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**NANYANG
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SINGAPORE

**TRANSITION METAL OXIDE CATALYSTS FOR
EXHAUST GAS OXIDATION**

WANG TING

Interdisciplinary Graduate School

Environmental Chemistry and Materials Centre

Nanyang Environment & Water Research Institute

2020

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**Interdisciplinary Graduate School
Environmental Chemistry and Materials Centre
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A thesis submitted to the Nanyang Technological University in
partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2020

Statement of Originality

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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.. Assoc Prof Xu Zhichuan, Jason. ...

[Input Supervisor Name Here]

Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journals where I was the first author.

Chapter 4 is published as T. Wang, Y. Sun, Ye Zhou, S. Sun, X. Hu, Y. Dai, S. Xi, Y. Du, Y. Yang, Z.J. Xu, Identifying influential parameters of octahedrally coordinated cations in spinel $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ oxides for the oxidation reaction. *ACS Catalysis*, **8** 8568-8577 (2018). DOI: 10.1021/acscatal.8b02376.

The contributions of the co-authors are as follows:

- Assoc. Prof Z.J. Xu and I conceived the idea and Assoc. Prof Z.J. Xu supervised the entire project.
- Dr Y. Sun conducted the Density Functional Theory computation calculations and corresponding data analysis.
- I prepared the manuscript drafts. Assoc. Prof Z.J. Xu, Dr Y. Sun and Dr Y. Zhou discussed and analyzed the measured data with me. Assoc. Prof Z.J. Xu and Prof Y. Yang revised the manuscript and provided valuable suggestions which helped in polishing the manuscript further.
- I performed all the catalytic activity measurements and analyzed the data. Dr Y. Zhou conducted the sample characterizations in the Facility for Analysis, Characterization, Testing and Simulation and assisted in analyzing of the characterization data. Dr S. Sun assisted in synthesis of the materials.
- Prof Y. Yang and Dr Y. Dai assisted in the temperature programmed desorption experiments and data analysis.
- Dr Y. Du and Dr S. Xi assisted in the collection of the X-ray absorption fine structure data in Singapore Synchrotron Light Source. Dr Y. Zhou and I analyzed the data.

Chapter 5 is published as T. Wang, J. Wang, Y. Sun, Y. Duan, S. Sun, X. Hu, S. Xi, Y. Du, C. Wang, Z.J. Xu, Origin of electronic structure dependent activity of spinel $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ oxides for complete methane oxidation. *Applied Catalysis B: Environmental*, **256** 117844 (2019). DOI: 10.1016/j.apcatb.2019.117844.

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- Assoc. Prof Z.J. Xu, Prof C. Wang and I conceived the idea and Assoc. Prof Z.J. Xu, Prof C. Wang supervised the entire project.
- I prepared the manuscript drafts. Assoc. Prof Z.J. Xu, Prof C. Wang discussed and analyzed the data with me. Assoc. Prof Z.J. Xu and Prof C. Wang revised the manuscript and provided valuable suggestions which helped in polishing the manuscript further.
- Mr. J. Wang and I performed all the catalytic measurements and analyzed the data. Mr. J. Wang and Dr S. Sun synthesized the materials.
- Dr Y. Sun conducted the Density Functional Theory computation calculations and corresponding data analysis.
- Ms. Y. Duan and Dr S. Sun conducted the sample characterizations in the Facility for Analysis, Characterization, Testing and Simulation and assisted in analyzing of the characterization data.
- Mr. J. Wang assisted in the temperature programmed desorption experiments and data analysis.
- Dr Y. Du and Dr S. Xi assisted in the collection of the X-ray absorption fine structure data in Singapore Synchrotron Light Source. Ms. Y. Duan and I analyzed the data.

[Input Date Here]

[Input Signature Here]

.... 01/01/2020.....

..... WANG TING

Date

[Input Name Here]

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Summary

Driven by the growing concern over air contamination, particularly the emission of exhaust gas, the development of air purification technologies is of paramount importance for maintaining a clean global environment. Heterogeneous catalysis as one of the most efficient responses to this pursuit has drawn a great deal of attention. While noble metal catalysts are an effective solution, their high cost and scarcity render them unsuitable to fulfill the growing demand. Attention has thus shifted to the more abundant transition metal oxides, with an expectation of designing highly effective catalysts. The rational design of efficient catalysts can be guided by gaining fundamental understandings on the structure-performance relationship, as well as identifying pertinent descriptors which can rationalize and predict the catalytic behaviors. Among the various earth-abundant oxide materials, cobalt-based spinel oxides or perovskite oxides have emerged as promising candidates, and thus in this thesis, specific attention has been given to those cobalt-based spinel oxide and perovskite oxide families. Two basic and major exhaust gas, i.e. CO and methane are employed. This dissertation first identifies the parameters that influence the activity of Co-Mn containing spinel oxide catalysts on CO oxidation. By tuning the ratio of octahedrally occupied Mn to Co in series of $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) spinel oxides, a correlation between the catalytic CO oxidation activity and e_g occupancy of Mn cations or the O p -band center relative to the Fermi level has been established. These two indices of how the electronic structure influences the oxygen addition- and removal-related processes, are proposed to be the activity descriptors. Second, the underlying origin of the structure and temperature-dependent complete methane oxidation over Co-Ni containing spinel oxides is examined. Ni is introduced to substitute the

octahedrally coordinated Co in series of $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$) for a tunable variation in electronic structure. Given a fair comparison of the catalyst intrinsic specific activity, it is found that the interplay between O p -band center and M_{oct} d -band center is correlated with not only the methane oxidation activity but also the thermal stability and reaction mechanism of the catalysts. CH_4 -TPD-MS and O_2 -TPD tests further confirmed the DFT results with featured involvement of adsorbed oxygen or lattice oxygen. It is accordingly proposed that the relative position between O p -band center and M_{oct} d -band center can serve as an activity/mechanism descriptor of the methane complete oxidation for spinel oxides. Third, efforts are devoted to unveiling the applicability of the as-established activity descriptor to perovskite oxides family. The structure-activity relationship of B-site substituted $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ ($x=0\sim 1.0$) perovskite oxides for complete methane oxidation is firstly investigated. It is revealed that the interplay between O p -band center and B site metal cation d -band center governs the catalytic comportment. The as-revealed governing role is further extended to the A-site substituted $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ perovskite oxides for catalytic performance prediction, which turns out to be effective. Briefly, the interplay between O p -band center and B-site metal cation d -band center can specify the catalysts' intrinsic property accountable for the catalytic performances and in turn predict the catalytic behavior.

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Figure 6.7 (a) BET measurements; (b) XRD patterns of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x=0.0, 0.25, 0.50, 0.75, 1.0$) perovskite oxides.

Figure 6.8 (a) PDOS of the d states of B-site Co and O p states in $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ ($x=0.25$) and SrCoO_3 ($x=1.0$), the up and down arrows refer to the spin up and spin down projection, respectively; (b) Specific values of the B-site Co d -band center relative to the Fermi level and O p -band center relative to the Fermi level in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x=0.0, 0.25, 0.5, 0.75, 1.0$), respectively; (c) The relative position values between the O p -band center and B-site metal cation d -band center in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x=0.0, 0.25, 0.5, 0.75, 1.0$); Insets are the schematic representation of the O p -band center and Co d -band center for $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ and SrCoO_3 ; (d) Catalytic performances of the A-site substituted $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ for complete methane oxidation in terms of the normalized specific activities and normalized peak areas of the produced CO_2 from CH_4 -TPD-MS experiment by $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$.

Figure 6.9 CO_2 detection from mass spectra during the CH_4 -TPD test for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x=0.0, 0.25, 0.50, 0.75, 1.0$) perovskite oxides. The produced CO_2 which reflects the activity of surface lattice O is well correlated with the O p -band center relative to the Fermi level calculated from DFT. This further confirms our proposal from the DFT calculations.

Abbreviations

TPD	Temperature Programmed Desorption
MS	Mass Spectrometry
E-R	Eley-Rideal
L-H	Langmuir-Hinshelwood
Mv-K	Mars-van Krevelen
DFT	Density Functional Theory
GWP	Global Warming Potential
TWC	Three-Way Converters
XAS	X-ray Absorption Spectroscopy
ROS	Reactive Oxygen Species
ORR	Oxygen Reduction Reaction
OER	Oxygen Evolution Reaction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
SAED	Selected Area Electron Diffraction
BET	Brunauer-Emmett-Teller
XRD	X-Ray Diffraction
XANES	X-ray Absorption Near Edge Structure
EXAFS	Extended X-ray Absorption Fine Structure

XPS X-ray Photoelectron Spectroscopy

ICP-OES Inductively Coupled Plasma-Optical Emission Spectrometry

List of Publications

1. **Ting Wang**, Yuanmiao Sun, Ye Zhou, Shengnan Sun, Xiao Hu, Yihu Dai, Shibo Xi, Yonghua Du, Yanhui Yang, Zhichuan J. Xu. Identifying influential parameters of octahedrally coordinated cations in spinel $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ oxides for the oxidation reaction. *ACS Catalysis*, 8 (2018) 8568–8577.
2. **Ting Wang**, Jieyu Wang, Yuanmiao Sun, Yan Duan, Shengnan Sun, Xiao Hu, Shibo Xi, Yonghua Du, Chuan Wang, Zhichuan J. Xu. Origin of electronic structure dependent activity of spinel $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ oxides for complete methane oxidation. *Applied Catalysis B*, 256 (2019) 117844.
3. Haiyan Li*, Shengnan Sun*, Shibo Xi, YuBo Chen, **Ting Wang**, Yonghua Du, Matthew Sherburne, Joel W. Ager, Adrian C. Fisher, and Zhichuan J. Xu. Metal-oxygen Hybridization Determined Activity in Spinel-based Oxygen Evolution Catalysts: A Case Study of $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$. *Chemistry of Materials*, 30 (2018) 6839-6848.
4. Linghui Yu, Jiajia Song, Luyuan Paul Wang, Samuel Jun Hoong Ong, Chengding Gu, Hanbin Liao, **Ting Wang**, Wei Chen, Ovadia Lev, Zhichuan J Xu. An Investigation on the Relationship between the Stability of Lithium Anode and Lithium Nitrate in Electrolyte. *Journal of The Electrochemical Society*, 166 (2019) A3570-A3574.

Patents held

Zhichuan Xu, **Ting Wang**, Xiao Hu, *An Active Catalyst Support*, Singapore professional Know-How

Chapter 1 Introduction

1.1 Background and Hypothesis

Air contamination primarily comes from waste gas emissions, has caused millions of death worldwide and is one of the worst toxic pollution problems^[1]. Among the various pollutants, carbon monoxide (CO) and methane (CH₄) have drawn extensive attention. CO as an easily overlooked but severe pollutant can cause fatal suffocation at a low concentration of hundreds of ppm^[2,3]. CH₄, the major constituent of natural gas, possesses a greenhouse effect that is much more prominent than CO₂^[4]. To meet the increasingly stringent environmental regulations, various technologies have been developed for the abatement of CO and methane atmospheric emissions^[5,6]. Currently, the most efficient and simple strategy is heterogeneous catalysis, through which CO or methane is completely oxidized into carbon dioxide^[7,8]. To date, the most successful example is the noble metal-based catalysts being applied in the toxic exhaust gas emissions from automobiles (three-way catalysts)^[5,9]. However, besides the high cost, noble metals prone to deactivation due to sintering, poisoning or decomposition under high temperatures, thus restraining their industrial applications^[10,11]. Exploring efficient and low-cost alternatives is therefore inevitable for the development of technology. Transition metal oxides, particularly the spinel oxides and perovskite oxides, are considered as promising alternatives due to their distinctly lower prices and superior catalytic activities.

Besides the detrimental effect of CO, the CO oxidation reaction, as an elementary reaction has widely been employed as a fundamental model for catalysts screening and mechanism understanding^[12]. Among the numerous investigated transition

metal oxide catalysts, cobalt-based or manganese-based spinel oxides are some of the most intriguing oxides due to their excellent CO oxidation performance^[12]. Numerous studies^[12–16] have focused on the activity of the catalysts but controversies still exist in explaining the influential parameters. Therefore, more investigations aiming to disclose the interactions and key parameters that influence the activity (e.g., with compositional changes) are in demand to understand the catalytic process. Particularly, parameters of octahedral sites have suggested to be the primary active sites^[13,17]. Moreover, as inspired by the proposed *d*-band center model in the CO oxidation over Pt alloys^[9] and the *d* electron states as an activity descriptor over Au nanoparticles^[18], we have a great interest in understanding the CO oxidation process over spinel oxides from another perspective such as molecular orbital theory. Though in the electrocatalysis process, the e_g filling state, metal–oxygen covalency, etc., have been established as activity descriptors for perovskite^[19–22] and spinels^[23], such descriptors that capturing the origin of CO oxidation activity by spinel oxides are rare. Therefore, the thesis tests the hypothesis in chapter 4 that there exist dominating parameters that governing the composition-dependent CO oxidation activity of substituted Co, Mn spinel oxides.

Compared with the CO oxidation process, the complete catalytic oxidation of methane is far more complicated, during which the CO oxidation is one of the multi-steps^[24]. As one of the basic hydrocarbon pollutants with high symmetry, understanding the mechanistic process of methane catalytic oxidation is of vital importance to the complex heterogeneous catalysis and environmental remediation. However, despite widespread investigations and attention on the complete methane oxidation, a definite reaction mechanism on the transition metal oxide catalysts has yet to be elucidated. The debates are mainly focused on the involvement of

dissociative adsorbed oxygen featured suprafacial Eley-Rideal (E-R)/Langmuir-Hinshelwood (L-H) mechanism^[8,25], or the lattice oxygen featured intrafacial Mars-van Krevelen (Mv-K) mechanism^[8,24,26]. In order to intrinsically understand at a molecular level of parameters that would trigger the E-R or Mv-K mechanisms, an exploration of the intrinsic origin of the structure-activity/mechanism relations and pertinent descriptors would provide us with a more comprehensive understanding of the oxidation reaction over spinel oxides. The thesis tests the hypothesis in chapter 5 that there exists a dominating parameter/descriptor governing the composition-dependent methane oxidation activity of substituted Co, Ni spinel oxides.

Perovskite type catalysts as another alternative to the noble-metal catalysts are preferable due to their low costs, excellent thermal stability, and their unique tunable structures with exceptional redox and oxygen mobility properties^[10,27,28]. Although the investigations of applying perovskite as catalysts for hydrocarbon oxidation reactions were started early from the 1970s^[29,30], the methane oxidation mechanism studies are mainly by means of kinetic data. A further step employing more theoretical tools like modeling, molecular simulations, *in situ* measurements, etc. are necessary for the mechanism study. Furthermore, despite the considerable studies on the interpretation of methane oxidation activities, rarely any attention has been paid on the descriptor studies of methane oxidation over perovskite catalysts. Thus, by investigating the A site or B site substituted La, Co-based perovskite oxides, chapter 6 tries to offer a landscape on the understanding of complete methane oxidation over perovskite oxides and to test whether the established descriptor on spinel oxides is applicable to the perovskite family.

1.2 Objectives and Scope

The overall objective of this dissertation is to develop fundamental understandings of waste gas complete oxidations over spinel oxide and perovskite oxide catalysts. Through probing the relationships between the physicochemical properties of catalysts and the catalytic performances, i.e. structure-performance relations, the oxidation mechanisms are intrinsically understood. Proper influential parameters are identified and proposed as activity descriptors, which capture the physical origin of catalytic behaviors and in turn, can help to predict the activities of catalysts. These fundamental understandings enable the rational design of efficient transition metal oxide catalysts for catalytic oxidation reactions.

Firstly, the simplest and widely investigated oxidation reaction model – CO oxidation – is employed to identify the parameters that influence the activity of spinel oxide catalysts. It is known that the octahedral sites of spinel oxides on the surface are suggested to be the primary active sites^[13,17], therefore a series of $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) spinel oxides are synthesized. With the inactive Zn^{2+} ^[31] occupied at the tetrahedral sites, the octahedral sites are exclusively investigated with a tunable ratio of Mn/Co. A correlation between the catalytic activity and e_g occupancy of Mn cations or the O p -band center relative to the Fermi level has been established.

Secondly, based on the probe of CO oxidation reaction over Co-based spinel oxides, the more complicated CH_4 oxidation reaction is subsequently explored on a series of $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) spinel oxides since the cobalt and nickel are considered as intriguing transition metals with promising activity for methane catalytic combustion^[5,26]. The physical origin of different catalytic behavior

(activity as well as reaction mechanisms) as a function of substitution element (Co by Ni) at the octahedral sites is revealed utilizing density functional theory (DFT) computation and temperature-programmed desorption techniques.

Thirdly, to check whether the established descriptors in spinel oxides applies to the perovskite family, two series of LaCoO_3 perovskite oxides with substitutions in either A position or B position (i.e. $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ or $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$) are synthesized as perovskite oxide catalysts for methane oxidation. The B-site substituted $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ ($x=0\sim 1.0$) perovskite oxides are firstly studied to check the structure-activity relationship. Methane oxidation mechanisms are understood assisting by the experiment results and DFT calculations. The feasibility of applying the descriptor to rationalize the catalytic activity and reaction pathways is investigated. Furthermore, a catalytic performance prediction study is carried out over A-site substituted $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x=0\sim 1.0$) perovskite oxides. This is made possible by the DFT calculations, followed by an analysis to predict activity patterns as a function of reaction temperatures. A comparison between the predictions and experimentally observed activities is made to justify the feasibility of applying the proposed descriptor for performance predictions.

1.3 Dissertation Overview

The thesis addresses the fundamental origin of the composition/temperature-dependent CO oxidation and methane oxidation by spinel and perovskite structured oxide materials (to be more specific, Co, Mn-based spinel oxides for CO oxidation; Co, Ni-based spinel oxides and La, Co-based perovskite oxides for methane oxidation).

Chapter 1 provides general background on catalytic CO and methane oxidations

over transition metal oxides. The goals and scope of the study are outlined.

Chapter 2 reviews the literature on CO and methane catalytic oxidations, the existing efficient catalysts being developed, particularly the spinel oxide and perovskite oxide catalysts. The mechanistic investigations on CO and methane oxidation and related activity influential parameters have also been summarized.

Chapter 3 elaborates on synthesis methods of transition metal oxides, characterization techniques and simple principles behind them.

Chapter 4 identifies the parameters of the octahedrally coordinated cations in Co, Mn-based spinel oxides that influence their activity towards CO oxidation.

Chapter 5 elaborates on the physical origin of catalytic activities and mechanisms of complete methane oxidation over the Co, Ni-based spinel oxides. Mechanism understandings depended on reaction temperatures and catalysts *per se* are revealed and corresponding activity descriptor is established.

Chapter 6 focuses on the applicability of the established methane oxidation descriptor to B-site substituted $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ perovskite oxides. A performance prediction study is also conducted over the A-site substituted $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ perovskite oxides. Mechanism understandings of complete methane oxidation towards perovskite oxides with tunable electronic structures have been discussed.

Chapter 7 draws together the threads of the thesis and recommendations for future investigations.

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Chapter 2 Literature Review

2.1 Introduction

As technology develops, environmental pollution has become an increasingly concerned issue due to the high health risk they pose on humans and animals. In particular, the air pollution has become one of the worst toxic pollution problems, which has caused millions of death worldwide and is the sixth-leading cause of death^[1]. Waste gas emission is one of the major sources for air pollution. There are two main sources for waste gas emissions, i.e. the transportation sources involving primarily automobile vehicles, and the stationary sources with combustion of fossil fuels like the power plants^[2]. Chemical plants are also a class of intensive emission sources for various chemical gases. Among the various sources, automobile exhaust is found to be the major waste gas contributor responsible for many pollutants, for instance, 90% or more of the total outdoor CO emissions in urban areas^[3] are originated from vehicle exhaust which stands for nearly half of the non-fire poisonings^[2].

The major pollutants in exhaust gas include carbon monoxide (CO), in-completely combusted hydrocarbons (HC), nitrogen oxides (NO_x), etc^[4]. Among the many ubiquitous contaminants of the environment, carbon monoxide (CO) is a severe but easily overlooked pollutant which may have caused more than a half of the reported fatal poisonings not even considering the grossly under-reported fact in fatal cases^[5]. It can cause headache, nausea, vomiting, permanent neurological damages or even fatal suffocation at a low concentration of hundreds of ppm^[3,6]. Another typical pollutant, methane, is actually the major component (over 90%) of a key fossil energy resource and raw material being used in our society - natural

gas^[7,8]. Compared with the coal and oil, natural gas is perceived as a low-carbon emission fuel and is projected to increase its production of 60% by the year 2040, which is approximately 5,765 billion cubic meter^[9]. However, when taking the climatic effect of methane emission into consideration, the scenario changes^[10]. As a potent greenhouse gas, methane possesses a global warming potential (GWP) 86 times higher than that of carbon dioxide (CO₂) over 20 years^[8]. In 2013, an increase of the concentration of methane in atmosphere by 150% since 1750 was reported^[8]. As a matter of fact, high concentration of waste gases will result in not only harmful biological impact to the livings, but also physical impact from the high concentration of physical gel particles suspended in air. These gel particles may host the bacterial and cause serious problems in urban living environment^[11]. On top of this, the emission of waste gas should be strictly controlled and reduced considering their associated serious health and environmental issues.

2.2 Heterogeneous catalysis technology for waste gas treatment

Intensive technologies have been developed to address the exhaust gas issues, and one of the most effective measures is to convert them into safer chemicals and/or materials so that the presence of waste gases in the air can be minimized and the urban area is more sustainable^[8,12–14]. Heterogeneous catalysis as a key option in catalytic conversion has become incredibly important^[15]. Currently, one of the most successful examples of industrial relevant applications of heterogeneous catalysts is the oxide-supported precious metal catalysts (mainly based on platinum-group metals like rhodium, platinum, palladium), which have been used in the automobile three-way converters (TWC)^[16] to reduce significantly the waste gas emissions from motor vehicles. According to the US EPA, the CO levels in air has decreased significantly since 1980 and can meet the outdoor standards (see

Figure 2.1) as most of the new cars were required to be equipped with catalytic converters from 1975 onwards^[17].

Figure 2.1 US national trend in CO based on 69 cities from the year 1980 to 2015^[17].

