diphenyl-1-butene mainly via Path 2 (Scheme 3.3).^{15,33} Based on our result (Table 3.3, entry 1), in the absence of any catalyst, styrene undergoes Path 1 to afford benzaldehyde, which is further oxidized to produce benzoic acid. Upon the introduction of Pd/PMO catalysts, styrene adopts Path 2 to give acetophenone. All the three Pd/PMOs prefer Path 2 over Path 1. As a result, markedly high SA was able to achieve.

Scheme 3.3: Possible catalytic products from the oxidation of styrene.

Based upon previously reported work,^{15,34} we proposed an analogous catalytic mechanism using Pd/PMO catalysts for selective oxidation of styrene to acetophenone with H_2O_2 as oxidant in the absence of copper or indium salts as co-catalyst (Scheme 3.4). According to our proposed mechanism, immobilized Pd^{2+} forms a palladium hydroperoxidic species by the addition of H_2O_2 (Scheme 3.4, step 1). This species is responsible for transferring oxygen to the olefin through a pseudocyclic hydroperoxypalladation process of the coordinated olefin, leading to the corresponding ketone and palladium hydroxyl species (Scheme 3.4, step 3). In the presence of an additional H_2O_2 , this palladium hydroxyl species regenerates the palladium hydroperoxidic species, completing the catalytic cycle (Scheme 3.4, step 4). The fate of the intermediate, palladium hydroxyl species, could be different in case of lacking H_2O_2 , where dehydroxypalladation will take place, affording $\text{Pd}(0)$ and causing the deactivation of

the catalysts (Scheme 3.4, step 5). Thus, less amount of H_2O_2 always disfavors the regeneration of active Pd^{2+} species.

Scheme 3.4: Proposed catalytic mechanism of using Pd/PMO catalysts for selective oxidation of styrene to acetophenone with H_2O_2 as oxidant.

In order to prove our hypothesized mechanism, another series of catalytic reactions were carried out to realize the variation of the conversion and selectivity as a function of different H_2O_2 : styrene molar ratio (H:S). The obtained results (Figure 3.11) indicate that the conversion rate increases quite remarkably as the ratio is increased, along with the conversion enhancement from 26% for a ratio of 1:1 to 84% for a ratio of 5:1. A consistent selectivity of 100% for the SA was observed when the H:S was up to 3:1. Furthermore the SA decreases to 93% and 90% for the H:S of 4:1 and 5:1, respectively. This apparent decrease in the SA upon increasing the H:S molar ratio is due to the formation of benzaldehyde and benzoic acid

through Path 1 (Scheme 3.3) under the influence of high concentration of oxidant. But the TOF has followed an increasing trend upon the increase of H:S under given reaction time mainly due to increase in the total conversion of styrene to acetophenone (Figure 3.11), So far, all experiments were carried out by adding H_2O_2 in several portions over a long period of time, preventing the rapid decomposition of H_2O_2 .

Figure 3.11: Catalytic activities of Pd/PMO-3 in terms of TOF for acetophenone as a function of H_2O_2 :styrene ratios.

Similar catalytic tests were performed for the H:S ratios of 3:1, 4:1 and 5:1, where H_2O_2 was added in a single portion at the beginning of the reaction. A significant decrease of styrene conversion was observed, which can be attributed to the unwanted decomposition of H_2O_2 (Figure 3.11). In addition, the SA was also decreased significantly resulting much lower TOF as compared to the previous cases where H_2O_2 was added in several portions over a long period of time (Figure 3.11). The deactivation of catalytic activity can be ascribed to the for-

mation of Pd(0) species on account of rapid decomposition of H_2O_2 resulting in incomplete catalytic cycle (Scheme 3.4, step 5). The formation of metallic Pd(0) nanoparticles was observed in the catalysts used in the reactions with one portion addition of H_2O_2 , whereas similar nanoparticles cannot be observed in the catalysts used in the previous cases with several portion additions of H_2O_2 (Figure 3.13 d & e). Thus, it can be concluded that prolonged addition of H_2O_2 supplies accessible peroxide during the course of the reaction, inhibiting the catalyst deactivation.

Figure 3.12: Catalytic activities of Pd/PMO-3 in terms of styrene conversion and selectivity of different products as a function of H_2O_2 :styrene ratios. Reaction conditions: Styrene/catalyst = 200:1 (mole ratio), 30 mL of acetonitrile as solvent at 60 °C.

Figure 3.13: TEM image of Pd/PMO-3 (a) before catalysis; (b) after the 5th cycle of catalysis with 5 h of reaction time; (d) after catalysis done by adding H₂O₂ in a single addition with a H:S of 5:1; (f) after the 2nd cycle of catalysis with 10 h of reaction time; (g) after the 4th cycle of catalysis with 10 h of reaction time. (c), (e) and (h) are respective XPS spectra of b, d and g.

Figure 3.14: Catalytic recycling experiments of Pd/PMO-3 by maintaining reaction time of 5 h in each cycle. Reaction conditions: Styrene/H₂O₂ = 1:3 (mole ratio) with a slow addition of oxidant, Styrene/catalyst = 200:1 (mole ratio), 30 ml of acetonitrile as solvent at 60 °C.

In the catalytic recycling experiments, reactions were carried out for 5 h and 10 h, respectively, by maintaining a slow addition of H₂O₂ over a period of 3 h with an H:S ratio of 3:1. In the case of 5 h reactions (Figure 3.14), Pd/PMO-3 presents a tremendous recyclability towards the acetophenone formation over 99% conversion of styrene up to 3 cycles. A slight catalytic deactivation was observed in the 4th and 5th catalytic cycles, although it was not significant. The ICP analysis of the reaction mixture as well as Pd/PMO-3 after the 5th cycle revealed no metal leaching during the catalysis. The ICP analysis of Pd/PMO-3 recovered after the 5th cycle of catalysis also eliminates the metal leaching from the solid catalyst (Table 3.2). Moreover, the formation of unwanted Pd(0) nanoparticles was also ruled out on the basis of the evidence obtained from the TEM and XPS experiments of the used catalyst (Figure 3.13 b & c). On the other hand, progressive decreases in the conversion as well as in SA were observed when the catalytic recycling experiment of Pd/PMO-3 was carried out for 10 h

(Figure 3.15). The severe deactivation of Pd/PMO-3 can be attributed to the progressive formation of Pd(0) nanoparticles, which were observed in the TEM images (Figure 3.13 f, g & h). The reason is that, when the reaction was carried out for 10 h, the amount of H_2O_2 decreased remarkably, resulting in the formation of Pd(0).

Figure 3.15: Catalytic recycling experiments of Pd/PMO-3 by maintaining reaction time of 10 h in each cycle. Reaction conditions: Styrene/ H_2O_2 = 1:3 (mole ratio) with a slow addition of oxidant, Styrene/catalyst = 200:1 (mole ratio), 30 ml of acetonitrile as solvent at 60 °C.

3.3. Conclusion

In conclusion, we have successfully synthesized a type of novel PMOs using β -diketiminate as the bridging unit in the silica network. Highly mesoporous architecture together with the β -diketimine centers render the PMOs to serve as an ideal scaffold for coordinating with $\text{Pd}(\text{OAc})_2$ for catalysis. The robust incorporation of $\text{Pd}(\text{OAc})_2$ into the PMOs through the formation of β -diketiminato-acetate Pd^{2+} complex facilitates homogeneous distribution of metal cation and prevents the formation of Pd(0) nanoparticles. The profound influence of H_2O_2 in the catalysis as well as the catalyst regeneration has been explored experimentally.

For the purpose of catalytic application, it has been demonstrated that the incorporation of a homogeneous catalyst, Pd(OAc)₂, into PMOs not only improves the selective conversion of styrene towards the acetophenone production, but also affords an excellent recyclability of the heterogeneous PMO catalyst, making the catalytic process more benign from environmental and commercial point of view. Thus, the current work presents a robust heterogeneous green catalyst for direct production of acetophenone from styrene with significantly high catalytic conversion, selectivity, and recyclability.³⁶

3.4. Experimental

3.4.1. Synthesis of β -diketimine (**1**)

β -Diketimine was synthesized according to a reported method with some modifications.¹⁸ In a typical synthesis of **1**, acetylacetone (1.0 g, 10 mmol) and 4-aminophenol (2.18 g, 20 mmol) were dissolved in absolute EtOH (50 mL) in a round bottom flask (100 mL) along with a magnetic stir bar inside. To the above mixture, conc. HCl (0.5 g) was added. After the reaction mixture was refluxed for 3 days, the mixture was cooled down to room temperature and treated with water (20 mL) containing Na₂CO₃. The solution was extracted with dichloromethane three times (20 mL each). The organic layers were dried through MgSO₄ and then concentrated under reduced pressure. The solid product was washed with cold ethanol and dried under vacuum to give compound **1**. ¹H NMR (CD₃OD, 300 MHz,) δ 7.30 (d, 4H), 6.72 (d, 4H), 2.08 (s, 6H), 1.29 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ ppm= 158.9, 153.4, 142.3, 121.2, 118.6, 40.0, 23.2; IR: ν = 3430, 3062, 2852, 1680, 1610, 1594 cm⁻¹; MS: calcd

for $C_{17}H_{18}N_2O_2$ $m/z = 282$, found: $m/z = 282$. Elemental analysis: calcd %: C 72.32, H 6.43, N 9.92, found %: C 72.88, H 6.08, N 10.1.

3.4.2. Synthesis of β -diketiminato bis(4,1-phenylene) bis(3-triethoxysilylpropylcarbamate) (2)

In a typical synthesis of **2**, synthesized compound **1** (1.0 g, 3.5 mmol) was dissolved in dry THF (50 mL) under N_2 in a two-necked round-bottom flask equipped with a condenser. 3-Isocyanatopropyltriethoxysilane (1.75 g, 7 mmol) was then added dropwise to the solution over 30 min. After the reaction mixture was allowed to reflux for 24 h, the reaction mixture was cooled down to room temperature. THF solvent was removed in vacuo, leaving a highly viscous liquid. Hexane was added to the viscous liquid and the precipitates were formed to afford compound **2**. 1H NMR (CD_3OD , 300 MHz,) δ 7.54 (d, 4H), 7.04 (d, 4H), 3.84 (q, 12H), 3.16 (t, 4H), 2.11 (s, 6H), 1.64 (s, 2H), 1.22 (t, 18H), 0.66 (t, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm= 159.4, 151.8 149.4, 144.2, 124.2, 121.0, 57.8, 45.0, 40.2, 24.8, 22.9, 18.4, 11.2; IR: $\nu = 3323, 2976-2887, 1714, 1670, 1551, 1506, 1207, 1082\text{ cm}^{-1}$; MS: calcd for $C_{37}H_{60}N_4O_{10}Si_2$ $m/z = 777$, found: $m/z = 778$ $[M+H]^+$. Elemental analysis: calcd %: C 57.19, H 7.78, N 7.21, found %: C 57.01, H 8.19, N 7.43.

3.4.3. Synthesis of PMO by hydrothermal process

PMO was prepared according to a reported method with some modifications.³⁵ Compound **2** and TEOS were used as silica sources and CTAB was used as the structure-directing agent. A gel was formed with a particular molar ratio of Si : CTAB : NH_3 (20%) : H_2O : EtOH = 1.0 : 0.12 : 8.0 : 114 : 10. Three different molar ratios of **2** to TEOS including 2%, 5% and 10% were used, leading to PMO-1, PMO-2, and PMO-3, respectively. In a typical synthesis of

PMO with 2% of **2**, CTAB (1.5 g, 4.1 mmol) was dissolved in H₂O (70 mL), and then NH₃ solution (20 mL, 25%) was added to the above solution. The mixture solution was stirred at 40 °C for 30 min to give a clear solution. A premixed solution of **2** (0.47 g, 0.6 mmol) and TEOS (5.8 g, 28.0 mmol) in EtOH (18 mL) was added to the above solution under vigorous stirring. After reacting for 2 h, the resulted gel was transferred to a polyethylene container and then heated to 90 °C for 4 d. The solid obtained was washed with H₂O and dried in air at 60 °C. The structure-directing agent was finally removed by extraction of the solid with dilute ethanolic HCl solution (20 mL of 0.5 M ethanolic HCl for 0.5 g of solid) at 40 °C for 2 h. PMO was obtained by filtration and dried in vacuo.

3.4.4. Synthesis of PMOs containing Pd complex (Pd/PMO-n)

In a typical synthesis of Pd/PMO, Pd(OAc)₂ (23 mg, 0.1 mmol) was dissolved in dry dichloromethane (10 mL), and then PMO-n (200 mg) was added. The mixture was stirring at room temperature for 24 h. The resulted solid was isolated by centrifugation and washed with dichloromethane using Soxhlet extraction for another 24 h, and then dried at 80 °C under vacuum for 12 h to yield a brown powder. After the incorporation of Pd(OAc)₂ into PMO-1, PMO-2 and PMO-3, the resulted materials were denoted as Pd/PMO-1, Pd/PMO-2 and Pd/PMO-3, respectively.

3.4.5. Catalytic tests

The catalytic tests were carried out in a two-necked round bottom flask. In a typical experiment, styrene (1.04 g, 10 mmol) was added to an acetonitrile solution (30 mL) containing Pd/PMO-n as catalyst. In order to avoid immediate decomposition of H₂O₂ and its strong effervescence, 30% H₂O₂ (3.4 g, 30 mmol) was added slowly to the mixture solution over a

period of 3 h. The resulting mixture was stirred under 400 rpm at 60 °C for 5 h. The products were then quantified using GC-MS for determining the response factors of the reactants and products individually. Then, the solvent from the reaction mixture was evaporated under vacuum and the crude product was purified by column chromatograph using silica gel with *n*-hexane/ethyl acetate (v/v 5:1) as eluent. The product acetophenone was obtained as a colorless liquid. Isolated product was also weighed to validate the GC-MS result and characterized by MS and NMR.

In order to check the catalyst recyclability, catalyst from the reaction mixture was recovered by centrifugation followed by washing with acetonitrile for several times. The recovered catalysts were kept under vacuum oven for complete dryness before using for the subsequent catalysis or various characterizations.

3.4.6. Characterization

^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometer operating at 400 MHz. The solid-state spectra were collected on an ECA400 NMR spectrometer (JEOL, 400 MHz), using a 4 mm CP/MAS probe at room temperature. TEM images were collected on a JEOL JEM-1400 instrument operated at 100 kV. FT-IR spectra were recorded as KBr pellets on a SHIMADZU IRPrestige-21 spectrometer with the sample powder diluted in KBr (1%). N_2 adsorption/desorption measurements for BET and BJH calculations were obtained using an autosorp-IQ instrument from Quantachrome Instruments Corporation. The BET method was utilized to calculate the specific surface areas of the materials whereas the BJH model derived from desorption branches of isotherms was adopted for the pore-size distributions of the PMOs. The

TEM images were obtained using a JEOL 2010. EA was obtained from EuroVector Euro EA Elemental Analyzer. Thermo Fischer iCAP 6000 series ICP-OES was used for performing trace metal analysis. XPS analysis was done by a SPECS HSA3500 plus spectrometer using Mg X-ray source. Quadrupole ion trap Mass Spectrometer equipped with Thermo Accela LC was used for analysis of catalytic reactions.

