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**STUDIES ON CONVERSION OF BIOMASS-BASED
MATERIALS INTO HMF-DERIVED CHEMICALS**

ZHAO JUN

SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

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ZHAO JUN

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School of Chemical and Biomedical Engineering

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Abstract

The demand for energy and resources of the world now outstrips the earth's ability to meet. With the decreasing of fossil fuel resource and serious environmental pollution caused by the overuse of fossil fuel, biomass energy has attracted more and more attention. As an important solution to the shortage of energy and resources, biorefinery can integrate biomass conversion process to produce energy and chemical building blocks for a diverse range of applications.

Among the various renewable building blocks, 5-hydroxymethylfurfural(HMF) plays an important role due to its rich chemistry and potential availability. It can be obtained from monosaccharides such as fructose, glucose, as well as cellulose directly. Moreover, HMF can also be used to produce many valuable molecules such as levulinic acid, dihydroxymethylfuran, 2,5-furandicarboxylic acid, 2,5-diformylfuran (DFF) and 5-hydroxy-4-keto-2-pentenoic acid. Here, the catalytic transformation of fructose to HMF and its derivatives are the study focus. Considering the separation of products and reuse of catalysts, heterogeneous reaction system with carbon-based solid catalysts was designed and applied in the conversion of fructose to HMF and DFF.

Dehydration of monosaccharides is the main method for the manufacture of HMF. Carbon spheres bearing high stability, low cost and abundant strong protonic acid sites were used as catalyst. The carbon spheres were prepared through a facile hydrothermal method with glucose as the carbon precursor. And then sulfonation treatment was used to increase the amount and strength of the acid sites on the surface of the carbon spheres. The carbon spheres based solid acid showed excellent performance in the dehydration of fructose to HMF. The influences of acid site density, reaction time, solvents, catalysts amount, temperature and mole ratio of catalyst to substrate were investigated. Under

optimized conditions, 90% yield of HMF was obtained with 100% fructose conversion in only 1.5h at 160°C.

DFF, which is an important monomer for industry can be synthesized by the selective oxidation of hydroxyl group of HMF. Vanadium-embedded mesoporous carbon microspheres were synthesized and applied in the aerobic oxidation of HMF to DFF, showing almost 100% selectivity towards DFF. The catalytic activity of the initially prepared vanadium-embedded carbon solid spheres is not ideal due to the limit contact chance between the reactant and the active site. However, after the introduction of mesoporous structure into the carbon sphere, the activity of the catalyst increased remarkably. But there was a slight decrease of the catalytic activity during the recycling test due to the leaching of the active sites.

Based on the successful synthesis of HMF and DFF through dehydration of fructose and selective oxidation of HMF respectively, molybdenum trioxide supported on carbon spheres were prepared and used as bifunctional catalysts for the one-pot and one-step conversion of fructose to DFF. The catalysts were prepared with a similar method as the vanadium-embedded carbon spheres. Different after-treatment methods were used to modify the physiochemical properties of the catalyst in order to achieve the best DFF yield. As a result, 77% DFF yield and 100% fructose conversion can be obtained under optimized conditions.

The component, morphology and structural properties of the catalysts were characterized by many techniques such as X-ray diffraction, Raman spectroscopy, Fourier transform infrared spectroscopy, Element analysis, X-ray absorption near edge structure, Thermo gravimetric analyzer and so on. Different reaction conditions were investigated to reach the highest yield of target product. In addition, the reusability of the catalysts was also tested.

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Chapter 1 Background and Philosophy

1.1 Background and biomass conversion via heterogeneous catalysis

Energy is needed for the survival of human society and is important in developing global economy and improving living standards; thus setting the pace of socioeconomic development[1]. With the development of global economy, the demand for energy is increasing rapidly, while the common energy sources like fossil fuels (namely oil and gas) are non-renewable, resulting in their long term supply crisis and high prices[2, 3]. However, this is only one side of the coin. On the other hand, the long history of man's misuse of oil and gas has led to some drastic changes on our environment[4]. The air pollution and water pollution can directly affect human health, and the global warming caused by the overproduction of carbon dioxide formed by burning of these non-conventional sources of energy has brought severe calamity to the creatures living on this planet including mankind[5-7]. Under the pressure from the shortages of energy resources and the serious environmental pollution, which even poses a great threat to man's existence and development, people from all around the world are trying to search and develop new, clean and safe energy resources to reduce the dependency on fossil fuels[8, 9]. Renewable energy sources like solar energy, wind energy, tidal energy, geothermal energy, nuclear energy etc. are increasingly attracting people's attention, and countries around the world are taking active measures to push the development of technologies in using these energies [10-12].

Among all the new types of energy resources, biomass energy is one of the most important energy sources to be benefited from in the future. Biomass is a form or carrier of solar energy. Solar energy harnessed by plants for photosynthesis is stored as chemical energy in biomass; it is in fact an effective and cost-effective way of utilising the infinite potential of solar energy[13-15]. Biomass is the most widely spread material on earth including all the animals,

plants and microorganisms and other derived organic materials. The energy that a plant uses during photosynthesis is 0.2% of the radiation of the solar energy reaching earth[16]. The absolute value of this energy is very huge, about forty times of the total energies consumed by humans worldwide. As the main ingredients of biomass, about 16 billion tons of lignin and cellulose can be regenerated every year, which is equal to 15-20 times of the oil production[17]. Besides, biomass comes from the carbon dioxide in the air and water, so even if the biomass was burnt to produce heat directly, it would not intensify the greenhouse effect. Replacing the traditional energy sources with biomass can reduce the dependence of coal, oil and gas and environment pollution as well. Generally, the abundant existence and renewability can guarantee the sustainable use of biomass; it's use reducing the carbon dioxide, sulphide and nitrous oxide level in atmosphere, thus making biomass an environment friendly energy source[18]. Biomass is easy to transport and the product quality is stable. In one word, biomass energy is the only storable and transportable renewable energy, and also the most promising substitute for conventional energy sources to realize the utilization on a large scale. But it comes with its own disadvantages such as dispersed distribution, low energy density, low calorific efficiency and complexity of the components.

Actually, biomass materials have been used as an energy source from time immemorial. Most of the time, they are burnt to provide heat energy. Until now, many farmers still rely on biomass for cooking and heating in many rural areas[18, 19]. This kind of unscientific use of biomass material can pollute the environment and waste energy sources. Therefore, it is necessary to develop new technical and scientific lines for systematically utilizing biomass materials.

As an energy source, biomass can either be used directly via combustion to produce heat or indirectly after converting it to various forms of biofuel.

Historically, humans have harnessed biomass derived energy since the time when people began burning wood to make fire, which should be replaced by new efficient and harmless utilization techniques. Biofuels are classified into two major categories based on the source of biomass. First generation biofuels are derived from sources such as sugarcane and corn starch etc.[20]. Second generation biofuels on the other hand utilize non-food based biomass sources such as agriculture and municipal waste[21, 22]. Despite being the favored alternatives, economical production of second generation biofuel is not yet achieved due to technological issues due to the chemical resistance and structural rigidity of lignocellulosic biomass.