The widely application of catalyst technologies in reducing the automobile exhaust emissions started from the original clean air act in the fall of 1974. Until around 1978, TWC were completely developed^[18]. Numerous scientific literatures and patents regarding the potential and commercialized three-way catalyst have appeared in the past forty years. Nevertheless, Air Products, The Catalyst Company, Degussa, Engelhard, W. R. Grace, Johnson Matthey, and UOP remains to be the major catalyst suppliers to the US automobile industry^[19]. The three-way catalysts are aimed to eliminate the three major exhaust pollutants CO, HC and NO_x. Both oxidation and reduction reactions are involved in the working mechanism of converters. For CO and CH, the desired product is CO₂ through oxidations, while the desired product is N₂ for NO_x through reduction reactions. Currently, these catalytic reduction and oxidation reactions are realized through the noble metals in the catalysts. For the reduction reactions, it is widely recognized that in a three-way catalyst, rhodium (Rh) is mainly responsible for the promoting reduction of NO_x to N₂, which exhibits excellent activity with a typical small usage

of 0.18 to 0.30 g per converter^[19]. Some drawbacks occurred when Rh plays the role as oxidation catalyst such as its high cost and sensitivity to preconditioning in oxygen. Here, in this thesis, we focus on the oxidation reactions, and catalytic reductions will be part of our future work. In a typical three-way catalyst, platinum (Pt) is mainly responsible for the oxidation conversion of CO and HC. Palladium (Pd) is sometimes added together with Pt for the catalytic oxidation or applied in dual-bed catalyst as the second oxidation catalyst^[16,19]. Other metals as iridium, ruthenium and so on have been investigated as alternative catalytic candidates but currently not yet commercialized.

2.3 Catalysts overview

As the heterogenous catalysis technology develops, developing high-performance catalysts has been a main topic to the research group. Various types of catalysts including noble metals, transition metal oxides, etc. have been produced and explored. Figure 2.2 gives an example of the catalysts being introduced for methane combustion^[20].

Figure 2.2 Catalysts being reviewed for methane combustion^[20].

2.3.1 Noble metal-based catalysts for catalytic oxidations

Nobel metal catalysts including Pd, Pt, Au, etc. are currently the most used and investigated catalytic materials for oxidation reactions including CO oxidation and complete methane oxidation.

Pd based catalysts has long been investigated and regarded as one of the most active catalysts towards oxidation reactions, particularly, for complete methane oxidation^[8,20]. Studies of Pd based catalysts mainly focus on the active state/phase during the methane oxidation process. Debates are usually concerning the metallic Pd^[21] or oxidised/partially oxidised PdO^[22], and some raises a mixed phase as Pd⁰/PdO_x^[23]. In fact, the behaviour of Pd as an oxidation catalyst is complicated with several active phases depending on the reaction conditions, sometimes they can be dynamic. For example, PdO^[22] is the mostly recognized active phase for the oxidation reactions, however, it will decompose into Pd metal at the temperature range of 923~1123 K. This decomposition process is reported to have negative effect on the catalytic reaction by lowering conversions. Nevertheless, when Pd is re-oxidised into PdO, the catalytic conversions are expected to be restored^[20]. Matam et al.^[24] tried to probe the nature of active phases on Pd/Al₂O₃ using the *in-situ* X-ray absorption spectroscopy (XAS) technique. The behaviour of Pd was monitored for the entire methane oxidation cycle up to 1130 K. The results manifest that the active Pd species are temperature dependent, PdO is responsible for activity under the temperature of 950 K, while the reduced Pd played an important role for the temperatures above. Recently, it has gradually become a common point that both reduced and oxidized forms of Pd contribute to the methane oxidation, but their effectiveness is temperature dependent^[25].

In contrast to the Pd based catalysts, the Pt based catalysts are less effective for the methane oxidation, whereas it is generally accepted they show better activity to the oxidation of higher hydrocarbons^[20]. Meanwhile, compared with the Pd catalysts, Pt catalysts would generally more resistant to some poisoning, for instance, the sulphur poisoning^[26]. One of the interests about the Pt catalysts is the particle size effect. For example, the activity of supported Pt nanoparticle is reported to depend on the average particle size of Pt by Beck etc.^[27]. Some contradictory opinions are also reported which doubts on the size effect. As they think the size differences may arise from the contamination of chlorine by using the Cl-containing Pt precursors. Sintering as another interference may lead to larger Pt particles during the sample preparation. To solve this problem, monodisperse Cl free Pt/Al₂O₃ catalysts were synthesized^[27]. A narrow size dependence of specific activity was observed. It was also found the dependence of apparent activation energy of CH₄ oxidation may result in this strong size sensitivity.

Compared with Pd or Pt based catalysts, Au based catalysts are not so widely studied in methane oxidation; however, it is more widely used in the CO oxidations as a potential alternative catalyst to solve the cold-start problem. The attentions started from a breakthrough made by Haruta and co-workers in 1987^[28], when they confirmed the properly prepared nanosized gold, supported on metal oxide showed extraordinary catalytic oxidation ability to CO at a temperature as low as -343 K. Motivated by the superior catalytic activity of gold, numerous studies have focused on the explanations of this phenomenon. Many potential factors may be introduced and concurrent in the complex gold catalytic system that can contribute to the catalytic activity. Both gold and the oxide support could be indispensable in determining the activity. Min and Friend^[15] classified the possible

contribute factors into two general categories as factors relate to gold and factors relate to the support as illustrated in the following scheme (Figure 2.3). Despite the seemingly confused situations full of debates and contradictions, some principle factors are generally agreed as responsible for the enhanced activity of gold. For example, size of the gold particles, which has been regarded to make a major effect on the activity. Generally, gold particles with diameter less than 5 nm proved to be highly active, with the highest rates to be at sizes of about 2 to 3 nm^[29]. And this is in regardless of the oxide support type^[30].

Figure 2.3 Schematic display of possible factors contribute to the catalytic activity of gold-based catalysts^[15].

Another consensual factor is the effect of oxide support. The support effect on Au catalysts are generally divided into two types. The reducible oxides type including TiO₂, Co₃O₄, Fe₂O₃ and so on which possess variable valence states and easy to be reduced. In contrast, the irreducible oxides usually refer to MgO, SiO₂, etc. that are relatively more difficult to be reduced. Normally, the reducible oxides are thought to be active sites for the catalytic reactions due to their participations in the catalytic process. They either supply oxygen or promote activation of oxygen in

the interface, or/and facilitate the CO₂ removal through the surface hydroxyl groups reactions^[31]. With regard to these irreducible oxides, they are thought to be inactive to the catalytic activity due to their inert role to the reactions, therefore, higher temperatures are required over the irreducible oxides supported gold catalysts than reducible oxides supported ones^[30,32]. Despite the high activity of noble metal-based catalysts, some drawbacks have hindered their applications, and one of the foremost is the high cost and shortage of these precious metals (Figure 2.4). It is therefore inevitable to explore efficient and low-cost alternatives, e.g. transition metal oxides.

Figure 2.4 Diagram of annual mine production of noble metals globally in 2012^[33].

2.3.2 Transition metal oxide catalysts for complete catalytic oxidations

2.3.2.1 Spinel oxides

Transition metal oxides make up one class of potential catalysts to noble metal catalysts due to their low cost and promising catalytic ability. Among them, spinel structured oxides are one of the most investigated materials. Since 1970s, some spinel type oxides have been found to be active for CO oxidation^[12]. Ever since, numerous studies had been carried out to improve the activity of spinel oxides and

to understand their oxidation mechanisms. The catalytic performances of mixed spinel oxides for the oxidation reaction are very often dependent, *inter alia*, on the composition, morphology, structure of the materials, coordination environment of the cations, etc.^[34,35]. Great effort has been spent on the catalytic mechanisms related to those factors, and some remarkable progress has been made. For example, the investigation of CO oxidation by both Co₃O₄ nanorods and nanoparticles revealed that octahedrally coordinated Co³⁺ ions are the active species^[36], which highlight the octahedral sites to be primary active sites in spinel oxides. Among the various compositions in spinel oxides, Co based spinel oxides are found to exhibit excellent activities. For instance, Co₃O₄ powder with a specific surface area of $\sim 5 \text{ m}^2 \text{ g}^{-1}$ showed a CO oxidation activity of $14 \times 10^{-6} \text{ mol s}^{-1} \text{ g}^{-1}$ ^[37], which is comparable to that of Pt alloys^[38]. A remarkably better catalytic performance has been further achieved for Co₃O₄ nanorods, which are capable of catalysing CO oxidation at a temperature as low as 196 K^[36]. The cobalt-based spinel oxides also exhibit high catalytic activities towards methane complete oxidations. For instance, different-shaped Co₃O₄ nanocrystals^[39] including sheets, belts, and cubes all display a T₉₀ (the temperature where 90% of methane is converted) lower than 673 K. Compared with cobalt-based spinel oxides, spinel manganites have generally been less studied^[37]; their activities are thereby still unclear to some extent, and some contradiction even exists. For instance, on one hand, the following order of activity has been reported^[40]: CuMn₂O₄ > CuCrO₂ $\approx$ Co₃O₄. On the other hand, Yang et al.^[35] found a lower activity for Mn-containing spinel oxides than for other spinels with Co and Cu. Nickel, as another active transition metal for methane catalytic combustion, has drawn great attention. Typically, Ni is added into the CeO₂ to form binary mixed oxides. The improved

catalytic combustion of hydrocarbons is due to the enhanced oxygen storage capacity and redox properties of the catalysts^[41,42]. A spectacular activity of the complete conversion below 673 K was reported on Ni incorporated cobalt spinel oxides^[43]. The monolithically integrated spinel $\text{Ni}_{0.5}\text{Co}_{0.25}\text{O}_4$ nanoarray has also been found having a higher methane oxidation activity than that of Co_3O_4 and $\text{Zn}_{0.5}\text{Co}_{0.25}\text{O}_4$ nanoarrays^[44].

2.3.2.2 Perovskite oxides

In all the transition metal oxides being investigated, perovskites with general structure ABO_3 is probably the most investigated catalysts for CO and methane oxidation^[12]. The A site possesses a typical lanthanide, alkaline or alkaline-earth cation, and B site possesses the transition metal cations. A typical cubic perovskite oxide unit cell is given in Figure 2.5., where the A cation coordinates with twelve O anions and B cation coordinates with six O anions^[45].

Figure 2.5 Unit cell schematic illustration of ABO_3 perovskite oxide^[45].

Preliminary study paved the way for the development of perovskite as catalysts for oxidation reactions since 1970s^[12,46,47], and abundant studies have thereafter been reported. Composition effect from substitutions at A site or B site are the most intensively investigated. For the partial A site substitutions, La based perovskite substituted by Sr is the most intriguing system^[12]. The introduction of Sr into

LaCoO₃ was reported can increase the surface areas of catalysts^[48,49]. However, a mediate substitution is reported to give higher activities. For instance, higher activities were observed by Parkash et al.^[50] in La_{1-x}Sr_xCoO₃ (x=0, 0.12, 0.3, 0.5) perovskite oxides than that of LaCoO₃, however, La_{0.7}Sr_{0.3}CoO₃ gave the best activity. Similarly, in the context of methane oxidation, a low degree of substitution is recommended by Gao and Wang^[51], where the methane oxidation activity for La_{1-x}Sr_xCoO₃ perovskites displayed in an order of x=0.1 > x=0.2 > x=0 or 0.3. La_{0.8}Sr_{0.2}MnO₃ in a series of La_{1-x}Sr_xMnO₃ perovskites (0 < x < 0.5) was also found to exhibit the highest intrinsic activity for methane catalytic combustion, although the BET surface area of these catalysts increases with higher Sr substitution^[52]. The partial substitution of La by Ce is also widely studied. The effects of Ce⁴⁺ substitution on the enhanced oxygen mobility are generally recognized^[53], which may result in the increase of catalytic activities.

For the B site substitution, for instance, the catalytic activity of LaBO₃ (B=V³⁺, Cr³⁺, Mn³⁺, Fe³⁺, Co³⁺, Ni³⁺) were investigated for CO oxidation, and the activity was correlate with the local symmetry of the number of d electrons of B site metal ions^[54]. Nanostructured LaBO₃ (B= Fe³⁺, Co³⁺, Mn³⁺) were prepared by Wei et al.^[55] for the methane catalytic combustion and it was found that the activity was follow the order as LaMnO₃ > LaCoO₃ > LaFeO₃. They ascribed the better activity of LaMnO₃ to its higher surface area. For the B site partial substitution in lanthanum cobaltite, Co was substituted by Fe in most cases^[56]. For instance, Royer et al.^[57] conducted an extensive study on the synthesis of partial Fe substituted LaCoO₃ perovskite oxides, i.e. LaCo_{1-x}Fe_xO₃ perovskites, using five different procedures and discussed the effect of synthesis conditions on catalytic

activity for methane oxidation. Double substitution in both the A and B positions have also been developed to further enhance the activity. For instance, the $\text{NdSrCu}_{1-x}\text{Co}_x\text{O}_{4-\delta}$ and $\text{Sm}_{1.8}\text{Ce}_{0.2}\text{Cu}_{1-x}\text{Co}_x\text{O}_{4+\delta}$ ^[58] for methane oxidations. However, some controversy was observed for double substitution. One order of magnitude higher specific activity was reported by Isupova etc.^[59] in $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.95}\text{Fe}_{0.05}\text{O}_3$ compared to $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ in CO oxidation. On the contrary, a progressive decrease in oxidation activity was observed when Fe was introduced in $\text{La}_{0.9}\text{Ce}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ ^[60].

2.3.2.3 Other transition metal oxides

The single metal oxide-based catalysts are a group of materials that display great potential on catalytic oxidations. The typical representatives of single metal oxide catalysts are copper oxide and manganese oxide-based catalysts. CuO is usually used with a porous substrate support. Various porous support including SiO_2 ^[61], Al_2O_3 ^[62], ZrO_2 ^[61] and so on have been investigated. The dominate role of Cu is well recognized by the investigations, while the nature of support has an important influence on the active Cu species on surface. Aguila et al.^[61] investigated the influences from different supports and the catalytic activity for methane oxidation was reported to follow the order of $\text{CuO}/\text{ZrO}_2 > \text{CuO}/\text{Al}_2\text{O}_3 \geq \text{CuO}/\text{SiO}_2$. The higher activity of CuO/ZrO_2 was attributed to the highly dispersed Cu species which was stabilized by zirconia. CuO nanoparticles have also been developed but with sever aggregation problems which hindered the further improvement of activity^[61]. CuO nanowires was developed by Feng et al., which exhibited not only excellent activity towards methane oxidation but also with remarkable stability^[63]. Manganese oxides have drawn great attention as effective oxidation catalysts due to their unique redox property. The catalytic activities of manganese oxides are

primarily dominated by the valence states of Mn as well as their oxygen storage capacity^[20]. Several oxidation states may co-exist in the manganese oxides-based catalysts with or without supports, which includes, Mn_3O_4 , Mn_2O_3 and MnO_2 . Various nanostructured manganese oxides have been developed, such as nanowires, nanoarrays, nanoparticles, and recently nano-coral like structure^[20,64]. Despite their promising activity, one of major problem faced by the manganese oxides catalysts is the sintering of some active phase e.g. $\alpha\text{-Mn}_2\text{O}_3$ grains, which causes the activity deactivation. Apart from the single oxides, mixed transition oxides are also widely investigated for the heterogenous oxidations. One or several transition metal oxides such as iron oxides, nickel oxides, manganese oxides, zirconium oxides are mixed with each other and used for CO oxidations or methane oxidations^[12,20,65,66]. For instance, a synergetic effect between MnO_x and NiO was observed in the $\text{MnO}_x\text{-NiO}$ oxides and therefore possessed a higher activity in methane oxidation than their counterparts^[65].

2.3.3 Catalytic oxidation mechanisms

The mechanism of CO oxidation or methane complete oxidation is a long-standing puzzle, which drives marvellous studies to address this issue. Compared with the noble metals, investigations on oxidation mechanisms towards transition metal oxide-based catalysts are not so mature. In particular to the spinel oxides and perovskite oxides, the situation is more complicated. Compared with the d^0 transition metal oxides, for instance V_2O_5 , WO_3 , which usually considered to follow the intrafacial Mars-van Krevelen mechanism for hydrocarbon and CO oxidation^[67,68], spinels or perovskites with $d^{n>0}$ enables more possibilities. Generally, two alternate mechanistic pathways are recognized to be involved in the complete oxidation of CO or lean methane, the suprafacial Langmuir-Hinshelwood

(L-H) mechanism or Eley-Rideal (E-R) mechanism (involvement of adsorbed oxygen), and the intrafacial Mars-van Krevelen (Mv-K) mechanism (participation of lattice oxygen)^[37,67].

For the suprafacial mechanism: the catalyst only provides sites for adsorption and activation of reactants. Surface reaction is subsequently occurred between the dissociative or molecular reactants. Figure 2.6 gives a schematic example of the suprafacial L-H mechanism for CO oxidation over supported transition metal oxides (inert and active supports).

Figure 2.6 Schematic illustration of L-H mechanism on CO oxidation over inert/active supported transition metal oxides^[12].

For the intrafacial mechanism: the catalyst is no longer an “inert” material which accommodates reaction sites. It participates in the reaction by providing bulk/lattice oxygen. The consumed oxygen is regenerated through incorporation of gaseous oxygen after adsorption and dissociation processes. In another word, the oxidation reaction takes place via the reduction-oxidation of catalysts’ surface. Tao etc.^[43] proposed a methane oxidation mechanism on NiCo₂O₄ spinel oxides with

lattice oxygen participation as shown below in Figure 2.7. This mechanism is understood at a molecular level through *in situ* studies and theoretical simulations. Despite widespread investigations and attentions, contradictory opinions have long been existed regarding to the above two oxidation reaction mechanisms over spinel or perovskite oxides. Taking the cobalt spinel as an example, some researches have considered the suprafacial reactive oxygen species (ROS), produced from the dissociative adsorption of O_2 , as the governing factor that is responsible for the high catalytic activity via the L-H mechanism^[69,70]. In contrast, the active lattice oxygen and the generated O vacancies implicated in the Mv-K mechanism are regarded to be of vital importance during the catalytic process by other researches^[71,72].

Figure 2.7 Proposed two different reaction pathways of methane complete oxidation on $NiCo_2O_4$ (110-B) of type I crystal by Tao etc. Either pathway A or pathway B involves the participation of lattice oxygen^[43].

Nonetheless, with a metal character for both valence and conduction bands in spinel or perovskite oxides, the preference or coexistence of the above two

mechanistic pathways are possible and is controlled by reaction conditions^[67]. This is called the two-term mechanism and the situation is more commonly recognized in the complete oxidation of methane by spinel or perovskite oxides. For instance, Pomonis et al.^[73] proposed a twin mechanism with simultaneous operation of suprafacial and intrafacial mechanisms depending on the reaction temperatures using two series of $\text{La}_{1-x}\text{Sr}_x\text{NiO}_{4-\lambda}$ prepared by two methods for methane oxidations. This is in consistent with the parallel mechanism proposed by Arai et.al^[74] based on the partially substituted La-Fe, La-Mn, and La-Co perovskite oxides. Recently, Zasada etc. offered a detailed landscape of the interplay between the L-H and Mv-K mechanism over cobalt spinel nanocubes with the help of both experiment and theoretical studies (as indicated in Figure 2.8), in which the catalytic process was divided into three temperature windows dominated by different mechanisms^[67,71]. From 573 K to 723 K, the L-H mechanism operates, while above 923 K, the Mv-K mechanism dominates. In between, these two mechanisms operate simultaneously. Follow up, their recent work employing the catalytic isotopic investigations and DFT modelling further confirms the operation of both the suprafacial and interfacial mechanisms. These two mechanisms may operate separately or in parallel depending on the reaction temperature and the O_2 pressure. Corresponding Co-O species are proposed to be responsible in the first C-H bond activation which is believed to be the kinetically relevant step. Two three-dimensional enthalpy diagrams have also been provided to discriminate between the above two mechanisms^[75].

Figure 2.8 Investigations on the interplay between suprafacial and intrafacial mechanisms on methane oxidation by spinel cobalt oxide nanocubes by means of isotopic experiment and DFT modelling^[76].

Along with the mechanism understandings, various factors have been proposed to be responsible for the catalytic activity, including BET surface areas^[77], oxygen mobility^[78], material texture property^[79], lattice O concentration^[80], reducibility of cations^[52] and so forth. Apart from them, the electronic structure of transition metal oxide is one of the most recognized factors that responsible for their activities. Salker^[81] tried to interpret the catalytic activities of spinel $\text{Co}_{1-x}\text{Cu}_x\text{Mn}_2\text{O}_4$ for CO oxidation by electronic and other physical properties (electrical resistivity, magnetic properties, etc.) and some others^[37,82] had correlated the CO oxidation activity to the electronic state of the transition metals in the perovskite structure. Despite the intensive attentions, limited studies have devoted to developing some intrinsic factors that relate to the origin of catalytic activity, which may serve as activity descriptor. The descriptor studies however are widely found in the field of electrocatalysis. One of the most investigated descriptors is the e_g orbital which directly points to the O p orbital, resulting in a strong overlap with that^[83]. Therefore it can strongly correlate to the catalytic OER

and ORR activities^[84,85]. For instance, as displayed in Figure 2.9, the OER activity of various perovskite oxides exhibits a volcano-shape as a function of the e_g electron of transition metal cations (B site) in perovskite oxides^[84].

Figure 2.9 The OER potential as a function of the occupancy of the e_g -symmetry electron of the B site metal in various perovskites^[84].

Another popular descriptor is the d -band model developed by Hammer and Nørskov^[86], which relates the adsorption strength of reactant and intermediates to the electronic states of the metal in terms of d -band center. In short, it describes the adsorption of reactants and intermediates on the metal catalysts. After refined by other researchers, it has been successfully used in predicting the ORR activity of perovskite oxides^[87] and spinel oxides^[83]. Several other oxidation reactions like CO oxidation^[38] (Figure 2.10) or propene oxidation are found to be suitable on metal alloy or mixed metal oxides^[88].

Figure 2.10 Specific CO oxidation activities as a function of calculated *d*-band centers for Pt and Pt alloys^[38].

Recently, the O *p*-band center relative to the Fermi level has been developed as another successful descriptor for electrocatalysis. It has been reported^[89,90] to be linearly correlated with the oxygen surface exchange kinetics and many other energetic parameters involving oxygen. Lee et al.^[90] explored the relationship of several ORR relevant reaction energies to the bulk oxygen *p*-band center and demonstrated that the LaBO₃ (B = Mn, Co, and Ni) bulk O vacancy, BO₂ surface oxygen vacancy and adsorption energies of BO₂ O-above-B-site are all linearly correlated with the bulk O *p*-band center as depicted in Figure 2.11.

Figure 2.11 (a) The bulk O vacancy and (b) surface O vacancy (solid symbols) and O above B site adsorption energies (empty symbols) in LaBO₃ perovskite oxides as a function of the bulk O *p*-band center calculated from DFT modelling^[90].

The effectiveness of the O *p*-band descriptor has also been qualitatively understood in terms of a simple rigid band model brought by Lee et al.^[90] as shown in Figure 2.12. Typically, moving electrons from the O *p*-band center to the Fermi level is equivalent to the processes involving removal of O from the reaction system. Correspondingly, moving electrons from the Fermi level to the O *p*-band center is equivalent to processes involving addition of O to the reaction system.

Figure 2.12 Schematic illustration of the correlation between the O p -band center and the ORR energetics rooted on the rigid band model^[90].

Enlightened by the aforementioned electronic factors which serve as effective descriptors for electrocatalysis due to their abilities to intrinsically reflect the redox properties of catalysts, potential descriptors studies on the heterogeneous oxidation reactions are in demand to better understand the catalytic mechanisms.