3.5. References

- (1) Gooßen, L.; Baumann, K. In *Handbook of C–H Transformations*; Wiley-VCH Verlag GmbH: 2008, p 277.
- (2) Tsuji, J. In *Palladium Reagents and Catalysts*; John Wiley & Sons, Ltd: 2005, p 27.
- (3) Lloyd, W. G.; Luberoff, B. J. *J. Org. Chem.* **1969**, *34*, 3949.
- (4) Barak, G.; Sasson, Y. *J. Chem. Soc., Chem. Commun.* **1987**, *0*, 1266.
- (5) Namboodiri, V. V.; Varma, R. S.; Sahle-Demessie, E.; Pillai, U. R. *Green Chem.* **2002**, *4*, 170.
- (6) Zhang, G.; Xie, X.; Wang, Y.; Wen, X.; Zhao, Y.; Ding, C. *Org. Biomol. Chem.* **2013**.
- (7) Wang, X.; Venkataramanan, N. S.; Kawanami, H.; Ikushima, Y. *Green Chem.* **2007**, *9*, 1352.
- (8) Feng, B.; Hou, Z.; Wang, X.; Hu, Y.; Li, H.; Qiao, Y. *Green Chem.* **2009**, *11*, 1446.
- (9) Ahn, J.-H.; Sherrington, D. C. *Macromolecules* **1996**, *29*, 4164.

-
- (10) Alandis, N.; Ricolattes, I.; Lattes, A. *New J. Chem.* **1994**, 18, 1147.
- (11) Maksimov, A. L.; Buchneva, T. S.; Karakhanov, E. A. *J. Mol. Catal. A* **2004**, 217, 59.
- (12) Betzemeier, B.; Lhermitte, F.; Knochel, P. *Tetrahedron Lett.* **1998**, 39, 6667.
- (13) Haimov, A.; Neumann, R. *Chem. Commun.* **2002**, 0, 876.
- (14) Jiang, H.; Jia, L.; Li, J. *Green Chem.* **2000**, 2, 161.
- (15) Chiappe, C.; Sanzone, A.; Dyson, P. J. *Green Chem.* **2011**, 13, 1437.
- (16) Franceschini, P. L.; Morstein, M.; Berke, H.; Schmale, H. W. *Inorg. Chem.* **2003**, 42, 7273.
- (17) Hadzovic, A.; Song, D. *Organometallics* **2008**, 27, 1290.
- (18) Lee, D.-H.; Jin, M.-J. *Organic Letters* **2010**, 13, 252.
- (19) Lee, D.-H.; Jung, J.-Y.; Jin, M.-J. *Chem. Commun.* **2010**, 46, 9046.
- (20) Lee, D.-H.; Taher, A.; Hossain, S.; Jin, M.-J. *Org. Lett.* **2011**, 13, 5540.
- (21) Shylesh, S.; Singh, A. P. *Microporous Mesoporous Mater.* **2006**, 94, 127.
- (22) Jin, Y.; Wang, P.; Yin, D.; Liu, J.; Qiu, H.; Yu, N. *Microporous Mesoporous Mater.* **2008**, 111, 569.
- (23) Hu, J.; Wu, Q.; Li, W.; Ma, L.; Su, F.; Guo, Y.; Qiu, Y. *ChemSusChem* **2011**, 4, 1813.
- (24) Modak, A.; Nandi, M.; Bhaumik, A. *Catal. Today* **2012**, 198, 45.
- (25) Silva, A. R.; Wilson, K.; Whitwood, A. C.; Clark, J. H.; Freire, C. *Eur. J. Inorg. Chem.* **2006**, 1275.
- (26) Jarrais, B.; Pereira, C.; Silva, A. R.; Carvalho, A. P.; Pires, J.; Freire, C. *Polyhedron* **2009**, 28, 994.
-

- (27) Chakraborty, B.; Viswanathan, B. *Catal. Today* **1999**, *49*, 253.
- (28) Hou, Z.; Theyssen, N.; Brinkmann, A.; Klementiev, K. V.; Grünert, W.; Bühl, M.; Schmidt, W.; Spliethoff, B.; Tesche, B.; Weidenthaler, C.; Leitner, W. *J. Catal.* **2008**, *258*, 315.
- (29) Sacco, L.; Lambert, S.; Pirard, J.-P.; Noels, A. F. *J. Catal.* **2005**, *232*, 51.
- (30) Kong, G.-Q.; Ou, S.; Zou, C.; Wu, C.-D. *J. Am. Chem. Soc.* **2012**, *134*, 19851.
- (31) Ding, S.-Y.; Gao, J.; Wang, Q.; Zhang, Y.; Song, W.-G.; Su, C.-Y.; Wang, W. *J. Am. Chem. Soc.* **2011**, *133*, 19816.
- (32) Borah, P.; Ramesh, A.; Datta, A. *Catal. Commun.* **2010**, *12*, 110.
- (33) Maurya, M. R.; Kumar, M.; Kumar, U. *J. Mol. Catal. A* **2007**, *273*, 133.
- (34) Roussel, M.; Mimoun, H. *J. Org. Chem.* **1980**, *45*, 5387.
- (35) Baleizao, C.; Gigante, B.; Das, D.; Alvaro, M.; Garcia, H.; Corma, A. *Chem. Commun.* **2003**, 1860.
- (36) Borah, P.; Zhao, Y. *J. Catal.* **2014**, *318*, 43.

Chapter 4: Synthesis of Urea Bridged PMO: A Heterogeneous Cooperative Organocatalyst for Henry Reaction

Abstract

A new urea-containing PMO was synthesized with excellent efficacy as a heterogeneous hydrogen bond donor (HBD) organocatalyst. However urea is often suffering from unwanted self-recognition and aggregation, resulting in loss of HBD catalytic competency. By embedding urea uniformly on the surface of silica network by the virtue of PMO preparation, we have able to revive the HBD catalytic ability of urea for Henry reaction with various substrates. Moreover the organic bridge of the PMO also contains a pyridine unit along with the urea linkages which eventually also acted as base to carry out the Henry reactions. The concept of constructing novel urea-pyridine bridged PMO with cooperative catalytic ability is the first approach so far in the field of PMO to conserve the HBD ability of urea towards the activation of electrophile through catalyst spatial isolation.

4.1. Introduction

Etymologically the term ‘organocatalysis’ means the use of small organic molecules to catalyze various organic transformations. In other words, it refers those catalytic organic transformations which are accelerated with the help of substoichiometric amount of organic molecule which doesn’t contain metal atoms. This fascinating area of research is a relatively new and over the past decade it has been emerged as a new dimension of synthetic organic chemistry. Being a part of green chemistry, organocatalytic methods often offer less expensive and more ecological alternative to metal carbenoid processes. These organocatalysts have the ability to interact with various substrates by the virtue of either Lewis acidity-basic or Brønsted acidity-basicity providing distinct reactivity, activity, and selectivity in the reactions.¹ Organocatalysts are often used to carry out nucleophile–electrophile reactions. Initially the activation of an electrophile in such reactions were carried out under the influence of a metal-based (or metal-ion based) Lewis acids which can accelerate the rate of the reaction by decreasing the energy of the lowest unoccupied molecular orbital (LUMO) of electrophile through the formation of a dative bond.² Last four decades extensive amount of research were done to develop many Lewis acidic metal based catalysts with advanced ligand designing - both chiral and achiral, which certainly helped to accelerate the synthetic organic chemistry. Likewise the Lewis acids, Brønsted acids also have the ability to catalyze various reactions which can be observed mainly in biocatalysis which includes a diverse array of reactions such as acyl and phosphoryl transfer, carbonyl addition, and pericyclic processes.^{3,4} In these reactions, it is the hydrogen bond (H-bond) interaction which features as Brønsted acid catalyst. Very recently electrophile activation by H-bond donors has emerged as new catalytic strategy in synthetic organic

chemistry including enantioselective catalysis. Among various types of organocatalysis, HBD catalysis is one of the special class biomimetic alternatives to Lewis acid activation which can aid in accelerating nucleophilic attack.^{2,5-7} In such catalysis, the catalyst coordinates to the electronegative atom (such as oxygen) on the reactant through H-bonding, decrease the electron density of the reactant species thus, activating it towards nucleophilic attack. A good hydrogen bond catalysis can be defined by having modest acidity ($pK_a \sim 30 - 5$), low dimerization potential and induce directionality within the substrate.⁶ Urea and thiourea are two the most applicable classes which have the potential to use as double H-bond donor in organocatalysis. Most of the HBD catalysts have been designed for liquid phase homogeneous catalysis. Thus solubility of the catalyst plays an important role towards the catalytic activity. Although urea is a potential HBD catalyst, it is greatly frowned upon due to its high propensity to dimerize attributed by its oxygen's ability to accept an H-bond.^{2,8} This unwanted and unproductive self-assembly behavior of urea significantly decreases the solubility leading to a potential decrease in catalytic reactivity. In case of homogeneous catalysis to avoid these problems often associated with the use of urea as HBD catalysts, more soluble thiourea analogues were investigated. The replacement of urea by thiourea rules out the possibility of self-assembly through the strong intermolecular H-bonding. But this new strategy often accompanied by poor thermal stability of thiourea group which restricts the applicability of these catalysts in broader range.⁸

Another smart way to improve the catalytic efficacy of homogeneous catalysts those are more inclined to self-quenching is via heterogenization. Moreover, organocatalysts are often associated with relatively low turnover efficiency which hinders organocatalytic reactions in large-scale synthesis making them incompetent for industrial usage.¹ This low TOF issue associated with organocatalysts can be circumvented by applying high loading and recycling

of catalysts. Heterogenization of those organocatalysts is only possible solution to get rid of such problems. But surprisingly only a few successful attempts have been reported so far regarding the incorporation of homogeneous HBD molecule into the solid architecture. Among these examples most of the solid HBD catalysts were prepared by post modification of the surface of various solid supports such as polymer,⁹ mesoporous silica,¹⁰ MOF etc.¹¹ However, the complex and expensive synthetic process, lack of stability due to the possibility of structural collapse and presence of metal in the framework make the MOF less compatible as solid support in heterogeneous catalysis than the other counterparts such as mesoporous silica, POP, zeolites etc. Although the successful preparation of urea based HBD supported on polymer,⁹ and mesoporous silica by post grafting method were reported but the probability of catalytic quenching of urea due to the dimerization with neighboring urea units cannot be overlooked (Scheme 4.1). Furthermore, post grafting method always enhances the unwanted hindrance inside the pore channels of the support materials making it difficult for substrate molecules' accessibility through diffusion during the reaction.

Scheme 4.1: Self-quenching of urea unit due to the dimerization with neighboring units after post grafting methods.

In order to circumvent the problems associated with urea as organocatalyst, we have designed a novel PMO incorporated with urea groups on the pore walls of PMO. This project seeks to explore the possibility of utilizing a urea class organic group as a precursor for

functionalizing PMO for HBD catalysis. Hence, since double hydrogen bonding is preferred for increasing the strength and directionality, 1,1'-(pyridine-2,6-diyl)bis(3-(3-(triethoxysilyl)propyl)urea) has been chosen as a precursor for PMO synthesis. This will restrict the anchored urea units from unwanted dimerization, unleashing its great potential in hydrogen bond catalysis activity. Through the preparation of PMO we can achieve hybrid material with the highest density of the organic functional groups. Since the organic groups are an integral part of the wall, it solves the problem of the reduction on pore size upon the incorporating organic groups in silica framework. Furthermore, it is highly homogeneous, even more than using co-condensation method. Moreover this PMO will serve as a heterogeneous architecture of organo-urea for heterogeneous catalysis which is essential for green catalysis. As a matter of fact, the predominant constituent of PMO is silica which is one of the most abundant elements on earth which makes the catalysts more benign from environmental as well as economical points of view.

This project aims to investigate the viability of incorporating urea groups in PMO to improve its HBD catalytic ability in heterogeneous phase which was evaluated by carrying out Henry reaction as model reaction. The Henry or nitroaldol reaction is a widely used classical reaction where diastereomeric mixtures of 2-nitroalcohols are formed on treatment of primary or secondary nitroalkanes and carbonyl derivatives in presence of a base through the formation of a new C-C bond. This reaction is the easiest pathway to generate pharmacologically important β -aminoalcohols derivatives including chloramphenicol, ephedrine, norephedrine and anthracycline antibiotics. But under various basic catalytic conditions, Henry reaction are often effected by other unwanted sides reactions such as aldol condensations and Cannizzarro reactions when acidic proton is present at α -carbon in the carbonyl sources. In general, Henry reaction requires a base which deprotonates the

nitroalkane on the α -carbon position forming a resonance stabilized anion followed by alkylation of the nitroalkane with the carbonyl. Motives behind choosing this reaction to evaluate catalytic activity of PMOs are: 1) to utilize urea as HBD catalyst to activate the LUMO of electrophile, 2) to exploit the basicity of pyridine unit present in the PMO-1 as co-operative catalyst which is selective enough to facilitate only Henry reaction without any side reactions and 3) to elevate the acidity of the proton on the α -carbon position of the nitroalkane due to the ability of urea to form H-bond with nitro group as well.

4.2. Results and discussion

4.2.1. Synthesis of organo alkoxy silane

Scheme 4.2: Schematic representation of the synthetic route for the organic silane precursor (3).

In order to prepare a PMO for catalytic applications, it is desirable to have a high degree of functionality within PMO by choosing an organic precursor with at least two terminal alkoxy silanes.¹²⁻¹⁴ In the current work, an essential organic precursor (3) with two urea linkages in it was synthesized (Scheme 4.2) through condensation between the amino group of 1 and the isocyanato unit of 2. Synthesis of such molecule has already been reported¹⁵ although never has been utilized for the preparation of PMO. The primary motivation behind choosing 3 as organic bridge in the PMO is to utilize its urea linkages for HBD catalysis as well as the pyridine unit as base to abstract proton. Using 3 as organic bridges, a novel PMO was synthesized through the co-condensation with TEOS using CTAB as SDAs under basic

condition. The prepared PMO grafted with **3** has been denoted as Urea/PMO for further discussion.

4.2.2. FT-IR study

Figure 4.1: FT-IR spectra of (a) compound **3** and (b) Urea/PMO.

The FT-IR spectrum (Figure 4.1a) of the organic precursor **3** revealed characteristic peaks at 1665 cm^{-1} which can be assigned to C=O stretching and the signals centered at 1445 cm^{-1} and 3248 cm^{-1} are accountable for the presence of N-H. The presence of these peaks gives evidences of the successful synthesis of our desired urea precursor. Furthermore, peaks at around 1072 cm^{-1} are attributed to Si-O-C indicating the successful silylation of the precursor. These characteristics peaks offered by the various functionalities such as C=O and C-N stretching from **3** can be observed in the FT-IR spectrum of Urea/PMO (Figure 4.1b) in

the range of 1600 to 1400 cm^{-1} . This provides clear evidence of the successful grafting of the precursor unit onto the organosilica framework. However, the predominant band at 1670 cm^{-1} to 1640 cm^{-1} is attributed to the bending frequency from surface absorbed H_2O molecules which unfortunately masked few other important signals attributed by **3**. The FT-IR spectrum of Urea/PMO (Figure 4.1b) has also shown the characteristic peaks of Si-O stretching at 1084 and 1231 cm^{-1} and Si-C stretching at 962 cm^{-1} , indicating the formation of network of silica. Furthermore, a broad band around 3426 cm^{-1} is attributed to the O-H stretching vibration of hydrogen bonded silanols on PMO.

4.2.3. ^{13}C and ^{29}Si solid NMR study of PMOs

Figure 4.2: ^{13}C CP-MAS solid state NMR of (a) Urea/PMO and (b) Urea/PMO_U^a.

^a catalyst recovered after 6 cycles of catalysis.