Conversion of biomass to biofuel can be achieved by different methods which are broadly classified into: thermal, chemical and biochemical methods. The thermal methods include biomass gasification technology, thermal cracking technology and biomass liquefaction technology. Biomass gasification technology is a process in which the transfer of the solid biomass into gas fuel happens through thermal chemical reactions[23]. It has a history of more than 100 years, the initial gasification reactor being set up in the year 1883, which used charcoal as raw material to produce gas to drive the internal combustion engine. According to the gasification temperature, biomass gasification can be classified into: room temperature gasification and high temperature gasification[24]. The room temperature gasification includes air gasification, oxygen gasification, steam gasification, steam-oxygen mixture gasification and hydrogen gasification. Usually, the efficiency of room temperature gasification is lower than high temperature gasification which occurs at 1000°C, where air is mixed with 10-20% steam as the gas intermediate. The pyrolysis of biomass is also one of the most promising ways of using these renewable forms of future energy, also known as liquefaction technology[25]. Organic molecules with larger molecular weight can be broken down into small molecular with relatively

fewer carbon atoms. Through the control of reaction temperature, reaction time, heating rate and active gas, different kinds of chemicals can be produced. The pyrolysis conducted under 400°C mainly produces coke while the main product becomes gas if the temperature is higher than 500°C[26]. Biomass liquefaction technology involves the transfer of biomass into liquid hydrocarbon under the conditions of high pressure(15MPa) and low temperature (250-400°C[27]. It can be classified into direct liquefaction and indirect liquefaction.

The biochemical methods of transformation of biomass include anaerobic fermentation technology, hydrolysis fermentation technology and biological hydrogen production technology. In the anaerobic environment, the biomass in fermentation tank is first converted to organic acid, alcohol, hydrogen and carbon dioxide by the bacterial action, then the organic acid and alcohol are metabolized to acetic acid and hydrogen, followed by the treatment with methanogens to produce methane. The hydrolysis fermentation technology was used to produce ethanol from sugar, starch and cellulose[27, 28]. First, the crushed cellulose was converted to sugar by catalyzing enzyme. Second, the sugar was converted to ethanol by leavening agent, but the concentration of ethanol was between 10-15%. Distillation and purification is essential to get 95% volume fraction ethanol. Algae and cyanobacteria can be used to produce hydrogen from biomass which is called biological hydrogen production[29].

Biomass can be transformed to to produce chemical that is more conveniently used, transported or stored, or to exploit some property of the process itself. For example, cellulose can be converted to intermediate platform chemical such sorbitol, glucose, hydroxymethylfurfural etc., and these chemicals are then further transformed to produce hydrogen or hydrocarbon fuels[30, 31]. The commercial production of wood sugars for ethanol production was first considered at the beginning of 20th century. Lignocellulose, a very abundant

material, are present as important polymers (cellulose, hemicellulose and lignin), of which cellulose and hemicellulose in particular are of high importance, since they are formed from monomers of glucose and they can be used as a carbon source in fermentation process for the production of ethanol[32, 33]. In order to produce industrial chemicals from biomass, it is important to find a range of chemical building blocks derived from renewable resources. One of these, 5-hydroxymethylfurfural(HMF), plays an important role, because it can be obtained not only from fructose but also from glucose as well as directly from cellulose. HMF is very useful not only as intermediate for the production of the biofuel dimethylfuran and other molecules, but also for important molecules such as levulinic acid, 2,5-furandicarboxylic acid(FDA), 2,5-diformylfuran(DFF), dihydroxymethylfuran and 5-hydroxy-4-keto-2-pentenoic acid[34-38].

In recent years, many kinds of sugars have been converted to value-added chemicals and it is of great significance. Hexoses are the six-carbon carbohydrates and they exist abundantly in nature. Among them, D-fructose and glucose are suitable to be used as the chemical feedstock[39]. The process of transformation of hexoses into furans and furan derivatives include many steps of reaction such as dehydration, hydrolysis, isomerization, reforming, aldol condensation, hydrogenation and oxidation[40, 41]. In the chemical conversion processes, the compounds like 5-HMF, FDCA, DFF and DMF are interrelated by reaction network. FDCA has been found useful as a fungicide, corrosion inhibitor and melting agent for foundry sands as well as an intermediate in pharmaceutical and photography fields and DFF is applied in the synthesis of special polymers as monomers are formed by the complete or partial oxidation of HMF[42, 43]. DFF is also used in the preparation of macrocyclic ligands, as intermediates of pharmaceuticals, as antifungal agents and as a cross-linking agent for poly(vinyl alcohol)[44].

Here, we focus on the chemical technologies for the utilization of biomass materials to enable the biomass materials to be converted into many kinds of value added chemicals through chemical reactions. As known to all, catalysts play a very important role during the reactions. Since the Swedish chemist Berzelius discovered a new force which was later called catalysis in 1835, the development of catalysis science and technology significantly promoted the progress of petroleum industry[45]. Various catalysts have been developed and applied in energy production, environment protection and agricultural production. In a homogeneous reaction system, the reactants and catalysts form a homogeneous phase, there is no phase boundary in the reaction, while in a heterogeneous reaction system, there exist multiple phase reactions, including gas-solid reaction, gas-liquid reaction, liquid-liquid reaction, liquid-solid reaction, gas-liquid-solid reaction and solid-solid reaction. Both of the mentioned catalytic reaction systems have advantages and disadvantages. The most obvious difference between the systems is that it is much easier to separate the catalysts from a heterogeneous reaction system than from the homogenous reaction system. Generally, the separation of catalysts is a cumbersome and energy-intensive process[46], which makes heterogeneous catalysts more popular in industry. Therefore, in order to realize a low-energy way for the reuse of catalyst, we will focus on the development of heterogeneous catalysts for the conversion of carbohydrates to value added chemicals.

1.2 Aims and outline of this dissertation

Synthesis of HMF and DFF from fructose was selected as the target reactions for investigation in this Ph.D. study, intending to understand and design optimal heterogeneous catalysts for specific reactions. The activity and selectivity of the catalysts were studied, and the properties of the catalysts were investigated through a series of characterizations.

The specific objectives of this research are:

- A. Design and prepare carbon based solid acids for the dehydration of fructose to HMF.
- B. Design and prepare catalysts for aerobic oxidation of HMF to DFF.
- C. Design and prepare bifunctional catalysts for one-pot synthesis of DFF from fructose.
- D. Investigate the properties of the catalysts through a series characterizations and optimize the reaction conditions to enhance the products yield.

The reaction consists of two steps: the dehydration of fructose to HMF and the aerobic oxidation of HMF to DFF (Scheme 1). The dehydration of fructose to HMF is an acid catalyzed reaction. Organic acids, inorganic acids, salts, Lewis acid and solid acids can be used in the dehydration of carbohydrates as catalysts in different reaction systems[47]. However, homogeneous reaction system has disadvantages in terms of separation and recycling while using solid acid catalysts can avoid these drawbacks. As for the oxidation of HMF to DFF, various catalysts have been prepared and tested with different kinds of oxidants such as NaOCl, BaMnO₄, Pb(OAc)₄-pyridine, trimethyl ammonium chlorochromate, oxalyl chloride, 2,2,6,6-tetramethylpiperidine-1-oxide and pyridinium chlorochromate[48, 49]. In order to save energy and reduce production costs, one-step transformation of fructose to DFF has attracted a lot of attention. However, at present the one-pot transformation of fructose to DFF is usually processed in two steps with acid catalysts for the dehydration of fructose to HMF and oxidative catalysts for the oxidation of HMF to DFF. What's more, the oxidative catalysts have to be added in to the system after the complement of the first step to prevent the direct decomposition of fructose to small organic acids. Thus it is still quite challenging to prepare bifunctional catalyst with both acid sites and oxidative sites for the direct synthesis process.