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Chapter 3 Experimental Methodology

3.1 Synthesis of cobalt based spinel and perovskite oxide catalysts

The synthesis of $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides and $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$, $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ perovskite oxides is using a sol-gel method, whilst the synthesis of $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ is using a thermal decomposition method. These two methods are selected respectively because the corresponding spinel oxides or perovskite oxides being produced possess high crystallinity and simple morphology. Since this thesis focuses mainly on the fundamental understanding of the transition metal oxide catalysts, potential morphological effect/influence is expected to be minimized *via* the above two synthesis methods.

3.1.1 Synthesis of cobalt based spinel oxides

$\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides were synthesized using a sol-gel auto combustion method^[1]. Proper amount of zinc, manganese, and cobalt in the form of acetate, i.e. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (99.999%), $\text{Mn}(\text{CH}_3\text{COO})_3 \cdot 2\text{H}_2\text{O}$ (97%) and $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (99.999%), were dissolved in diluted nitric acid with a molar ratio of $1:x:(2-x)$, $x = 0.0, 0.2, 0.6, 1.0, 1.4, 1.8, 2.0$. Citric acid as the chelating agent was then added into the solution with a molar ratio of cations: citric acid of 1:3 under constant stirring. The obtained mixture was heated and then maintained at 363 K under stirring for several hours until a viscous gel was formed through hydrolysis and condensation reactions. Afterwards, the gel was transferred to an oven and dried at 443 K for 12 hours and annealed in air at 873 K for an additional 6 hour (heating rate: 10 K min^{-1}) after being ground into powder. $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides were then harvested and kept in dry places prior to use. Typically, the

sol-gel auto combustion method enables a yield of crystalized particles as high as 90%.

$\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides were synthesized *via* a thermal decomposition method. In a typical preparation process of precursors, certain amount of zinc, nickel, and cobalt in the form of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, were dissolved in 3 mL nitric acid and 30 mL de-ionized water with a molar ratio of 1:x:(2-x). The mixture was then heated at 383 K under magnetic stirring to obtain a homogeneous solution. Afterwards, this homogeneous solution was transferred to an oven and dried for 12 hours, followed by calcination in air at the desired temperature for another 6 hours (heating rate: 10 K min^{-1}). After being grinded into powder, $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides were then collected and kept in dry place prior to use.

3.1.2 Synthesis of cobalt based perovskite oxides

All the $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ oxides were synthesized *via* a sol-gel method. Specifically, for the synthesis of $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ ($x=0.0, 0.25, 0.5, 0.75, 1.0$), proper amount of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added stoichiometrically into a mixed solution of urea (15 mmol), nitric acid (3 mL), citric acid (15 mmol) and 30 mL of deionized (DI) water. For the formation of LaCoO_3 , 3.75 mmol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 3.75 mmol $\text{Co}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ were added in the above mixture, whilst for the formation of LaFeO_3 , 3.75 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ instead of $\text{Co}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ were added. These solutions were heated to 353 K under constant stirring with a magnetic stirrer until a gel generated. The gel was then dried at 443 K for 12 h followed by calcination at 873 K for 6 h crystallization.

For the synthesis of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x=0.0, 0.25, 0.5, 0.75, 1.0$), proper amount of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added into the solution of ammonium hydroxide (NH_4OH) mixed with ethylenediaminetetraacetic acid (EDTA) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$). The mixture was then stirred to dissolve and heated at 503 K for several hours to dry. After which, a homogenous viscous gel was formed, and it was then further heated at 523 K for 5 hours followed by calcination in a furnace at 1273 K for 6 hours to obtain the crystallized product. As for LaCoO_3 , the procedures are the same except that $\text{Sr}(\text{NO}_3)_2$ was excluded.

All the chemicals were of analytical reagent grade purchased from Sigma Aldrich Corporation (USA), without further purifications.

3.2 Catalyst Characterizations

3.2.1 Electron Microscopy

The SEM (JEOL JSM-7600/7800 F) was applied for the observation of morphological characteristics of all the transition metal oxide catalysts in this thesis. By employing a focus beam of electrons, SEM is being able to produce various signals at the surface of samples. A wide variety of information such as morphology, size distribution and so forth can be obtained through analysing the generated signals. Here, the secondary electrons obtained in SEM which are mainly for visualizing the surface roughness and texture of sample are used in the thesis. Images of our samples can thus be produced and analysed to acquire the morphological information. To those oxide samples with poor conductivity, a thin layer of Au/Pt needs to be coated on the surface. The resolution of SEM can be adjusted by adjusting the wavelength of the electron source. Generally, to get a higher resolution, a reduced wavelength of electron source is needed. Meanwhile,

according to the de Broglie equation, the wavelength is proportional to the accelerating voltage of the electron source^[2].

TEM is mainly used in Chapter 5 to analyse the crystalline state of the $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides. Compared with SEM, TEM possess a much higher voltage in the range of 40~300 kV, which results in a better resolution. In contrary to the SEM, the beam of electrons in TEM passes through the samples and generates some interactions at the same time. The projected images by TEM is naturally two-dimensional images. From the brightness of the images, information on several factors can be tell, which includes the density and morphology of the sample, size of the particle etc. The electrons in TEM are regarded as wave-like instead of particle-like, which possess a wavelength that is about 10 times larger than that of the crystal lattice spacing. Based on this, the SAED model is used to explore information on the samples' orientation, crystalline state, lattice spacing and so on.

3.2.2 BET

To intrinsically understand the catalytic oxidation mechanisms by the synthesized transition metal oxides, the catalytic conversions of each catalyst are normalized to their surface areas, denoted as the intrinsic activity. The surface areas are obtained through the BET analysis and performed with an ASAP Tristar II 3020 physisorption analyzer at 77 K. The BET theory is actually extended from the Langmuir theory, which engages with the monolayer molecular adsorption in specific. Whilst the BET theory deals with the multilayer molecular adsorption^[3]. The BET analysis is based on several hypotheses which are not elaborate here and can be found in many literatures^[3-5]. By using a vacuum pump, the measurement starts with a de-gas process coupling with a heating setup for water vapor removal.

During the measurement, quantity of pure nitrogen gas is purged in and the pressure changes in terms of equilibrium pressure/saturation pressure (p/p_0) are recorded in the meantime. The specific surface areas results will be automatically determined and presented by the BET instrument.

Information on the pore size distribution of samples can be acquired *via* the adsorption isotherms. Typically, six representative types of physisorption isotherms^[6] can be observed and illustrated in Figure 3.1^[5].

Figure 3.1 Six types of gas physisorption isotherms with various surface features and pore size distributions^[5].

Judging from the types of isotherms, some information on the pore size and surface features can be revealed. In typical, type I isotherm represents the samples are of microporous structures (< 2 nm). Type II isotherm indicates the samples are non-porous or macroporous (> 50 nm). With a weak interaction between the adsorbate and adsorbent, type III isotherm stands for samples with nonporous structure. Type IV isotherm with a characteristic hysteresis loop indicates a mesoporous sample with capillary condensation within the solid samples. Similar to the differences between type II and type III isotherms, the differences between type V and type IV isotherms are the same. Type V isotherms represent the

mesoporous adsorbents with weak interactions between the adsorbent and adsorbate; Lastly, with a characteristic isotherm like type VI, suggesting a homogeneous surface of the sample.

3.2.3 XRD

In this thesis, we aim to establish a structure-catalytic performance relationship of the transition metal oxides. XRD is therefore an indispensable technique to confirm the correct phase and phase purity of the synthesized oxides.

During operation, X-ray beam passes into the lattice of the crystalline sample and are scattered when in contact with atoms. As a response, the array of atoms generates interference patterns. It is when the diffraction angle θ satisfies the Bragg's Law as below that the constructive interference happens^[7]:

$$n\lambda = 2d\sin\theta$$

Where, n is the order of reflection, λ refers to the wavelength of the X-ray, d is the d-spacing of the crystal plane, θ denotes the incidence angle. And here, in this thesis, the X-ray source is Cu ($\lambda=1.5418 \text{ \AA}$). During the scanning, the angel range is set to be within 2θ , which gives all possible constructive interferences. Therefore, XRD patterns with diffraction peaks as a function of 2θ are produced, through which we are able to identify different phase compositions in the powder sample. This is made possible because each sample has a distinctive set of XRD patterns, which can be considered as the fingerprint for phase identification. In this dissertation, a Shimadzu XRD-6000 instrument with Cu $K\alpha$ radiation at a scan rate of $2^\circ/\text{min}$ is used.

3.2.4 XAS

Considering that the thesis focuses on the transition metal oxide catalysts, i.e. the spinel oxides and perovskites oxides, where metal cations may occupy in either the tetrahedral or octahedral coordination sites (A site or B site for the perovskite oxides), the distribution and coordination environment of the cations should be unambiguously revealed. The XAS technique is thus employed in this study to probe the cation distribution and occupation, the valence states of the cations are quantified as well. XAS is a popular technique that examines how X-rays are absorbed by an atom at energies near or above the discrete core-level binding energies^[8]. Since the absorption ability of each element is different, by measuring the sample response to the absorption of X-ray, the unique extent of X-ray absorption therefore can provide information on the coordination environment and chemistry. Specifically, the XAS spectrum can be divided into two parts, the XANES and the EXAFS.

When the energy of the incident X-ray is higher than the binding energy of a core-level electron, a photoelectron is generated. In the meantime, the core electron level is left empty. This will lead to a sharp jump in the XANES spectrum and this energy value is known as the edge value of XANES. As the different valence states of one element possesses different binding energy of a core-level electron, the differential curves of XANES will be used to measure the oxidation and reduction state of a target element.

The other application of XAS in this thesis is to employ the EXAFS model to determine the local structure, for instance, the cation distribution of certain catalyst. The EXAFS technique measures the oscillations at energy levels far beyond the

absorption edge values. When the outgoing photoelectron wave hits the neighbouring scattering atoms, the backscattered photoelectron wave is generated. And the interference between the outgoing wave and the backscattered wave would generate the EXAFS spectrum. A detailed information on the local structure including the coordination numbers, interatomic distances, neighbouring environment can therefore be acquired.

In the study, XANES and EXAFS experiments were conducted in transmission mode at beamline XAFCA of the Singapore Synchrotron Light Source. Boron nitride powder ($\sim 1\ \mu\text{m}$, 98%, Sigma Aldrich, USA) was mixed with each sample to form pellets for analysis. The data reduction and data analysis were performed with the Athena, Artemis and IFEFFIT software packages^[9]. The EXAFS data were extracted from the measured absorption spectra using standard procedures. A cubic-spline-fit procedure was used to determine the post-edge background with a subsequent subtraction. Normalization was performed by dividing the data by the height of the absorption edge at 50 eV. Experimental phase shifts and back-scattering amplitudes were obtained from reference samples.

3.2.5 XPS

XPS is one of the most used electron spectroscopic techniques due to its surface sensitive ability. It is usually used for probing chemical environment of the element in samples. In addition, this technique allows an identification of the elemental composition only around 10 nm in the near surface of the sample. The basic principle behind XPS technique is the photoelectric effect. When X-ray photons are irradiated to the sample (incoming electrons), the initially bound core-level electrons are ejected out. Along with the emission, an electron energy

analyser filters the emitted electron kinetic energy, which inherited from the incident X-ray. Since binding energy is independent of the X-ray energy whilst the kinetic energy is not, therefore, the binding energy value is usually derived *via* the Ernest Rutherford equation^[10,11] to construct the spectrum:

$$E_{\text{Binding}} = E_{\text{Photon}} - (E_{\text{Kinetic}} + \Phi)$$

Where E_{Binding} refers to the binding energy of the electron, E_{Photon} is the initial energy of the incoming X-ray photon, E_{Kinetic} denotes the measured kinetic energy of the electron, Φ is the work function of the instrument. From the XPS data, particularly the position and intensity of the peaks, several information regarding to the samples can be derived. From the peak positions, some characteristics information on the samples' electronic structure can be obtained. While for the peak intensity, it represents the concentration of certain species on the surface. Similar to the XRD, this is based on the fact that each element has a distinctive spectrum and position of its own. In this thesis, XPS is mainly used in Chapter 4 to probe the valence states of octahedrally coordinated Co and Mn in $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ spinel samples obtained after synthesis.

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Chapter 4

Co, Mn-based spinel oxides towards CO oxidation:

Identifying the catalytic-critical influential parameters

4.1 Introduction

Driven by the increasing concern of air pollution, particularly the CO emissions from various sources, the development of air purification technologies is of paramount importance to maintain a clean mother earth^[1]. Heterogeneous catalysis as one of the most efficient response to this pursuit has drawn great attention^[1]. The most successful example is the noble-metal-based catalysts for the degeneration of toxic exhaust gases from automobiles^[2,3]. However, the high-cost and shortage of these precious metals make them difficult to meet the future growing demand, the exploration of efficient and low cost alternatives is therefore of great interesting and becomes inevitable^[3]. Transition metal oxides are one class of potential catalysts that are expected to meet the above need due to their low-cost and promising catalytic ability. Among them, spinel structured oxides possess unique advantages, such as high stability and facile synthesis^[4]. Besides, the electron exchange between neighboring cations in spinel oxides can be also optimized for promoting their catalytic ability^[5,6]. Great efforts on the catalytic mechanisms related to some factors such as composition, morphology, coordination environment, etc.^[7,8] thereby have been made and some remarkable progress has been gained. Particularly in the spinel oxides, octahedral sites on the surface have been suggested to be the primary active sites^[6,7,9].

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Among the numerous investigated transition metal oxides, cobalt-based oxides are one of the most intriguing oxides ascribing to their excellent CO oxidation performance, which is approaching to noble metals^[5]. Manganese, as another commonly involved transition metal for CO oxidation, is usually combined with other elements (such as copper^[8], cobalt^[5], lanthanum^[10,11]) to form manganites. Despite the intensive studies trying to interpret their catalytic behaviours^[2,5,8,12,13], it is far from enough, aimed to disclose the interactions and key parameters that influence the activity (e.g. with the compositional changes) in the catalytic process. In addition, further efforts are needed to investigate the relationships between the electronic structures and the catalytic mechanisms, especially for the spinel oxides. Inspired by the proposed *d*-band center model in the CO oxidation over Pt alloys^[3] and the *d* electron states as activity descriptor over Au nanoparticles^[14], it is of great interest to understand the CO oxidation process over spinel oxides from another perspective such as the molecular orbital theory. Typically, as in the electro-catalysis process, *e_g* filling state, metal-oxygen covalency, etc. have been established as activity descriptors for perovskite^[15–18] and very recently for spinels^[19] as well.

In this chapter, a series of spinel oxides $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ with compositional changes (*x* ranging from 0 to 2.0) were synthesized to exclusively investigate the catalytic activity of octahedrally occupied cations, i.e. Mn and Co for CO oxidation. In these spinel oxides, the inactive element Zn^{2+} occupied tetrahedral sites^[20] and thus the catalytic contribution from the tetrahedral sites can be ruled out. It is found that Mn cations to be the primary active sites for catalyzing CO oxidation when Mn and Co co-exist in the octahedral sites. The effects of $\text{Mn}^{4+}/\text{Mn}^{3+}$ were then explained in detail in association with the CO oxidation

mechanism. In addition, the moderate distance of O p -band center relative to the Fermi level computed by DFT calculations further interpreted the enhanced activity of $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ by well balancing the oxygen addition and removal related processes during the CO oxidation. Based on the above, the e_g occupancy of active Mn cations and the O p -band center relative to the Fermi level were proposed to be important influential parameters which accounts for CO oxidation on these spinel oxides.

4.2 Experimental section

4.2.1 Catalytic activity evaluation

Catalytic activity measurement in terms of CO oxidation was performed under atmospheric pressure in a continuous-flow fixed bed micro reactor, equipped with an on-line gas chromatograph (6890N, Agilent Technologies, USA) for inlet and outlet gas streams analysis. 20 mg of catalyst was loaded into the quartz reactor supported by two plugs of quartz wool. Prior to the reaction, the catalyst was pretreated *in situ* at 623 K under helium flow for 1 h. The desired operation temperature was controlled through an insert thermocouple with an adjustable range of room temperature to 773 K. A gas mixture of 1 vol.% CO, 3 vol.% O₂ and He at a flow rate of 100 mL/min, corresponding to a space velocity of 300, 000 mL h⁻¹ g⁻¹_{cat} was introduced. For all samples, the experiments were carried out under temperature gradient conditions and data were taken under steady state (at least 1 h). Typically, the system temperature was ramped with a rate of 2 K/min to the desired temperatures under a flow of helium, after which the reagent gas mixture was introduced. All experiments were undertaken in triplicate.

4.2.2 Temperature programmed reduction/desorption

H₂-TPR The reduction behaviors of ZnMn₂O₄, ZnMn_{0.2}Co_{1.8}O₄ and ZnCo₂O₄ were investigated by H₂-TPRs (temperature-programmed reduction). The experiment was carried out on a Micromeritics Autochem 2920 instrument equipped with a TCD detector. Typically, powdered catalysts were added to a U-shape quartz tube reactor and were supported by quartz wool. Helium was purged into the reactor to remove residual air, followed by a heating to 623 K for 1 h in He and then cooled to 298 K. The catalysts were reduced in a 10 % H₂/He flow with the temperature raising from 298 K to 1073 K at a rate of 283 K/min.

O₂-TPD Temperature programmed desorption of oxygen (O₂-TPD) experiments were carried out using the Micromeritics Autochem 2920 with a chemisorption analyzer. For each experiment, catalysts were placed in a quartz reactor and preconditioned in flowing He for 1 h at 623 K. They were then exposed to 10% O₂/He for 30 min, followed by cooling to 298 K in 10% O₂/He flow. For desorption of O₂, samples were purged with He and heated up from 298 K to 1073 K at a rate of 283 K/min.

4.2.3 DFT studies

All the density functional theory (DFT) calculations were performed by the Vienna *Ab initio* Simulation Package^[21], employing the projected augmented wave (PAW) model. The exchange and correlation effect were described by using Perdew-burke-Ernzerhof (PBE) function^[22], within the generalized gradient approximation (GGA) approach. The GGA + U calculations were performed using the model proposed by Dudarev et al.^[23], with the U_{eff} (U_{eff} = Coulomb U–exchange J) values of 4.0 eV, 3.3 eV, and 4.7 eV for Mn, Co, and Zn, respectively. The cutoff energy

was set to be 450 eV for all the calculations. For bulk geometry optimization, the Monkhorst–Pack^[24] k-point mesh of $6 \times 6 \times 6$ was employed; while for computing the electronic structure, a $9 \times 9 \times 9$ mesh was adopted. Of all the calculations, the Brillouin zone was integrated using tetrahedron method with Blöch corrections. The force and energy convergence tolerance were set to be 0.05 eV Å⁻¹ and 10⁻⁵ eV, respectively.

4.3 Results and discussion

4.3.1. Materials Characterizations

The morphologies of the as-prepared $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ oxides ($x=0\sim 2.0$) were examined by SEM as presented in Figure 4.1a. All of these samples are irregularly shaped particles. These irregularly shaped particles are then randomly stack or aggregated into some pore structures. It can be seen from Figure 4.2 that all the spinel $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ oxides exhibit a narrow pore-size distribution centered at around 25 nm. The large pore size suggest that these oxides catalysts are not porous materials and the porosity observed from the SEM images could originates from some form of irregular stacking of the oxide particles or aggregated oxide particles. A relatively larger size is obtained on ZnCo_2O_4 ($x=0$) particles without Mn substitution. The difference in particle size is in consistent with the results of BET measurements, where the specific surface area of ZnCo_2O_4 is merely around 8 m² g⁻¹ whereas that of Mn-contained samples are in the range from 20 to 30 m² g⁻¹ (Figure 4.1b and Table 4.1). A similar size scale has also been reported for ZnCo_2O_4 particles synthesized under analogous conditions^[25]. Through the similar morphology, possible morphology effects on CO oxidation in terms of different particle shapes can thereby be excluded.

Figure 4.1 (a) SEM images; (b) BET measurements (the detailed data results are given in Table S1) and (c) XRD patterns of $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) spinel oxides.

Figure 4.1c shows the XRD patterns of as-synthesized $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides. The diffraction pattern of ZnCo_2O_4 ($x=0$), which is readily indexed to the standard cubic spinel ZnCo_2O_4 (JCPDS Card No. 23-1390) without detectable impurity peaks, indicates the pure spinel structure. Nevertheless, as the substitution of Mn for Co increased, the characteristic peaks gradually shifted to the body-centered tetragonal spinel structure of ZnMn_2O_4 ($x=2.0$, JCPDS Card No. 24-1133). The spinel structure is well retained during this composition change induced crystallographic phase transformation. It should be noticed that the cubic spinel phase prefers a low Mn/Co molar ratio ($x \leq 1.0$) while tetragonal spinel phase prefers a high Mn/Co proportion ($x > 1.0$). This crystal phase transition is often found in the manganese-cobalt containing spinels when varying the Mn/Co molar ratio and is sensitive to the Mn content^[26,27]. The prominent Jahn-Teller effect of octahedral Mn^{3+} in Mn-enriched spinels is responsible for the lattice distortion, causing the low symmetry from cubic spinel to tetragonal spinel phase^[26]. Namely, the observed structure transition from cubic phase (Mn-poor) to tetragonal (Mn-

rich) phase in $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ thereby can be ascribed to the ascended distortion. Such crystal phase change is also reported to be existed in the $\text{Cu}_{1-x}\text{Mg}_x\text{Cr}_2\text{O}_4$ and $\text{CuCr}_{2-x}\text{Al}_x\text{O}_4$ spinel oxides^[12].

Figure 4.2 Pore size distribution of $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) oxides, obtained from BET results.

Table 4.1 Summary of BET surface area, half conversion temperatures (T_{50}), and complete conversion temperatures (T_{100}) of $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ oxides.