The ^{13}C CP-MAS NMR spectrum of Urea/PMO (Figure 4.2a) displays clear evidence in support of the successful incorporation of compound **3** into the silica framework. The respective ^{13}C CP-MAS solid state NMR (Figure 4.2a) exhibits strong signals ranging from 10 to 43 ppm, which can be attributed to different aliphatic primary and secondary carbon atoms from the organic bridging unit (**3**). Strong signals from aromatic carbons on the pyridine ring can be identified at ~105 ppm as well as in the range from 140 to 160 ppm. In addition to these signals, one strong signal at 151.6 ppm can be assigned to the carbonyl carbon from urea linkage. The same characteristic signals were even observed from the recovered Urea/PMO_U catalyst after 6 consecutive cycles of catalysis. It is a solid evidence to realize that the organic moiety within the silica framework in PMO is stable enough for prolonged catalytic usage. ^{29}Si CP-MAS NMR analysis was also carried out for Urea/PMO to realize the covalent incorporation of the organic bridge (**3**) into the inorganic siloxane network. ^{29}Si NMR spectra of Urea/PMO (Figure 4.3a) show signals with major intensities centered at -110 and -100 ppm with a small shoulder at -90 ppm which can be attributed to Q^4 [$(=\text{SiO})_4\text{Si}$] and Q^3 [$(=\text{SiO})_3\text{Si}(\text{OR})$] respectively, where R = Et or H. Along with these signals prepared Urea/PMO also displayed one more peak at -64 ppm which is corresponding to T^3 resonance from silicon species attached to the organic group [$-\text{CH}_2-\text{Si}(\text{OSi}\equiv)_3$]. Apart from T^3 signal the spectrum doesn't display any other signals corresponding to T^0 , T^1 and T^2 . This is solid evidence in support of complete grafting of organic precursors in to the silica framework through the hydrolysis of terminal alkoxysilanes. The ^{29}Si CP-MAS NMR spectrum for Urea/PMO_U (Figure 4.3b) is essentially similar to its pristine condition revealing the stable grafting of **3** in the polysiloxane network.

Figure 4.3: ^{29}Si CP MAS NMR spectra of (a) Urea/PMO and (b) Urea/PMO_U.

4.2.4. Isothermal N_2 adsorption/desorption measurements of PMOs

Figure 4.4: Isothermal N_2 adsorption/desorption plot of Urea/PMO (black) and Urea/PMO_U (red) along with respective BJH pore size distribution plot in the inset.

The isothermal N₂ adsorption/desorption measurements were carried out for Urea/PMO and the same catalyst after 6 cycles of catalysis (Urea/PMO_U) to determine the surface areas and pore size distributions (Table 4.1). From the N₂ adsorption isotherm under the lowest pressure, BET surface area of Urea/PMO was measured to be 951 m²g⁻¹ and BJH model for the pore-size distribution indicates the presence of mesopores with an average pore diameter 3.8 nm. While the same analysis were carried out for the Urea/PMO_U catalysts recovered after 6 cycles of catalysis, a slight decrease in the BET surface area was observed which was found to be 892 m²g⁻¹ although the pore diameter was found to be remained as 3.8 nm. The N₂ adsorption analysis for both the samples displays similar type of isotherms from which we can rule out the chance of structure collapse during the catalysis. Isotherms can be assigned as typical Type IV with H4 type adsorption hysteresis (Figure 4.4) with a narrow pore size distribution. From these characteristics we can infer that the PMO contains narrow slit like pores in the range of mesopores.

Table 4.1: Analytical, textural, and porosity data of different catalysts.

S. No.	Catalyst	BET Surface area (m ² g ⁻¹)	BJH Pore diameter (nm)	Content of 3 in PMOs (mmol/g)
1	Urea/PMO	951	3.8	0.64
2	Urea/PMO_U	892	3.8	0.634

4.2.5. Elemental analysis of PMOs

The EA was carried out for PMOs to determine the amount of nitrogen (N) present in the material. Since precursor **3** is the only source of nitrogen in the PMO and each mole of precursor contains 5 moles of N- from which we quantified the final loading of **3** grafted in the PMOs before and after the catalysis. From the analysis the loading of **3** in Urea/PMO was

found to be 0.64 mmol g^{-1} and the value became $0.634 \text{ mmol g}^{-1}$ in case of Urea/PMO_U (Table 4.1).

4.2.6. Mesostructural morphology of PMOs

Figure 4.5: TEM images (a) Urea/PMO and (b) Urea/PMO_U.

TEM analysis [Figure 4.5 (a and b)] shows nice mesostructural morphologies for both Urea/PMO and Urea/PMO_U. It can be clearly seen the pores with regular porosity with pore diameters concurrent with BJH analysis.

4.2.7. Catalytic evaluation of Urea/PMO

Scheme 4.3: Henry reaction used a test reaction for the evaluation of Urea/PMO at R.T. using acetonitrile as solvent.

A series of Henry reactions between 4-nitrobenzaldehyde ($\text{X} = p\text{-NO}_3$) and nitromethane were carried out (Scheme 4.3) in order to evaluate the catalytic efficacy of Urea/PMO. The

results showed that the Urea/PMO catalyst is efficient enough to facilitate the Henry reaction at

Figure 4.6: Catalytic activities of Urea/PMO in terms of yield of 2-nitro-1-(4-nitrophenyl)ethanol as a function of catalyst loading for the reaction in scheme 4.3 where . Reaction conditions: Aromatic aldehyde: Nitromethane=1:1.2 (mole ratio); reaction time: 6h; Solvent: Acetonitrile.

room temperature (RT) to yield respective β -nitro alcohol i.e. 2-nitro-1-(4-nitrophenyl)-ethanol as product without any additional base. The catalytic conditions were optimized by varying catalyst loading (mole ratio of **3** present in Urea/PMO with respect to aldehyde) in acetonitrile as solvent for duration of 6 h. Results show that 46% yield with a turn over frequency (TOF) of 0.77 h^{-1} can be achieved for a 10 mol% loading of the catalyst (Figure 4.6). The yield of product can further excel up to 54% for a 12% loading of catalyst; however the corresponding TOF decreased to 0.75 h^{-1} . Therefore 10 mol% loading has been

considered as optimum loading of the catalyst for further catalytic evaluations. With 10 mol % of catalyst loading, the test reaction was further carried out as a function of reaction

Figure 4.7: Catalytic activities of Urea/PMO in terms of yield of 2-nitro-1-(4-nitrophenyl)ethanol as a function of reaction time for the reaction in scheme 4.3 where X = *p*-NO₃. Reaction conditions: 4-nitrobenzaldehyde: Nitromethane=1:1.2 (mole ratio); catalyst loading: 10 mol%; Solvent: Acetonitrile.

time. A progressive increase of the product yield was observed and a maximum yield of 96% for corresponding β -nitro alcohol was achieved during 16 h of reaction. Surprisingly as similar to the previous case, the TOF remained constant till 12 h of reaction followed by a dramatic drop of TOF at 16 h of reaction. From these, 12 h of reaction time with 10 mol % of catalyst loading have been determined as optimum reaction conditions and these conditions were used for further investigations for catalytic studies at RT using acetonitrile as solvent.

In a typical Henry reaction of 4-nitrobenzaldehyde and nitromethane as substrates in acetonitrile over a period of 12 h of reaction yields corresponding β -nitro alcohol with conversion of 93% while 10 mol% of Urea/PMO was applied whereas the same reaction

Table 4.2: Catalytic activities in terms of yield of 2-nitro-1-(4-nitrophenyl)ethanol with different catalysts for the reaction in scheme 4.3 where X = *p*-NO₃. Reaction conditions: 4-nitrobenzaldehyde: Nitromethane = 1:1.2 (mole ratio); reaction time: 12h; Solvent: Acetonitrile.

S No	Catalyst	Loading (mol %)	Yield (%)	TOF (h ⁻¹)
1	Urea/PMO	10	93	0.60
2	No catalyst	-	0	-
3	3	10	23	0.14
4	Pyridine	10	26	0.18
5	Et ₃ N	10	31	0.19
6	MCM-41	(equal weight of used in entry 1)	0	-
7	MCM-41+ Et ₃ N	Combined amount from entry 5 and entry 6	22	-

cannot proceed without any catalyst (Table 4.2, entry 1 and 2). Under similar reaction conditions, **3** as catalyst afford a conversion of only 23 % (Table 4.2, entry 3). Since Henry reaction demands a base, we carried out this model reaction in presence of pyridine and triethylamine (Et₃N) without using Urea/PMO. The results showed significantly low conversion rate as compared to Urea/PMO under given conditions (Table 4.2, entry 4 and 5). Moreover, bare mesoporous silica materials such as MCM-41 also contain lot of surface hydroxyl groups which also have the ability to form various sort of hydrogen bonding. However, it is apparent that these hydroxyl groups show sheer apathy towards the catalysis

(Table 4.2, entry 6). Even after adding Et_3N as base in the reaction alongside of MCM-41, only an insignificant improvement was achieved (Table 4.2, entry 7). From all these observations, we can rationally rule out the involvement of bare silica surface in catalysis through any sort of interactions. Therefore, we can conclude that it is the surface embedded **3** units responsible for the catalytic activities which not only act as base but also activate LUMO of electrophiles. These results helped us to realize that Urea/PMO satisfies all there three major expectations mentioned above and proved it as an efficient HBD catalyst with cooperative activities.

Scheme 4.4: Schematic presentation of proposed mechanism involved during in the surface catalysis.

The Henry reaction is initiated by the deprotonation of the nitroalkane on the α -carbon position forming a resonance stabilized anion. However due to the presence of urea on the surface of Urea/PMO, the nitromethane can interact with urea through hydrogen bonding interactions (Scheme 4.4) which eventually enhances the acidity of the proton on the α -carbon making deprotonation process easier for the surface bound pyridine units triggering

the deprotonation of nitromethane. Consequently these deprotonated anions react to the aldehydic carbon which electrophilicity has been enhanced due to the formation of two-point hydrogen bonding through acidic N–H bonds of surface embedded urea units with the aldehydic oxygen. When the reaction continues for a long time the pyridine units may be protonated which may decrease the basic nature of Urea/PMO. This fact attributes to the lowering of TOF while reaction continued for 16 h (Figure 4.7).

Figure 4.8: Catalytic recycling experiments of Urea/PMO for the reaction in scheme 4.3. Reaction conditions: Aromatic aldehyde: Nitromethane=1:1.2 (mole ratio); catalyst loading: 10 mol%; reaction time: 12h; Solvent: Acetonitrile, room temperature.

In order to evaluate the catalytic recyclability of Urea/PMO, we performed catalytic cycles using recovered catalyst for same reaction (Scheme 4.3) under optimum catalytic conditions.

It is evident from results that Urea/PMO presents a tremendous recyclability with consistent conversion up to 6 catalytic cycles without any significant catalytic deactivation (Figure 4.8).

The recovered catalyst after 6th cycle (Urea/PMO_U) was further characterized thoroughly by

various analytical techniques such as ^{13}C and ^{29}Si solid NMR, Isothermal N_2 adsorption/desorption measurements and TEM. These characterizations reveal Urea/PMO_U is essentially similar to its pristine form i.e. Urea/PMO which also advocates the chemical and morphological stability of Urea/PMO during catalysis.

Table 4.3: Catalytic activities of Urea/PMO for the reaction in Scheme 4.3 as a function of various substituted benzaldehydes in terms of yield of corresponding β -nitro alcohols.

S. No	X-	Isolated yield (%)
1	<i>p</i> -NO ₂	93
2	<i>p</i> -Br	81
3	<i>o</i> -Cl	79
4	<i>m</i> -Cl	76
5	<i>p</i> -Cl	76
6	H	73
7	<i>o</i> -OH	71
8	<i>p</i> -OH	68
9	<i>o</i> -OMe	47
10	<i>p</i> -OMe	43

Furthermore, we have successfully optimized the cooperative catalytic activities of Urea/PMO for a series of substituted benzaldehydes and nitromethane in acetonitrile as a solvent for a period of 12h at RT (Scheme 4.3). In most of the cases, it was observed that the rate of condensation reaction for aromatic aldehydes attached with electron withdrawing groups is greater than that of the electron donating group substituted aromatic aldehydes

(Table 4.3). In general electron-withdrawing substituents on the phenyl ring of aldehyde favored the reaction (entries 1-5 in Table 4.3). The strong electron-withdrawing substituent facilitates aromatic aldehyde to undergo Henry reaction much faster with better yield (entry 1 in Table 4.3) than those substituents with weak electron-withdrawing abilities (entries 2-5 in Table 4.3). On the other hand, substituent with electron-donating reduces the reactivity of the aromatic aldehydes markedly even lower yields than benzaldehydes (entries 6-10 in Table 4.3). Besides, a trend of higher reactivity was also observed for an ortho-substitution over para-substitution.

Table 4.4: Catalytic activities of different catalysts for the reaction in Scheme 4.3 as a function of mixture of substituted benzaldehydes in terms of yield of corresponding β -nitro alcohols.

S. No	X-	Catalyst	Isolated yield (%)	
			p-OMe	p-NO ₂
1	<i>p</i> -OMe + <i>p</i> -NO ₂ = 1:1	Urea/PMO	33	82
2	<i>p</i> -OMe + <i>p</i> -NO ₂ = 1:1	Et ₃ N	0	25
3	<i>p</i> -OMe + <i>p</i> -NO ₂ = 1:1	Pyridine	0	17

In order to demonstrate the HBD catalytic activity offered by urea units of **3** embedded on Urea/PMO, three controlled Henry reactions were carried out using a mixture of *p*-methoxybenzaldehyde (S1) and *p*-nitrobenzaldehyde (S2) maintaining a mole ratio of 1:1 under three different catalytic conditions. Since S1 has electron donating group at para position, it requires a LUMO activation of the aldehyde whereas the aldehyde group is much activated due to the presence of electron withdrawing nitro group at the para position. At first catalysis was carried out using Urea/PMO as catalyst which offered successfully corresponding β -nitro alcohols for both S1 and S2 (Table 4.4, entry 1). On the other hand, β -

nitro alcohol corresponding to S2 was formed while Et₃N and pyridine were used as base with significantly low yield (Table 4.4, entry 2 and 3) although, due to the absence of LUMO activation of electrophile through HBD, S1 did not undergo Henry reaction to give corresponding products. From these reactions we can firmly conclude that the urea group present in the Urea/PMO successfully acts a HBD catalyst to activate the electrophile and facilitates the Henry reaction.

4.3. Conclusion

We have demonstrated the first time synthesis of a PMO based HBD catalyst which shows tremendous co-operative catalytic activities toward Henry reaction. The immobilization of urea based catalysts through PMO preparation; we are able to enhance the activity of urea based HBD catalysts preventing their self-dimerization. The HBD catalysts have already been proved as an important class of catalysts for the activation of small molecules. But the uses of these catalysts are limited to homogeneous liquid phase catalysis which restricts them within the vicinity of academic research only. However, immobilization of urea based catalysts through PMO preparation we can able to develop easy approach towards catalysts' separation and recyclability which are key ingredients for the commercialization of catalysts.

4.4. Experimental

Materials: All starting materials used in the synthesis and catalysis were purchased from Sigma Aldrich or Alfa Aesar and used without further purification.