The wide variety of catalysts and catalysis systems designed and used for biomass conversion will be discussed in Chapter 2.

Scheme 1 Conversion of fructose to HMF and DFF

Carbon-based solid acid was used as the catalyst for the dehydration of fructose to HMF in this thesis. Carbon-based solid acid is environment friendly and is insoluble in common organic solvents, and is widely used as supports to load various metal or metal oxide to form carbon composites and applied in catalysis. Here, we prepared carbon spheres by hydrothermal method using carbohydrates as starting materials. The as-synthesized carbon sphere can be easily modified with various functional groups to meet the requirements of the reaction. More specifically, we modified the carbon spheres with $-\text{SO}_3\text{H}$ to enhance its acidity to meet the requirements of dehydration of fructose to HMF. These results will be presented in detail in Chapter 4.

The work we have done on the oxidation of HMF to DFF will be presented in Chapter 5. As we mentioned above that carbon materials are widely used as supports to load various metal or metal oxide, vanadium doped carbon spheres were synthesized and applied in the aerobic oxidation of HMF to DFF in this thesis. Metal oxide or supported noble metal such as Pt/C, Pd/C and Ru/C are usually used as catalysts for the aerobic oxidation of HMF to DFF[50-52]. The reaction results are significantly influenced by the reaction conditions such as the temperature, ratio of reactant to catalyst, the reaction time and solvents. Generally, higher temperature and longer reaction time can lead to a higher conversion of reactant and higher yield of target product if it is stable under the

reaction conditions. Though a lot of catalysts have been developed for the oxidation of HMF to DFF, it is still quite a challenge to produce DFF in high yield, because the aldehyde groups can be further oxidized to carboxyl groups.

Investigation on the one-pot conversion of fructose to DFF will be presented in Chapter 6. DFF, as a valuable intermediate, a highly potential chemical used in the production of furanic polymers and renewable furan urea resin, has not been able to achieve industrial production. One of the reasons behind this is that the separation and purification of HMF is a high energy consuming process, resulting in the high price of HMF and the high cost for production of DFF from HMF. Therefore, to produce DFF from sugars directly without the separation and purification of HMF will be a greener and more economical way. A lot of efforts have been made to realize a one-pot synthesis of DFF from fructose with the combination of the acid catalyst and oxidative catalyst. Based on this idea, molybdenum trioxide supported on carbon spheres were prepared and applied in the one-step conversion of fructose to DFF in this thesis.

All the synthesized catalysts were characterized using a series of characterization techniques, e.g., field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD), RAMAN spectra, Fourier transmission infrared spectroscopy (FTIR), X-ray absorption fine structure (XAFS), Element analysis (EA) and thermal gravimetric analysis (TGA), $\text{NH}_3/\text{CO}_2/\text{CO}$ temperature programmed desorption (TPD). This part will be presented in Chapter 3.

Chapter 2 Literature Review

During the last few decades, the conversion of biomass via platform molecules or building blocks to biomass-based value added chemicals has attracted sharply increasing interests. Among the considerable range of renewable building blocks derived from biomass materials, HMF is regarded as an important intermediate due to its rich chemical properties and the possibility of its easily available synthesis strategy from fructose, glucose, sucrose and even directly from cellulose[53-56]. In this process, catalysts play an important role in activating the reaction and promoting the yield of the target products and product quality. A significant issue in the dehydration of sugars is the formation of humins, which are generally undesirable for chemical purposes. Therefore, developing new catalysts with high surface area and catalytic activity, which can solve the problems of mass transfer resistance, time consumption and fast deactivation commonly faced by heterogeneous catalysts, has attained a great deal of attention. So far, considerable efforts have been made on the catalytic transformation of biomass materials into HMF and HMF derived chemicals[57, 58]. The principles for designing heterogeneous catalyst applied in carbohydrates conversion will be discussed and the advances in the strategies for biomass conversion are also reviewed in this chapter.

2.1 Synthesis of HMF from carbohydrates

Scheme 2 Conversion of sugars to HMF and other derived chemicals.

As shown in Scheme 2, HMF is a versatile and multi-functional compound and a good starting point for the synthesis of precursors of pharmaceuticals, thermoresistant polymers, and macrocyclic compounds and particularly for the synthesis of dialdehydes, ethers, amino alcohols, and other organic intermediates[34, 47, 59]. It was first separated from the reaction system consisting of fructose, sucrose and oxalic acid, though not until 1909, the structure of HMF was assigned, because the extraction of HMF from aqueous phase was not easy due to the fact that the distribution coefficient between the inorganic and organic phase was not favorable[34, 60]. A similar method was provided by Kiermayer who produced HMF starting from sugar cane[61]. Later, HMF was found to be the product of carbohydrates dehydration reactions by Harris[62]. Up to now, over 1000 papers have been published on the synthesis of HMF, which is an evidence for the great importance of HMF as a platform molecule. HMF is mainly synthesized by the dehydration of monosaccharides after loss of three water molecules. It is a very complex process because of the acid catalyzed dehydration leads to various by-products such as formic acid,

levulinic acid apart from HMF. With the increasing interests in carbohydrates dehydration reactions, a series of catalysts have been developed for the synthesis of HMF. Generally, the catalysts can be classified into five groups: organic acids, inorganic acids, salts, Lewis acid, and others[63].

Sulfuric acid, phosphoric acid and hydrochloric acid are the most commonly used acid catalysts for the dehydration of carbohydrates to HMF[64-66]. Hydroiodic acid was also found to be active in the conversion of hexoses to HMF[34]. Organic acids such as oxalic acid, levulinic acid and p-toluenesulfonic acid can also act as catalysts[67-69]. H_2SO_4 worked as a catalyst in sub-critical water at 250°C and the yield of HMF was as high as 53%[70]. HCl and H_3PO_4 can also catalyze the reaction in subcritical water to a HMF yield of 40-50%. It was found that lower pH can lead to more rehydration of HMF to levulinic and formic acids. Among hydrochloric, sulfuric, phosphoric, oxalic, citric, maleic and p-toluenesulfonic acids, phosphoric acid showed best catalysis effect at lower pH while at higher pH HCl was the best. Moreover, HMF can also be produced from glucose, but usually the reaction rate and selectivity are lower than that of fructose. For example, when H_3PO_4 was used as the catalyst for the dehydration of glucose, only 15.5% HMF yield can be obtained[71]. The ring structure of glucose is stable, thus there is little open-chain molecules in the reaction system, making the HMF generating speed limited by the low speed of enolization.