Mn content (x) in $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$	Sample name	BET surface area (m^2/g)	T_{50} (K)	T_{100} (K)
0	ZnCo_2O_4	7.8	513	623
0.2	$\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$	27.5	408	473
0.6	$\text{ZnMn}_{0.6}\text{Co}_{1.4}\text{O}_4$	30.1	481	598
1.0	ZnMnCoO_4	26.5	534	648
1.4	$\text{ZnMn}_{1.4}\text{Co}_{0.6}\text{O}_4$	22.9	504	648
1.8	$\text{ZnMn}_{1.8}\text{Co}_{0.2}\text{O}_4$	20.4	501	598
2.0	ZnMn_2O_4	26.0	529	648

To further explore whether Mn and Co are chiefly occupied in octahedral sites as expected, extended X-ray absorption fine structure (EXAFS) measurements were employed to identify the cation distribution. The Fourier transform (FT) of the absorption fine structure is given in Figure 4.3a. Through revealing bond distances

between the absorbing atom and backscattering atoms^[28], it can provide information on site occupation. The first shell peaks at ~ 1.5 Å are corresponding to scattering from the nearest neighbor crystal oxygen around the absorbing transition metal sites (TM-O bond distance)^[29,30]. The peaks at ~ 2.5 Å ($\text{TM}_{\text{Oh}}\text{-TM}_{\text{Oh}}$) and ~ 3.0 Å (e.g. $\text{TM}_{\text{Td}}\text{-TM}_{\text{Td}}$ or $\text{TM}_{\text{Td}}\text{-TM}_{\text{Oh}}$) are due to contributions from metal ion scattering to its closest neighboring metal ion around octahedral or tetrahedral sites^[29,30]. In all $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ with ascended Mn substitution, the FT spectra of both Co and Mn barely change and generally keep the same with the pristine samples (either octahedral-Co in ZnCo_2O_4 or octahedral-Mn in ZnMn_2O_4), indicating that all Mn and Co cations are octahedrally coordinated and the substitution does not change the coordination environment of these two cations in $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$. In addition, the different oscillating structures observed at radial distance of 2-3 Å in the spectra of Mn K-edge is caused by the prominent conversion from cubic (Mn-poor) to tetragonal (Mn-rich) spinel phase. This phase transition caused by the Jahn-Teller distortion is typical for high Mn concentration spinel oxides^[26] and is evidenced in the XRD analysis.

On the other hand, the single metal ion-metal ion scattering peak (at ~ 3.0 Å, $\text{Zn}_{\text{Td}}\text{-Zn}_{\text{Td}}$) in FT of Zn EXAFS spectra (Figure 4.3a) implies that Zn is preferentially fixed at the tetrahedral sites. This is based on the fact that tetrahedrally coordinated cations possess only one TM-TM distance, octahedrally coordinated cations on the contrary have two different TM-TM distances^[30]. Actually, the strong preference of Zn^{2+} cation for tetrahedral site has been previously reported in various spinel oxides and is considered to be caused by its inactive d^{10} electronic structure^[20,28]. On the basis of above, it can be confirmed that all the synthesized $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$

($x=0\sim 2.0$) oxides well maintained the spinel structure with both Mn and Co cations occupying in the octahedral sites whilst Zn cations in the tetrahedral sites.

Figure 4.3 (a) Fourier transform of EXAFS spectra of Co K-edge, Mn K-edge, and Zn K-edge in $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) spinel oxides; (b) Normalized XANES spectra of Co K-edge, Mn K-edge, and Zn K-edge in $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) spinel oxides, the quantified oxidation states of Co, Mn, and Zn are in the respective insets.

The oxidation states of cations in $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ were probed using X-ray absorption near edge structure (XANES), where the positions of K-edge as an indicator were determined by the integral method described previously^[19,31]. The decrease of oxidation states is observed with the progressive Mn substitution, where the edge positions of both Mn and Co exhibit significant shift and approach to lower binding energies (Figure 4.3b). To acquire the quantified oxidation state of Mn and Co, their edge positions were compared with the reference oxides. As shown in the insets of Figure 4.3b, the average oxidation state of Co decreases

from +3.0 to +2.4 and that of Mn reduces from +3.6 to +3.1 with the increase of Mn substitution, indicating the diminished presence of Co^{3+} and Mn^{4+} . This redistribution of cation oxidation states, in general, was caused by the charge redistribution between these two transition cations through the redox reaction of $\text{Mn}^{3+} + \text{Co}^{3+} \rightarrow \text{Mn}^{4+} + \text{Co}^{2+}$ [8]. As Co was gradually replaced by Mn, electron hopping may occur, and the electronic states changed subsequently. This phenomenon of oxidation state redistribution can be often found in the Mn and Co mixed oxides such as $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ [32]. Meanwhile, as illustrated in Figure 4.3b, the oxidation state of Zn almost remained unchanged at +2. The above results obtained from XANES were further confirmed by X-ray photoelectron spectroscopy analysis in Figure 4.4 and Table 4.2. Therefore, the chemical formula of the as-prepared spinels can be signified approximately as $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_{4+\delta}$ with δ as oxygen non-stoichiometry with range from 0.02 to 0.17 [19].

Figure 4.4 XPS spectra of Co and Mn 2p of $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) spinel oxides. The Co^{2+} (Co(II)) and Co^{3+} (Co(III)) XPS peak separation fittings for Co 2p_{3/2} and Mn^{3+} (Mn(III)) and Mn^{4+} (Mn(IV)) XPS peak separation fittings for Mn 2p_{3/2} are plotted.

Table 4.2 Relative peak areas of Co2p and Mn2p derived from XPS for the $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) oxides.

Mn content (x) in $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$	Sample name	Relative peak area Co(II)/Co(III)	Relative peak area Mn(III)/Mn(IV)
0	ZnCo_2O_4	0/100	/
0.2	$\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$	33.5/66.5	45.7/54.3
0.6	$\text{ZnMn}_{0.6}\text{Co}_{1.4}\text{O}_4$	39.6/60.4	65.5/34.5
1.0	ZnMnCoO_4	47.2/52.8	75.2/24.8
1.4	$\text{ZnMn}_{1.4}\text{Co}_{0.6}\text{O}_4$	59.0/41.0	80.3/19.7
1.8	$\text{ZnMn}_{1.8}\text{Co}_{0.2}\text{O}_4$	79.5/20.5	84.1/15.9
2.0	ZnMn_2O_4	/	100/0

Note: Binding energy of Co2p: Co(II) – 780.03 eV, Co(III) – 780.89 eV.

Binding energy of Mn2p: Mn(III) – 641.90 eV, Mn(IV) – 643.93 eV.

4.3.2. Evaluation of catalytic activity for CO oxidation

The CO oxidation measurement was performed to evaluate the catalytic performance of the as-synthesized spinels. Figure 4.5a shows the temperature dependence of CO conversion of all $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ catalysts ($x=0\sim 2.0$). It can be seen clearly that $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$), which achieves 100% conversion at around 473 K and 50% conversion at 408 K, exhibits a much higher catalytic activity than the rest six oxides. For a more straightforward comparison, the temperatures when 50% of CO is converted (T_{50}) by each catalyst are listed in Table 4.1. However, it is noteworthy that the activity obtained from these results can not reflect the intrinsic specific activity since catalytic process basically involves only the atoms on the surface^[33]. Thereby, the normalized specific activities of these catalysts to their surface areas were calculated using the BET

result. Although the BET surface area may not be perfectly equivalent to the real active surface area, it is reasonable to use it for the oxidation activity assessment^[5,19]. As a matter of fact, the BET surface area has already been widely employed for metal oxide catalyst comparison/screening in catalytic oxidation process^[5,8,34].

Figure 4.5 (a) CO oxidation percentage as a function of temperature for ZnMn_xCo_{2-x}O₄ (x=0~2.0) spinel oxides; (b) Normalized specific catalytic activities as a function of catalyst compositions for ZnMn_xCo_{2-x}O₄ (x=0~2.0) under three different temperatures; (c) Correlation between Mn and Co valence and the specific CO oxidation activity at 448 K; (d) The e_g filling state and average outer electron number d_{avg} of Mn cations as a function of catalyst compositions for substituted ZnMn_xCo_{2-x}O₄ (x=0.2~1.8).

Figure 4.5b depicts the surface area normalized specific activity under various temperatures plotted as a function of Mn content in ZnMn_xCo_{2-x}O₄ (x=0~2.0)

spinel. Similarly, the $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$) catalyst displays the best specific activity under all three temperatures, leaving the normalized activities of the rest spinels with various Mn and Co contents much lower. For the bimetallic spinels, ZnCo_2O_4 ($x=0$) exhibits relatively higher activity than ZnMn_2O_4 ($x=2.0$) under all circumstances but without significant differences. Generally, a higher temperature leads to a better specific activity, with the best reaction rate of $9.32 \times 10^{-5} \text{ mol m}^{-2} \text{ min}^{-1}$ achieved by $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$) at 448 K. An increased availability of bulk oxygen at higher temperatures^[35] seems to be responsible for the variations under different temperatures.

Furthermore, the stability test of $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ in Figure 4.6 indicates the superior stability of the oxide catalyst, which decrease only ~8% after reaction for 24 h. Notably, this excellent activity is comparable to, or outperform most of the reported transition metal spinel oxides or mixed oxide catalysts such as spinel Co_3O_4 powder^[8], MnCuO_x ^[8], CuCo_2O_x ^[8], MnCr_2O_4 ^[36], $\text{Co}_{1-x}\text{Cu}_x\text{Mn}_2\text{O}_4$ ^[13] and $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ perovskite^[5]. It is even approaching to some spinel nanomaterials, for instance, the $\text{M}_x\text{Co}_{3-x}\text{O}_4$ ($\text{M}=\text{Co}, \text{Ni}, \text{Zn}$) nanoarrays^[2] being reported. In addition, the comparison of activities of CoAl_2O_4 and ZnCo_2O_4 also highlights the critical role of octahedral sites in spinels. Since Co cations in CoAl_2O_4 spinels are accommodated in the tetrahedral sites and Al in its octahedral positions is considered to be inactive towards CO oxidation^[1,7,37], the comparison of CoAl_2O_4 and ZnCo_2O_4 offers an opportunity to reveal the roles of octahedral and tetrahedral sites in spinels. As displayed in Figure 4.7, ZnCo_2O_4 shows nearly five-times higher activities than that of CoAl_2O_4 , indicating the octahedrally coordinated Co is remarkably more active than the tetrahedral coordinated Co ion. This result is line with several reports^[7,9,19] on other catalysis by spinel oxides.

Figure 4.6 The stability test of ZnMn_{0.2}Co_{1.8}O₄ (x=0.2) for CO oxidation.

Figure 4.7 (a) Comparison of CO oxidation percentage as a function of temperature for spinel CoAl₂O₄ and ZnCo₂O₄; (b) Comparison of normalized specific catalytic activities of spinel CoAl₂O₄ and ZnCo₂O₄ under three different temperatures.

In our work, the phase transition from cubic to lower tetragonal symmetry as evidenced in the XRD does not appear to be influential on the CO oxidation activity significantly. In fact, the influence from phase transition to the reaction process can be very limited in ordinary cases unless the rate of catalytic reaction and the rate of phase transition are comparable^[12].

4.3.3. Exploration of parameters influencing the catalytic activity of octahedral cations

The possible effects from the cations in tetrahedral sites and the differences in particle morphology on CO oxidation have been excluded by the EXAFS and SEM analysis, respectively. Considering that catalytic activity is highly related to the surface electronic structure [3,15,38], the role of the oxidation state of cations in determining the CO oxidation performance is then investigated and discussed. Co sites are generally considered to be more active than Mn sites in the form of single metal oxides (e.g. Co_3O_4 vs. $\text{MnO}_2/\text{Mn}_2\text{O}_3$)^[5]. However, situation may differ for the oxides with more than one metal due to the interactions of dual- or multi-elements. For instance, both the Co- and Mn-containing perovskite oxides exhibit comparable CO oxidation activities and both are significantly more active than other transition metal containing perovskite oxides (e.g. Ni-, Fe-, V-, etc.)^[5]. In the case of spinel oxides here, it is proposed that both Mn and Co on the octahedral sites contribute to catalyzing the CO oxidation and their oxidation states are the decisive factors. The specific catalytic activities of $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) spinels are then correlated to the Mn and Co oxidation states as displayed in Figure 4.5c. With a very minor Mn substitution ($x=0.2$), the activity of $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ significantly improved for nearly three-fold over ZnCo_2O_4 . It can be noticed that the oxidation state of Co in ZnCo_2O_4 and $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$, however, barely changed and same at $\sim +3.0$. Meanwhile, Mn in $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ shows a high oxidation state of $\sim +3.6$, representing that Mn^{4+} is the dominant oxidation state rather than Mn^{3+} . As Mn substitution increased from $x=0.2$ ($\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$) to $x=0.6$ ($\text{ZnMn}_{0.6}\text{Co}_{1.4}\text{O}_4$), the catalytic activity strikingly dropped back to an activity that is similar to ZnCo_2O_4 but marginally lower. Under this circumstance,

the oxidation states of Co and Mn cations in $\text{ZnMn}_{0.6}\text{Co}_{1.4}\text{O}_4$ both decreases compared with that of $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$. Specifically, Co oxidation state slightly decreases from +3.0 in $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ to +2.9 in $\text{ZnMn}_{0.6}\text{Co}_{1.4}\text{O}_4$, but a relatively remarkable decrease is found in Mn valence. The decrease of Mn oxidation state from +3.61 in $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ to +3.35 in $\text{ZnMn}_{0.6}\text{Co}_{1.4}\text{O}_4$ indicates that Mn^{3+} instead of Mn^{4+} becomes the predominate species. With more Mn substitution ($x=1.0$ to $x=2.0$), the catalytic activities roughly keep the same with very tinny fluctuations. For these samples, the oxidation state of Co is found gradually decreased from +2.83 ($x=1.0$) to +2.43 ($x=2.0$). On the contrary, the oxidation state of Mn shows a minimal drop from +3.29 to +3.17. Based on the fact that the catalytic activity changes generally follow the variation of oxidation state of Mn cations, we suggest that here Mn cations are the dominant active sites for CO oxidation.

Apparently, an optimal nominal oxidation state of Mn cations in these spinel oxides is the key to achieve the high specific CO oxidation activity. The nominal oxidation state of Mn cations above +3 is the result of co-existence Mn^{4+} and Mn^{3+} in these spinel oxides (the existence of Mn^{2+} should be excluded in these $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ based on the stoichiometry). Previous investigations^[39] on $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ perovskite oxides have indicated that having Mn oxidation state approaching to 4+ provides the highest CO oxidation performance. By substituting La^{3+} with the divalent cations of Sr^{2+} , which led to a rise in Mn^{4+} concentration, the CO conversion increases. Similarly, the Ce^{4+} substitution in $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x=0\sim 0.3$) show that the increase in the molar ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ contributed to the increase in catalytic activity^[10,11]. The mixed Mn valency which brings about favorable charge transfer for oxygen adsorption is proposed to render the high

catalytic activity^[40]. On the other hand, either a high content of Mn^{3+} or fully Mn^{4+} in La- and Ca-based perovskite oxides cannot provide a satisfying activity^[41]. Considering the fact that in both perovskite and spinel oxides, the active cations are octahedrally coordinated, these cations in spinel may work in a similar way as proposed in perovskite^[16]. It is thereby proposed that a proper ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$, i.e. $\text{Mn}^{4+}/\text{Mn}^{3+} > 1$, is essential for high CO oxidation activity based on the observed catalytic activity results. This conclusion is coherent with the previous observations. For instance, $\text{LaMn}_{0.6}\text{Cu}_{0.4}\text{O}_3$ with Mn valence of 3.67+ gives a specific activity for CO oxidation higher than LaMnO_3 , in which the Mn oxidation state is 3+^[42].

The crucial role of Mn^{4+} in achieving high CO oxidation activity can be rationalized by the interplay of its electronic structure and the oxygen adsorption. In term of the electronic structure, e_g filling of Mn cations can sign as a dictation to the O_2 adsorption strength on the Mn site^[16]. The e_g antibonding orbital directly points to O p orbital, resulting in a strong overlap with that^[19]. This rationalizes that the electron filling of e_g orbital can directly affect the binding strength of oxygen on Mn cations. According to the Mars-van Krevelen redox mechanism^[43,44], the CO oxidation include the following steps (Figure 4.8): Step 1, the adsorption of CO onto the surface of metal oxide ($\text{M}_{\text{oct}}\text{-O-M}_{\text{oct}}$); Step 2, the surface reaction between CO and the adjacent O, during which an important step is the formation of intermediate carbonate; Step 3, the desorption of produced CO_2 , and thus the formation of O vacancy (V_o); Step 4, the adsorption of oxygen and the intermediary formation of O species (e.g. O^{2-}); Step 5, the trapping of O in the vacancy (V_o) for the vacancy refilling to reform the metal oxide surface. Among this process, the oxygen adsorption for subsequent O vacancy refilling (Steps 4 and

5) has been considered to be the rate-determining steps for metal oxides catalyzed CO oxidation^[1,5]. Consequently, when going from Mn^{3+} to Mn^{4+} , e_g filling goes from one to zero, and thus the strength of O_2 adsorption increases and facilitates the subsequent oxygen vacancy refilling. With an eye to the oxygen adsorption and vacancy refilling, a low e_g filling ($e_g < 0.3$) represents too strong adsorption, which hinders the desorption (mobility) of oxygen and thus limiting the trapping and refilling rate of O in the vacancy (Step 5), while a high e_g filling ($e_g > 0.5$) hinders the oxygen adsorption (Step 4). Therefore, a high catalytic performance needs an optimum e_g filling state which is in the range of 0.3 to 0.5. This is therefore corresponding to the ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ in these spinel oxides. The ratio in $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ is 1.58 (a nominal valency of 3.61) and it gives the e_g filling at 0.4. This optimal e_g filling state explains the observed high catalytic activity on $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$. The corresponding e_g filling states of Mn cations in $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ from $x=0.2\sim 1.8$ are given in Figure 4.5d. Accordingly, it is proposed that the e_g filling state of the octahedrally coordinated Mn cations can be used as a descriptor for the CO oxidation activity of these $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides.

Figure 4.8 The proposed reaction pathway on these spinel oxides based on the Mars-van Krevelen mechanism. M_{oct} refers to cations at the octahedral site and V_o refers to oxygen vacancy. The rate-limiting steps are Step 4 and 5 (marked with green).

In addition, the average outer electron number of Mn cations in $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ oxides can be another parameter to describe their CO oxidation activity^[3,38]. A linear relation of the adsorption energy of OER intermediates (*O, *OH and *OOH) to the oxidation state of series metal cations (M) in monoxides, La-based and Sr-based perovskite oxides (MO , LaMO_3 and SrMO_3) has been demonstrated by Federico et al., in which decreasing the oxidation state corresponds to stronger binding of the reaction intermediates or adsorbates^[15]. Similar conclusion was also supported by a theoretical calculation of CO oxidation over Au nanoparticles^[14]. With the co-existence of Mn^{4+} and Mn^{3+} , excessively a low ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ means low oxidation degree, representing the excessively strong adsorption of the reaction intermediates (including the intermediate O and CO species). This will restrain the desorption of O intermediates and O refilling (rate-limiting steps, Step 4 and 5 in Figure 4.8) as well as the desorption of CO_2 (Step 3 in Figure 4.8). Meanwhile, excessively a high ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ is an over-oxidized state, giving the weak adsorption of the intermediates and limiting the surface reaction rates. The optimum situation is at a proportion where Mn^{4+} is a bit over Mn^{3+} , just as the Mn oxidation state in $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$, which balanced the intermediates adsorption and desorption strength for surface reactions. In ionic compound, the number of outer electrons is equivalent to the resulting number of valence electrons in an ion being oxidized or reduced^[15]. The electron configuration of Mn is $3d^5 4s^2$, hence, Mn^{4+} has three outer electrons, while Mn^{3+} has four outer electrons. The average outer electrons d_{avg} shown in Figure 4.5d are calculated as the average of outer electrons of Mn^{4+} and Mn^{3+} after counting into their ratios, which can be deducted from the XANES results. It is clearly seen that, in $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ where the average outer electrons of Mn are slightly lower than

3.5, favors the reaction activity through the moderate adsorption of O and CO intermediates. As the number of average outer electrons increases ($d_{\text{avg}} > 3.5$), however, the adsorption of intermediates gets too strong and hinders the desorption of intermediates and CO_2 , leading to a lower activity.

4.3.4. DFT studies

Figure 4.9 (a) Spinel structures; (b) PDOS of the O p states and M_{oct} d states; and (c) schematic representation of the O p -band center for ZnCo_2O_4 , ZnMn_2O_4 and $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$. The arrows in (b) refer to spin up and down spin projection.

The DFT calculations were carried out on all the seven spinel $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) oxides through the Vienna *Ab initio* Simulation Package and details for the calculation can be found in the Experimental section. Compared with the metal d -band, which has shown great importance in elucidating some catalytic

oxidization reactions at metal surface^[3,19], the O *p*-band with a more delocalized nature is more accurate in capturing the electronic structure characteristics of transition metal oxides^[17,18]. Meanwhile, the *d*-band characters can still be reflected from the delocalized nature of the O *p*-band through the hybridized density of states (Figure 4.9).

According to PDOS of ZnCo₂O₄ (Figure 4.9b), the peaks below Fermi level (E_F) are mainly composed of O (*p*) and Co (*t_{2g}*) orbitals; while the peaks above the E_F originate from *e_g* orbitals. The energy level of *e_g* is close to E_F , indicating a low crystal field splitting energy (Δ_{cf}) between *e_g* and *t_{2g}*. The completely empty *e_g* explains the low spin state of Co, suggesting the Hund exchange energy Δ_{ex} is smaller than Δ_{cf} . Since the energy difference between Δ_{ex} and Δ_{cf} determines the spin state, the small gap implies the possibility of the change of spin state in ZnCo₂O₄. In contrast, a lower Δ_{cf} is found on ZnMn₂O₄ and the partially occupied *e_g* near E_F illustrates an evident high spin state. The majority of spin *e_g* near E_F are split due to the Hahn-Teller effect^[45]. The calculated magnetic moments per Mn is 4.03 μ_B , consistent with previous report^[46]. A small amount of Mn substitution in ZnCo₂O₄ (resulting in ZnMn_{0.2}Co_{1.8}O₄) does not change the PDOS dramatically; however, two sharp peaks emerge above E_F , implying that *e_g* is slightly occupied, which results in a relatively higher spin state than pure ZnCo₂O₄. PDOS of the O *p* states and *M_{oct}* *d* states for ZnMn_{*x*}Co_{2-*x*}O₄ (*x*=0.6~1.8) spinel oxides are given in Figure 4.10. From the schematic display (Figure 4.9c) of *M_{oct}* *d*-band and O *p*-band derived from PDOS, it is obvious that the change of spin state has led to the gradual change of O-*p* band center, with the ZnMn_{0.2}Co_{1.8}O₄ showing an intermediate value of band center. Generally, the values of O *p*-band center relative to the Fermi level of these spinel ZnMn_{*x*}Co_{2-*x*}O₄ oxides are found to gradually

decrease with increasing contents of Mn from $x=0$ to $x=0.6$ and then stay in the same level with little fluctuations from $x=0.6$ to $x=2.0$ (Figure 4.11a).

Figure 4.10 PDOS of the O p states and M_{oct} d states for (a) $\text{ZnMn}_{0.6}\text{Co}_{1.4}\text{O}_4$; (b) ZnMnCoO_4 ; (c) $\text{ZnMn}_{1.4}\text{Co}_{0.6}\text{O}_4$; (d) $\text{ZnMn}_{1.8}\text{Co}_{0.2}\text{O}_4$ spinel oxides. The arrows refer to spin up and down spin projection.