4.4.1. Synthesis of bis-alkoxyorganosilane (3)

The silylated precursor 1,1'-(pyridine-2,6-diyl)bis(3-(3-(triethoxysilyl)propyl)urea) was synthesized as follows:

Pyridine-2,6-diamine (0.5 g, 4.58 mmol) was added to a 100 mL two necked oven-dried round bottom flask (RBF) equipped with a magnetic stirring bar. 30 ml of anhydrous DCM was introduced into system to afford clear brown solution. Then 3-isocyanatopropyltriethoxysilane (3.4 mL, 13.75 mmol, 3 equiv.) was injected to the brown solution. The mixtures were allowed to reflux and reaction completion was monitored by TLC. After 36 h on completion of the reaction solvent was removed *in vacuo* resulting in oily crude products. Excess hexane was then added after cooling down to room temperature. The solid precipitates were filtered and dried under vacuum to afford brown solid (2.5 g, 4.14 mmol, yield: 90%). The product was identified by ^1H NMR and MS. ^1H NMR (CDCl_3 , 400 MHz) δ 7.50 (1H, t, PyH), 6.92 (2H, d, PyH), 3.85 (12H, q, OCH_2), 3.35 (4H, t, NCH_2), 1.70 (4H, quint, CH_2), 1.23 [18H, t, $\text{CH}_3(\text{OEt})$], 0.76 (4H, t, SiCH_2). ^{13}C NMR (100 MHz, CDCl_3) δ ppm= 157.8, 153.3, 139.8, 101.4, 57.3, 44.8, 24.3, 18.1, 12.6. MS (ES) m/z = 604.5 ($\text{M} + \text{H}$) $^+$.

4.4.2. Synthesis of PMO (Urea/PMO)

4.4.3. Co-condensation method was adopted to prepare PMO using tetraethyl orthosilicate (TEOS) and precursor **3** as silica sources.

An already reported procedure has been adopted¹⁶ and modified in order to prepare PMO with co-condensation of TEOS and precursor (**3**) using CTAB as the structure-directing template. A gel was formed with a particular molar ratio of Si: CTAB: NH_3 (25%): H_2O : EtOH = 1.0: 0.12: 8.0: 114: 10. In a typical synthesis of PMO, CTAB (0.319 g, 0.876 mmol) was dissolved in H_2O (15 mL) and then NH_3 solution (1.106 mL, 25%) was added to the above solution. The mixture was stirred at 40 $^\circ\text{C}$ for 30 min. A premixed solution of **3** (0.221

g, 0.365 mmol) and TEOS (1.445 g, 6.94 mmol) in EtOH (5 mL) maintaining a mole ratio of 5:95 was added dropwise to the mixture solution under vigorous stirring within 0.5 h. After the reaction was kept for overnight at 40 °C, the resulting gel was transferred to a polyethylene container and heated to 90 °C for 4 days. The solid obtained was washed with H₂O and dried in vacuum oven at 60 °C for 12 h. The structure-directing agent was finally removed by extraction of the solid with dilute ethanolic HCl solution (20 mL of 0.5 M ethanolic HCl for 0.5 g of solid) at 40 °C for 2 h. PMO was obtained by filtration and washed thoroughly with H₂O and ethanol and dried in vacuum oven for complete dryness. A weight of 0.57 g PMO has been isolated and denoted as **Urea/PMO**.

4.4.3. Catalytic tests

In a typical experiment of Henry reaction, 50 mg of nitromethane (0.819 mmol) and 103 mg of 4-nitrobenzaldehyde (0.683 mmol) were added to 10 ml acetonitrile contained with 10 mol% of Urea/PMO (mol % of organic units in the Urea/PMO with respect to 4-nitrobenzaldehyde). The resulting mixture was stirred under 400 rpm at room temperature for next 12 h. After completion of the reaction, the catalyst from the reaction mixture was recovered by centrifugation followed by the solvent evaporation under vacuum to yield crude product. At last the product (β -nitro alcohol) was isolated from the unreacted substrates by preparative TLC using *n*-hexane/ethyl acetate (v/v 4:1) as eluent. Isolated product was also weighed to quantify the isolated product yield and characterized by MS and NMR.

In order to check the catalyst recyclability, catalyst from the reaction mixture was recovered by centrifugation followed by washing with acetonitrile for several times. The recovered catalysts were kept under vacuum oven for complete dryness before using for the subsequent catalysis or various characterizations.

Analytical data of various products of Henry reaction:

- (i) 2-Nitro-1-(4-nitrophenyl)-ethanol (Table 4.3, entry 1): Off-white liquid with isolated yield of 93%; ^1H NMR (400MHz, CDCl_3): δ ppm = 8.28 (d, 2H), 7.65 (d, 2H), 5.61-5.64 (m, 1H), 4.56-4.66 (m, 2H), 3.23 (1H, br s); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ = 70.1, 80.7, 124.3, 127.1, 145.1, 148.3. IR (KBr film, cm^{-1}): ν = 3401, 2919, 1555, 1416, 1382, 1349, 1086, 856, 754, 727, 697. ESI-MS: m/z Calcd. for $\text{C}_8\text{H}_8\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 213.05; Found, 213.05.
- (ii) 2-Nitro-1-(4-bromophenyl)-ethanol (Table 4.3, entry 2): Yellow oil with isolated yield of 81%; ^1H NMR (400 MHz, CDCl_3): δ ppm = 7.54–7.52 (m, 2H), 7.30–7.25 (m, 2 H), 5.45–5.42 (m, 1H), 4.59–4.46 (m, 2H), 3.00 (s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ = 70.4, 81.0, 123.0, 127.7, 132.2, 137.2. IR (KBr film, cm^{-1}): ν = 3540, 2922, 1592, 1554, 1489, 1412, 1344, 1292, 1212, 1075, 1011, 907, 825, 733, 646. ESI-MS: m/z Calcd. for $\text{C}_8\text{H}_8\text{BrNO}_3$ $[\text{M}+\text{H}]^+$: 244.97; Found, 246.03 $[\text{M}+\text{H}]^+$.
- (iii) 2-Nitro-1-(2-Chlorophenyl)-ethanol (Table 4.3, entry 3): Yellow liquid with isolated yield of 79%; ^1H NMR (400 MHz, CDCl_3): δ ppm = 8.10 (d, 1H), 7.89 (d, 1H), 7.47 (t, 1H), 7.20 (t, 1H), 5.72 (dd, 1H), 4.55 (dd, 1H), 4.33 (dd, 1H), 3.52 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ = 68.0, 79.4, 127.6, 127.7, 129.8, 130.0, 131.6, 135.7. IR (KBr film, cm^{-1}): ν = 3589, 2924, 2256, 1557, 1473, 1442, 1416, 1379, 1344, 1285, 1211, 1131, 1086, 1037, 905, 734, 650, 610. ESI-MS: m/z Calcd. for $\text{C}_8\text{H}_8\text{ClNO}_3$ $[\text{M}+\text{H}]^+$: 202.03; Found, 202.03.
- (iv) 2-Nitro-1-(3-Chlorophenyl)-ethanol (Table 4.3, entry 4): Dark yellow oil with isolated yield of 76%; ^1H -NMR (400 MHz, CDCl_3): δ ppm = 7.32 (s, 1H), 7.25 (m, 3H), 5.26 (dd, 1H), 4.59 (dd, 1H), 4.38 (dd, 1H), 3.48 (br s, 1H); ^{13}C NMR

(CDCl₃, 100 MHz, ppm): δ = 70.4, 81.1, 124.2, 126.3, 129.2, 130.4, 135.1, 140.2.

IR (KBr film, cm⁻¹): ν = 3563, 1597, 1557, 1477, 1422, 1378, 910, 739. ESI-MS:

m/z Calcd. for C₈H₈ClNO₃ [M+H]⁺ : 202.03; Found, 202.03.

- (v) 2-Nitro-1-(4-Chlorophenyl)-ethanol (Table 4.3, entry 5): Yellow viscous liquid with isolated yield of 76%; ¹H-NMR (400 MHz, CDCl₃): δ ppm = 7.48 (d, 2H), 7.28 (d, 2H), 5.30 (dd, 1H), 4.58 (dd, 1H), 4.38 (dd, 1H), 3.41 (br s, 1H); ¹³C NMR(CDCl₃, 100 MHz, ppm): δ = 70.4, 81.1, 127.4, 129.3, 134.9, 136.7. IR (KBr film, cm⁻¹): ν = 3446, 2924, 2255, 1557, 1493, 1379, 1090, 1015, 909, 829, 735, 651, 530. ESI-MS: m/z Calcd. for C₈H₈ClNO₃ [M+H]⁺ : 202.03; Found 202.03.
- (vi) 2-Nitro-1-phenyl-ethanol (Table 4.3, entry 6): Colorless oil with isolated yield of 73 %; ¹H-NMR (400 MHz, CDCl₃): δ ppm = 7.28-7.42 (m, 5H), 5.43 (dd, 1H), 4.62 (dd, 1H), 4.50 (dd, 1H), 3.08 (br s, 1H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ = 71.0, 81.2, 126.0, 129.0, 129.0, 138.3. IR (KBr film, cm⁻¹): ν = 3535, 3032, 2920, 1554, 1495, 1453, 1418, 1379, 1290, 1212, 1066, 895, 764, 702, 608. ESI-MS: m/z Calcd. for C₈H₉NO₃ [M+H]⁺ : 168.07; Found 168.07.
- (vii) 2-(1-Hydroxy-2-nitroethyl)-phenol (Table 4.3, entry 7): Colorless oil with isolated yield of 71%; ¹H-NMR (400 MHz, CDCl₃): δ ppm = 7.27 (m, 4H), 5.61 (dd, 1H), 4.57 (dd, 1H), 4.36 (dd, 1H), 3.23 (br s, 2H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ = 39.5, 75.4, 116.4, 120.5, 121.7, 130.3, 130.5, 153.6. IR (KBr film, cm⁻¹): ν = 3446, 3043, 2923, 1597, 1556, 1505, 1458, 1433, 1380, 1340, 1273, 1233, 1109, 840, 758, 630. ESI-MS: m/z Calcd. for C₈H₉NO₄ [M+H]⁺ : 184.06; Found 184.06.

- (viii) 4-(1-Hydroxy-2-nitroethyl)-phenol (Table 4.3, entry 8): Yellow oil with isolated yield of 68%; ^1H -NMR (400 MHz, CDCl_3): δ ppm = 7.53 (d, 2H), 7.13 (d, 2H), 5.30 (dd, 1H), 4.59 (dd, 1H), 4.40 (dd, 1H), 3.80 (br s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ = 70.9, 81.4, 116.4, 129.5, 132.6, 156.7. IR (KBr film, cm^{-1}): ν = 3348, 2923, 2852, 1675, 1601, 1553, 1515, 1495, 1449, 1378, 1261, 1219, 1157, 1108, 1042, 910, 838, 734, 698. ESI-MS: m/z Calcd. for $\text{C}_8\text{H}_9\text{NO}_4$ $[\text{M}+\text{H}]^+$: 184.06; Found 184.06.
- (ix) 2-Nitro-1-(2-methoxyphenyl)-ethanol (Table 4.3, entry 9): Isolated yield of 47%. ^1H NMR (CDCl_3 , 400 MHz): δ ppm = 7.43 (d, 1H), 7.32-7.30 (m, 1 H), 7.03-6.98 (m, 1 H), 6.91 (d, 1 H), 5.63-5.60 (m, 1 H), 4.66-4.56 (m, 2 H), 3.88 (s, 3 H), 3.15 (br, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ = 55.4, 67.8, 79.9, 110.6, 121.1, 126.1, 127.2, 129.8, 156.1. IR (KBr film, cm^{-1}): ν = 3538, 3011, 2944, 1556, 1492, 1347, 1290, 1073, 1026, 910, 859, 735, 616. ESI-MS: m/z Calcd. For $\text{C}_9\text{H}_{11}\text{NO}_4$: 197.19; Found 197.23.
- (x) 2-Nitro-1-(4-methoxyphenyl)-ethanol (Table 4.3, entry 10): Isolated yield of 43%. ^1H -NMR (400MHz, CDCl_3): δ ppm = 7.34 (d, 2H), 6.94 (d, 2H), 5.41-5.44 (m,1H), 4.62 (dd, 1H), 4.49 (dd, 1H), 3.84 (s, 3H), ~2.3-3.0 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ = 55.4, 70.8, 81.3, 114.5, 129.4, 130.4, 160.1. IR (KBr film, cm^{-1}): ν = 3464, 2934, 1553, 1514, 1462, 1420, 1379, 1304, 1249, 1178, 1076, 1030, 896, 834, 784, 731, 693. ESI-MS: m/z Calcd. For $\text{C}_9\text{H}_{11}\text{NO}_4$: 197.19; Found 197.07.

4.4.4. Characterization

^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometer operating at 400 MHz. The solid-state spectra were collected on an ECA400 NMR spectrometer

(JEOL, 400 MHz), using a 4 mm CP-MAS probe at room temperature. TEM images were collected on a JEOL JEM-1400 instrument operated at 100 kV. FT-IR spectra were recorded as KBr pellets on a SHIMADZU IRPrestige-21 spectrometer with the sample powder diluted in KBr (1%). N₂ adsorption/desorption measurements for BET and BJH calculations were obtained using an autosorp-IQ instrument from Quantachrome Instruments Corporation. The BET method was utilized to calculate the specific surface areas of the materials whereas the BJH model derived from desorption branches of isotherms was adopted for the pore-size distributions of the PMOs. EA were obtained from EuroVector Euro EA Elemental Analyzer. Quadrupole ion trap Mass Spectrometer equipped with Thermo Accela LC was used for analysis the mass.

4.5. References:

- (1) Lee, J.-W.; Mayer-Gall, T.; Opwis, K.; Song, C. E.; Gutmann, J. S.; List, B. *Science* **2013**, *341*, 1225.
- (2) Taylor, M. S.; Jacobsen, E. N. *Angew. Chem. Int. Ed.* **2006**, *45*, 1520.
- (3) *Comprehensive Biological Catalysis*, 1998.
- (4) Silverman, R. B. *The Organic Chemistry of Enzyme-Catalyzed Reactions*, 2000.
- (5) Schreiner, P. R. *Chem. Soc. Rev.* **2003**, *32*, 289.
- (6) Doyle, A. G.; Jacobsen, E. N. *Chem. Rev.* **2007**, *107*, 5713.
- (7) Zhang, Z.; Schreiner, P. R. *Chem. Soc. Rev.* **2009**, *38*, 1187.
- (8) Connon, S. J. *Chem. Eur. J.* **2006**, *12*, 5418.
- (9) Tuchman-Shukron, L.; Portnoy, M. *Adv. Syn. Catal.* **2009**, *351*, 541.

- (10) Chen, H.-T.; Trewyn, B.; Wiench, J.; Pruski, M.; Lin, V. Y. *Top Catal* **2010**, 53, 187.
- (11) Dong, X.-W.; Liu, T.; Hu, Y.-Z.; Liu, X.-Y.; Che, C.-M. *Chem. Commun.* **2013**.
- (12) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, 402, 867.
- (13) Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, 121, 9611.
- (14) Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1999**, 11, 3302.
- (15) Liu, F.; Fu, L.; Wang, J.; Meng, Q.; Li, H.; Guo, J.; Zhang, H. *New J. Chem.* **2003**, 27, 233.
- (16) Borah, P.; Ma, X.; Nguyen, K. T.; Zhao, Y. *Angew. Chem. Int. Ed.* **2012**, 51, 7756.

Chapter 5: Design, Synthesis and Application of Azobenzene Gated PMO: An Efficient Protecting Scaffold for an Unsymmetrical NIR-Squaraine Dye

Abstract

Herein, a new phenylene bridged PMO with azobenzene gated pores was prepared. Upon activation, azobenzene gate undergoes trans- to cis-isomerization which entraps an unsymmetrical near-infrared squaraine dye inside the pores. Gate closure results in the safe loading of dye inside pores in monomeric state even in aqueous medium. Further, dye inside gated-PMO exhibits excellent generation of reactive oxygen species upon excitation at 664 nm, which causes the oxidation of phenol into benzoquinone. The new hybrid PMO was loaded inside a microfluidic device and a free-flow technique was employed to demonstrate the photooxidation of phenol in presence of 664 nm light to benzoquinone with ~20-23% yield.