Lewis acid, such as CrCl_2 , CrCl_3 , FeCl_2 , CuCl_2 , VCl_3 , MoCl_3 , PdCl_2 , PtCl_4 , RuCl_3 and RhCl_3 are found to be effective in the catalytic dehydration of fructose to HMF. AlCl_3 was used as catalyst for fructose dehydration in water, and the yield of HMF is 53.9%. 29.4% HMF yield was obtained when inulin was used as the starting material under the same reaction conditions[72]. A combination of FeCl_3 and tetrathylammonium bromide (Et_4NBr) worked more effective than FeCl_3 for the conversion of fructose to HMF, in which the active species were thought to be FeCl_3Br^- ion, the yield of HMF can reach as high as 86% in

NMP[73]. According to recent reports, IrCl_3 and GeCl_4 showed good catalytic activity for the dehydration of HMF in $[\text{BMIM}]\text{Cl}$, 89.2% and 92.1% HMF yields were obtained respectively under mild conditions[74, 75]. In addition, rare earth metal trifluoromethanesulfonates exhibited high activities as new type of Lewis acid[76]. In the presence of DMSO, 83.8% HMF yield was observed by using $\text{Sc}(\text{OTf})_3$ as the catalyst. Under similar reaction conditions, HMF yields of 80.2%, 78.1%, 73% and 63.5% were achieved in the presence of $\text{Yb}(\text{OTf})_3$, $\text{Ho}(\text{OTf})_3$, $\text{Hm}(\text{OTf})_3$ and $\text{Nd}(\text{OTf})_3$ respectively.

Solid acid catalysts have several advantages over liquid acid catalysts. First, solid acid catalyst can be easily separated from the reaction system and can be reused. Second, solid acid catalyst can work at higher temperature by which the reaction can become shorter thus it can reduce the side reactions to a distant. Third, the acid density on the surface of solid acid can be adjusted since the acid groups are the active sites for the dehydration of fructose to HMF. A fructose conversion of 76% and a HMF selectivity of 92% were achieved by using dealuminated H-form mordenite at 165°C in a solvent consisting of water and MIBK[77]. The conversion of fructose and selectivity of HMF are influenced by the kind of acid and the structural properties of the acid. When the Si/Al ratio was 1:1, the H-mordenite showed best catalytic activity[78]. In the presence of the vanadylphosphate(VOP), a 40% yield of HMF was obtained for 6wt.% aqueous solution of fructose[79]. Introducing different trivalent metal ions can enhance the VOP catalytic activity. The yield and selectivity increased to 50% and 87% respectively using Fe-containing VOP catalyst. Nb-based catalysts like Nb_2O_5 , niobium phosphate(NbOPO_4) exhibited high catalytic activity[80, 81]. The Nb_2O_5 prepared at 400°C shows 100% fructose conversion with 86% yield of HMF in DMSO at 120°C after 2h[35][82]. Zr- and Ti-based catalyst with different structures were employed in the dehydration of fructose[83]. An optimized HMF yield of 47% was obtained within 4h at 403K over $\text{SO}_4^{2-}/\text{ZrO}_2$.

Al₂O₃ with Zr-Al mole ratio of 1:1[84]. The yield of HMF reached 38% catalyzed by TiO₂ under microwave irradiation with 83% conversion of fructose at 200°C[85]. In the same conditions, 30% HMF yield and 65% fructose conversion can be obtained by ZrO₂ instead of TiO₂[86]. Cheap and readily abundant Zr(O)Cl₂ catalyst produce 63% HMF from fructose in water using methylisobutylketone(MIBK) as the organic phase in biphasic solvent system[87]. Sulfated zirconia is an effective catalyst which can catalyze fructose to HMF with the conversion of 94% and HMF yield of 72%[88]. 98% conversion of fructose with 85% HMF yield in 2h at 120°C using 10wt.% acidity modified silver exchanged silicotungstic acid catalyst was achieved. Ion-exchange resins also can be applied for the synthesis of HMF from sugars[89]. Nakamura developed a strongly acidic ion-exchange resin for the dehydration of fructose to HMF and obtained an 80% yield of HMF. An even higher HMF yield of 90% was obtained by the employment of Diaion[®]R PK-126 resin, which can be used in water-MIBK biphasic system by using DMSO or NMP as an aqueous-phase modifier[90]. Lansalot-Matras and Moreau used Amberlyst-15 as a catalyst in ionic liquids such as 1-butyl-3-methyl imidazolium tetrafluoroborate([BMIM]BF₄) and 1-butyl-3-methyl imidazolium hexafluorophosphate([BMIM]PF₆) for the dehydration of fructose to HMF[91]. The reaction took place in a micro-batch reactor at 80°C. The yield of HMF was around 50% and 80% respectively by [BMIM]BF₄ and [BMIM]PF₆ after reaction for 3h.

Researchers tried different solvents in the dehydration of glucose with mineral acid as catalyst. The selectivity of HMF was about 6% in water. Unlike fructose, even in an aprotic solvent such as DMSO and DMF, the yield of HMF was also very low[92]. Li Recently, a specially designed biphasic reactor which can help improve the yield of HMF from 11% to 53% was developed for the dehydration of glucose[93]. Compared with mineral acid catalysts, solid acid performed better in transferring glucose to HMF.

Solvents play an important role in the dehydration of carbohydrates to HMF[94]. DMSO, DMF, DMA, acetone, acetic acid, methanol, THF, MIBK and isopropanol were the most commonly used solvents for the dehydration of fructose to HMF. When HCl was used as the catalyst for the dehydration of fructose to HMF, 70% and 83% yield of HMF were achieved in the presence of tert-butanol and isopropanol respectively[95]. The same thing happened when H₂SO₄ was used to catalyze the fructose dehydration reaction. 57% yield of HMF was obtained in isopropanol at 120°C after 2h[95], while HMF yield of 82.9% can be achieved at 100°C in 50min by using [BMIM]Cl as the solvent[96]. Lewis acid catalyst such as FeCl₃ combined with tetraethylammonium bromide exhibited different activities and selectivities towards fructose dehydration to HMF in different solvents. In the presence of NMP, the HMF yield can reach 86%, while this value dropped to 62% when the reaction was conducted in DMF[73]. Formic acid and levulinic acid are the common byproducts formed during the reaction when organic solvents such as DMF, methanol and toluene are used as the solvents. However, when the reaction was carried out in DMSO, the formation of byproducts was inhibited and the HMF yield will increase. Musau and Munavu further studied the effect of DMSO and found that DMSO could facilitate the formation of HMF and prevent HMF from decomposing to formic acid and levulinic acid[97]. Similar findings were also reported when ionic liquids were applied in the dehydration of carbohydrates to HMF. Ionic liquids serve as both good solvents and catalysts during the reaction. Because of the special properties such as negligible vapor pressure and comparative thermal stability, there is more hope to develop more green approaches for the utilization of carbohydrates, thus ionic liquids are considered as more environmentally friendly solvents than the other organic solvents. Molten salts were first used in the dehydration of monosaccharides in 1983[98]. 70% yield of HMF converted from fructose was achieved in the presence of pyridinium chloride, which laid a solid foundation

for the development of ionic liquids used in carbohydrates transformation. In recent years, 1-butyl-3-methylimidazolium bisulfate, N-methyl-2-pyrrolidonium methyl sulfonate, diethylene glycol-bis(3-methylimidazolium)dimesylate, triethylene glycol-bis(3-methylimidazolium) dimesylate and tetraethyleneglycol-bis(3-methylimidazolium) dimesylate were prepared and applied in the dehydration of fructose to HMF as catalysts and solvents[99-103]. Results showed that Lewis acidic ionic liquids were more effective than Bronsted acidic ionic liquids for the conversion of fructose to HMF.