Since oxygen interacting processes governs many key aspects of oxidation, it is thus rational to correlate the intrinsic specific activities of CO oxidation in this study with the O p -band center relative to the Fermi level (Figure 4.11b). A volcano trend is found with the peak close to $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$) at O p -band center of -2.1 eV, which stays intermediately from the Fermi level among all the $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) oxides. Specifically, ZnCo_2O_4 ($x=0$), of which the O p -band center is too close to the Fermi level (-1.4 eV), shows a much lower activity ($3.6\times 10^{-5} \text{ mol m}^{-2} \text{ min}^{-1}$). In contrast, the other five spinel $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.6\sim 2.0$) oxides, where the O p -band center are around -2.6 eV, which are too

far from the Fermi level, also exhibit much lower activities ($1.7 \sim 3.1 \times 10^{-5} \text{ mol m}^{-2} \text{ min}^{-1}$). It is only when the O p -band center is neither too far nor too close to the Fermi level, such as $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$), that shows an enhanced activity ($9.3 \times 10^{-5} \text{ mol m}^{-2} \text{ min}^{-1}$).

Figure 4.11 (a) The O p -band center relative to the Fermi level; (b) Correlation of the specific CO oxidation activity and the O p -band center relative to Fermi level (E_F) of all seven spinel $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) oxides.

The O p -band center relative to the Fermi level has been reported^[17,18] to be linearly correlated with the oxygen surface exchange kinetics and many other oxygens involved energetic parameters, for instance, activation energy of oxygen/vacancy hopping, oxygen dissociations, etc. Typically, moving electrons from the O p -band center to the Fermi level equivalents to the processes involving O removal from the reaction system. Correspondingly, moving electrons from the Fermi level to the O p -band center equivalents to processes that involving O addition to the reaction system^[17,47]. Since the rate-determining steps for CO oxidation are the oxygen adsorption and O vacancy refilling (Steps 4 and 5, respectively in Figure 4.8) which involve multiple oxygen addition and removal related processes, the O p -band can serve as an effective descriptor for the CO

oxidation activity. When the O p -band center is too close to the Fermi level, the oxygen is too active and this will hinder the stability for oxygen adsorption (Step 4 in Figure 4.8). However, if the O p -band center is too far from the Fermi level, the oxygen is so inactive that will retard the surface reactions for O vacancy refilling (Step 5 in Figure 4.8). Having the O p -band center that is neither too close nor too far to the Fermi level well balances the oxygen addition and removal related processes, therefore interpreters the activity enhancement. Moreover, this moderate oxygen adsorption and desorption on the surface of $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$) is also supported by the H_2 -TPR and O_2 -TPD tests as shown in Figure 4.12.

Figure 4.12 (a) H_2 -TPR profiles and (b) O_2 -TPD spectra of ZnCo_2O_4 ($x=0$), $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$) and ZnMn_2O_4 ($x=2$).

As displayed in Figure 4.12 a, ZnMn_2O_4 presents a single peak centered at 682 K, which recognized to be in the region of reduction of Mn^{3+} ions to Mn^{2+} [48]. A similar reduction profile was also observed in the reported ZnMn_2O_4 spinel[49]. For ZnCo_2O_4 , two major peaks at about 591 K and 653 K can be distinguished. These two peaks are reported[50] to be assigned to two reduction steps of the ZnCo_2O_4 species to Co^{2+} and subsequently Co^0 . In the profiles of $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ however, three sharp peaks located at 570 K, 606 K and 634 K respectively are distinguished,

which incorporates both the main peaks from ZnMn_2O_4 and ZnCo_2O_4 . Notably, all the reduction peaks shifted toward the lower temperature, implying that $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ have a relatively lower reduction temperature, which would make the redox reaction easier^[51]. H_2 -TPR results indicated that with a small amount Mn substitution in ZnCo_2O_4 , i.e. the $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ becomes more readily to be reduced, which corresponding to a higher capacity to provide oxygen for the reaction in a reducing environment^[52].

As shown in Figure 4.12 b, generally, two types of oxygen species can be desorbed by spinels similar to that of perovskites: the α oxygen desorption peaks which locate at lower temperature region are broad and small, while the β oxygen desorption peaks extend from above 873 K are sharp and strong^[48,53]. These α oxygen desorption peaks are refer to oxygen adsorbed on the catalyst surface, whereas the β desorption peaks are recognized as the lattice oxygen of the spinel oxides^[48,53]. Typically, for the catalytic reactions, only α oxygen is concerned^[53]. In the α oxygen-TPD profile of ZnMn_2O_4 , the desorption peak is observed to be rather small, indicating a relatively difficult oxygen desorption. In contrast, the α oxygen desorption peak of ZnCo_2O_4 is much larger, implying a much easier oxygen desorption. For $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ which exhibits an α oxygen desorption peak that is larger than that of ZnMn_2O_4 but smaller than ZnCo_2O_4 , suggesting a mediate oxygen desorption potential. Besides, both ZnMn_2O_4 and $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ exhibit a lower desorption temperature, which indicates a higher activity at low temperatures. This might explain their higher CO catalytic activities at the starting lower temperatures in Figure 4.5. O_2 -TPD results manifest that ZnMn_2O_4 is rather inactive in the oxygen adsorption and desorption, whereas ZnCo_2O_4 is too active.

In between, $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ possess a mediate activity for the oxygen adsorption and desorption, which is in agree with the e_g estimation and DFT calculations.

Similar trend has been reported^[18] on using the the O p -band center relative to the Fermi level as OER activities descriptor of perovskite and results indicate moving the the O p -band center closer to the Fermi level increase the OER activity in some degree, but further uplifts result in the decrease of oxide activity and stability. In addition, our DFT calculation results also verify the proposed e_g estimation that the enhanced activity originates from the moderate (neither too strong nor too weak) oxygen adsorption thus facilitating the O vacancy refilling.

4.4. Conclusion

In this chapter, we have investigated the composition effect of spinel $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) oxides on CO oxidation. The structure characterizations showed that Zn cations prefer staying in tetrahedral sites and Mn and Co cations prefer staying in octahedral sites. The intrinsic activities of these spinel oxides for CO oxidation were found different and composition dependent. The best performance was achieved by $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$), which is nearly three-times higher than others. The origin of such activity variation among these spinel oxides was further investigated with the aid of cations' local chemistry and valency characterizations. The catalytic performance of $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides containing Mn (i.e. $x=0.2\sim 1.8$) basically follow the variation of the nominal oxidation state of Mn. It is accordingly proposed that Mn cations to be the key species in determining the CO oxidation activity on these spinel oxides. The co-presence of Mn^{4+} and Mn^{3+} with a ratio a bit over one ($\text{Mn}^{4+}/\text{Mn}^{3+}=1.58$) is the key to achieve the high activity. Under this circumstance, the oxygen adsorption strength is moderate, thus

facilitating the O vacancy refilling, which are the rate-determining steps during the CO oxidation. Moreover, a moderate binding energy of the reaction intermediates that balance the adsorption and desorption strength also contribute to a high activity. The DFT calculations further verifies the enhanced activity originates from a moderate location of the O *p*-band center to the Fermi level, which well balance the oxygen interacting processes during the CO oxidation. On the basis of the above, the e_g filling state of Mn and the O *p*-band center relative to the Fermi level are proposed to be influential parameters for CO oxidation on spinel $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ oxides.

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Chapter 5

Co, Ni-based spinel oxides towards complete methane oxidation: Explorations on origin of the structure-performance relationship

5.1 Introduction

Methane, as the major constituent of natural gas, possesses a greenhouse effect that is much more prominent than CO_2 ^[1–3]. With the widely application of natural gas in auto-vehicles, power plants and other industries, the abatement of methane (CH_4) atmospheric emission is of paramount importance to meet the increasingly stringent environment regulations^[2,4,5]. Currently, the most efficient and simple strategy to reduce the detrimental environmental effect of methane is the catalytic combustion, through which methane is completely oxidized into carbon dioxide and water^[2,6]. To date, the most intensively studied catalysts are the noble metals, especially the Pd and Pt, which are found to be the most active for the catalytic combustion^[7,8]. However, precious metals impose various constraints, including high cost, scarcity and strict operating temperatures (they deteriorate easily by sintering at high temperatures)^[6,7,9]. Transition metal oxides such as spinels^[1,4,10–12], perovskites^[8,13–15] and some mixed oxides^[2,8,16,17] are considered as potential alternatives due to their distinctly lower prices and promising catalytic activities. Among them, the cobalt-based spinel oxides are found to be one of the most intriguing catalysts which exhibit high catalytic activities^[1,4,10–12].

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Nickel, another active transition metal for methane catalytic combustion, is usually combined with other metals^[4,10]. Despite widespread investigations and attentions on the complete methane oxidation, a definite reaction mechanism on the transition metal oxide catalysts has yet to be elucidated. Debate has been focused on the involvement of dissociative adsorbed oxygen featured suprafacial Langmuir-Hinshelwood (L-H) mechanism, which is often preceded by an Eley-Rideal (E-R) step^[6,18], or the lattice oxygen featured intrafacial Mars-van Krevelen (Mv-K) mechanism^[6,9,10,19]. While a temperature dependent coexisted mechanism is more acknowledged over many other mixed metal oxides and spinels^[2,4,6,19,20]. Aside from the intensive studies, the routine way to recognize a L-H/E-R or Mv-K pathway is still under study by the reaction rate^[6-8]. However, the mechanisms may not be identified properly according to the kinetic data, which exhibit similar rate equations for both L-H/E-R or Mv-K catalytic turnovers^[6]. Therefore, simple ways other than kinetic study are in demand to identify and predict the preferential reaction mechanism of certain metal oxide catalyst. Additionally, it is not yet intrinsically understood at a molecular level of parameters that would trigger the E-R or Mv-K mechanisms. Therefore, further efforts are needed on the exploration of intrinsic origin of the structure-activity/mechanism relations which would provide us with a more comprehensive understanding of the oxidation reaction over transition metal oxides. In particular, there is still lack of pertinent descriptors that are able to capture the physical origin of the activity, which could in turn be used to predict the catalytic behavior of the catalysts.

Using CO oxidation reaction as a probe reaction, the previous chapter^[21] has provided some fundamental insights into the physiochemical properties of spinel oxides catalysts. These studies interpret the catalytic performance from the view of

molecular orbital theory. Nevertheless, compared with the CO oxidation process, the complete catalytic oxidation of methane is far more complicate, during which the CO oxidation is one of the multi-steps^[9]. As one of the basic hydrocarbon pollutants with high symmetry, understanding the mechanistic process of methane catalytic oxidation is of vital importance to the complex heterogeneous catalysis and the environmental remediation.

Thus, in Chapter 5, a series of spinel oxides $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ (x ranging from 0 to 0.8) were synthesized to investigate the origin of the structure-activity/mechanism relationship for complete catalytic oxidation of methane. The catalytic mechanistic process was understood from the perspective of molecular orbital theory by means of experimental results, corroborated by the DFT calculations. Similar to the $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides in Chapter 4, tetrahedral sites were occupied by the inactive Zn^{2+} ^[19] in $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ spinels to ruling out their catalytic contributions, and focus on the catalytically more active octahedral sites^[1,22]. Ni was introduced to substitute the octahedrally coordinated Co for a tunable variation in electronic structure. The specific activity normalized by surface area was found to exhibit two different catalytic behaviors under different temperature ranges. Experiment results are supported by the first principle DFT+U calculations, where the interplay between O p -band center and M_{oct} d -band center was found to be correlated with not only the methane oxidation activity but also the thermal stability and reaction mechanism of the catalysts. Thermal stable Ni-poor spinel oxides with the M_{oct} d -band center in a higher position relative to the O p -band center, exhibit greater metal character, indicative of an E-R mechanism. In turn, thermal metastable Ni-rich spinel oxides with the O p -band center in a higher position relative to the M_{oct} d -band center, display greater oxygen character, indicative of the Mv-K

mechanism. The effects of M_{oct} d -band center and O p -band center were then explained in association with the methane oxidation mechanism. In addition, CH_4 -TPD-MS and O_2 -TPD tests further confirmed the DFT results with featured involvement of adsorbed oxygen or lattice oxygen. Based above, the relative position between O p -band center and M_{oct} d -band center was proposed to be activity/mechanism descriptor of the methane complete oxidation on the $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$) spinel oxides.

5.2 Experimental section

5.2.1 Synthesis of $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ oxides

$\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides were synthesized *via* a thermal decomposition method as described in Chapter 3. Notably, the substitution of Ni for Co, i.e. the value of x in $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ merely varied from $x=0$, 0.2, 0.4, 0.6 to $x=0.8$. When the Ni replacement reached $x=1$, which means equal molar number of $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ were added, a mixed phase containing spinel phases, NiO and ZnO phases started to form. When Co was thoroughly replaced by Ni ($x=2.0$), a mixture of NiO and ZnO oxides was formed instead of ZnNi_2O_4 . Similar situation was reported for the synthesis of $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ nanoparticles^[23].

5.2.2 Catalytic activity measurement and DFT studies

The methane total oxidation catalytic performance was also measured in a fixed bed micro reactor with continuous flow under atmospheric pressure. An on-line gas chromatograph with a flame ionization detector (FID) (GC 2060, Sensitive instrumental Co., Ltd, China) was equipped for the inlet and outlet gas stream analysis. Typically, certain amount of catalyst was loaded into the quartz reactor between two plugs of quartz wool. The desired operation temperature with an

adjustable range of room temperature to 873 K was controlled by a furnace with an insert thermocouple for the temperature monitoring. A gas mixture of 1.1% methane and 98.9% air controlled through their own mass flow meters was introduced into the system with a flow rate of 90 mL/min, corresponding to a space velocity of 36,000 mL h⁻¹ g⁻¹_{cat}. All the experiments were carried out in triplicate under temperature gradient conditions and data were taken under steady state. The DFT calculations were performed similar to that as described in Chapter 4.

5.2.3 Temperature programmed desorption

O₂-TPD and CH₄-TPD experiments were carried out using the Micromeritics Autochem 2920 with a chemisorption analyzer. For each experiment, catalysts were placed in a quartz reactor and preconditioned in flowing He for 1 h at 573 K, followed by cooling to 323 K in He. They were then exposed to 10% O₂/He or pure CH₄ for 30 min. The physically adsorbed O₂ or CH₄ were removed by purging with helium flow at 323 K for 30 min. For desorption of O₂ or CH₄, samples were purged with He. The reactor was heated up from 373 K to 1173 K at a rate of 283 K/min. Mass spectrometry (Hidden analytical QGA) is coupled with the CH₄-TPD process for identification of the desorbed components in the desorption flow.

5.3 Results and discussion

5.3.1. Materials characterizations

The morphology of ZnNi_xCo_{2-x}O₄ oxides (x=0~0.8) was examined by FESEM. As depicted in Figure 5.1a, all samples consist mainly of irregularly shaped particles which are randomly aggregated or stacked into some pore structures. The particle sizes were determined by the N₂ adsorption measurements as presented in Figure

5.1b and Table 5.1. ZnCo_2O_4 possess the largest specific surface area of $57 \text{ m}^2 \text{ g}^{-1}$, whereas when Ni was incorporated, the surfaces areas of these Ni-contained samples are gradually decreased from 56 to $38 \text{ m}^2 \text{ g}^{-1}$ (Table 5.1). Figure 5.1c exhibits the XRD patterns of $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ oxides ($x=0\sim 0.8$) being synthesized. The diffraction peaks of ZnCo_2O_4 ($x=0$) can be readily indexed to the standard cubic spinel ZnCo_2O_4 (JCPDS Card No. 00-023-1390) without detectable parasitic phases. All the diffraction patterns indicate the retainment of pure cubic spinel structure up to $x=0.8$ wherein Co is replaced by Ni.

Table 5.1 Summary of BET surface area, crystallite size and lattice parameter of $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$) spinel oxides.

Ni content (x) in $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$	Sample name	BET surface area (m^2/g)	Lattice parameter a (Å)
0	ZnCo_2O_4	56.6	8.124(7)
0.2	$\text{ZnNi}_{0.2}\text{Co}_{1.8}\text{O}_4$	56.4	8.14(1)
0.4	$\text{ZnNi}_{0.4}\text{Co}_{1.6}\text{O}_4$	49.4	8.149(5)
0.6	$\text{ZnNi}_{0.6}\text{Co}_{1.4}\text{O}_4$	43.8	8.165(5)
0.8	$\text{ZnNi}_{0.8}\text{Co}_{1.2}\text{O}_4$	38.1	8.180(7)

Nevertheless, as the level of substitution of Co by Ni further increases, additional NiO and ZnO phases are formed as shown in Figure 5.2. For those pure spinel $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ oxides ($x=0\sim 0.8$), an increased lattice parameter (a) is observed from 8.124(7) Å to 8.180(7) Å (Figure 5.3 and Table 5.1) with an increase of Ni substitution. Similar lattice expansion has been reported^[24] and can be attributed to the the Jahn-Teller distortion induced by the incorporation of low spin Ni^{3+} ($t_{2g}^6 e_g^1$) into the structure^[25,26]. The real atomic ratios of Zn:Co:Ni in the series $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$) oxides are confirmed by the ICP-OES as shown in Table 5.2.

Figure 5.1 (a) FESEM images; (b) N₂ adsorption measurements and (c) XRD patterns of the as-prepared ZnNi_xCo_{2-x}O₄ (x=0~0.8) spinel oxides.

Figure 5.2 XRD patterns of ZnNi_{0.2}Co_{1.8}O₄ (x=0.2), ZnNi_{1.2}Co_{0.8}O₄ (x=1.2) and ZnNi₂O₄ (x=2.0). Characteristic peaks corresponding to ZnO wurtzite structure and NiO rock-salt structure can be identified.

Figure 5.3 XRD refinement on spinel $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ oxides ($x=0\sim 0.8$) patterns obtained by D8 ADVANCE with Pawley refinement method on TOPAS software.

Table 5.2 ICP-OES analysis results of spinel $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$) oxides.

Ni content (x) in $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$	Weight (mg)	Solution volume (mL)	Elements	Element Concentration in solution (ppm)	Dilution factor	Atomic ratio of Zn:Co:Ni
0	10	50	Zn	5.028	10	1:1.97
			Co	8.946		
			Ni	/		
0.2	10	50	Zn	5.477	10	1:1.89:0.21
			Co	9.354		
			Ni	1.038		
0.4	10	50	Zn	5.476	10	1:1.58:0.39
			Co	7.802		
			Ni	1.930		
0.6	10	50	Zn	5.253	10	1:1.41:0.66
			Co	6.695		
			Ni	3.111		
0.8	10	50	Zn	5.483	10	1:1.15:0.84
			Co	5.693		
			Ni	4.132		

To verify whether Ni and Co remain occupied in octahedral sites as expected when Ni is introduced, EXAFS and XANES measurements were carried out to probe the cation occupancy and valency. Figure 5.4a gives the Fourier transform (FT) of the absorption fine structure. Information on site occupation is inferred through revealing bond distances between the absorbing atom and backscattering atoms^[27].

Generally, the shell peaks at ~ 1.5 Å are assigned to single scattering from the closest neighboring crystal oxygen around the absorbing transition metal sites (TM-O bond distance) [27,28]. The peaks at ~ 2.5 Å ($\text{TM}_{\text{Oct}}\text{-TM}_{\text{Oct}}$) and ~ 3.0 Å (e.g. $\text{TM}_{\text{Td}}\text{-TM}_{\text{Td}}$ or $\text{TM}_{\text{Td}}\text{-TM}_{\text{Oct}}$) correspond to scattering of the metal ion to its nearest neighboring metal ion around octahedral or tetrahedral sites [27,28]. That is, octahedrally coordinated cations possess a typical atom-atom bond distance of ~ 2.5 Å from their neighboring metal ions while tetrahedrally coordinated cations keep the atom-atom bond distances at ~ 3.0 Å [29]. The FT patterns of both Ni and Co in all the $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$) oxides remain the same with a characteristic interatomic distance of ~ 2.5 Å, suggesting that all Ni and Co cations are octahedrally coordinated and their coordination environment is not changed by the substitution. This preferential octahedral coordination of Ni and Co cations with a $3d^{6-8}$ electron configuration is also supported by the crystal field stability energy [30].

Figure 5.4 (a) Fourier transform of EXAFS spectra and (b) Normalized XANES spectra of Co K-edge, Ni K-edge, and Zn K-edge in $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$) spinel oxides.

In contrast, the FT EXAFS spectra of Zn with a metal ion-metal ion scattering peak at ~ 3.0 Å ($Zn_{Td}-Zn_{Td}$) (Figure 5.4a) indicates that Zn is preferentially accommodates at the tetrahedral sites for all the $ZnNi_xCo_{2-x}O_4$ ($x=0\sim 0.8$) oxides. The strong preferential tetrahedral site occupancy of divalent Zn in various spinel oxides is attributed to its inactive d^{10} electronic structure^[29,31] as reported as well as the large formation energy for antisite defects^[32]. Therefore, it can be confirmed that the spinel structure of all the synthesized $ZnNi_xCo_{2-x}O_4$ ($x=0\sim 0.8$) oxides is well maintained with Ni, Co cations stays in the octahedral sites and Zn cations fixed in the tetrahedral sites. In addition, the HRTEM image, STEM-EDS image and mapping of $ZnNi_{0.8}Co_{1.2}O_4$ ($x=0.8$) provided in Figure 5.5 and Figure 5.6 further confirm the phase purity and homogenous distribution of element Zn, Co, Ni and O.

Figure 5.5 (a) HRTEM image and (b) STEM-EDS image and analysis of $ZnNi_{0.8}Co_{1.2}O_4$ ($x=0.8$).

Figure 5.6 Elemental mapping of Zn, Co, Ni, O of the as synthesized $\text{ZnNi}_{0.8}\text{Co}_{1.2}\text{O}_4$ ($x=0.8$). The maps obtained *via* TEM demonstrate a homogeneous distribution of the elements Zn, Co, Ni and O consistent with the formation of spinel $\text{ZnNi}_{0.8}\text{Co}_{1.2}\text{O}_4$.

It can be seen from the HRTEM image in Figure 5.5a, the synthesized $\text{ZnNi}_{0.8}\text{Co}_{1.2}\text{O}_4$ catalyst shows a characteristic lattice interplanar spacing (d) of 0.245 nm for the (311) lattice plane of spinel, which is consistent with the XRD results. The inset selected area electron diffraction (SAED) patterns for the sample can be indexed to (311), (222), (622) and (620) planes. From Figure 5.5b, a homogenous distribution of element Zn, Ni, and Co is observed on both the surface and in the bulk of the catalyst.

The valency of Co, Ni, Zn in $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ were probed using XANES. The integral method^[31,33] was employed to determine the positions of K-edge as shown in Figure 5.4b. With the progressive Ni substitution (from $x=0$ to $x=0.8$), the edge positions of Co, Ni and Zn rarely change and generally keep the same as the pristine ZnCo_2O_4 sample, manifesting an unchanged oxidation state of Co, Ni and Zn cations in the $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ when x increases from 0 to 0.8.

Figure 5.7 (a) Normalized Co K-edge and Ni K-edge XANES spectra of $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.2, 1.2, 1.6, 2.0$). (b) Normalized Zn K-edge XANES spectra of $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.2, 1.2, 1.6, 2.0$) (left panel). The right panel shows the circled area of spectra in the left panel.