5.1. Introduction

PMOs prepared by the polycondensation of small hydrocarbon bridged silane molecules have been proven to be very potential for various applications including catalysis.¹ Relatively hydrophobic nano confinement inside the mesopores inherited from the hydrocarbon bridges makes these PMOs a suitable porous domain for various organic molecules especially in an aqueous environment.¹ These covalently bonded organic bridges especially phenylene and ethenylene units in the siloxane network of PMO can further be functionalized chemically via direct sulfonation², bromination³, amination^{4,5}, hydroxylation⁶, and Diels–Alder reaction⁷. The chemical modification of the organic bridges in PMOs have been considered as very effective approach to achieve highly functionalized nanopores with uniform mesopore spacing. Among these transformations, direct amination is very much advantageous since the amino group offers us further functionalization via amide, imine, urea, diazo etc. bond formation. Inagaki *et.al.* demonstrated for the first time the successful direct amination of the phenylene bridges in the mesoporous benzenesilica network of PMO via a two-step chemical transformation (Scheme 5.1).⁵

Scheme 5.1: Direct amination via two steps of phenylene-bridged PMO.

In the last decade a novel fascinating field related to switchable-gated nano hybrid material has been developed. Due to the immense scope of applications of these gated nano-devices, many hybrid materials were developed by anchoring organic molecules or supramolecules onto certain inorganic scaffolds. These switchable-gated hybrids can provide supramolecular

behaviors to accommodate various host molecules within robust solid domain protecting them from wide range of outside chemical environment in a ‘closed’ mode of anchored molecules as gate. An efficient gated hybrid demands two important components viz - (i) a switchable molecule which can undergo “opened” or “closed” modes upon the application of certain external stimuli; (ii) a suitable nanocontainer made of robust inorganic material which also offers easy surface functionalization of desired gate-like organic molecules.⁸ Mesoporous silicas of different morphologies as well as pore sizes have been proven as a promising class of inorganic scaffolds to construct various fascinating gated nanohybrids especially for the purpose of delivery applications. Till date various gated mesoporous silica hybrids have been developed which switchable gates can be readily modulated by various external stimuli such as pH value changes,^{9,10} chemical treatments,¹¹ electrostatic interactions,¹² enzymatic actions,¹³ redox changes,^{14,15} and photoirradiation¹⁶⁻¹⁹. Azobenzene is well known for its *trans*–*cis* isomerization property upon alternating irradiation with UV and visible light or heating. Based upon this unique photo induced isomerization property, azobenzene and its derivatives have been utilized in large extent to design various photothermal-powered molecular machines which can be reversibly operated without generation of any byproducts. Photo-switchable azobenzene functionalized mesoporous silica based gated hybrids have been widely applied in catalysts,²⁰ sensors,²¹ soft materials,²² and even in biological systems.²³ Having this motivation to design a new gated hybrid material we made an approach to functionalized azobenzene moieties directly to the phenylene bridges of a benzene-PMO where the azobenzene will play a photo-responsive gate to tune the internal pore size of PMO while the benzene-PMO will act as nano container with hydrophobic confinement. Besides the direct aminated phenylene bridges of such PMO offers a perfect platform to anchor azobenzene moieties uniformly.

In another context, molecular oxygen (O_2) exhibits two low-lying singlet excited states, $^1\Delta_g$ (22.5 kcal mol⁻¹) and $^1\Sigma_g^+$ (31.5 kcal mol⁻¹) above the triplet state.²⁴ But due to the spin forbidden transition from the $^1\Delta_g$ state to the $^3\Sigma_g^-$ state, the $^1\Delta_g O_2$ is a relatively long-lived species. On the other hand, the second singlet state of oxygen is short lived due to a spin-allowed transition from $^1\Sigma_g^+$ to $^1\Delta_g$ state. It has been found that oxygen is *ca.* 1 V more oxidizing in its singlet excited state (1O_2) which makes it significantly more reactive species.²⁴ Consequently, 1O_2 has been utilized as a versatile reagent to carry out various organic reactions where substrates were normally unaffected by oxygen in its normal energy state. Besides, 1O_2 produced from ground state oxygen also has ability to kill biological cell by either necrosis and/or apoptosis for which 1O_2 has been exploited to develop various photo dynamic therapies (PDTs) for cancerous cell.²⁵

Photosensitized generation of 1O_2 , is a simple and controllable method amongst all the possible processes for the production of 1O_2 . This method requires a suitable photosensitizer in presence of O_2 under the irradiation of light of an appropriate wavelength which can be absorbed by a photosensitizer to excite oxygen to its singlet state. An ideal photosensitizers necessary to have following properties:²⁶

- (1) High absorption coefficient in the spectral region of the excitation light.
- (2) The energy of the triplet state should be appropriate so that efficient energy can be transferred to ground state oxygen.
- (3) The life time of the triplet state should be long enough ($\tau_T > 1\mu s$) with a high corresponding quantum yield ($\Phi_T > 0.4$).
- (4) High photostability.

Among various photosensitizer squaraine dyes, a class of zwitterionic dyes which exhibit excellent photophysical properties in the near-IR (NIR) region,^{27,28} emerged as efficient sensitizers to produce $^1\text{O}_2$ through an energy transfer process under the light as stimulus proving these dyes as the second generation of photosensitizers for photodynamic therapy (PDT).²⁹ This fascinating class of dyes have also been proven to be potential candidates in various biological applications such as metal ion sensing,^{30,31} NIR fluorescent labeling,³² two-photon absorption,²⁶ and detection and estimation of thiol-containing amino acids.^{33,34} However, there are two major challenges in using these dyes for biological applications, especially for PDT and imaging applications: preventing easy formation of dye aggregates in aqueous environments and protecting the photophysical characteristics from nucleophilic attack on the squaryl rings. Although approaches such as (i) supramolecular encapsulation using macrocyclic host molecules (e.g., β -cyclodextrin³⁵ and serum albumins³⁶) and (ii) the formation of squaraine-derived rotaxanes³⁷ can enhance their stability and prevent chromophore interactions, the real bottleneck in maintaining the photophysical characteristics of these dyes in aqueous environments remains unresolved. Recently Zhao *et. al.* demonstrated an innovative way to protect squaraine dye from nucleophilic attack by loading into mesoporous silica nanoparticles followed by wrapping the nanoparticles with ultrathin graphene oxide sheets.³⁸ In this project we have attempted to design a new hybrid material composed of azobenzene grafted PMO where the size of the pore channels can be tuned upon the irradiation of light.

However, it is important to mention that $^1\text{O}_2$ exhibits a short half-life time ($0.6\ \mu\text{s}$) and diffusion distance ($0.1\ \mu\text{m}$) of in aqueous media,²⁴ for which efficient utilization of this reactive oxygen species is a great challenge especially in catalysis. As an approach to overcome this we can use the micro-channels of microfluidics system as a microreactor since

micro-dimension presents short diffusion time for the reactants which attributes improved mass transportation in the reactor.³⁹ It is however important to mention that microfluidics deals with the behavior of fluids in micro domain typically sub-millimeter, scale. The microtechnology, technology associated with microfluidics, has been undergoing a rapid growth ever since its inception. Through various advanced and impressive demonstrations of microfluidics devices till date, microtechnology has emerged as potential tool for many areas of application. Among them microfluidics systems were used to construct microreactors with three-dimensional structures with the inner dimensions between ten and a hundred micrometers rendering several vital advantages over traditional large-scale batch chemistry. Since the heat-transfer coefficient is inversely proportional to the channel diameter, microstructured reactors allow fast heating and cooling as compared to conventional chemical reactors resulting higher selectivity, yield, and product quality.³⁹ The hydrodynamic flow in the microchannels makes the reactants' flow laminar, directed, and highly symmetric. Apart from all merits related to microprocess engineering, the microreactor is a suitable system for the synthesis and use of potentially hazardous compounds, as only very small amounts of compounds/reagents are handled.⁴⁰

Herein we designed a novel phenylene bridged PMO based functionalized with azobenzene units which serve as multi-level gates inside the pore walls. The gate opening and closing functions can be operated reversibly with the help of light induced *cis-trans* isomerization ability of azobenzene. Later an unsymmetrical NIR squaraine dye has been loaded inside the pores and multi-level gates inside the pores were closed to prevent the dye from aggregation in aqueous medium preventing its photophysical properties. The dye loaded porous hybrid exhibits excellent photosensitizing ability to generate $^1\text{O}_2$ upon excitation at 664 nm light.

The oxidation of phenol to benzoquinone was further investigated using $^1\text{O}_2$ generated by our dye loaded hybrid material inside a microfluidic based micro reactor.

5.2. Results and discussions

Scheme 5.2: Synthetic routes to prepare compound 4.

5.2.1. Preparation of amino modified phenylene-PMO

A phenylene bridged PMO (denoted as Ph-PMO) was at first prepared by adopting an established synthesis route. In order to achieve larger pore size, P123 was used as template under acidic condition. The prepared Ph-PMO was further subjected to a nitration process (denoted Ph-PMO- NO_2) followed by a reduction to generate amino functionality (Ph-PMO- NH_2) (scheme 5.1). After successful preparation of Ph-PMO- NH_2 , the compound 4 (Scheme 5.2) was grafted through amide coupling and the hybrid PMO was denoted as azo@PMO for further discussions. The motive behind preparing phenylene bridged PMO is to create relatively higher hydrophobic environment inside the pore channels which was already realized in many previous reports.⁴¹⁻⁴³ The functionalization of azobenzene group with terminal ethoxy functionality will presumably reinforce the internal hydrophobicity of the pore channels. Besides direct amination of these phenyl bridges help to graft 4 more uniform fashions with a constant distance from the surface of PMO's wall.

5.2.2. FTIR Study of PMOs

Figure 5.1: FT-IR spectra of (a) Ph-PMO, (b) Ph-PMO-NO₂, (c) Ph-PMO-NH₂ and (d) azo@PMO.

Successful functionalization was characterized by FT-IR method where Ph-PMO shows all the characteristic peaks in the range of 1000-1200 cm⁻¹ corresponding to polysiloxane network alongside the overtones of benzene ring vibrations (1300–2000 cm⁻¹) (Figure 5.1a). After the nitration, the resultant Ph-PMO-NO₂ produces two strong bands at 1354 and 1540 cm⁻¹ attributed by symmetrical and asymmetrical stretching modes of N–O respectively (Figure 5.1b).⁵ These bands are found to be disappeared or decreased significantly upon the treatment with SnCl₂–HCl giving rise of new band centered at 1392 cm⁻¹ corresponding to N–H (Figure 5.1c).⁵ Other characteristic bands attributable to the bending and stretching modes of N–H have been found to be masked by broad peaks by silanol groups and the strong signal by surface absorbed water molecules. These results are very much concurrent with the previously reported results supporting the successful reduction of -NO₂ into -NH₂ functionality to form Ph-PMO-NH₂. On the other hand, azo@PMO displays new peaks centered at 1634, 1602 and 1544 cm⁻¹ which can be attributed to various combinational vibrations related to secondary amide along with weak signals by azo bond centered at

$\sim 1500\text{--}1400\text{ cm}^{-1}$ (Figure 5.1d). These observations provide firm support towards the successful formation of desired azo@PMO through the grafting of compound **4** via amide linkage.

5.2.3. ^{13}C and ^{29}Si solid NMR study of PMOs

Figure 5.2: ^{13}C CP-MAS solid state NMR of (a) Ph-PMO, (b) Ph-PMO-NH₂ and (c) azo@PMO.

The ^{13}C CP-MAS NMR was carried out to support the successful amination of the Ph-PMO followed by the grafting of **4** to form azo@PMO. The Ph-PMO displays strong resonance at ~ 134 ppm corresponds to the aromatic carbons along with few small peaks in the region 0 to 50 ppm as well as at 234 ppm related to the presence of some non-extracted template (Figure 5.2a).^{5,44} The ^{13}C CP-MAS NMR spectrum of Ph-PMO-NH₂ displays resonances at *ca.* 122, 135 and 151 ppm assigned to three different types of sp^2 carbons from the amine substituted phenylene group in accordance with previously reported results (Figure 5.2b).⁵ The subsequent grafting of compound **4** through amide can also be identified by the resonances

(Figure 5.2c). Signal at 172 ppm corresponds to the carbon from the amide linkage and signals at 63 and 14.5 ppm, attributed by aliphatic carbons from ethoxy group, provide solid evidence of the successful grafting of compound **4**. Other aromatic sp^2 carbons from grafted **4** are also visible in the range 110-165 ppm although few signals are masked by strong resonance signals from the phenylene carbons of PMO.

Figure 5.3: ^{29}Si CP-MAS solid state NMR of (a) Ph-PMO-NH₂ and (d) azo@PMO.

The ^{29}Si CP-MAS NMR analyses were performed for Ph-PMO-NH₂ and azo@PMO (Figure 5.3). ^{29}Si CP-MAS NMR spectrum of Ph-PMO-NH₂ exhibits three T^n signals ($n = 1, 2, 3$) corresponding to Si species covalently bonded to carbon atoms i.e. T^1 at $\delta = -60.7$ ppm [C–Si–(OSi)(OH)₂], T^2 at $\delta = -69.6$ ppm [C–Si–(OSi)₂(OH)] and T^3 at $\delta = -77.4$ ppm [C–Si–(OSi)₃] (Figure 5.3a). Similar spectrum can be observed for azo@PMO which confirms the

retention of the stable network of organosilica after the grafting of compound 4 through amide linkage (Figure 5.3b). Moreover, both spectra confirm the absence of additional Q^n signals indicating that there was no any cleavage of Si–C bonds during the synthesis procedure.

5.2.4. UV/Vis study of azo@PMO

Figure 5.4: UV/Vis absorption spectrum of (a) Ph-PMO-NH₂ and (b) azo(*trans*)@PMO (both 1.5 mg mL⁻¹ in aqueous solution). (c) Changes in the UV/Vis absorption spectrum azo(*cis*)@PMO (1.5 mg mL⁻¹) after irradiation for 20 minutes with 383 nm UV light. Inset: the change in absorbance at 383 nm of azo@PMO as a function of cycles upon either alternating UV irradiation or heating at 55 °C.

The UV/Vis studies have been carried out to understand the photothermal-responsive activities of azo@PMO in aqueous solution. The UV/Vis absorption spectrum of Ph-PMO-NH₂ exhibit broad scattering in water with a maximum at 320 nm corresponding to phenyl backbone in the PMO skeleton (green curve, Figure 4.5a). Similarly, in water azo(*trans*)@PMO exhibit signature absorption peak corresponding to π - π^* transitions in azo-

units at 380 nm (blue curve, Figure 4.5b). Irradiation of azo(*trans*)@PMO with 380 nm light for 20 min shows a decrease in the intensity of absorption at 380 nm with concomitant formation of a new band at 460 nm corresponding to *cis* isomer, azo(*cis*)@PMO (black curve, Figure 4.5c). The process of *cis* to *trans* isomerization was found to be repeatable up to several cycles as shown in the inset of Figure 4.5.

Scheme 5.3: External stimuli responsive reversible isomerization of azo@PMO.

5.2.5. Loading of an unsymmetrical Squaraine Dye into azo@PMO

Scheme 5.4: A schematic representation of Sq loading into azo@PMO.