There are two main reasons for the low HMF yield in some reaction systems, one is the rehydration of the formed HMF, the other is the formation of humins through reaction between HMF and carbohydrates. To solve the above problems, biphasic solvent systems were developed to separate HMF from the reactant by extraction of HMF into organic phase. For example, mix solvents reactions were examined for the conversion of fructose to HMF using HCl as the catalyst. Under the same reaction conditions, HMF yields of 54.6%, 53.1%, 32% and 49.9% were observed in H₂O/MIBK, H₂O/1-butanol, H₂O/1-hexanol, and H₂O/(2-butanol-toluene) respectively[103-105]. HMF yield of 97% was reported in a DMSO/MIBK biphasic system at 76°C. H-Y faujasites and H-mordenite catalysts were examined in a H₂O/MIBK system for the conversion of fructose to HMF[106, 107]. The ratio of Si/Al affected the catalytic performance significantly. HMF yield can be achieved as high as 69% with 76% fructose conversion in the presence of H-mordenite with Si/Al ratio of 11. Dumesic et al. prepared propylsulfonic acid-functionalized and thiopropyl-modified silicas and applied in the dehydration of fructose to HMF in MIBK/2-butanol (7:3 w/w) at 180°C[108]. Results suggested that the catalytic effect was enhanced only after the acid functionalization. Later, Dumesic et al also studied the effect of the ratios of water/DMSO and water/NMP mixtures on the dehydration of fructose to HMF in the presence of acidic ion-exchange resin DIAION PK216 at 90 and 120°C[93].

The highest yield was 83% and fructose conversion was 98%, with ratio of water/NMP as 4:6 (w/w). It was found that lower fructose concentration could benefit the selectivity of HMF. Yang et al. reported a very high yield of HMF and selectivity by using niobic acid treated with phosphoric acid[109]. The reaction was carried out in water and 1.5 equiv (v/v) 2-butanol at 160°C, resulting in 89% HMF yield and 90% fructose conversion. Fan et al. conducted the dehydration of fructose to HMF in water/MIBK in the presence of $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ which is a solid heteropolyacid[110]. Under the optimized conditions, HMF yield of 78% and fructose conversion of 83% were obtained at 120°C after 1h. Analogously, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ was applied in the catalytic dehydration of fructose in water/MIBK, yielding 74% HMF and 78% fructose conversion at 115°C after 1h[111]. HMF can also be produced with glucose as the precursor. 21-25% isolated yield of HMF was reported in water/MIBK after 9h at 160°C from glucose[112]. Rigal and Gaset studied the aldose dehydration in water/MIBK with an acidic ion-exchange resin as the catalyst and HMF yields below 10% were obtained[113]. HCl was also used in the catalytic conversion of glucose to HMF, a HMF yield of 24% with glucose conversion of 50% was attained in MIBK/2-butanol at 170°C[93]. A relatively high HMF yield up to 62% was achieved by the combination of AlCl_3 and HCl[114]. Yang et al. reported a comparable result in a biphasic water –NaCl/THF systems in the presence of AlCl_3 [115]. Solvents systems such as H_2O -DMSO/2-BuOH-MIBK were also investigated, giving the highest HMF yield of 35% [116]. It can be seen that even in a biphasic system, conversion of glucose to HMF with high yield is more difficult than the conversion of fructose. Roman-Leshkov and Dumesic then investigated the influences of different types of organic solvents as extracting agents in combination with inorganic phase[117]. Typically, experiments were conducted with 30 wt% fructose in the aqueous phase with HCl as the catalyst at 150°C, the volume ratio of the organic and inorganic solvent is 3.2. The study

focused on the tests of primary and secondary alcohols, ketones and cyclic ethers. HMF yield of around 69% was the highest yield which can be achieved by using 2-butanone and 2-pentanol as the organic phase.

2.2 Synthesis of 5-hydroxymethylfurfural-based furan derivatives

Based on the further catalytic transformation of HMF, many furan derivatives such as DFF, HMFCFA and FDA can be synthesized, that is the oxidation of HMF can be performed selectively to the formyl or hydroxyl groups or can involve both groups[118, 119].

The selective oxidation of the formyl group of HMF leads to the formation of HMFCFA. Silver oxide and mixture of silver and copper were used as catalysts for the selectivity oxidation of the formyl group of HMF to HMFCFA[120]. HMFCFA was considered to be the intermediate product during the aerobic oxidation of HMF to FDA. Au/TiO₂ was applied in the oxidation reaction of HMF, it was found that a lower pressure or low concentrations of base resulted in more of the intermediate oxidation product HMF than FDA[121]. Davis et al. reported that 92-93% selectivity towards HMFCFA with 100% conversion of HMF were obtained in the presence of Au/C in basic conditions[122]. Beside oxygen, H₂O₂ can be used as the oxidant also. As a minor product, HMFCFA of 40% yield can be attained using chloroperoxidase as the catalyst[123].

The selectivity oxidation of hydroxyl group of HMF can produce DFF which is an important monomer for industry[124]. However, due to the high reactivity of the aldehyde function, the selective oxidation of HMF to DFF is still challenging. In early reports, DFF can be get from the oxidation of HMF by hydrogen peroxide and catalyzed by synthetic titanium silicalite, while the yield of DFF was only 25%[125]. Various catalytic systems have been developed towards the selective oxidation of HMF to DFF. In early reports, classical oxidants such as pyridinium chlorochromate, NaOCl, 2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO) have been applied for the oxidation of

HMF into DFF[118, 126, 127]. By using a DMSO-potassium dichromate oxidative complex at 100°C, 58% yield of DFF was obtained[128]. The trimethylammonium chlorochromate(TMACC)-Al₂O₃ and pyridinium chlorochromate(PCC)-Al₂O₃ oxidative system was tested and obtained DFF in 75% and 58% yield respectively[126, 128]. Homogeneous metal/bromide catalysts were also used in the aerobic oxidation of HMF to DFF, like Co/Mn/Zr/Br was used with air as oxidant, it was found that Co/Mn/Zr/Br was activity which mean that it can provide high conversion and selectivity, resulting in 57% DFF yield[36]. However, these methods showed some distinct drawbacks such as high cost and large amount of toxic waste. From the viewpoint of sustainable development, it is recognized that the oxidation process of HMF using molecular oxygen as the oxidant with heterogeneous catalysts is much more economical and environmentally friendly. The conversion of HMF to DFF with oxygen, air or other environmental friendly oxidants has long been a hot research topic. Supported V₂O₅/TiO₂ catalyzed oxidation of HMF with air as the oxidant and toluene or MIBK as solvents was also investigated[129]. The yield of DFF can reach as high as 90% at 1.6MPa with in 4h. The influence of solvents, pH value, pressure of oxygen and temperature was investigated when Pt/C catalyst was used in the reaction[130]. It was found that DFF was prone to form at high temperature and natural pH.. Metal-modified unsupported or SiO₂-supported vanadyl phosphate(VOP) catalysts were also tested in the oxidation of HMF to DFF under oxygen and air pressure[131]. The influence of different solvents was investigated and researchers found that DMF was one of the solutions which performed best for this transformation. By using NaClO as oxidant and Mn(III)-salen catalysts, HMF can be converted to DFF at room temperature without any by products like FDA[132]. V₂O₅ and VOHPO₄·0.5H₂O were used for the oxidation of HMF to DFF. It was found that this kind of V catalyst can not only catalyzed pure HMF to DFF but also the DFF produced by

dehydration of fructose[131]. Supported platinum catalysts were also applied in the conversion of HMF to DFF such as the Pt/SiO₂ and Pt-ZrO₂ for the oxidation of pure HMF[133].