However, as illustrated in Figure 5.7, the K-edge positions of Ni in $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=1.2, 1.6, 2.0$) progressively shift and approach lower binding energies which are closer to that of NiO, suggesting the decrease in oxidation state of Ni cations. Furthermore, a significant increase of peak features at around 9665 eV and a decrease of peak features at around 9675 eV in the Zn K-edge in $\text{ZnNi}_{1.2}\text{Co}_{0.8}\text{O}_4$, $\text{ZnNi}_{1.6}\text{Co}_{0.4}\text{O}_4$ and ZnNi_2O_4 (Figure 5.7) indicate the appearance of ZnO wurtzite phase^[34]. The information presented above further supports the formation of additional NiO and ZnO when the Ni substitution exceeds 0.8 as observed in XRD.

5.3.2. Evaluation of catalytic activity for complete methane oxidation

A complete oxidation of methane using the as-synthesized $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ spinels ($x=0\sim 0.8$) was then performed. For a better reflection of the intrinsic specific activity instead of the mass activity, the methane conversion of these catalysts was normalized to their BET surface areas since catalytic process basically occurs only on the catalyst surface^[33,35]. Even though the BET surface area is not perfectly equivalent to the real active surface area, it has been widely used as the best representative for the activity assessment^[2,31,36,37]. Typically, the BET surface area has been established as a methodology for activity assessment and screening for metal oxide catalysts^[31,36,38]. Figure 5.8a shows the surface area normalized specific activity plotted as a function of Ni content in $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$) spinels under various temperatures (from 573 K to 823 K). Generally, the results enable us to distinguish different activity trends depending on the temperatures. Under low temperatures (below 673 K), $\text{ZnNi}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$) catalyst exhibits a higher specific activity with a volcano trend than the other four spinels ($x=0, 0.4, 0.6, 0.8$). As the temperature increases (above 673 K), the specific activities are increased for all the catalysts. Under the situation of relatively higher temperatures (673 K to 773 K), two distinct catalytic behaviors can be observed. For catalysts with Ni content less than 0.4, the volcano trend remains, indicating the specific activities increase at a similar rate with elevated temperatures. By contrast, for those catalysts with Ni content exceed 0.4, the activities increase more significantly than that of the catalysts with Ni content less than 0.4. It is noteworthy, this activity increment difference becomes more obvious under high temperatures (i.e. 723 K and 773 K). The reaction rate of $\text{ZnNi}_{0.8}\text{Co}_{1.2}\text{O}_4$ ($x=0.8$) has achieved $11.7\times 10^{-8} \text{ mol m}^{-2} \text{ min}^{-1}$ at 823 K, keeping pace with the superior

activity of $\text{ZnNi}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$). Meanwhile, the reaction rates of $\text{ZnNi}_{0.6}\text{Co}_{1.4}\text{O}_4$ and $\text{ZnNi}_{0.4}\text{Co}_{1.6}\text{O}_4$ have increased to a comparable level of $10 \times 10^{-8} \text{ mol m}^{-2} \text{ min}^{-1}$. Notably, the excellent activity of $\text{ZnNi}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$) and $\text{ZnNi}_{0.8}\text{Co}_{1.2}\text{O}_4$ ($x=0.8$) is comparable, or superior to many of the reported metal oxides catalysts, such as the spinel $\text{M}_x\text{Co}_{3-x}\text{O}_4$ ($\text{M}=\text{Co}, \text{Ni}, \text{Zn}$)^[4], MgCr_2O_4 and CoCr_2O_4 spinels^[39], $\text{NiO/Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ ^[40], LaMO_3 perovskites^[8,14] and so on. It is even approaching to some noble metal catalysts, for instance, the $\text{Pt/Al}_2\text{O}_3$ and $\text{Pd/Al}_2\text{O}_3$ being reported^[7,8]. Kinetic studies including Arrhenius plots of the catalysts for the catalytic methane oxidation and their corresponding activation energies (E_a) are given in Figure 5.9 and Table 5.3.

As shown in Figure 5.9, the Ni-poor $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.4$) spinel oxides give rise to similar plots that in a close regime, indicating a similar kinetic behavior of these catalysts. Whilst the Ni-rich $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0.6$ and 0.8) spinel oxides give rise to close plots in another regime with different slopes, suggesting a similar kinetic behavior of these two catalysts. Table 5.3 gives the values of activation energy of all the spinel oxides. It can be seen, $\text{ZnNi}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$) and $\text{ZnNi}_{0.8}\text{Co}_{1.2}\text{O}_4$ ($x=0.8$) show relatively lower activation energies than the other four catalysts, which is in consistence with their better catalytic activities exhibit in Figure 5.8a. Moreover, the activation value of these two catalysts (98.1 kJ/mol for $\text{ZnNi}_{0.2}\text{Co}_{1.8}\text{O}_4$ and 88.9 kJ/mol for $\text{ZnNi}_{0.8}\text{Co}_{1.2}\text{O}_4$) also falls in the range of activation energies reported for methane oxidation over Pd, Rh and Pt catalysts (71-100 kJ/mol)^[6].

With regarding to the mechanistic pathways of methane oxidation, despite the existence of ambiguities on various transition metal oxides catalysts, a consensus is met with the temperature dependent reaction kinetic that the L-H/E-R

mechanism operates at low temperature range, whilst the Mv-K mechanism features at high temperatures. In between, these two mechanisms engaged simultaneously and may compete with each other^[6,9,19,41,42].

Figure 5.8 (a) Normalized specific activities of complete methane oxidation as a function of catalyst compositions for ZnNi_xCo_{2-x}O₄ (x=0~0.8) under increasing temperatures; (b) PDOS of the O *p* states and M_{oct} *d* states in ZnNi_{0.2}Co_{1.8}O₄ and ZnNi_{0.8}Co_{1.2}O₄, the arrows refer to spin up and spin down projection; (c) Calculated M_{oct} *d*-band center relative to the Fermi level and O *p*-band center relative to the Fermi level of ZnNi_xCo_{2-x}O₄ (x=0~2.0); (d) Calculated bulk volume and O *p*-band center relative to M_{oct} *d*-band center of ZnNi_xCo_{2-x}O₄ (x=0~2.0). Three regions are distinguished with the increased amount of Ni ratio.

Based on the above mechanistic pathways, we hereby proposed that the spinel catalysts presented here may operate in two different mechanisms depending not only on the reaction temperatures but also on the catalysts *per se*. ZnNi_xCo_{2-x}O₄ spinels with Ni content less than 0.4 (Ni-poor spinels) prefer to follow the suprafacial E-R model, while ZnNi_xCo_{2-x}O₄ spinel catalysts with Ni content exceed

0.4 (Ni-rich spinels) are predominated by the intrafacial Mv-K mechanism. In the temperature range predominated by certain reaction pathways, the activity of those catalysts that follow the same mechanistic pathways gets strengthened; in the converse situation the activity is relatively weakened. Therefore, below 673 K where the suprafacial E-R mechanism operates, the specific activities of Ni-poor spinels are higher than that of the Ni-rich spinels. At the temperature of 673 K to 773 K, due to the onset of the intrafacial Mv-K mechanism the specific activities of Ni-rich spinels gradually increased and the activity increment become more significant than that of the Ni-poor spinels. Particularly, when the temperature reaches above 723 K, where the intrafacial Mv-K mechanism gradually dominates the scheme, the activities of Ni-rich spinel catalysts increase much more. In between, $\text{ZnNi}_{0.4}\text{Co}_{1.6}\text{O}_4$ ($x=0.4$) may possess a property that follows both suprafacial and intrafacial mechanisms. This explains why its specific activity increases at a rate comparable to the Ni-rich spinels under high temperature ranges (Mv-K mechanism gradually dominates) but follow the volcano trend of the Ni-poor spinels (coexists of E-R and Mv-K mechanisms).

Figure 5.9 Arrhenius plots of the corresponding $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim0.8$) catalysts for the catalytic oxidation of methane.

5.3.3. Origin exploration of structure-performance relationship

Taking into account that catalytic activity is highly related to the catalyst's electronic structure^[21,30,43,44], first-principles DFT+U calculations were carried out to testify and interpret the intrinsic structure-performance relationship being proposed. It is well known that the suprafacial E-R mechanism is featured by the dissociative adsorption of dioxygen^[16,19,45], while remarkable lattice O activation and oxygen vacancies generation features to the intrafacial Mv-K mechanism^[4,6,10]. Therefore, the metal *d*-band center which relates to the adsorption of molecules at metal surface and subsequent adsorbate-metal interactions^[46,47], as well as the O *p*-band center which correlated with many oxygen interacting processes, for instance, oxygen dissociation, activation of oxygen, O vacancy hopping, etc. ^[21,44,48], are employed as parameters for the investigation. Furthermore, the interplay between the metal *d*-band center and the O *p*-band center is also examined for the intrinsic catalytic mechanism exploration.

As shown in Figure 5.8b, lattice oxygens are observed to be substantially bound to the cations for spinel $\text{ZnNi}_{0.2}\text{Co}_{1.8}\text{O}_4$. In this case, the M-O bond is relatively tighter, indicating a higher possibility to follow the suprafacial E-R mechanism without participation of lattice O. With increased Ni content, non-bonding oxygen *p* states appear on spinel $\text{ZnNi}_{0.8}\text{Co}_{1.2}\text{O}_4$. The appearance of non-bonding oxygen suggests that lattice O is more prone to participate *via* the intrafacial Mv-K reaction pathway. PDOS of the O *p* states and M_{oct} *d* states in ZnCo_2O_4 ($x=0$), $\text{ZnNi}_{0.4}\text{Co}_{1.6}\text{O}_4$ ($x=0.4$), and $\text{ZnNi}_{0.6}\text{Co}_{1.2}\text{O}_4$ ($x=0.6$) are given below in Figure 5.10. The This mechanistic pathway alteration is then further elucidated from the relative position relationship between M_{oct} *d*-band center (relative to E_F) and O *p*-band center (relative to E_F).

Figure 5.10 PDOS of the O p states and M_{oct} d states in (a) ZnCo_2O_4 ($x=0$), (b) $\text{ZnNi}_{0.4}\text{Co}_{1.6}\text{O}_4$ ($x=0.4$), and (c) $\text{ZnNi}_{0.6}\text{Co}_{1.4}\text{O}_4$ ($x=0.6$), the arrows refer to spin up and spin down projection.

The specific values of M_{oct} d -band center and O p -band center relative to the Fermi level for $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) are given in Figure 5.8c. It can be seen, the position of M_{oct} d -band centers gradually move further to the Fermi level with increasing amount of Ni from $x=0$ to $x=2.0$. For the spinel $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$), the values of M_{oct} d -band center decrease from -0.74 eV to -1.68 eV and gets even lower to -2.77 eV for the non-spinel ZnNi_2O_4 ($x=2.0$). On the contrary, the O p -band centers progressively move closer to the Fermi level. The values of O p -band centers increase from -1.52 eV to -0.70 eV for the five spinel catalysts, and further increases to -0.43 eV for the non-spinels. To elucidate the interplay of M_{oct} d -band center and O p -band center, the relative positions between them (the position of O

p -band center to the Fermi level minus the position of M_{oct} d -band center to the Fermi level) have been calculated in Figure 5.8d and Figure 5.11 (schematic display). Realizing that the relative position of O p -band and M_{oct} d -band level offers a dimension in which both cationic and anionic redox capacities of the catalysts can be cumulated^[49], affecting both the reactivity/mechanism and to some extent, the structural thermal stability of the catalysts^[50], we therefore compared them with the calculated bulk volume of all the $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) oxides. For Ni-free ZnCo_2O_4 ($x=0$), the position of O p -band center is 0.71 eV lower than of the position of M_{oct} d -band center. This position difference with a lower O p -band center is narrowed to 0.46 eV for $\text{ZnNi}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$) spinel. When the Ni content increases to $x=0.4$, the position of O p -band center becomes higher than that of the M_{oct} d -band center, and this position difference with a higher O p -band center grows larger with the increase Ni content ($x>0.4$).

With regarding to the catalysts' thermodynamic stability which associated with the surface structure, it is found to be correlated to the activation of surface oxygen atoms (surface lattice O)^[49,50]. For those Ni-poor spinels with a lower energy state of O than that of the M_{oct} , indicating a relatively inactive lattice oxygen and a strong binding of adsorbates to the cations^[47]. At this energy state, the surface structure of Ni-poor spinels are thermodynamically stable and their corresponding bulk volume is relatively small. When the Ni content continuously increased to $x=0.4$ ($\text{ZnNi}_{0.4}\text{Co}_{1.6}\text{O}_4$), the energy state of O becomes higher than that of M_{oct} , suggesting the trigger of lattice oxygen activation^[49,50]. Due to a relatively close energy state of O (-1.0 eV) and M_{oct} (-1.3 eV), the surface structure of $\text{ZnNi}_{0.4}\text{Co}_{1.6}\text{O}_4$ ($x=0.4$) is still stable. As the Ni content further increase to $x=0.8$, the energy gap between O and M_{oct} gradually increases with a higher O energy

state. Under this energy state situation ($x=0.6\sim0.8$), the lattice oxygen gets more active and consequently destabilize the surface^[50] of the Ni-rich spinels to a thermodynamically metastable state.

Figure 5.11 Spinel structures and schematic representation of the O p -band center and M_{oct} d -band center for $ZnNi_{0.2}Co_{1.8}O_4$ (top left panel) and $ZnNi_{0.8}Co_{1.2}O_4$ (top right panel); the proposed reaction pathways based on the Eley-Rideal (E-R) mechanism (bottom left panel) for Ni-poor spinel oxides and Mars-van Krevelen (Mv-K) mechanism (bottom right panel) for Ni-rich spinel oxides. M_{oct} refers to cations at the octahedral site, O_{ads} refer as reactive oxygen species and V_o refers to oxygen vacancy. The rate-limiting steps are marked with green; the important adsorbates on the M_{oct} sites in the E-R pathway and the lattice O and generated oxygen vacancies in the Mv-K pathways are marked with orange; the series intermediate reactions are marked with purple.

Moreover, when the Ni substitution gets too high, to the extent where the energy state of O p -band center is much higher than that of the M_{oct} d -band center ($x>0.8$),

drastic structural reorganization might occur^[50] and both the surface and bulk structure becomes too unstable to be maintain in a pure-phase spinel structure. This result is in line with the constantly increased bulk volume being calculated (Figure 5.8d) and is evidenced by the XRD characterization, where an increased lattice parameter in spinel $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$) is observed as well as the detection of phase separation into wurtzite structure and rock-salt structure with the Ni substitution exceeds 0.8 ($x>0.8$).

This relative position relationship between O p -band center (relative to E_F) and M_{oct} d -band center (relative to E_F) also render the change of mechanistic pathways. As can be seen from the schematic display in Figure 5.11, Ni-poor spinels with the M_{oct} d -band center in a higher position relative to the O p -band center, exhibit greater metal character, indicative of a mechanism centered on the interaction on the metal cation sites^[49,51]. Therefore, the L-H/E-R mechanism featured by the adsorption of O_2/CH_4 on the metal surface, dominates the reaction pathway of Ni-poor spinels. In contrast, the Ni-rich spinels with the O p -band center in a higher position relative to the M_{oct} d -band center, and the Fermi level moves closer to the O p states, display greater oxygen character, indicates an enhanced activation of lattice oxygen^[51] and a mechanism highlight by the high involvement of lattice oxygen, i.e. the Mv-K mechanism. The interplay between the O p -band center and M_{oct} d -band center well rationalizes the reactivity of spinel $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$) towards methane conversion and their different mechanistic pathways being predicted previously. This changing of reaction pathways with compositional variation has also been reported for the Ce-doped SnO_2 , where the reaction pathway for Sn-rich catalysts follow the Mv-K model, and shift to a more complex model upon the Ce-rich ones^[2].

To explicate the reactivity behavior more specifically, the possible E-R and Mv-K pathways for methane oxidation over the Ni-poor and Ni-rich spinel catalysts are proposed in Figure 5.11. For Ni-poor spinels that follows the suprafacial E-R mechanism: Step 1, the adsorption of O_2 on the surface of metal oxide ($O-M_{oct}-O$) and formation of the reactive oxygen species (O_{ads}); Step 2, adsorption and activation of gaseous CH_4 by the adsorbed reactive O, at this step, the surface stabilized $-O_{ads}H$ and $-CH_3$ species are formed; Step 3, with the activation of methane oxidation, some intermediate oxygenates are derived, leading to the subsequent formation of H-O, C-O bonds and the cleavage of residual C-H bonds. Notably, these series intermediates steps, depending on the exact reaction conditions, may create complex networks of consecutive or parallel processes^[6]; Step 4, desorption of the produced CO_2 and H_2O for the recovery of active sites on the surface of metal oxides. Among this process, the first C-H cleavage and the H_2O desorption are generally considered to be the rate-determining steps^[2,6,16,52] for the methane oxidation. Consequently, when the M_{oct} d -band center is too far from the Fermi level ($x=0.4$), adsorption of the surface intermediates (reactive O species, etc.) on the metal cations is too weak, leading to a lack of stability for the subsequent surface reactions (including the rate-determining step, C-H bond dissociation/activation). In contrast, if the M_{oct} d -band center is too close to the Fermi level ($x=0$), represents the adsorption is too strong, inhibits the desorption (mobility) of formed H_2O (rate-determining step) and thus passivating the active sites. The moderate M_{oct} d -band center of $ZnNi_{0.2}Co_{1.8}O_4$ ($x=0.2$) optimizes/counterbalances the binding strength of reaction intermediates on surfaces (neither too strong nor too weak), not only facilitates the H_2O transfer but also stabilize the surface intermediates, thus interprets its activity outperformance.

Actually, this volcano-type correlation between the catalytic activity and the d -band center has widely been reported in the oxygen evolution reaction^[50,51,53] and CO oxidation^[54] over metal alloy and transition metal oxides. Furthermore, the moderate binding on the surface of $\text{ZnNi}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$) is also supported by the temperature programmed desorption of oxygen (O_2 -TPD) and temperature programmed desorption of methane coupled with mass spectra (O_2 -TPD-MS) tests as depicts in Figure 5.12 and Figure 5.13.

Figure 5.12 O_2 -TPD spectra of $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$). Insert is the α oxygen desorption peaks of these spinel oxides.

As displayed in Figure 5.12, two types of oxygen species can be desorbed by the $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$) spinels which are similar to that of perovskites. The α oxygen desorption peaks which are generally broad and small locate at lower temperature region, whilst the β oxygen desorption peaks are usually sharp and strong extend from around 873 K^[21,55,56]. The α oxygen desorption peaks are identified as oxygen adsorbed on the catalyst surface, whereas the β desorption peaks are recognized as the lattice oxygen of the spinel oxides^[21,56]. Generally, in

the α oxygen-TPD profile of $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$), the desorption peak areas are observed to gradually reduced. Specifically, for the Ni-poor $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.4$) spinel oxides: the desorption peak of ZnCo_2O_4 ($x=0$) is observed to be the largest, implying an easier adsorption of oxygen. In contrast, the α oxygen desorption peak of $\text{ZnNi}_{0.4}\text{Co}_{1.6}\text{O}_4$ ($x=0.4$) is much smaller, indicating a relatively weak and difficult oxygen adsorption. For $\text{ZnNi}_{0.2}\text{Co}_{1.8}\text{O}_4$ ($x=0.2$) which exhibits an α oxygen desorption peak that is larger than that of $\text{ZnNi}_{0.4}\text{Co}_{1.6}\text{O}_4$ ($x=0.4$) but smaller than ZnCo_2O_4 , suggesting a mediate oxygen adsorption potential. O_2 -TPD results manifest that $\text{ZnNi}_{0.4}\text{Co}_{1.6}\text{O}_4$ ($x=0.4$) is relatively inactive in the oxygen adsorption and desorption, whereas ZnCo_2O_4 is too active. In between, $\text{ZnNi}_{0.2}\text{Co}_{1.8}\text{O}_4$ possess a mediate activity for the oxygen adsorption and desorption, which is in agree with the M d -band center estimation from DFT calculations. In terms of the β desorption peaks recognized as the lattice oxygen of the oxides, it can be seen the desorption temperature is gradually shift from 1050 K to lower temperature at 940 K as the Ni content increase from $x=0$ to $x=0.8$. This decrease of desorption temperature indicative of an increased activity of lattice oxygen, which is in consistent with the O p -band center estimation from DFT calculations.

With the help of mass spectra displayed below in Figure 5.13, the produced CO_2 from the reaction between the adsorbed CH_4 and the surface lattice oxygen of the catalysts is identified. Since there is no adsorbed oxygen on the surface of catalysts (removed by preconditioned in flowing He) and no contact with any free oxygen during the whole process, the generated CO_2 is correlated directly with the availability/activity of lattice O. Notably, the lattice O participation seems early at around 600 K, but the real situation can be very different. In the real reaction situation with excessive supply of gaseous O_2 and lean methane, the adsorbed O_2

will compete with lattice O for the reaction with methane, leading to a much more complicated process as observed in the experiment. Generally, the produced CO_2 which reflects the activity of surface lattice O is well correlated with the calculated O p -band center relative to the Fermi level from DFT. This further confirms our proposal from the DFT calculations.

Figure 5.13 CO_2 detection from mass spectra during the CH_4 -TPD test for $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$). (a)~(e) Evolution of the carbon dioxide signals for various spinels with Ni content increase from $x=0$ to $x=0.8$; (f) Comparison of normalized peak areas of the produced CO_2 from the spinel catalysts and the correlation with O p -band center relative to the Fermi level.

Regarding the Ni-rich spinels that follows the intrafacial Mv-K mechanism: Step 1, adsorption and dissociation of gaseous CH_4 on the metal cations ($\text{O-M}_{\text{oct}}\text{-O}$); Step 2, after dissociation of first C-H in CH_4 , the H species will couple with the O atom of the lattice O to form OH, follow by the oxidation of CH_3 species to CH_3O . After that, intermediates CH_2O is formed through dehydrogenation by the OH species

and generates the oxygen vacancies; Step 3, molecular oxygen adsorbs and dissociates on the surface O vacancies and fills in; Step 4, H atoms dissociate from the intermediate CH_2O couple with the dissociated intermediate O to form OH and the intermediate CHO is formed by the formation of lattice O vacancy; intermediate CHO is transformed to intermediate CO through dehydrogenation by the formed OH species; Step 5, with further O_2 adsorption and O vacancy refilling, CO is oxidized to CO_2 and be desorbed from the metal cation's surface, leaving the recovered active sites. Among the above processes, the multiple lattice O involved steps instead of one or two rate-determining steps are crucial for the entire methane oxidation, depending mainly on the activity/availability of surface lattice O^[3,9,12]. Besides, the well-recognized critical C-H bond cleavage step is also largely controlled by the redox mechanism involving lattice O^{[52][57]}. Therefore, Ni-rich spinels with increased amount of Ni, the O *p*-band center moves closer to the Fermi level, the surface lattice O becomes more active and thus facilitates the proceeding of multiple lattice O involving steps, results in the higher specific activity of $\text{ZnNi}_{0.8}\text{Co}_{1.2}\text{O}_4$ ($x=0.8$) under high temperature ranges. This enhanced active lattice oxygen participation with increased substitution of Co by Ni in $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$) is also testified by CH_4 -TPD-MS and O_2 -TPD tests as discussed previously. Nevertheless, if the O *p*-band center gets further close to the Fermi level ($x>0.8$), the surface lattice O gets so active that destabilize the surface and bulk structure and leads to the phase separation as mentioned previously. As a matter of fact, the O *p*-band center relative to the Fermi level is found to be capable of describing O involved reaction energies, activation energies and can be used as descriptors for the O addition and removal related processes^[48]. For instance, an increase of OER activity has been reported when the O *p*-band center moves closer

to the Fermi level using double perovskites, but further upshifts the O *p*-band center to the Fermi level result in decrease of the oxide stability and no increase in the activity^[44]. Similar situation is also observed in our previous study regarding the CO oxidation^[21].