An unsymmetrical squaraine dye (Sq) shown in the Scheme 5.4 has been synthesized by a synthetic process mentioned in the experimental section. Sq has a characteristic absorption maximum at 667 nm (Figure 5.7(i) a) and corresponding emission maximum at 685 nm (Figure 5.7(ii) a). The molar absorptivity (ϵ) of this dye in dichloromethane was found to be $165620 \text{ M}^{-1}\text{cm}^{-1}$. The Sq-dye has been loaded into azo@PMO following the procedure mentioned in the experimental section which has been depicted schematically in the Scheme 5.4. The new dye loaded azo@PMO has been denoted as Sq-azo@PMO for further discussion. The amount of Sq-dye loaded in Sq-azo@PMO was determined by extracting thoroughly out all dye molecules from the pores by opening the gates under UV light

irradiation in DCM. Then, all the extracted Sq-dye in DCM solution was quantified by its UV/vis absorbance intensity and dye loading was found to be 0.2 wt%.

5.2.6. N₂ adsorption measurements of PMOs

Figure 5.5: (i) Isothermal N₂ adsorption/desorption plot of (a) Ph-PMO, (b) Ph-PMO-NH₂, (c) azo@PMO and (d) Sq-azo@PMO. Along with BJH pore size distribution plots of (ii) Ph-PMO, (iii) Ph-PMO-NH₂, (iv) azo@PMO and (v) Sq-azo@PMO.

The isothermal N₂ adsorption/desorption measurements were carried out for all Ph-PMO, Ph-PMO-NH₂, azo@PMO and Sq-azo@PMO to determine the surface areas and pore size distributions (Table 5.1). From the N₂ adsorption isotherm under the lowest pressure, the BET equation was used to determine surface area and BJH model for the pore-size. It has been found that Ph-PMO, Ph-PMO-NH₂ and azo@PMO demonstrate typical Type IV isotherms with H1 type adsorption hysteresis indicating the presence mesoporous matrix with uniform pore distribution [Figure 5.5 (i)]. Although the starting Ph-PMO exhibits very high surface area with larger pore diameter, but the subsequent surface modifications reduces the pore sizes as well as the surface areas (Table 5.1; Figure 5.5). The pore diameter was

dramatically reduced to 2.3 nm after the final functionalization of compound **4** although the hybrid still exhibited a narrow pore size distribution. Upon the subsequent loading of dye in to the pores of azo@PMO, resultant Sq-azo@PMO underwent further reduction of both surface area as well as pore size. However the N₂ isotherm for Sq-azo@PMO can also assigned to Type IV isotherm without any distinguishable adsorption hysteresis [Figure 5.5 (i)d] indicating presence of dyes occupying the voids of meso channels.

Table 5.1: Textural and porosity data of different PMOs.

Sr No	PMOs	BET (m ² g ⁻¹)	Pore diameter (nm)
1	Ph-PMO	1099	5.8
2	Ph-PMO-NH ₂	733	3.6
3	azo@PMO	524.6	2.3
4	Sq-azo@PMO	488.8	1.7

5.2.7. Morphological study of PMOs by TEM

TEM images of the Ph-PMO, Ph-PMO-NH₂ and azo@PMO are shown in the Figure 5.6. Result suggests that in case of Ph-PMO, large mesopores having dimension *ca.* 5-6 nm are arranged uniformly in a honey comb like hexagonal array throughout the sample (Figure 5.6a). The regular mesoporous structure of pristine Ph-PMO remained preserved in the other hybrids as well upon the subsequent modifications (Figure 5.6 b and c). However after loading of Sq-dye, the extent of regularity and the pore dimension the pore channels has been reduced due to interchelation of the dye molecules inside the pores (Figure 5.6d). These textural observations of all four phases of PMOs are in good agreement with the behavior of pore sizes determined from the N₂ isotherm data.

Figure 5.6: TEM images (a) Ph-PMO, (b) Ph-PMO-NH₂, (c) azo@PMO and (d) Sq-azo@PMO. The scale bar represents 100 nm.

5.2.8. Spectroscopic analysis of Sq-azo@PMO

An aqueous solution Sq-azo(*trans*)@PMO exhibit a broad absorption showing characteristic peaks corresponding to *trans*-azo moiety at ~380 nm and peak around 664 nm corresponding to the dye intercalated inside the pores [Figure 5.7 (i) c]. Relative to the corresponding absorption of Sq in DCM, Sq-azo(*trans*)@PMO shows no shift in the absorption maximum at 664 nm in aqueous solutions. Similarly, when excited at 650 nm, Sq-azo(*trans*)@PMO

shows blue shifted emission max at 680 nm when compared to Sq in DCM [Figure 5.7 (ii) b]. The observed blue shift in the emission maximum could be attributed to the effect of hydrophobic environments inside azo intercalated pores of PMO. Hence we prove that the azobenzene units grafted in the pore-walls act as “closed-gate” in its *trans*- form as well as spacer between Sq molecules effectively preventing aggregation inside the pores of PMO.

Figure 5.7: (i) UV/Vis absorption spectrum of (a) Sq-Dye in DCM (b) azo@PMO in water and (c) Sq-azo@PMO in water. (ii) Emission spectra of (a) Sq-dye in DCM and (b) Sq-azo@PMO in water.

However, upon the prolong irradiation of UV light with 383 nm to Sq-azo@PMO dispersed in water different spectral features can be observed. The obtained spectrum on such event displays disappearance of the absorption band at 664 nm contributed by Sq-dye along with the absorption band at 383 nm due to azo(*trans*)@PMO isomerizes to azo(*cis*)@PMO [Figure 5.8] causing the pores opened. As a result the monomeric Sq in presence of aqueous medium suffered aggregation which results deactivation of the photophysical properties. Hence we can rationally claim that azobenzene units in Sq-azo(*trans*)@PMO act as ‘closed gate’ as well as spacer between the Sq molecules preventing them from aggregation.

Figure 5.8: UV/Vis absorption spectra of (a) Sq-azo@PMO in water and (b) Sq-azo@PMO in water after irradiation of UV light with 383 nm for 60 min.

5.2.9. Generation of $^1\text{O}_2$ by Sq-azo@PMO in aqueous medium

Figure 5.9: UV-vis absorption changes between 340 and 420 nm corresponding to the absorption of ADMA upon the irradiation of 664 nm light to an aqueous solution of ADMA along with (a) Sq-azo@PMO and (b) azo@PMO.

The photo-induced $^1\text{O}_2$ generation capability of the Sq-azo@PMO hybrid was investigated through an indirect chemical method using ADMA as the $^1\text{O}_2$ trap agent. ADMA reacts with $^1\text{O}_2$ to produce corresponding endoperoxide that can be realized by absorption changes of ADMA. ADMA aq. (8.2×10^{-5} M) solution of was mixed with aqueous suspension of Sq-azo@PMO (0.3 mg ml^{-1}) under stirring. A typical absorption spectrum of the mixture shows two characteristic regions (Figure 5.9a); i.e., absorption corresponding to ADMA is at 350–415 nm, and absorption for Sq is from 630 to 700 nm. Upon the irradiation of 664 nm light for 50 minutes the absorption of ADMA decreased continuously. The distinct photobleaching of ADMA indicates the photo-induced generation of $^1\text{O}_2$ by the monomeric Sq protected inside Sq-azo@PMO hybrid in aqueous medium. In another controlled experiment, 664 nm light was irradiated to same concentration of aqueous solution of ADMA containing azo@PMO to check the photo-induced $^1\text{O}_2$ generation capability of the hybrid PMO without Sq. No photo-induced generation of $^1\text{O}_2$ was observed until 60 minutes of light irradiation (Figure 5.9b). Therefore, the phenomenon of effective $^1\text{O}_2$ generation of Sq-azo@PMO in aqueous condition provides a proof-of-concept for our novel strategy to protect Sq-dye in its monomeric state inside the nanochannels of PMO preserving its photophysical properties.

5.2.10. $^1\text{O}_2$ assisted oxidation of phenol in microreactor

Among various applications of $^1\text{O}_2$, paramount interests have been given towards the synthesis of fine chemicals and in the treatment of wastewater using $^1\text{O}_2$ as a reactive reagent. Phenol and its derivatives are infamous as toxic compounds commonly found in the wastewater of paper, dye manufacturing industries and oil refineries due to their resistance to biodegradation. One common approach to deal with such water contaminants is to oxidize them into corresponding oxygenated compounds which are easily biodegradable.^{9,36,37} Many

extensive studies have been done to execute oxidation of phenols in organic solvents via in situ generation of $^1\text{O}_2$ in presence of photosensitizers such as eosin, rose bengal, methylene blue, riboflavin, and Zn(II) tetraphenylporphyrin. Similar reactions have also been investigated in aqueous solution with various dyes as well as metal complexes as photosensitizer and from the results it is evident that the presence of monomeric state of the photosensitizer in solution is crucial to achieve its highest efficacy. However, such photo-oxidation in aqueous medium is highly desirable since it is closely related to wastewater treatment. Unfortunately most of the organic dyes face severe aggregation in aqueous medium which also kill their ability to generate $^1\text{O}_2$ as well.

Figure 5.10: (a) Visualization of microfluidic channels by using a red dye; (b) loading of Sq-azo@PMO in the cavity and (c) schematic representation of the cross sectional view of the prepared microreactor.

Herein, we have attempted to carry out oxidation of phenol to benzoquinone using $^1\text{O}_2$ generated by Sq-azo@PMO under light in aqueous medium. For this purpose we have designed a microfluidics based micro reactor. The microfluidics device has been designed with two inlets for two reactants namely 0.1 M aqueous solution of phenol and O_2 . The microchannel can be visualized with the help of an aqueous solution of a red dye as shown in the Figure 5.10 (a). A cavity was also created to make a catalyst bed which was later filled with Sq-azo@PMO as shown in Figure 5.10 (b). The whole device was manufactured by using PDMS which was fixed on top of a glass platform [Figure 5.10(c)].

Figure 5.11: Operational mode of the Sq-azo@PMO loaded microreactor under the irradiation of 664 nm light.

Before carrying out the photo-oxidation in microreactor, we have attempted to carry out oxidation of phenol to benzoquinone (BQ) using $^1\text{O}_2$ generated by Sq-azo(*trans*)@PMO under 664 nm light irradiation in aqueous medium. In this case, at first 3 mg of Sq-azo(*trans*)@PMO was dispersed in 1.5 ml of 0.1 M aqueous solution of phenol in a 2 ml glass cuvette under constant stirring. A laser light with 664 nm wavelength has been

irradiated focusing at the reaction mixture inside the cuvette along with the continuous bubbling of O_2 using a balloon containing O_2 under 1atm pressure. The reaction mixture was collected and analyzed time to time until the completion of the reaction. But this process was found to be associated with few drawbacks such as: prolonged reaction time to achieve 100% conversion of phenol into BQ i.e slow rate of conversion as well as rapid declination of conversion rate as reaction proceeded (Figure 5.12) and limitation over the area for light irradiation.

Figure 5.12: Production of BQ as a function of time under above mentioned conditions.

However, it has been already mentioned that 1O_2 exhibits a short half-life time ($0.6 \mu s$) and diffusion distance ($0.1 \mu m$) of in aqueous media,²⁴ for which efficient utilization of this reactive oxygen species is a great challenge especially in macro scale. As an approach to

circumvent all above mentioned issues, we use the micro-channels of microfluidics system as a microreactor since micro-dimension presents short diffusion time for the reactants which attributes improved mass transportation in the reactor.³⁹ In order to investigate the oxidation of phenol to BQ by generating $^1\text{O}_2$ in presence of Sq-azo@PMO under the irradiation of light with a wavelength of 664 nm, the catalyst bed was initially packed with 3 mg of Sq-azo@PMO [Figure 5.10 (b)]. 0.1 M aqueous solution of phenol was injected into the microchannel through inlet 1 maintaining constant flow of 2 ml/h with the help of a syringe pump. The other inlet was also used to apply a flow of O_2 into the micro channel from an O_2 filled balloon under 1atm. The 2 ml/h flow of phenol was found to be optimum since any flow rate above that caused leakage problem and any flow rate less than the optimum one can't create enough pressure inside the microchannel to pass the reactant through the catalytic bed efficiently. Keeping a constant flow of both reactants, we carried out the oxidation reaction under room temperature upon the irradiation of a laser light with a wavelength of 664 nm (2.5 mW/cm^2) (Figure 5.11). Products were collected from the outlet for over a period of 30 minutes. After qualitative and quantitative analysis of the product, the results show that during the course of oxidation reaction phenol has selectively converted into BQ. Under identical conditions except the 664 nm light source was ON and OFF periodically for a period of 30 minutes for each action. The results showed that no product was obtained without the irradiation of light whereas 22-23% yield of BQ was obtained in every cycle of reaction under the irradiation of 664 nm light [Figure 5.13 (a)]. This is a clear evidence of generation of $^1\text{O}_2$ by Sq-azo@PMO under the influence of 664 nm light which eventually oxidized efficiently phenol into BQ within the close confinement of the micro reactor. On the other hand, in absence of light irradiation, the evolution of $^1\text{O}_2$ was discontinued which brought the production of BQ into a halt.

Figure 5.13: Oxidation of phenol inside the microfluidic channel (a) as a function of cycles upon alternating irradiation of 664 nm light and (b) continuous irradiation of 664 nm light.

The same reaction was further investigated for longer reaction time under continuous irradiation of light and products were collected and analyzed periodically. Results show that for every 30 minutes of reaction under given conditions result a consistent production of BQ with ~21-23% up to 210 minutes [Figure 5.13 (b)].

Figure 5.14: UV/Vis absorption spectra of Sq-azo@PMO in water (a) before reaction and (b) recovered after the prolonged reaction.

After the end of all the oxidation reactions, the used Sq-azo@PMO was recovered and photophysical property has been characterized by using UV/Vis spectroscopy. After comparing the spectra of Sq-azo@PMO corresponding to before and after the catalysis, we can conclude that the Sq-dye remained stable in its monomeric state even after generation of $^1\text{O}_2$ for long time in aqueous environment [Figure 5.14 (b)]. However, slight decrease in absorbance in the region corresponding to Sq-dye was observed which can be attributed to the photo bleaching of dye due to the prolong use of laser light with 664 nm wavelength.

5.3. Conclusion

In conclusion, herein we reported the preparation of a novel phenylene bridged gated-PMO appended with azobenzene gates inside the pore walls (azo@PMO). The functionalized azobenzene moieties inside the pores serve as gate for the nanochannels of PMO which can be closed and opened reversibly by virtue of *cis-trans* isomerization induced by external stimuli. Later, an unsymmetrical squaraine dye (Sq) was loaded inside the pores which existed inside the pores in monomeric state owing to its intercalation into the gaps of *trans*-azo spacers. The monomeric Sq existed inside the nanochannels of azo@PMO shows high efficiency to generate $^1\text{O}_2$ in aqueous environment upon light irradiation. In order to achieve efficient *in situ* utilization of generated $^1\text{O}_2$, a microfluidic reactor has been fabricated and oxidation of phenol was carried out. Up to 23% production of BQ with 100% selectivity was achieved.

5.4. Experimental

Materials: All starting materials used in the synthesis and catalysis were purchased from Sigma Aldrich or Alfa Aesar and used without further purification.

5.4.1. Preparation of Ph-PMO

The phenylene bridged PMO was prepared by following a previously reported procedure.⁴⁵ In a typical synthesis, 0.99 g of P123 was dissolved in 36 ml of distilled water containing 200 ml of hydrochloric acid (36 wt%). In to this solution BTEB (1.01 g) was added under continuous stirring maintaining a molar composition of the reaction mixture as BTEB:P123:HCl:H₂O = 1:0.034:0.48:400. The mixture was stirred for another 1 h at 0 °C. The mixture was then heated at 50 °C for 20 h with stirring, and followed by aging in a closed vessel at 100 °C for 24 h. The white precipitate was recovered by filtration and washed with water repeatedly to yield mesoporous material. Then the material was subsequently dispersed in water at 100 °C for 72 h. The surfactant was removed by solvent extraction with ethanol followed by calcination at 250 °C in air for two hour.