FDA which is a potential bio-renewable replacement monomer for terephthalic acid in polyethylene terephthalate plastics and can be formed by the oxidation of both formyl and hydroxyl groups of HMF[134-136]. It was first reported to be synthesized by electrochemical oxidation of HMF in a H-shaped cell near an anode[137]. Strasser et al. studied the electrochemical oxidation of HMF using a Pt electrode at pH 10[138]. Later, carbon-black-supported noble-metal catalysts were applied in the electrocatalytic oxidation of HMF and it was found that the reaction results were greatly affected by the potential and the electrocatalyst[139]. N₂O₄ and nitric acid can oxidize HMF to FDA in DMSO and obtained FDA in 24% yield[140]. Pt/Al₂O₃ as a more economical and environmentally friendly heterogeneous metal catalyst was used under basic reaction conditions using air as oxidant at 60°C[133]. When Pt-ZrO₂ and air were used in the synthesis of FDA from HMF, a 100% conversion and 98% selectivity were obtained. Au/TiO₂ nanoparticle catalyst catalyzed HMF to FDA in aq.NaOH at 20 bar O₂ and ambient temperature lead to a 71% yield[122]. Through conducting the oxidation reaction with various gold nanoparticle catalysts, it was found that the rate-limiting step was the oxidation of HMFCa to FDA[139]. The most active and efficient catalysts were Au- CeO₂ and Au-TiO₂. According to the experiments conducted in the presence of supported platinum catalysts at different pH, Pt/Al₂O₃ and Pt/C was found to be the most efficient catalysts in aqueous Na₂CO₃ while Pt-ZrO₂ provided the best oxidation results under acidic conditions. Compared to Au/C and Au/TiO₂, Pt/C and Pd/C were more selective towards FDA under basic aqueous conditions. However, chemical oxidation reactions are usually conducted under high temperature and high pressure. Conversely, biocatalytic conversion is typically performed under

relatively mild reaction conditions with less toxic chemicals. DFF was oxidized to FDA with high yield (>99%) in the presence of lipases as biocatalysts and hydrogen peroxide as oxidant[141]. Most enzymes are restricted to either oxidation of formyl groups or hydroxyl groups, making the full oxidation of HMF to FDA very challenging. Fraaije et.al recently developed an FAD-dependent oxidase of the glucose-methanol-choline oxidoreductase family for the HMF oxidation. Up to 95% yield of FDA was obtained at ambient pressure and temperature after 24h[142, 143].

Though various HMF-derived chemicals are very good starting materials for further transformations and chemical building blocks for industry, the industrial production of HMF-derived chemicals has not been realized because of the high costs using HMF as raw material. The high price of HMF is caused by the high energy cost and process complexity during the separation and purification of HMF from the reaction system. However, most existing catalysts are efficient only for the oxidation of pure HMF, it means that the catalysts show no activity for the in situ oxidation of HMF generated from carbohydrates. Thus it is necessary to develop new catalysts which are able to catalyze the one-pot synthesis of HMF-derived chemicals directly from carbohydrates in order to save energy and make the synthesis process greener. So far, vanadium based catalysts were found to be active for the air-oxidation of not only pure HMF but also HMF produced via dehydration of fructose. V_2O_5 was the least expensive and most readily available catalyst that was used for the one-pot transformation of fructose to DFF[144]. A 58% yield of DFF calculated on HMF and 43% calculated on fructose were obtained by adding the V_2O_5 into the reaction system after the fructose was fully converted to HMF. $VOHPO_4 \cdot H_2O$ was prepared and used in the one-pot reaction, exhibiting 61% DFF yield calculated on HMF and 45% calculated on fructose. Since the whole reaction consists two steps: the dehydration of carbohydrates to HMF and the oxidation of HMF to DFF, it is

easy to imagine that the combination of acid sites and oxidative sites may lead to the formation of bifunctional catalysts which can catalyze both the dehydration reaction and oxidation reaction, resulting in a one-pot conversion of carbohydrates to DFF without the separation and purification of HMF. H-form cation and VOHPO_4 were jointly used for the direct transformation of fructose to DFF in DMSO[145]. $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}/\text{NaBr}$ and $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ were applied in the one-pot synthesis of DFF from glucose in DMA with a DFF yield of 55% based on glucose[146]. High yield of DFF was obtained from fructose by using the combination of $\text{Fe}_3\text{O}_4\text{-SBA-SO}_3\text{H}$ and K-OMS-2. $\text{Fe}_3\text{O}_4\text{-SBA-SO}_3\text{H}$ can produce HMF from fructose with 81% yield in DMSO at 110°C , while K-OMS-2 can catalyze the oxidation of HMF with nearly 100% selectivity. However, when $\text{Fe}_3\text{O}_4\text{-SBA-SO}_3\text{H}$ and K-OMS-2 were added together into the reaction system at the initial stage, the DFF yield became quite low due to the formation of humins or the unwanted oxidation of fructose by K-OMS-2[147]. Further study showed that K-OMS-2 did promote the decomposition of fructose to unknown compounds. Therefore, a one-pot but two-step reaction was conducted by stepwise addition of catalysts to overcome this problem. Similarly, a combination of HT, Amberlyst-15, and Ru/HT was found to be active for the production of DFF from fructose and glucose via base-catalyzed isomerization, acid-catalyzed dehydration and selective oxidation in a one-pot reaction[148]. The reaction was carried out under atmospheric pressure of molecular oxygen, DFF yield of 13% and HMF yield of 44% were obtained starting from fructose. DFF yield raised from 13% to 34% by a one-pot two-step reaction, during which the reaction reacted under N_2 for 3h before bubbling oxygen into the system. Furthermore, one-pot synthesis of DFF from glucose in the presence of Amberlyst-15, HT and Ru/HT was investigated. DFF yield of 25% was obtained by a two-step but one-pot reaction without separation of catalysts. While this value was only 8% by a one-step synthesis method due to the decomposition of

glucose. For the above examples, DFF was produced through a one-pot but two-step reaction. Typically, the reaction was catalyzed by only acid catalyst first to convert fructose to HMF as much as possible, then the oxidative catalysts were added into the reaction system for the further oxidation of HMF generated from fructose to DFF. Another process is that acid catalysts and the oxidative catalysts were added together at the initial stage of the reaction, but the oxidant wasn't fed in until the fructose was totally dehydrated to HMF, inert gas was usually purged during the dehydration process to prevent the oxidation degradation of fructose. Recently, composite catalysts bearing both acid sites and oxidative sites were developed and applied for the one-step approach to DFF from fructose. As a solid acid, graphitic carbon nitride showed good performance in the dehydration of fructose to HMF, and vanadium-doped graphitic carbon nitride can act as the oxidative catalyst for the aerobic oxidation of HMF to DFF. Thus the combination of protonated graphitic carbon nitride and vanadium-doped graphitic carbon nitride can be applied in a one-pot and two-step synthesis method for the transformation of fructose to DFF. Since the acid sites and oxidative sites were supported on the same carrier, Jinzhu Chen et al. prepared a bifunctional catalyst made of protonated vanadium-doped graphitic carbon nitride and applied in the one-step approach to DFF from fructose, leading to a DFF yield of 45% [149]. Most recently, keggins-type heteropolyacids were found to be active in acid and oxidation catalysis for the transformation of hydrocarbons, hydrogenation of cellulose and hydrodeoxygenation of lignin-derived monomers [150-152]. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{FePW}_{12}\text{O}_{40}$ have been applied in the dehydration of fructose and degradation of cellulose [111]. They are well known for the well-defined structure, strong Bronsted acidity, fast multi-electron transfer, high proton mobility and resistance to hydrolytic and oxidative degradations in solution. Hu et al. synthesized several Keggin-type heteropoly acids such as $\text{H}_4\text{PMo}_{11}\text{V}_1\text{O}_{40}$, $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$, $\text{H}_4\text{PW}_{11}\text{V}_1\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and