At the point of $x=0.4$ ($\text{ZnNi}_{0.4}\text{Co}_{1.6}\text{O}_4$), where the position of O *p*-band center (-1.0 eV to E_F) and M_{oct} *d*-band (-1.3 eV to E_F) is quite close to each other (Figure 5.8c and d), possessing a property predominated by both the E-R mechanism and Mv-K mechanism. This well explains the activity behavior of $\text{ZnNi}_{0.4}\text{Co}_{1.6}\text{O}_4$ which follows the volcano trend of Ni-poor spinels under low temperature range but increases at a comparable rate to Ni-rich spinels under higher temperatures. Accordingly, we thereby propose that the position of M_{oct} *d*-band center and O *p*-band center relative to the Fermi level may serve as effective descriptors for the surfacial E-R mechanism and intrafacial Mv-K mechanism, respectively.

5.4. Conclusion

In this chapter, a series of spinel oxides $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 0.8$) were synthesized to investigate the origin of their electronic structure dependent activities and mechanisms for methane oxidation. The interplay between O *p*-band center and M_{oct} *d*-band center was found to be responsible for the methane oxidation activity. Ni-poor $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ spinels with the M_{oct} *d*-band center positioned higher relative to the O *p*-band center, exhibited greater metal character, indicative of a dissociative adsorbed oxygen featured surfacial Eley-Rideal (E-R) model. In contrast, Ni-rich $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ with the O *p*-band center in a higher position relative to the M_{oct} *d*-band center, displayed greater oxygen character, predominated by the intrafacial Mars-van-Krevelen (Mv-K) mechanism featuring

the involvement of lattice oxygen. Consequently, the relative position between O *p*-band center and M_{oct} *d*-band center is proposed as pertinent activity descriptor that also exhibit predictive power on the preferential reaction pathways. These findings may provide steps towards the rational design of better spinel oxides for catalytic oxidation reactions.

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Chapter 6

Co, La-based perovskite oxides towards complete methane oxidation: Descriptor feasibility and predictability study

6.1 Introduction

Natural gas, consists of over 90% of methane (CH_4), is perceived as one of the cleanest fossil energy resources^[1,2]. However, when taking the climatic effect of methane emission into consideration, the scenario changes^[3]. As a potent greenhouse gas, the emission of methane should be strictly controlled and reduced^[2]. Intensive technologies have been developed to address this issue, among which complete catalytic oxidation of methane into carbon dioxide (CO_2) is the most efficient and mature one, particularly to the vehicle exhaust emissions^[2,4,5]. Noble metals, especially, the partially oxidized palladium, are the most active catalysts for methane oxidation^[2,5,6]. However, besides the high cost, they are prone to deactivation due to sintering, poisoning or decomposition under high temperatures, thus restraining their industrial applications^[7,8]. Therefore, developing efficient alternative catalysts from non-noble metal materials is inevitable for the technology. Among the non-noble metals, perovskite-type oxide catalysts outstand as a preferable choice due to their low costs, excellent thermal stability, and their unique tunable structures with exceptional redox and O mobility^[7,9,10]. Particularly, the lanthanum and cobalt-based perovskites as the most widely studied perovskite oxides are noted to exhibit superior catalytic performance for methane oxidation^[7,9,11,12]. Early from 1970s, when the potential of applying perovskite as catalysts for hydrocarbon oxidation reactions was

discovered^[13,14], extensive studies have been made to improve the activity of perovskite catalysts. Changing the composition of catalysts by partial substitution in the A position or B position has been verified to be an effective way to tune the catalytic performance. In the context of A site substitution, the low valence Sr substitution are extensively explored. Substitutions at B-site are also explored to improve the catalytic performance. One of the most investigated cases is the substitution of B-site cobalt by iron.

Along with the investigations on improving the catalytic activity of perovskite type catalysts, various factors have been proposed to be responsible for the catalytic activity, however, combined factors should be reckoned to interpret/predict catalytic activity^[15,16]. Despite the considerable studies on interpretation of methane oxidations activities, rarely any attentions have been paid on the descriptor studies of perovskite catalysts for methane oxidation. A descriptor can specify the physicochemical properties of catalysts which are responsible for catalytic performance, thereby enables the rational design of efficient catalysts with superior activity^[17]. Actually, descriptor studies on transition metal oxides for some other catalytic reactions have been widely carried out and are proven to be quite fruitful^[17]. Nevertheless, the descriptor study is still in lack with regarding to the methane catalytic combustions. Chapter 5 demonstrated that the interplay of O *p*-band center and metal *d*-band center can serve as an activity descriptor for methane complete oxidations over spinel oxides, however, it is still unknown whether it is applicable to the perovskite family. Apparently, identifying such descriptors, particularly for perovskite oxides, that associate the observed catalytic activity with catalysts' intrinsic properties are highly in demand, which would predict the catalytic behavior and in turn guide the design of catalysts with

requisite property. In addition to exploring the reactivity of catalysts, it is also important to understand the mechanism of methane complete oxidation. In spite of the extensive investigations, the mechanism studies over perovskite oxides are mainly by means of kinetic data. A further step employing more theoretical tools like modelling, molecular simulations, *in situ* measurements, etc. is necessary towards the mechanism study. As compared to the spinel oxides, the understanding of reaction mechanisms in the context of methane oxidation over perovskite oxides is far from enough.

Herein, in Chapter 6, series of LaCoO_3 perovskites with either substitution in A site by Sr or substitution in B site by Fe, i.e. $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ perovskite oxides ($x=0.0, 0.25, 0.5, 0.75, 1.0$) were prepared for the study of activity descriptors and understanding of methane oxidation process. The B-site substituted $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ perovskite oxides with tunable electronic structures were firstly employed to identify the suitable activity descriptor for methane oxidation. By means of DFT calculations and experimental characterizations, the relative positions between O *p*-band center and B-site metal cation *d*-band center are found to be responsible for the observed catalytic performances. Therefore, as a potential descriptor, this index was further extended to the catalytic performance prediction study over A-site substituted $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ perovskite oxides, which turns out to be very effective. Briefly, the interplay between O *p*-band center and B-site metal cation *d*-band center can specify the catalysts' intrinsic property accountable for the catalytic performances and in turn predict the catalytic behavior.

6.2 Experimental section

Series of $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ oxides ($x=0.0, 0.25, 0.5, 0.75, 1.0$) were synthesized *via* a sol-gel method as described in Chapter 3. The methane total oxidation catalytic performance was also measured in a fixed bed micro reactor with continuous flow under atmospheric pressure which is the same as stated in Chapter 5. The DFT calculations were performed similar to that as described in Chapter 4 and 5. O_2 -TPD and CH_4 -TPD experiments were carried out using the method in Chapter 5.

6.3 Results and discussion

6.3.1. $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ catalysts characterizations

The morphologies of $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ oxides ($x=0.0, 0.25, 0.5, 0.75, 1.0$) examined by FESEM are displayed in Figure 6.1. As depicted, similar morphologies with porous networks are recognized in all the $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ samples, which are formed from randomly aggregated or stacked particles.

Figure 6.1 SEM images of $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ ($x=0.0, 0.25, 0.5, 0.75, 1.0$) perovskite oxides.

The corresponding particle sizes measured by the BET technique are presented in Figure 6.2a and Table 6.1. The substitution of Co by Fe in LaCoO_3 increases the specific surface area over a small range from $10.8 \text{ m}^2 \text{ g}^{-1}$ to $13.9 \text{ m}^2 \text{ g}^{-1}$ (Table 6.1). The Type V adsorption and desorption isotherms as an indicate of mesoporous structures^[18] in the samples are in consistence with the SEM observations. The crystal structures characterized by XRD are exhibited in Figure 6.2b. As displayed, the diffraction peaks of the as-prepared LaCoO_3 ($x=0.0$) matched well with the standard rhombohedral perovskite LaCoO_3 structure (JCPDS Card No. 25-1060). No detectable parasitic peaks including CoO , Co_3O_4 and La_2O_3 can be found implying the successful formation of pure phase LaCoO_3 oxide. Nevertheless, as Co gradually substituted by Fe ($x=0.25$ and 0.5), an additional phase is formed which can be indexed to orthorhombic. In another word, the $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$ and $\text{LaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ exhibit a mixed rhombohedral and orthorhombic structure. As the level of Fe substitution further increases ($x=0.75$ and 1.0), the characteristic peaks shift to orthorhombic structure of LaFeO_3 (JCPDS Card No. 37-1493). Besides, the diffraction peak appears to gradually shifts to lower angle with the increase of Fe substitution (Figure 6.3), which can be induced by the different ionic radius of Co^{3+} and Fe^{3+} cations ($\text{Fe}^{3+} > \text{Co}^{3+}$)^[19].

Figure 6.2 (a) BET measurements; (b) XRD patterns of the as-synthesized $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ perovskite oxides; (c-d) Fourier transform of EXAFS spectra; (e-f) Normalized XANES spectra (Insets provide the respective quantified oxidation states of Co and Fe) of Co K-edge and Fe K-edge respectively in $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ ($x=0.0, 0.25, 0.5, 0.75, 1.0$) perovskite oxides.

Table 6.1 Summary of BET surface area of $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ perovskite oxides.

Fe content (x) in $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$	Sample name	BET surface area (m^2/g)	Sr content (x) in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$	Sample name	BET surface area (m^2/g)
0.0	LaCoO_3	10.8	0.0	LaCoO_3	1.1
0.25	$\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$	13.9	0.25	$\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$	1.7
0.5	$\text{LaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$	12.5	0.5	$\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$	6.6
0.75	$\text{LaFe}_{0.75}\text{Co}_{0.25}\text{O}_3$	12.6	0.75	$\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_3$	8.1
1.0	LaFeO_3	10.8	1.0	SrCoO_3	0.7

Figure 6.3 XRD patterns of the as-synthesized $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ ($x=0.0, 0.25, 0.5, 0.75, 1.0$) perovskite oxides in the scan range of 30 degree to 35 degree.

To explore the possible impact of Fe substitution in LaCoO_3 , X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were conducted to probe the coordination environment and electronic structure changes. The Fourier transformed (FT) EXAFS spectra in Figure 6.2c and d are employed to identify the local atomic environment of Co and Fe cations in substituted $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ perovskite oxides. By revealing the peak distance and intensity related to the coordination shells of Co and Fe, information on site occupation can be extracted^[20,21]. Specifically, the first shell peak features at $\sim 1.5 \text{ \AA}$ represents the Co-O/Fe-O shell caused by scattering from the absorbing metal atom (Co/Fe) to its closest neighboring O^[21,22]. From Figure 6.2c and d, the FT patterns of Co or Fe barely changed in all $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ samples, manifesting that Fe substitution has barely any effect on the bond lengths of Co-O or Fe-O. Generally, the FT patterns between the Co K-edge and Fe K-edge are similar, implying that Fe substitution in $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ causes no significant impact on the coordination environment of all Co and Fe atoms.

From the Co and Fe K-edge XANES spectra in Figure 6.2e and f, the nominal Co and Fe valence states are illustrated. Positions of K-edge as an indicator when compared to corresponding reference oxides was determined using the integral method^[23,24]. After progressive Fe substitution, the K-edge energies/positions of Co (Figure 6.2e) exhibits almost no shift and remains the same as the pristine LaCoO_3 , indicating an unchanged valency of Co cations in the substituted $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$. A similar situation is observed in the K-edges of Fe, where unshifted edge positions are found in all substituted catalysts (Figure 6.2f) with relative to the reference Fe_2O_3 . Moreover, the quantified oxidation state of Co and Fe acquired from comparing the edge positions to those of the reference materials are given in the inset. It is discerned that the valence states of both Co and Fe maintain constant at approximately 3+ despite an increased level of Fe substitution. Therefore, based on the unchanged coordination environment and valence states of both Co and Fe, it can be confirmed that Co is successfully substituted by Fe at the B site of $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ as expected.

6.3.2. Evaluation of catalytic activity of B-site substituted $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ for complete methane oxidation

The B-site substituted $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ was investigated firstly, where the redox specifications of these transition metal ions control the catalytic property of perovskite oxides^[7,9,25]. The catalytic activity was evaluated in terms of the complete oxidation of methane. In order to interpret the intrinsic property of the catalysts and their associated reaction mechanisms, the BET surface area normalized specific activities are employed. Despite that the BET surface area is not perfectly identical to the real active surface area, it is reasonable to use it for the activity assessment. Actually, assessing activity by the BET surface area has

been widely used as an effective method for transition metal oxide catalysts screening^[26–30]. The BET surface area normalized specific activity of methane oxidation plotted as a function of Fe amount in $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ at increasing temperatures from 623 K to 823 K is displayed in Figure 6.4a. Generally, it can be distinguished that the catalysts exhibit different manners under three different temperature zones: the low temperature zone (623 K and below), medium temperature zone (from 623 K to 773 K), and high temperature zone (above 773 K). Under the low temperature zone, where the catalytic activity starts to light-off, a volcano pattern with $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$ ($x=0.25$) showing higher specific activity than other catalysts can be observed. As the temperature increases to the medium temperature zone, an increase in specific activities are found for all the $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ catalysts. To be more specific, the medium temperature zone can be divided into two stages according to the specific activity increment in Figure 6.4b. When the temperature below 723 K, it can be seen that LaFeO_3 ($x=1.0$) and $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$ ($x=0.25$) increase the most, followed by $\text{LaFe}_{0.75}\text{Co}_{0.25}\text{O}_3$ ($x=0.75$) and $\text{LaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ ($x=0.5$), while LaCoO_3 ($x=0.0$) increases the least. From 723 K to 773 K, the activity of $\text{LaFe}_{0.75}\text{Co}_{0.25}\text{O}_3$ ($x=0.75$) increases more making its activity increment exceeding that of $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$ ($x=0.25$). When the temperature further increases to the high temperature zone, an obvious decrease of activity increment for LaCoO_3 ($x=0.0$) and $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$ ($x=0.25$) is observed. Meanwhile, the rest three $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ ($x=0.5\sim 1.0$) catalysts exhibit higher activity increments. The reaction rate of $\text{LaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ ($x=0.5$) has achieved $20.6\times 10^{-8} \text{ mol m}^{-2} \text{ min}^{-1}$ at 823 K, approaching to that of $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$ ($x=0.25$). Meanwhile, the superior activity of LaFeO_3 has reached $26.9\times 10^{-8} \text{ mol m}^{-2} \text{ min}^{-1}$, which is comparable, or superior to many of the reported perovskite oxides

catalysts, for instance, the nonporous $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskite^[31], ZrO_2 supported La, Mn oxide and ZrO_2 - LaMnO_3 perovskite catalysts^[32], A-site substituted ACoO_3 (La, Sr, Nd) perovskites^[16], and some noble metal-based catalysts, including $\text{Pd/Co}_3\text{O}_4$ ^[33], bimetallic $\text{Ru-Re}/\gamma\text{-Al}_2\text{O}_3$ ^[34] and so forth.

The mechanism of methane complete oxidation is a long-standing puzzle, which drives marvellous studies to address this issue. For perovskite oxides, the E-R model is perceived as a popular suprafacial model, whereas the L-H model is more fitted for the noble metals^[2,7,16,35]. In spite of the contradictions on reaction pathways, the two-term mechanism with simultaneous participation of suprafacial and intrafacial processes varies with temperatures has gradually become a consent^[12,25,36,37]. This two-term model is possible over the $d^{n>0}$ perovskite oxides, where both the valence and conduction bands are of metal character^[36]. This possibility can also be supported by the fact that La-based perovskites are able to adsorb enormous oxygen species both on the surface and in the bulk, vice versa, desorb corresponding two types of O, surface oxygen species and lattice oxygen^[9,27]. Our prior work^[38] suggests that particular spinel catalysts may prefer to follow certain mechanistic pathways (either the suprafacial E-R model or the intrafacial Mv-K mechanism). And in the temperature window predominated by certain reaction pathways, catalysts that follow the same reaction model behave better; in the converse situation, those do not undergo the same mechanism model get weakened. Briefly, the property of catalysts *per se* works together with the reaction temperature that leads to the observed catalytic activity. In order to explore whether the perovskite oxide catalysts follow the same principle, DFT calculations with particular attention on the *p*-band center of oxygen and *d*-band center of B-site metal cations in substituted LaCoO_3 perovskite are performed.

Figure 6.4 (a) Catalytic performances of the B-site substituted LaFe_xCo_{1-x}O₃ (x=0.0, 0.25, 0.5, 0.75, 1.0) perovskite oxides for complete methane oxidation in terms of the normalized specific activities; (b) Specific activity increments as a function of Fe substitution in LaFe_xCo_{1-x}O₃ under increasing temperatures; (c) The values of B-site metal cation *d*-band center relative to the Fermi level and O *p*-band center relative to the Fermi level in LaFe_xCo_{1-x}O₃ (x=0.0, 0.25, 0.5, 0.75, 1.0), respectively; (d) The relative position values between the O *p*-band center and B-site metal cation *d*-band center in LaFe_xCo_{1-x}O₃ (x=0.0, 0.25, 0.5, 0.75, 1.0) (the position of O *p*-band center to the Fermi level minus the position of B-site metal cation *d*-band center to the Fermi level). Insets are the PDOS of the *d* states of B-site Co, Fe and O *p* states in LaFe_{0.25}Co_{0.75}O₃ (x=0.25) and LaFeO₃ (x=1.0).

6.3.3. Interpretation of catalytic activity from DFT calculations

To characterize the suprafacial mechanism featured by dissociative adsorption of gaseous oxygen on the catalysts' surface^[39,40], the *d*-band center of metal cations is

being introduced. This is because the *d*-band center has been developed to describe the adsorption of reactants/intermediates at the metal surface as well as related adsorbate-metal interactions, and is proved to be effective by numerous studies^[17,41,42]. In contrast, the *p*-band center of oxygen is proposed in accounting for the alternative intrafacial mechanism, featured with the involvement of lattice/bulk oxygen^[7,12,36,43]. The effectiveness of establishing O *p*-band as representor for O relevant surface reactions has been qualitatively understood and testified in a number of catalytic oxidation reactions^[24,38,44–46].

In Figure 6.4c, the values of calculated B-site metal *d*-band centers of Co and *p*-band centers of O relative to the Fermi level are provided respectively for the $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ oxides. In general, the *d*-band centers progressively move apart from the Fermi level, with a value of -2.01 eV for LaCoO_3 ($x=0.0$) to -3.25 eV for LaFeO_3 ($x=1.0$). Inversely, the O *p*-band centers gradually approach to the Fermi level, from -2.63 eV for LaCoO_3 ($x=0.0$) to -1.74 eV for LaFeO_3 ($x=1.0$). Their interplay in terms of the relative positions between oxygen *p*-band center (relative to E_F) and B-site metal cation *d*-band center (relative to E_F) are obtained (values are given in Figure 6.4d) to further elucidate the structure-performance relations. This relative position enables us a dimension to cumulate both the cationic and anionic redox capacities^[38,47] which influence the catalysts' activity and mechanism. The negative relative position value (-0.63 eV) of LaCoO_3 ($x=0.0$), with a higher position of B-site metal cation *d*-band center indicates a greater metal character^[47,48]. Thus it preferentially follow the suprafacial E-R mechanistic pathway highlighted with dissociative adsorption of dioxygen on the metal surface (suprafacial model-driven catalysts). When Fe is introduced to substitute Co at the B-site, the relative position has shifted to a positive value of 0.08 eV for

$\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$ ($x=0.25$). At this point, the relative position value is close to zero, suggesting a very close position between the B site metal cation d -band center and O p -band center in $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$. It is therefore result in a property dominated by both the suprafacial and intrafacial models (two-term model). Under such circumstances, the intrinsic property of the catalyst is more complicated subjecting to some synergistic effect. Here, though the relative position value of $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$ ($x=0.25$) is positive, it is proceeded with a two-term pathway with preference to the suprafacial model (suprafacial model-driven catalysts) due to its relatively low O p -band center value, which will be elaborated later on. As the Fe substitution further increases, the relative position values further increase for the $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ ($x=0.5\sim 1.0$). These mounted positive values with a shifted higher position of O p -band center than that of the B-site metal cation d -band center, implying a greater oxygen character of the catalysts^[48,49]. They prefer to follow the intrafacial Mv-K reaction pathways featured with the critical participation of bulk oxygen (intrafacial model-driven catalysts). This interplay can not only specify the properties of the catalysts but also render the catalytic performances. When rationalizing the catalytic performance, the reaction temperature should always be considered. For the $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ catalysts, the lattice oxygen participation temperature starts early from around 673 K, which may be attributed to the crucial role of materials textural property^[9,50]. This early engagement of lattice oxygen around the light-off temperature has also been reported on layered LaSrCoO_4 ^[39]. For a better interpretation of the activity behavior exhibited in Figure 6.4a, we divide the temperatures into three zones accordingly. At the low temperature zone, where the suprafacial E-R mechanism operates, the specific activities of suprafacial model-driven catalysts, i.e. LaCoO_3 ($x=0.0$) and $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$

($x=0.25$) are relatively higher. When the temperature increases to 723 K (the first stage of medium temperature zone), the lattice oxygen starts to get involved, leading to a scenario where the suprafacial and intrafacial mechanism co-exist and compete with each other^[36,43]. At this temperature zone, we can observe an increase in all catalysts and a comparable increase for both the suprafacial model-driven catalysts (LaCoO_3 and $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$) and the intrafacial model-driven catalysts ($\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$, $x \geq 0.5$). However, when the temperature rises to 773 K (the second stage of medium temperature zone), where the suprafacial and intrafacial mechanisms still exist concurrently and the reaction mechanism is gradually dominated by the intrafacial one due to the governing involvement of lattice oxygen. This mechanism change results in a small activity increment of the suprafacial model-driven catalysts (LaCoO_3 and $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$) as shown in Figure 6.4b, but a bigger increment for the intrafacial model-driven catalysts ($\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$, $x \geq 0.5$). When the temperature reaches the high temperature zone, where the intrafacial Mv-K mechanism rules, significantly higher activity and larger activity increment can be observed for the intrafacial model-driven catalysts ($x=0.50$, $x=0.75$, $x=1.0$). It is noteworthy, the substitution of Co by Fe at the B-site of LaCoO_3 has directly altered the catalytic properties from the suprafacial-model to the intrafacial-model driven, and subsequently results in the observed catalytic performances. Similar behaviour was also reported in the Ce doped La-ferrite perovskites, where the suppression of suprafacial activity and the enhancement of intrafacial activity was observed^[40].