5.4.2. Preparation of Ph-PMO-NO₂

Ph-PMO-NO₂ was synthesized according to a previously reported procedure.⁵ In a typical procedure, the above synthesized Ph-PMO (0.524 g) was mixed in an acid solution of 96% v/v sulfuric acid (15.2 g) and 69% v/v nitric acid (3.47 g). After stirring the reaction mixture at room temperature for 3 days, the solution was poured into cold distilled water (300 mL). The solid product was isolated by filtration and repeatedly washed with a large amount of distilled water.

5.4.3. Preparation of Ph-PMO-NH₂

Ph-PMO-NH₂ was synthesized according to the previously reported procedure.⁵ In a typical procedure, the above mentioned synthesized Ph-PMO-NO₂ powder (0.400 g) was suspended in 15 mL of 37% v/v HCl solution containing SnCl₂ (2 g) and the suspension was stirred continuously at room temperature for 3 days. After reaction the suspension was poured into

distilled water (300 mL) and filtered to collect the products. The obtained material was further washed with a large amount of distilled water, followed by isopropylamine (10 mL) and ethanol (100 mL). Recovered material was finally vacuum-dried to afford Ph-PMO-NH₂.

5.4.4. Synthesis of 4-(4'-hydroxy-phenylazo)benzoic acid (**3**)

4-(4'-hydroxy-phenylazo)benzoic acid (**3**) was synthesized according to a previously reported procedure.⁴⁶ 4-aminobenzoic acid (1 g, 7.3 mmol) was suspended in a mixture of 10 mL of acetone/water (1:1) under constant stirring at 0 °C using an ice bath. To this cold solution concentrated HCl (1.15 mL) was added dropwise. After 5 min of stirring, a solution of NaNO₂ (0.63 g, 9.12 mmol) in water (3 mL) was added dropwise into the reaction mixture. This solution was stirred for 1 h at 0°C and then cannulated in a mixture of water/acetone (1:1) (10 mL) containing phenol (0.57 g, 6.08 mmol), Na₂CO₃ (1.3 g, 12.15 mmol) and NaOH (0.97 g, 24.3 mmol) at 0°C. Stirring was continued for 3 h while the mixture was warmed up to RT. Acetone was evaporated and a mixture of 1M HCl solution and dichloromethane was added to the residue. Layers were separated and aqueous layer was extracted twice with dichloromethane. The combined solution were washed with brine and dried over Na₂SO₄. The crude was purified by chromatography on silica gel using dichloromethane/MeOH (9:1) to give **3** (1 g, 73%) as an orange solid. ¹H NMR (400 MHz, MeOD-*d*₄) δ, 8.15 (d, *J* = 8.4 Hz, 2H), 7.87 (m, 4H), 6.92 (d, *J* = 8.9 Hz, 2H); ¹³C NMR (100 MHz, MeOD-*d*₄) δ 169.4, 163.0, 156.9, 147.7, 133.1, 131.9, 126.6, 123.3, 117.0. ESI-MS: *m/z* Calcd. for C₁₃H₁₀N₂O₃ [M+H]⁺ : 243.2; Found, 243.2.

5.4.5. Synthesis of 4-(4'-ethoxy-phenylazo)benzoic acid (**4**)

4-(4'-ethoxy-phenylazo)benzoic acid (**4**) was synthesized according to a previously reported procedure with little modifications.⁴⁷ In a typical synthesis 4-(4'-hydroxy-phenylazo)benzoic

5 + 6 $\xrightarrow{\text{i)}$ 7

Sq; R = $\text{---CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OCH}_3$

The squaraine dye, **Sq** was synthesized by the condensation reaction of the semisquaraine derivative (**5**) (218 mg, 1.0 mmol) with styrylpyrrole chromophore (**6**) (375 mg, 1.0 mmol) in 1:1 butanol/benzene mixture (80 mL) under azeotropic conditions (Scheme 5.5). After refluxing for 12 hours, the reaction mixture obtained was cooled followed by the removal of the solvents. The crude product was precipitated from petroleum ether, filtered and redissolved in CHCl₃. The crude product obtained was purified by column chromatography over silica gel using 3% methanol/dichloromethane. **Sq**: Yield 50%, ¹H NMR (400 MHz, CDCl₃) δ (ppm): 12.62 (s, 1H), 8.05 (d, 1H, Ar H), 7.70 (d, 1H, Ar H), 7.57 (d, 1H, vinylic, *J*

= 16.0 Hz), 7.27 (d, 1H, vinylic, $J = 15.0$ Hz), 7.13 (s, 1H, Ar H), 6.91 (d, 1H, Ar H), 6.83 (d, 2H, Ar H), 6.35 (d, 1H, Ar H), 6.11 (s, 1H, Ar H), 4.87 (t, 2H), 3.85 (s, 6H), 3.82 (t, 2H), 3.55 (t, 2H), 3.53 (t, 2H), 3.45 (t, 2H), 3.36 (t, 2H), 3.27 (s, 3H), 3.14 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 40.43, 55.83, 56.14, 58.89, 70.50, 70.53, 71.03, 71.82, 98.71, 107.54, 111.39, 112.12, 112.21, 115.12, 116.81, 126.17, 129.70, 151.99, 153.73, 157.92, 163.27. HRMS (FAB) calcd for $\text{C}_{33}\text{H}_{40}\text{N}_2\text{O}_8$ (M^+): 592.68, found: 593.30.

5.4.7. Preparation of azo@PMO

At first 300 mg of compound 4 was dissolved in 5 ml of SOCl_2 and the solution was stirred for 6 h at 343 K. After that SOCl_2 was removed by using vacuum distillation. The reddish solid compound was found and repeatedly washed using dry toluene to remove unreacted traces of SOCl_2 by using vacuum distillation. Once SOCl_2 was removed completely, the recovered compound was dissolved into dry DCM and 300 mg of Ph-PMO- NH_2 was also added to it. The reaction mixture was allowed to reflux under N_2 atmosphere for overnight. After completion of reaction solid product was collected by filtration and washed with DCM and ethanol under sonication. Finally the solid product was vacuum-dried to afford azo@PMO.

5.4.8. Preparation of Sq_azo@PMO

In a typical process 20 mg of azo@PMO at first dispersed in 10 mL of acetonitrile and mixture was stirred under a UV light source with a wave length of 380 nm for 1 h in order to convert all surface functionalized azobenzene units from the *trans* form to the *cis* form. The photostationary state *cis*-azobenzene units were confirmed by UV/Vis absorption. To this mixture, 5 mL already prepared 0.4 mM Sq solution in acetonitrile was added and stirred under UV irradiation for under 15 min. Subsequently the whole mixture was stirred at 55 $^\circ\text{C}$

under visible light for 2 h. Solid materials were separated by centrifuge and washed thoroughly by acetonitrile followed by DCM under sonication. The greenish blue material was vacuum dried to afford Sq-azo@PMO.

5.4.9. Microfluidic chip fabrication

Soft lithography is used for the creation of PDMS (polydimethyl siloxane) chips. It involves two steps: the creation of a mold followed by the creation of PDMS chips.⁴⁸ The mold is created by photolithography whereby a negative photoresist (SU-8 25, Microchem Inc., Newton, MA, USA) is coated on a silicon substrate and exposed to UV radiation at 365 nm through a photomask. Once exposed, the substrate is baked and developed to obtain the final mold with a channel thickness of approximately 40 μm . PDMS (Sylgard 184, Dow Corning, MI, USA) is prepared by mixing an elastomer and a curing agent in the ratio of 10:1 by weight. Once PDMS is prepared it is poured over the mold and curing is performed at 70 $^{\circ}\text{C}$ for two hours at the end of which PDMS polymerizes and the chip can be cut out from the mold.

5.4.10. Oxidation of Phenol in microfluidic chip

At first 3 mg of Sq-azo@PMO was loaded into the cavity in the prepared microfluidic chip [Figure 5.10 (b)]. A thin cotton plug was also used in front of the outlet channel to prevent unwanted leakage of Sq-azo@PMO from the cavity. A microscopic cover glass was used to close the cavity using vacuum grease and transparent sellotape. The openings of two inlets in the microfluidic chip were connected to a syringe pump containing 0.1 M aqueous solution of phenol and to a balloon containing O_2 by using a plastic capillary tube with 1 mm diameter. Likewise the opening of the outlet was also connected to a sample vial through similar capillary tube to collect the reaction mixture after reaction. The 0.1 M phenol solution was

allowed to pass through the reactor cavity via micro channel at continuous flow of 2 mL/h with help of the syringe pump along with O₂. Under such reaction conditions, a laser light with 664 nm wavelength (2.5 mW/cm²) has been irradiated focusing at the reactor cavity (Figure 5.11). The reaction mixture collected from the outlet was analyzed after an interval of 30 minutes. The product and unreacted reactant were identified and quantified by using an Agilent 6890 GC system equipped with a flame ionization detector after determining the response factors for the reactants and products individually.

5.4.11. Characterization

¹H and ¹³C NMR spectra were recorded on a Bruker spectrometer operating at 400 MHz. The solid-state spectra were collected on an ECA400 NMR spectrometer (JEOL, 400 MHz), using a 4 mm CP-MAS probe at room temperature. TEM images were collected on a JEOL JEM-1400 instrument operated at 100 kV. In order to prepare samples for TEM, materials were dispersed in methanol using sonication and mixtures were drop cast on TEM grid. The sample loaded TEM grids were allowed long hours to dry under air. FT-IR spectra were recorded as KBr pellets on a SHIMADZU IRPrestige-21 spectrometer with the sample powder diluted in KBr (1%). N₂ adsorption/desorption measurements for BET and BJH calculations were obtained using an autosorp-IQ instrument from Quantachrome Instruments Corporation. The BET method was utilized to calculate the specific surface areas of the materials whereas the BJH model derived from desorption branches of isotherms was adopted for the pore-size distributions of the PMOs. Electronic absorption spectra were recorded on a Shimadzu UV-3101 PC NIR scanning spectrophotometer and the emission spectra were measured on a Shimadzu RF5301 spectrofluorimeter. Quadrupole ion trap Mass Spectrometer equipped with Thermo Accela LC was used for analysis the mass and product

was quantified by using an Agilent 6890 GC system equipped with a flame ionization detector after determining the response factors for the reactants and products individually.

5.5. References

- (1) Yang, Q.; Liu, J.; Zhang, L.; Li, C. *J. Mater. Chem.* **2009**, *19*, 1945.
- (2) Inagaki, S.; Guan, S.; Ohsuna, T.; Terasaki, O. *Nature* **2002**, *416*, 304.
- (3) Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1999**, *11*, 3302.
- (4) Ide, A.; Voss, R.; Scholz, G.; Ozin, G. A.; Antonietti, M.; Thomas, A. *Chem. Mater.* **2007**, *19*, 2649.
- (5) Ohashi, M.; Kapoor, M. P.; Inagaki, S. *Chem. Commun.* **2008**, 841.
- (6) Polarz, S.; Kuschel, A. *Adv. Mater.* **2006**, *18*, 1206.
- (7) Nakajima, K.; Tomita, I.; Hara, M.; Hayashi, S.; Domen, K.; Kondo, J. N. *Adv. Mater.* **2005**, *17*, 1839.
- (8) Coll, C.; Bernardos, A.; Martínez-Máñez, R.; Sancenón, F. *Acc. Chem. Res.* **2012**, *46*, 339.
- (9) Zhao, Y.-L.; Li, Z.; Kabehie, S.; Botros, Y. Y.; Stoddart, J. F.; Zink, J. I. *J. Am. Chem. Soc.* **2010**, *132*, 13016.
- (10) Park, C.; Oh, K.; Lee, S. C.; Kim, C. *Angew. Chem. Int. Ed.* **2007**, *46*, 1455.
- (11) Lai, C.-Y.; Trewyn, B. G.; Jeftinija, D. M.; Jeftinija, K.; Xu, S.; Jeftinija, S.; Lin, V. S. Y. *J. Am. Chem. Soc.* **2003**, *125*, 4451.
- (12) Grattoni, A.; Fine, D.; Zabre, E.; Ziemys, A.; Gill, J.; Mackeyev, Y.; Cheney, M. A.; Danila, D. C.; Hosali, S.; Wilson, L. J.; Hussain, F.; Ferrari, M. *ACS Nano* **2011**, *5*, 9382.

-
- (13) Patel, K.; Angelos, S.; Dichtel, W. R.; Coskun, A.; Yang, Y.-W.; Zink, J. I.; Stoddart, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 2382.
- (14) Nguyen, T. D.; Tseng, H.-R.; Celestre, P. C.; Flood, A. H.; Liu, Y.; Stoddart, J. F.; Zink, J. I. *PANS* **2005**, *102*, 10029.
- (15) Nguyen, T. D.; Liu, Y.; Saha, S.; Leung, K. C. F.; Stoddart, J. F.; Zink, J. I. *J. Am. Chem. Soc.* **2007**, *129*, 626.
- (16) Mal, N. K.; Fujiwara, M.; Tanaka, Y. *Nature* **2003**, *421*, 350.
- (17) Liu, R.; Zhang, Y.; Feng, P. *J. Am. Chem. Soc.* **2009**, *131*, 15128.
- (18) Ferris, D. P.; Zhao, Y.-L.; Khashab, N. M.; Khatib, H. A.; Stoddart, J. F.; Zink, J. I. *J. Am. Chem. Soc.* **2009**, *131*, 1686.
- (19) Angelos, S.; Yang, Y.-W.; Khashab, N. M.; Stoddart, J. F.; Zink, J. I. *J. Am. Chem. Soc.* **2009**, *131*, 11344.
- (20) Mooibroek, T. J.; Schoon, L.; Bouwman, E.; Drent, E. *Chem. Eur. J.* **2011**, *17*, 13318.
- (21) Cheng, X.; Li, Q.; Li, C.; Qin, J.; Li, Z. *Chem. Eur. J.* **2011**, *17*, 7276.
- (22) Bleger, D.; Yu, Z.; Hecht, S. *Chem. Commun.* **2011**, 47, 12260.
- (23) Beharry, A. A.; Woolley, G. A. *Chem. Soc. Rev.* **2011**, *40*, 4422.
- (24) DeRosa, M. C.; Crutchley, R. J. *Coord. Chem. Rev.* **2002**, 233–234, 351.
- (25) Ma, X.; Sreejith, S.; Zhao, Y. *ACS App. Mater. Interfaces* **2013**, *5*, 12860.
- (26) Beverina, L.; Crippa, M.; Landenna, M.; Ruffo, R.; Salice, P.; Silvestri, F.; Versari, S.; Villa, A.; Ciaffoni, L.; Collini, E.; Ferrante, C.; Bradamante, S.; Mari, C. M.; Bozio, R.; Pagani, G. A. *J. Am. Chem. Soc.* **2008**, *130*, 1894.
- (27) Ajayaghosh, A. *Acc. Chem. Res.* **2005**, *38*, 449.
- (28) Ajayaghosh, A. *Chem. Soc. Rev.* **2003**, *32*, 181.
-