$\text{H}_5\text{SiMo}_{11}\text{V}_1\text{O}_{40}$ and studied their catalytic performance for the conversion of fructose to DFF[153]. Effects of the amount of catalyst, the redox potential and acidity were investigated and results showed that higher Bronsted acidity of heteropoly acids lead to higher yield of HMF from fructose and higher redox potential favors the oxidation of HMF to DFF. Under optimized conditions, DFF yield of 60.3% can be obtained at 160°C in 2h in the presence of PMo_{12} HPA.. Considering the reusability of catalysts, homogeneous PMo_{12} HPA was converted to heterogonous catalyst by partial substitution of H^+ for Cs^+ . A series of $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}$ catalysts were prepared and used in the one-step transformation of fructose to DFF. An impressive DFF yield of 69.3% was attained over $\text{Cs}_{0.5}\text{H}_{2.5}\text{PMo}_{12}$ under optimized reaction conditions. Analogously, a series of acidic cesium salts of molybdovanadophosphoric heteropolyacids were developed by Chen et al[154]. as bifunctional catalysts for one-step approach to DFF from fructose with molecular oxygen as the oxidant under mild and environmental friendly conditions. The acid density and vanadium content are the two key factors influencing the catalytic performance. A maximum yield of 60% from fructose was achieved with $\text{Cs}_3\text{HPMo}_{11}\text{VO}_{40}$ as a catalyst under atmospheric pressure of oxygen. Moreover, the heterogeneous $\text{Cs}_3\text{HPMo}_{11}\text{VO}_{40}$ showed very good reusability during the recycling test. K-10 clay-Mo, a heterogeneous catalyst was successfully prepared by immobilization of bis(acetylacetonato) dioxo-molybdenum on montmorillonite K-10 clay[155]. In addition, a magnetic bifunctional $\text{WO}_3\text{HO-VO-SiO}_2@\text{Fe}_3\text{O}_4$ nanocatalyst was prepared by using chlorosilylated $\text{SiO}_2@\text{Fe}_3\text{O}_4$ nanoparticles as the platform for the acidic and oxidative function groups[156]. The catalyst showed good performance in the fructose dehydration reaction with 82% HMF yield in 1h, and upon co-oxidant H_2O_2 DFF yield of 71% was achieved addition after 15h under ambient air. It can be inferred that metal oxides represented by vanadium oxide and molybdenum oxide usually act as the oxidative sites to work along with the

acid sites in order to make the catalysts active both for the dehydration of fructose and the oxidation of HMF to DFF. Most recently, graphene oxide served as a bifunctional and metal-free catalyst was applied in the direct synthesis of DFF from fructose[157]. Under optimized conditions, 93.3% yield of HMF from fructose dehydration was obtained and 90% yield of DFF was achieved from aerobic oxidation of HMF. Besides, the GO can catalyze the one-pot and one-step transformation of fructose to DFF in a yield of 53%, and this value can increase to 72.5% when the reaction was conducted in two-steps, that is, to use nitrogen as the protection gas during the dehydration of fructose to HMF to prevent the oxidative degradation of fructose, and oxygen was fed in after the fructose has been converted to HMF.

2.3 Synthesis and applications of carbon-based acid catalysts

With efficient activity, high selectivity, long catalytic life and easy in separation and reuse, heterogeneous acid catalysts have attracted much attention for its potential in efficiently transforming biomass materials to value added chemicals[158]. There are five groups of solid acid catalysts which has long been used in the process of utilization of biomass materials. They are H-form zeolites, transition-metal oxides, cation-exchange resins, supported solid acids and heteropoly compounds[159].

Being non-toxic and no-corrosive, various zeolites are used in the transformation of biomass as good reusable catalysts[160, 161]. The acid sites are usually the active sites for the catalytic process, thus the acid density is a key factor for the performance of the catalysts[162]. The ratio of Al/Si influences the Bronsted acid sites significantly for H-form zeolites[163]. Modified H-zeolites showed good stability, which can keep the framework at temperatures up to 127°C[161]. Moreover, the physical properties such as hydrophilic or hydrophobic surfaces of a zeolite can be adjusted without influence of the functionalized acid sites.

Metal oxide can have both Lewis acid sites and anions with Bronsted base sites on its surface[164]. Transition-metal oxides such as Nb₂O₅, WO₃, Zr-TMS, TiO₂ and Ta₂O₅-WO₃ are usually used as solid acid catalysts for biomass hydrolysis[165-168]. They are easy to reuse and have good stability during the reactions and can be classified into two types: single metal oxides and mix metal oxides. High surface area, adjustable pore size and good thermal stability are usually the special structure of mesoporous metal oxides which showed high catalytic efficiency[169-173].

Cation-exchange resins are widely used in esterification, alkylation, hydration, dehydration and condensation reactions as solid acids[174-178]. Acidic resins were used in the hydrolysis of cellulose since 1960[179]. Since then, cation-exchange resins such as NKC-9, Amberlyst-15 and Nafion NR50 are developed and applied in cellulose hydrolysis to glucose and showed considerable activity[180, 181]. Cation-exchange resins have many favorable properties and of these properties, most notably is the unique merit that inhibitors in the hydrolyzates can be removed by the resins themselves[182].

Having strong Bronsted acidity, stability and high proton mobility, heteropolyacids are used as environmentally benign and economical solid catalysts in homogeneous, biphasic and heterogeneous systems. Keggin heteropoly anion is the first characterized heteropoly acid. Heteropolyacids are soluble in water and their acidic strength is comparable with sulfuric acid. Moreover, they can be heterogenized through ion-exchange of H⁺ with Cs⁺ to form insoluble acidic cesium salts, Cs_xH_{3-x}PW₁₂O₄₀ [183, 184]. Other ions such as V⁵⁺, Co²⁺ and Zn²⁺ can substitute the metal ions of the heteropoly acids during the synthesis process[185]. In addition, heteropoly acids can be loaded onto functional carriers like amorphous silica, molecular sieve MCM-41 and activated-carbon. The supported heteropoly acids can keep the activity and have better stability in liquid-phase reaction systems[186-193].

Compared with zeolites and transition-metal oxides, supported solid acid catalysts are promising for the utilization of biomass materials due to the substantial surface acidic species[194-196]. Supported metal oxide solid acid and supported carbonaceous solid acid are the two main types of supported solid acids. Typically, supported metal oxide solid acid catalysts are prepared by impregnating the hydroxide from ammonia precipitation of corresponding metal salt solution with sulfuric acid solution followed by calcination[197, 198]. The advantages of this kind of catalysts are their excellent thermal and mechanical stability, high surface area and large pore size. The disadvantage is that leaching of the acidic sites exist under hydrolytic conditions[199].