Figure 6.5 The schematic diagrams of the proposed suprafacial Eley-Rideal (E-R) mechanism (left panel) and intrafacial Mars-van Krevelen (Mv-K) mechanism (right panel) for lanthanum, cobalt-based perovskite oxide catalysts.

To further explicate the superior activity of $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$ ($x=0.25$) and LaFeO_3 ($x=1.0$), the possible suprafacial E-R pathway and intrafacial Mv-K pathway over the La, Co-based perovskites are proposed as in Figure 6.5. Similar mechanistic pathways can be found in our prior work regarding the spinel catalysts^[38]. As observed, the distinct difference between the two mechanisms is the involvement of lattice oxygen. For the suprafacial E-R model (left panel in Figure 6.5), gaseous oxygen is adsorbed on the B-site metal cation surface of the perovskite oxide with subsequent formation of reactive O species. The gaseous CH_4 is then adsorbed and activated by the reactive O species. After successive intermediate reactions, the active sites on the perovskite oxides surface is recovered *via* desorption of the formed CO_2 and H_2O ^[51,52]. The entire process proceeds without the involvement of lattice oxygen. For this suprafacial process, a moderate B-site metal *d*-band center value which is neither too close nor too far from the Fermi level^[47,49,53] can facilitate the rate-determining steps^[36,51] thereby improving the activity of the suprafacial model-driven catalysts. Therefore, LaCoO_3 ($x=0.0$) with the Co *d*-band center too close to the Fermi level inhibits the rate-determining steps and results in

the low activity. For the intrafacial Mv-K model (right panel in Figure 6.5), the gaseous CH_4 is adsorbed directly on the B-site metal cation surface of perovskite catalysts. After dissociation, the H species react with the lattice oxygen and generates the O vacancies^[51]. The generated vacancies will be refilled *via* the gaseous O_2 adsorption and dissociation. With consecutive intermediate steps coupled with O vacancy generation and refilling, the active surface of the catalysts will be recovered^[12,36]. As a result, the activity of those intrafacial model-driven catalysts is determined by lattice oxygen-involving steps, and mainly by the activity/availability of lattice oxygen^[39,54,55]. From $x=0.25$ to $x=1.0$, the O p -band center of these catalysts moves closer to the Femi level, indicating a more active lattice oxygen which favors the lattice oxygen involving procedures and brings about higher catalytic activities in the end. It is worth mention, at $x=0.25$ ($\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$), though its relative position value is positive (0.08 eV), it is regarded as a catalyst driven by the two-term mechanism. In addition, as its value of O p -band center relative to the Fermi level is relatively low (-2.15 eV), suggesting a less active lattice oxygen, the corresponding intrafacial activity is thus easily suppressed. Accordingly, $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$ is perceived as catalyst driven by the suprafacial model. With a combination of a two-term pathway property and a moderate B-site metal d -band center, the outperformance of $\text{LaFe}_{0.25}\text{Co}_{0.75}\text{O}_3$ ($x=0.25$) taking place at low and mediate temperature ranges, is within expectation.

Based above, it can be concluded that analysis of methane oxidation using the p -band center of oxygen and d -band center of B-site metal cations in $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ perovskite oxide allows clarifying the reaction models of the catalytic process, as well as interpreting the intrinsic structure-activity relationship.

6.3.4. Prediction of methane oxidation on the A-site substituted $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$

To further testify the feasibility of using the relative position of O p -band center and B-site metal cation d -band center as an activity descriptor, A-site substituted $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ perovskites were synthesized and investigated. In this part, $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x=0.0, 0.25, 0.5, 0.75, 1.0$) perovskite oxides are prepared, their morphological and structural analysis are provided in Figure 6.6 and Figure 6.7, which proves the successful substitution of A-site La by Sr. Here, the corresponding values of cobalt d -band center and oxygen p -band center were calculated. The catalytic performance in terms of methane oxidation over series $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ was predicted through analyzing the interplay of O p -band center and Co d -band center, and subsequently testified *via* methane oxidation experiments.

Figure 6.6 (a) SEM images; (b) Fourier transform of EXAFS spectra; (c) Normalized XANES spectra of Co K-edge in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x=0.0, 0.25, 0.50, 0.75, 1.0$) perovskite oxides.

Figure 6.7 (a) BET measurements; (b) XRD patterns of the La_{1-x}Sr_xCoO₃ (x=0.0, 0.25, 0.50, 0.75, 1.0) perovskite oxides.

Firstly, the B-site Co *d*-band center relative to the Fermi level and O *p*-band center relative to the Fermi level are calculated as displayed in Figure 6.8 a-c. From the general trends shown in Figure 6.8b, the Co *d*-band center is found to be apart from the Fermi level gradually, whereas the O *p*-band centers progressively get closer to the Fermi level as the substitution of La by Sr increases from x=0.0 to x=1.0 in La_{1-x}Sr_xCoO₃. To predict the catalytic performances of La_{1-x}Sr_xCoO₃ in a general way, the relative positions between the O *p*-band center and Co *d*-band center is then obtained as depicting in Figure 6.8c. Based on the information provided above, some properties regarding the La_{1-x}Sr_xCoO₃ oxides can be deduced. Firstly, LaCoO₃ (x=0.0) with a negative relative position value of -0.63 eV, is a typical suprafacial model-driven catalyst. Secondly, La_{0.75}Sr_{0.25}CoO₃ (x=0.25) with a negative relative position value (-0.15 eV) is also perceived as a suprafacial model-driven catalyst. Nevertheless, due to its small value around zero, it still possesses some two-term model properties. Thirdly, as the Sr substitution increases, the relative position value of La_{0.5}Sr_{0.5}CoO₃ (x=0.5), La_{0.25}Sr_{0.75}CoO₃

($x=0.75$) and SrCoO_3 ($x=1.0$) gets increasingly positive (from 0.44 eV to 1.79 eV), indicative of the intrafacial model-driven catalysts. In the previous section, it has been elaborated that the activity of the suprafacial model-driven catalyst is subjected to its metal d -band center, whilst the activity of the intrafacial model-driven catalyst is dominated by its O p -band center. Accordingly, the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ oxides are anticipated to present a catalytic manner as follows. The typical suprafacial model-driven catalyst - LaCoO_3 ($x=0.0$) is expected to exhibit a good activity at the low-temperature zone predominated by the suprafacial mechanism. At the medium temperature zone where the suprafacial and intrafacial mechanism co-operates, the activity LaCoO_3 will keep increasing but the increment is expected to decrease when intrafacial mechanism gradually dominates the two-term model. However, with its Co d -band center too close to the Fermi level, the activity of LaCoO_3 is not expected to be superior to other Sr substituted $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ oxides. As for the $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ ($x=0.25$), it is believed to have a better activity than that of LaCoO_3 at the temperature ranges where suprafacial mechanism and two-term mechanism operate. This is due to the unique property of $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ ($x=0.25$), which is driven by the two-term model, as well as its moderate d -band center that is neither too far nor too close to the Fermi level. Similarly, its increment is also expected to slightly decrease at the end of the moderate temperature zone. For the three intrafacial mechanism-driven $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ oxides ($x=0.5\sim 1.0$), their catalytic activities are expected to be low under the low-temperature zone and start to increase at the moderate temperature zone where the intrafacial mechanism starts to participate. The activity increase increment is believed to increase with the rising temperatures. Among them, the SrCoO_3 is expected to show the best activity under moderate and high temperatures attributed

to its O p -band center which is the closest to the Fermi level. Generally, the activity will exhibit a volcano trend with a superior activity of $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ ($x=0.25$) at the beginning, followed by a faster increase in activity for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ oxides ($x=0.5\sim 1.0$) as the temperature further increases. At the end, either $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ ($x=0.25$) or SrCoO_3 ($x=1.0$) will be the most active catalyst

Figure 6.8 (a) PDOS of the d states of B-site Co and O p states in $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ ($x=0.25$) and SrCoO_3 ($x=1.0$), the up and down arrows refer to the spin up and spin down projection, respectively; (b) Specific values of the B-site Co d -band center relative to the Fermi level and O p -band center relative to the Fermi level in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x=0.0, 0.25, 0.5, 0.75, 1.0$), respectively; (c) The relative position values between the O p -band center and B-site metal cation d -band center in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x=0.0, 0.25, 0.5, 0.75, 1.0$); Insets are the schematic representation of the O p -band center and Co d -band center for $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ and SrCoO_3 ; (d) Catalytic performances of the A-site substituted $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ for complete methane oxidation in terms of the normalized specific activities and normalized peak areas of the produced CO_2 from CH_4 -TPD-MS experiment by $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$.

To testify our predictions, the catalytic performances of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ oxide series for complete methane oxidation are evaluated and displayed in Figure 6.8d. It tells that the experimental results generally fit our predicted patterns. The $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ ($x=0.25$) with a two-term model property shows the best activity under low and mediate temperatures, exhibiting a volcano trend. In the meantime, the intrafacial model-driven catalysts exhibit an increase in activity when the temperature further increases, particularly to the range where the intrafacial mechanism dominates, i.e. under high temperatures. At 973 K, the activity of SrCoO_3 ($x=1.0$) has exceeded $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ ($x=0.25$) to be the most active one. In general, it can be seen from Figure 6.8d, for the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ oxides series, the participation of lattice oxygen seems late from 873 K and the suprafacial mechanism seems to dominate during its entire reaction temperature range. On the contrary, the participation of lattice oxygen in $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ oxides series starts early from the light-off temperature, implying that the intrafacial mechanism generally dominates the entire reaction temperature range. This temperature difference is subject to different material texture properties and reaction environments. This is also one of the reasons why we can only predict the activity in a general way at the current state. To acquire a more accurate prediction, further investigations are in need, for instance, descriptors for temperature dividing (low, moderate or high-temperature zones) including the light-off temperatures identification (high or low light-off temperature category), etc.

Figure 6.9 CO₂ detection from mass spectra during the CH₄-TPD test for La_{1-x}Sr_xCoO₃ ($x=0.0, 0.25, 0.50, 0.75, 1.0$) perovskite oxides. The produced CO₂ which reflects the activity of surface lattice O is well correlated with the calculated O *p*-band center relative to the Fermi level from DFT. This further confirms our proposal from the DFT calculations.

To offer support to DFT calculations, CH₄-TPD-MS (Figure 6.9) was conducted. From the results of CH₄-TPD-MS, the produced CO₂ by various La_{1-x}Sr_xCoO₃ oxides ($x=0.0\sim1.0$) was quantified and normalized by surface areas as shown in Figure 6.8d (dash line). Since there is no adsorbed oxygen on the surface of catalysts (removed by flowing He during precondition in CH₄-TPD) and no contact with any free oxygen during the whole desorption process, the generated CO₂ can, therefore, reflect the availability/activity of lattice oxygen to some degree. It can be seen, the normalized amount of CO₂ by LaCoO₃ ($x=0.0$) is relatively lower, indicating a lower activity of lattice oxygen, which is consistent with our DFT result. The normalized amounts of CO₂ produced by La_{0.75}Sr_{0.25}CoO₃ ($x=0.25$), La_{0.5}Sr_{0.5}CoO₃ ($x=0.5$), and La_{0.25}Sr_{0.75}CoO₃ ($x=0.75$) gradually increases but with

no significant differences. This explains why the increase of specific activities of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ ($x=0.5$) and $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_3$ ($x=0.75$) are not significant at high-temperature ranges, though they are intrafacial model-driven catalysts. SrCoO_3 ($x=1.0$) however produces a much higher amount of CO_2 , implying a much higher activity/availability of lattice oxygen, which leads to the superior activity of SrCoO_3 observed in Figure 6.8d under high temperatures. The similar patterns between the produced amount of CO_2 by intrafacial model-driven catalysts, i.e. $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x=0.5\sim 1.0$), and their corresponding specific activities being observed (Figure 6.8d) which are dominated by the activity/availability of lattice oxygen, confirms our estimations from DFT calculations.

To conclude, there are some rules can be proposed for the activity prediction, particularly within certain catalyst series: If the catalysts series exhibit a relative low light-off temperature, the activity of intrafacial model-driven catalysts among the series are expected to exhibit superior activities than that of the suprafacial model-driven catalysts, with the best one usually be the catalyst with the most active lattice oxygen. On the contrary, if the catalyst series display a high light-off temperature, then the activity of those suprafacial model-driven catalysts among the series are expected to exhibit better activities than the intrafacial model-driven catalysts. Under low and moderate temperature ranges, the best activity is believed to be the one with the moderate B site metal cation d -band center, which usually be the one with the unique two-term property. In such circumstances, it is, however, difficult to predict the best-activity catalyst at high-temperature zone. Whether it is the intrafacial model-driven catalysts with the most active lattice oxygen or the suprafacial model-driven catalysts with a moderate d -band center is subject to some complex synergistic effect.

6.4. Conclusion

In summary, the involvement of suprafacial mechanism and intrafacial mechanism in the course of complete methane oxidation over a series of B-site substituted $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ were studied *via* a combination of experiments and theoretical calculations. It was revealed that the catalytic performance alteration in terms of the catalytic activity and reaction pathways can be well rationalized by the relative positions between O *p*-band center and B-site metal cation *d*-band center of perovskite oxides. With a negative relative position value, the perovskite catalysts are predominantly driven by the suprafacial model, exhibiting an improved activity in the low-temperature range where the suprafacial mechanism operates. Those catalysts with a positive relative position value, on the contrary, are intrinsically driven by the intrafacial model, showing superior activity at high temperatures, where the intrafacial mechanism dominates. The as-revealed governing role of B-site metal cation *d*-band center and O *p*-band center relative to the Fermi level was further extended to the A-site substituted $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ perovskite oxides. Through the interplay of these two band centers, the catalytic performance of complete methane oxidation over $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ catalysts was predicted and then testified. The catalytic activity from experimental results showed a consistent activity pattern as predicted. This work demonstrated that the interplay between O *p*-band center and B-site metal cation *d*-band center as an activity descriptor is applicable to the perovskite oxide family.

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Chapter 7 Conclusions and Future Work

7.1 Conclusions

In this thesis, we present in depth studies to understand the relationship between the physiochemical properties of cobalt based transition metal oxides and their catalytic oxidation performances in terms of CO oxidation and complete methane oxidation. Some fundamental understandings have been developed which enables a rational design of efficient transition metal oxide for catalytic oxidation reactions.

We started from a simple oxidation model - catalytic CO oxidation. Note that the octahedral sites in spinels are responsible for their catalytic activities, and the cobalt- or manganese-based spinel oxides have gained consistent interests due to their superior catalytic performances, a series of $\text{ZnMn}_x\text{Co}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) spinel oxides were synthesized. And particular attention was put on the activity variation caused by tuning the ratio of octahedrally occupied Mn to Co. In these spinel oxides, the inactive element Zn^{2+} occupied tetrahedral sites^[1] and thus the catalytic contribution from the tetrahedral sites can be ruled out. It was revealed that both Mn and Co contribute to the activity with Mn cations as the primary active species when they co-exist, the intrinsic specific activity was found composition-dependence and the highest activity was given by the Mn/Co molar ratio of 0.11. The presence of Mn^{4+} and Mn^{3+} in a proper ratio was a key for achieving high oxidation activity and can be rationalized by the moderate oxygen adsorption during the CO oxidation, which facilitates the O vacancy refilling. This was also supported by the density function theory (DFT) calculation, showing that the high activity of $\text{ZnMn}_{0.2}\text{Co}_{1.8}\text{O}_4$ originates from having the O p -band center neither too far nor too close to the Fermi level. The e_g occupancy of Mn cations and the O p -

band center relative to the Fermi level, which are the indexes of how the electronic structure influences the oxygen addition- and removal-related processes, are proposed to serve as the activity descriptors.

Following the CO oxidation as a probe model, the target is set to the more complicated complete methane oxidation reaction. As one of the basic hydrocarbon pollutants with high symmetry, understanding the mechanistic process of methane catalytic oxidation is of vital importance to the complex heterogeneous catalysis and the environmental remediations. Cobalt based spinel oxides are also chosen for the investigation with combined to nickel, another active transition metal for methane catalytic combustion. Similarly, in the series $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ spinels, tetrahedral sites were occupied by the inactive Zn^{2+} [1] to ruling out their catalytic contributions and focus on the catalytically more active octahedral sites^[2,3]. Ni was introduced to substitute the octahedrally coordinated Co for a tunable variation in electronic structure. Similar to the CO oxidation investigation, we target to identifying an influential parameter that can reveal the origin of structure-performance relationship and serve as the activity descriptor. Through the investigation, it is found out that the activity and reaction pathway difference can be rationalized by the interplay between O *p*-band center and M_{oct} *d*-band center. Ni-poor $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides with a higher positioned M_{oct} *d*-band center relative to the O *p*-band center, exhibit greater metal character, indicative of a L-H/E-R mechanism centered on the interaction on the metal cation sites. In contrast, Ni-rich $\text{ZnNi}_x\text{Co}_{2-x}\text{O}_4$ spinel oxides with the O *p*-band center in a higher position relative to the M_{oct} *d*-band center and the Fermi level moves closer to the O *p* states, display greater oxygen character; this suggests a Mv-K mechanism highlight by the enhanced involvement of lattice oxygen. In the

temperature range predominated by certain reaction pathways, the activity of those catalysts that follow the same mechanistic pathways gets strengthened; in the converse situation the activity is relatively weakened. In addition, CH₄-TPD-MS and O₂-TPD tests further confirmed the DFT results with featured involvement of adsorbed oxygen or lattice oxygen. Accordingly, it is proposed that the relative position between O *p*-band center and M_{oct} *d*-band center, captures the physical origin of methane oxidation activity, and can serve as pertinent descriptor of the methane oxidation activity for the ZnNi_xCo_{2-x}O₄ (*x*=0~0.8) spinel oxides. It also helps to predict the preferential reaction pathways, providing a strategy to rationalize and tailor highly active spinel oxide catalysts for complete methane catalytic oxidation.

In order to further testify the feasibility of the as-establish activity descriptor to perovskite oxides, series of La_{1-x}Sr_xCoO₃ and LaFe_xCo_{1-x}O₃ with substitutions in either A position or B position were synthesized as perovskite oxide catalysts for methane oxidation. Firstly, the involvement of suprafacial mechanism and intrafacial mechanism in the course of complete methane oxidation over a series of B-site substituted LaFe_xCo_{1-x}O₃ were studied. It was revealed that the catalytic performance alteration in terms of the catalytic activity and reaction pathways can be well rationalized by the as-established descriptor: relative positions between the O *p*-band center and B-site metal cation *d*-band center of perovskite oxides. With a negative relative position value, the perovskite catalysts are predominantly driven by the suprafacial model, exhibiting an improved activity in the low temperature zone where the suprafacial mechanism operates. Those catalysts with a positive relative position value, on the contrary, are intrinsically driven by the intrafacial model, showing superior activity at high temperatures, where the intrafacial

mechanism dominates. Subsequently, the as-revealed governing role of B-site metal cation d -band center and O p -band center relative to the Fermi level was further extended to the A-site substituted $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ perovskite oxides. Through the interplay of these two band centers, the catalytic performances of complete methane oxidation over $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ catalysts were predicted and testified. The catalytic activity from experimental results showed a consistent activity pattern as predicted. It is therefore proved that the interplay between the O p -band center and B-site metal cation d -band center as a potential methane oxidation activity descriptor is applicable to not only the spinel oxides but also the perovskite oxides.

7.2 Recommended Future Work

(1) In Chapter 6, we have proposed some general rules on the activity prediction using the established descriptor on methane oxidation. However, these rules are mainly applicable within certain catalyst series, i.e. $\text{LaFe}_x\text{Co}_{1-x}\text{O}_3$ or $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$. Some questions arise over the as-established descriptor, for instance, whether it is applicable to catalysts with different material textures. Therefore, future work may look into the following aspects:

Take the perovskite oxides as an example, certain perovskite catalysts (i.e. LaBO_3) with different material textures including LaCuO_3 , LaNiO_3 , LaCoO_3 , LaFeO_3 , LaMnO_3 , LaCrO_3 , LaVO_3 , LaTiO_3 , LaScO_3 etc. will be synthesized using the same method (e.g. sol-gel method) and applied for complete methane oxidation. Their corresponding structure-performance relationships will be investigated to identify the proper influential parameters that can specifying the origin of the activity and subsequently serve as the activity descriptor for perovskites with various textures/compositions. Similar descriptor study is needed to the spinel oxides with

different material textures.

(2) Except for the investigations on different catalysts, different target pollutants should also be considered. In this dissertation, we start from the probe oxidation model – CO oxidation, and then to the more complex model –methane oxidation. The future work can extend to the even more complicated pollutants –the volatile organic compounds (VOC), which is another major contribution to the air contamination. There are several major types^[4] of VOC including the halogenated VOCs (e.g. the most commonly found one, polychloromethanes), aldehydes (represented by formaldehyde and acetaldehyde), aromatic compounds (e.g. benzene, toluene, and ethylbenzene which occurred in the petroleum fuels), polycyclic aromatic hydrocarbons (naphthalene with two rings, phenanthrene with three rings and so on), and alcohols and ketones (which are widely used in personal care products). Widely investigations were reported on the VOC oxidations by transition metal oxide catalysts, such as the Co_3O_4 spinels^[5], partially substituted lanthanum-based perovskites^[4], ceria based mixed metal oxides^[6] and so on. Despite the increasing attentions, the fundamental understanding of the VOC oxidation on various catalysts is far from enough. Therefore, it is of vital importance to investigate the VOCs oxidation process on transition metal oxide catalysts.

(3) For all the efforts we have made is to better design and develop efficient, robust catalysts that can replace the noble metals being used in the market now. Therefore, our next move will focus more on the industrial application aspect. For example, we can integrate our efficient transition metal oxide catalyst onto the large commercial cordierite monolithic substrates to test their activities, stabilities and other mechanistic functions. Through this way, usability of the developed catalysts

will be re-evaluated and improved accordingly. Meanwhile, simulated exhaust gas including water vapor, CO₂ etc. will be applied to the testing.

(4) Hereby, most of the efforts in this dissertation have been devoted to the understanding of transition metal oxides towards complete oxidation reactions, including CO oxidation and methane oxidation. Actually, the partial oxidation of methane to syngas is another topic worth paying attention to. Methane as a widely used feedstock to produce synthesis gas, H₂ and other clean energies^[7], its commercial value should always be aware of. In addition, there are some principles from the complete oxidation reactions that can be used in the partial oxidations, therefore, partial oxidation of methane by transition metal oxide catalysts is another prospect that can be cover in the future work.

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