-
- (29) Avirah, R. R.; Jayaram, D. T.; Adarsh, N.; Ramaiah, D. *Org. Biomol. Chem.* **2012**, *10*, 911.
- (30) Ajayaghosh, A.; Arunkumar, E.; Daub, J. *Angew. Chem. Int. Ed.* **2002**, *41*, 1766.
- (31) Arunkumar, E.; Chithra, P.; Ajayaghosh, A. *J. Am. Chem. Soc.* **2004**, *126*, 6590.
- (32) Renard, B.-L.; Aubert, Y.; Asseline, U. *Tetrahedron Lett.* **2009**, *50*, 1897.
- (33) Ros-Lis, J. V.; García, B.; Jiménez, D.; Martínez-Máñez, R.; Sancenón, F.; Soto, J.; Gonzalvo, F.; Valdecabres, M. C. *J. Am. Chem. Soc.* **2004**, *126*, 4064.
- (34) Sreejith, S.; Divya, K. P.; Ajayaghosh, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 7883.
- (35) Arun, K. T.; Jayaram, D. T.; Avirah, R. R.; Ramaiah, D. *J. Phys. Chem. B* **2011**, *115*, 7122.
- (36) Jisha, V. S.; Arun, K. T.; Hariharan, M.; Ramaiah, D. *J. Am. Chem. Soc.* **2006**, *128*, 6024.
- (37) Arunkumar, E.; Forbes, C. C.; Noll, B. C.; Smith, B. D. *J. Am. Chem. Soc.* **2005**, *127*, 3288.
- (38) Sreejith, S.; Ma, X.; Zhao, Y. *J. Am. Chem. Soc.* **2012**, *134*, 17346.
- (39) Jähnisch, K.; Hessel, V.; Löwe, H.; Baerns, M. *Angew. Chem. Int. Ed.* **2004**, *43*, 406.
- (40) Basavaraju, K. C.; Sharma, S.; Maurya, R. A.; Kim, D.-P. *Angew. Chem. Int. Ed.* **2013**, *52*, 6735.
- (41) Rác, B.; Hegyes, P.; Forgo, P.; Molnár, Á. *App. Catal. A* **2006**, *299*, 193.
-

- (42) Rat, M.; Zahedi-Niaki, M. H.; Kaliaguine, S.; Do, T. O. *Microporous Mesoporous Mater.* **2008**, *112*, 26.
- (43) Shylesh, S.; Wagener, A.; Seifert, A.; Ernst, S.; Thiel, W. R. *Angew. Chem. Int. Ed.* **2010**, *49*, 184.
- (44) Lourenco, M. A. O.; Siegel, R.; Mafra, L.; Ferreira, P. *Dalton Trans.* **2013**, *42*, 5631.
- (45) Goto, Y.; Inagaki, S. *Chem. Commun.* **2002**, 2410.
- (46) Leriche, G.; Budin, G.; Brino, L.; Wagner, A. *Eur. J. Org. Chem.* **2010**, *2010*, 4360.
- (47) Gao, J.; He, Y.; Liu, F.; Zhang, X.; Wang, Z.; Wang, X. *Chem. Mater.* **2007**, *19*, 3877.
- (48) McDonald, J. C.; Duffy, D. C.; Anderson, J. R.; Chiu, D. T.; Wu, H.; Schueller, O. J. A.; Whitesides, G. M. *Electrophoresis* **2000**, *21*, 27.

Chapter 6: Summary of the Research Work

In the 21st century, we have witnessed in many ways that the discovery of various versatile materials is impetus for the growth and betterment of humanity. However the development of new material can be constructive towards humanity if its quest has been done maintaining harmony with nature. As a result, efforts have been given to develop novel materials which are more environmentally friendly, recyclable, energy efficient and inexpensive to achieve holistic progress of mankind. Similarly mesoporous silica based materials have also undergone a chronologically evolution ever since the discovery during early 90s in the last century. Due to the lower cytotoxicity of silica to the physiological environment as well as its flexibility towards chemical modifications, tunable mesostructure such as pore size, surface area, and pore volume provide lots of possibilities for varieties of applications, including heterogeneous catalysis in the development for green chemistry, drug/gene delivery, protein or enzyme delivery, biological imaging and so forth. Very recently PMO has emerged as new addition to mesoporous silica based materials with numerous potential for various applications owing to its hybrid nature. Due to the possibility of homogeneous distribution of organic units in silica network at molecular level, PMOs satisfy one of the prime requirements of surface catalysis. In the first chapter a detailed introduction to the utilization of PMO based materials as heterogeneous catalysts is presented. We have also discussed the fascinating transition of hybrid mesoporous silica based materials from surface functionalization techniques to PMOs and tried to provide the chronological development of PMOs in catalysis. Therefore, even though PMO based materials have been extensively

studied, still PMO exhibits great potentials in developing its applications such as catalysis, in particular, due to its versatile physicochemical properties as well as material structural variations.

One of the crucial aspects in the preparation of PMO is to design and synthesis of appropriate organic bridge with terminal alkoxysilane. With that motivation we attempted to design and synthesis three different organic bridges with two terminal alkoxysilanes according to our further catalytic requirement. These organic precursors were utilized to develop respective PMOs by using co-condensation techniques. In the second chapter, we developed a direct route to immobilize $\text{VO}(\text{acac})_2$ by grafting into the framework of silica through the preparation of PMO. For this purpose we designed a prerequisite organic bridge molecule having a vanadyl center with two terminal alkoxysilane. The vanadyl grafted PMO is capable of catalyze the direct hydroxylation of benzene to phenol with 100% product selectivity as well as catalytic recyclability without catalytic deactivation. Generally hydrothermal technique is widely recognized to prepare PMO. Under such conditions co-condensation of the organosilicon compound and TEOS is often suffered from unwanted phase separation, preferential self-condensation and metal leaching as well as aggregation especially in the case of organosilane containing metal center. Therefore, in chapter three we adopted a different approach to prepare a novel metal centered PMO where at first we developed a series of PMO where β -diketimate units were embedded into the siloxane network. These PMOs were found to be excellent scaffold for the immobilization of palladium acetate ($\text{Pd}(\text{OAc})_2$) through the complexation between iminic nitrogen atoms of β -diketimate and $\text{Pd}(\text{OAc})_2$, leading to resulting in efficient heterogeneous catalysts for the oxidation of styrene. With these two examples we attempted to establish a

novel strategy for transforming a catalytically important transition-metal complex into a heterogeneous catalyst by means of designing catalytically active PMOs.

Apart from the heterogenization of catalytically important transition-metal complexes, PMO can be extended further to immobilize various organocatalysts as well. In chapter four, 1,1'-(pyridine-2,6-diyl)bis(3-(3-(triethoxysilyl) propyl)urea) has been chosen as a precursor for PMO synthesis which contains two urea linkages and a pyridine unit. This PMO is not only capable enough to address the common demerits associated with homogeneous organocatalysts such as low TOF, stability, reactivity, and recyclability but also it can successfully prevent urea from unwanted self-recognition and aggregation unleashing its HBD catalytic competency. The concept of constructing novel urea-pyridine bridged PMO with cooperative catalytic ability is the first approach so far in the field of PMO to conserve the HBD catalytic ability of urea towards the activation of electrophile through catalyst spatial isolation.

Apart from being heterogeneous catalyst, PMO can play perfect role as host to accommodate various guest molecules inside the pores. Moreover PMO materials can be functionalized with some organic molecules which can behave as gates to the mesopores and the closing and opening of gate can be motorized by some external stimuli. Such 'closed' gated PMO can be perfect scaffold to various guest molecules inside the mesopores protecting them from unwanted hostile conditions prevailing outside. In chapter five we have prepared phenylene bridged PMO which pores were functionalized by azobenzene units through direct amination of phenylene bridges. Upon activation by UV light with appropriate wavelength, azobenzene gate was subjected to undergo *trans*- to *cis*-isomerization which entraps an unsymmetrical near-

infrared squaraine dye inside the pores. Gate closure results in the safe loading of dye inside pores in monomeric state even in aqueous medium. Further, dye inside gated-PMO exhibits excellent generation of $^1\text{O}_2$, a reactive oxygen species upon excitation at 664 nm, which causes the oxidation of phenol inside a microfluidic device with ~20-23% yield of benzoquinone.

Comprehensive materials characterizations were carried out to realize all the novel materials in terms of their structure and chemical constituents. For example, TEM analysis was used to observe the morphologies of prepared PMOs and determine its real size. BET and BJH methods were employed to find out the porosity information of the formed materials. FT-IR and NMR were utilized in the tracking of chemical modifications on the surface. XPS, ICP and EA were performed to analyze and quantify the various elements of PMOs. UV/Vis and fluoresce techniques were also employed to understand the photophysical properties of various PMO based hybrids.

In summary, exploration of PMO based inorganic-organic hybrids is a fascinating area of research which able to create interest remarkably in the field of material and related sciences in the past one decade. However, continuous efforts of researchers are being invested into this research field and a large number of publications on PMO are reports every year, suggesting the vitality and great potentials of this traditional material.

APPENDIX

1. N₂ Adsorption/Desorption Measurements of PMOs (Chapter 2) **Figure A1.** Isothermal N₂ adsorption/desorption plot of PMO-1. **Figure A2.** BJH Pore size distribution of PMO-1.

Figure A3. Isothermal N₂ adsorption/desorption plot of PMO-2.

Figure A4. BJH Pore size distribution of PMO-2.

2. XPS spectra of Pd/PMOs (Chapter 3)

Figure A5. XPS spectrum of Pd/PMO-1.

Figure A6. XPS spectrum of Pd/PMO-2.

Figure A7. XPS spectrum of Pd/PMO-3.

Figure A8. FTIR spectra of (a) Pd/PMO-3, and (b) Pd/PMO-3 recovered after 5th catalytic cycle.

LIST OF PUBLICATIONS, PATENT and CONFERENCES

A. *Publications:*

1. **Parijat Borah**, Sivaramapanicker Sreejith, Palapuravan Anees, Nishanth Venugopal Menon, Yuejun Kang, Ayyappanpillai Ajayaghosh, Yanli Zhao “Photo-Oxidation of Phenol Catalyzed by NIR Squaraine Dye-Loaded and Azobenzene-Gated Periodic Mesoporous Silica in a Continuous-Flow Device” Manuscript under preparation.
2. **Parijat Borah**, John Mondal, Yanli Zhao, “Urea Bridged Periodic Mesoporous Organosilica as Efficient Hydrogen-Bond Donating Heterogeneous Cooperative Organocatalyst for Henry Reaction” Manuscript under preparation.
3. **Parijat Borah**, Yanli Zhao, “ β -Diketimine Appended Periodic Mesoporous Organosilica as a Scaffold for Immobilization of Palladium Acetate: An Efficient Green Catalyst for Wacker Type Reaction” *Journal of Catalysis* **2014**, 318, 43–52.
4. Kim Truc Nguyen, Sivaramapanicker Sreejith, James Joseph, Tingchao He, **Parijat Borah**, Eng You Guan, Sun Woh Lye, Hangdong Sun, Yanli Zhao, “Poly(acrylic acid) Capped and Dye Loaded Graphene Oxide-Mesoporous Silica: A Nano-Sandwich for Two-Photon and Photoacoustic Dual Mode Imaging” *Particle & Particle Systems Characterization* **2014**, DOI: 10.1002/ppsc.201400044.
5. John Mondal, Kim Truc Nguyen, Avijit Jana, Karina Kurniawan, **Parijat Borah**, Yanli Zhao, Asim Bhaumik “Efficient alkene hydrogenation over magnetically

-
- recoverable and recyclable $\text{Fe}_3\text{O}_4@\text{GO}$ nanocatalyst using hydrazine hydrate as the hydrogen source” *Chemical Communications* **2014**, DOI: 10.1039/C4CC04770B.
6. John Mondal, Sivaramapanicker Sreejith, **Parijat Borah**, Yanli Zhao *ACS Sustainable Chemistry & Engineering* **2014**, ASAP article.
 7. Vivek Nair, Sivaramapanicker Sreejith, **Parijat Borah**, Steffen Hartung, Nicolas Bucher, Yanli Zhao, Madhavi Srinivasan, “Crystalline $\text{Li}_3\text{V}_6\text{O}_{16}$ rods as high-capacity anode materials for aqueous rechargeable lithium batteries (ARLB)” *RSC Advances*, **2014**, DOI: 10.1039/C4RA02804J.
 8. John Mondal, **Parijat Borah**, A Modak, Yanli Zhao, Ashim Bhaumik, *Organic Process Research & Development* **2014**, 18 (1), 257–265.
 9. Xing Ma, Cathleen Teh, Quan Zhang, **Parijat Borah**, Cleo Choong, Vladimir Korzh, Yanli Zhao, *Antioxidant & Redox Signaling* **2013**, *accepted*.
 10. Kim Truc Nguyen, Dehui Li, **Parijat Borah**, Xing Ma, Zhaona Liu, Liangliang Zhu, George Grüner, Qihua Xiong, Yanli Zhao, *ACS Applied Materials and Interfaces* **2013**, 5 (16), 8105-8110.
 11. **Parijat Borah**, Xing Ma, Kim Truc Nguyen, Yanli Zhao, *Angewandte Chemie International Edition* **2012**, 51, 7756–7761.
 12. Xiao-Jun Wang, Pei-Zhou Li, Lei Liu, Quan Zhang, **Parijat Borah**, Jinye Daniel Wong, Xiu Xiang Chan, Ganguly Rakesh, Yongxin Li, Yanli Zhao, *Chemical Communications* **2012**, 48, 10286-10288.
 13. Xing Ma, Kim Truc Nguyen, **Parijat Borah**, Chung Yen Ang, Yanli Zhao, *Advanced Healthcare Materials* **2012**, 1, 690–697.
 14. **Parijat Borah**, Arjun Ramesh, Arunabha Datta, *Catalysis Communications* **2010**, 12, 110-115.
-

15. Parijat Borah, Chandrashekar Pendem, Arunabha Datta, *Studies in Surface Science and Catalysis*, **2010**, 175, 541-545.

16. Parijat Borah, Arunabha Datta, *Applied Catalysis A: General*, **2010**, 376, 19-24.

B. Patent:

1. Yanli Zhao, **Parijat Borah**, John Mondal, "Preparation of pyridine-urea bridged periodic mesoporous organosilica: a novel heterogeneous H-bond donating organocatalyst for cooperative catalysis of henry reaction" *US Patent 61/914,536*, submitted on **11 December 2013**.

C. Conferences:

1. Humboldt Kolleg, International Symposium on Environment and Health in the 21st Century, 22nd September 29, 2014 at Center for Life Sciences, NUS, Singapore.
2. 2013 Reaxys PhD Prize Symposium (Reaxys Inspiring Chemistry Conference), September 22-24, 2013 Grindelwald, Switzerland.
3. International Symposium on Macrocyclic and Supramolecular Chemistry (8-ISMSC), July 7th-11th, 2013 at Arlington, Virginia, USA.
4. International Congress for Innovation in Chemistry (PERCHCIC Congress VIII) May 5th – 8th, 2013, Pattaya, Thailand.
5. 2nd International Conference on Molecular and Functional Catalysis (ICMFC-2)" 30 - 31 July 2012 Biopolis, Singapore.

-
6. 2nd Molecular Materials Meeting (M3)@Singapore: An international conference on “Frontiers in Materials Science, Chemistry & Physics” 9 - 11 January 2012 Biopolis, Singapore.
 7. 20th National Symposium on Catalysis”, Organized on behalf of the Catalysis Society of India by the National Centre for Catalysis Research, Indian Institute of Technology Madras, December, 2010.
 8. 10th International Symposium on the "Scientific Bases for the Preparation of Heterogeneous Catalysts", Louvain-la-Neuve, Belgium, July 2010.