Among the various types of solid acid catalysts, carbon based catalysts attracted the most attention, because researchers are trying to prepare catalysts from renewable sources such as biomass material in order to make the chemical production process fully environmentally friendly and green. Compared with other materials, carbon material is considered as a very promising material due to its excellent properties such as low material cost, high surface area and good thermal stability[200]. They are good support materials and can be functionalized with acids or bases on the carbon surface. generally, there are two methods to prepare carbon-based acid catalysts, one is direct sulfonation of carbon material, the other is sulfonation of carbon material via reductive alkylation/acylation[180, 201, 202]. Carbon materials such as sugars, polycyclic aromatic compounds, polystyrene resins, activated carbon, biochar and lignin can act as the carbon sources during the sulfonation process[203]. Sulfonation agent, sulfonation time and carbon precursors are the main factors which influence the physical and chemical properties of the carbon-based acid catalysts. Various low polycyclic aromatic hydrocarbons such as naphthalene, anthracene were used as raw materials and directly applied in the incomplete sulfuric acid carbonization to prepare carbon-based solid acid, which showed high activities in esterification,

hydrolysis reactions[204, 205]. But the sulfuric groups on the carbon supports is not stable, resulting in leaching of functional groups during the reaction at somewhat high temperature. It is of great significance to prepare carbon-based solid acid with biomass materials as starting materials to reduce the cost. Pyrolysis, gasification, flash carbonization and hydrothermal carbonization are the most commonly used methods for the carbonization of biomass or biomass derived materials[204].

In a typical direct sulfonation process, carbohydrates such as glucose, fructose, sucrose, and cellulose are heated under nitrogen to produce a brown-black solid. Then the solid was sulfonated by concentrated sulfuric acid or fuming sulfuric acid at 150°C. The carbon-based solid acid is collected after washing repeatedly with hot distilled water until no impurities such as sulfate ions were detected in the wash water[201]. Lower pyrolysis temperatures with longer time were found to be more suitable for the thermal carbonization of biomass materials to produce carbon materials which were more prone to be sulfonated to a high degree. For the hydrothermal carbonization method, the needed reaction temperature is much lower than pyrolysis, and the produced biochar has more surface oxygen containing groups.

Concentrated and fuming sulfuric acid are usually used as the sulfonation agents, and the latter is favorable for the synthesis of carbon-based solid acid with higher acid density and higher catalytic activity. For example, sulfonated-active carbon catalysts were tested in the esterification of higher fatty acids in ethanol-oleic acid mixture and ethanol-stearic acid mixture and the results showed that sulfonated-active carbon prepared with fuming sulfuric acid showed higher acid density and better catalytic performance. However, considering the safety and operation problems brought by fuming sulfuric acid, the application of concentrated sulfuric acid is more advocated. But when carbon nanotubes, graphene, and ordered mesoporous carbon are used as the carbon supports, it is

difficult to sulfonate these materials by concentrated or fuming sulfuric acid. Special sulfonating agents such as 4-benzenediazoniumsulfonate, p-styrenesulfonic acid and Chlorosulfuric acid are used for the sulfonation of these “rigid” carbon materials[206-212]. The advantage of using these sulfonating agents is that the sulfonation temperature is very low, which can help maintain the original structure of the carbon materials. Recently, p-toluenesulfonic acid and hydroxyethylsulfonic acid were also used in the sulfonation process. However, they can only be used with some special carbon materials which are mainly hydroxyl compounds and aldehydes so that they can polymerized together to form carbon-based acid in hydrothermal conditions[213-215]. For instance, glucose/resorcinol/TsOH mixtures are used as raw materials and polymerized to monolithic carbons with sulfonic groups. Moreover, glucose/ceric acid/hydroxyethylsulfonic acid mixtures can be used to prepare carbon-based solid acid through hydrothermal method. The effect of carbon precursor on the activity of such catalysts was studied by using different carbohydrates such as glucose, fructose, cellulose, sucrose and starch, and results showed that starch was the best starting material for the hydrothermal preparation of carbon-based solid acid due to high acid density, large surface area, pore volume and pore size[216, 217].

Carbon-based solid acid catalysts with special polymeric structure can be prepared by using resin as the carbon source[218-220]. Phenolic resin was used as raw material to synthesize carbon-based solid acid through two steps: carbonization and sulfonation[221]. The final products owed higher recyclability and higher $-\text{SO}_3\text{H}$ than the carbon-based solid acid prepared from traditional nafion resin. Similarly, mesoporous carbon-based solid acid can be prepared from resorcinol-formaldehyde resin and showed excellent catalytic performance for the selective dimerization of α -methylstyrene. In addition, polyvinyl chloride

was as used to prepare carbon-based solid acid which performed better on the diffusion of reactants[222].

Carbon-based solid acid catalyst bearing $\text{-SO}_3\text{H}$, -COOH , and -OH function groups, were efficient catalysts for the hydrolysis of cellulose[222-228]. The catalytic effect depends greatly on the ability of adsorbing β -1,4 glucan, the large effective area in water and acid groups tolerable to hydration[222]. A remarkable glucose yield of 40% with a high selectivity of 90% was obtained for the cellulose hydrolysis reaction in the presence of carbon-based solid acid[225]. Moreover, the carbon-based solid acid catalysts were found to be active for hydrolysis of hemicellulose to xylose and glucose, the dehydration from xylose to furfural and dehydration of fructose to furfural and HMF, which are important reactions in the utilization of biomass resources[229-232]. Carbon-based solid acid catalysts can be used in the production of biodiesel. It was found that the carbon-based solid acid with higher surface area and higher acid density usually showed better reaction performance[233]. Glycerol etherification with isobutylene can also be catalyzed by carbon-based solid acid catalysts with high selectivity[234]. Vegetable oil asphalt and s-MWCNTs were used as carbon precursors to prepare carbon-based solid acid catalysts. Though the asphalt-based catalyst had a lower surface of $7.48\text{m}^2/\text{g}$ compared to the higher surface area of $43.9\text{m}^2/\text{g}$ of s-MWCNTs-based solid acid, it showed higher activity for the production of biodiesel because of its high acid site density and large pores presented in the structure which allowed the diffusion of reactant easily into the internal acid groups[235, 236]. This result is consistent with the work presented by Lou et al. in which the catalytic activity of as-synthesized catalysts was primarily affected by acid sites densities but not the surface area[237]. De-oiled canola meal was used as carbon precursor by Similarly Rao et al. to prepare carbon-based solid acids in four different ways: direct sulfuric acid sulfonation, partial carbonization of de-oiled canola metal at 400°C followed by sulfuric acid

treatment, partial carbonization of de-oiled canola metal at 400°C followed by steam activation and sulfuric acid sulfonation and partial carbonation of de-oiled canola metal at 300°C followed by sulfuric acid treatment. Results showed that the acid densities were greatly affected by the carbonation temperature. The acid sites density of the carbon-based solid catalysts prepared by direct sulfonation of de-oiled canola metal was the lowest compared with the other catalysts[238]. This is probably because of that the direct sulfonation destroyed the main components such as carbohydrates and proteins of de-oiled canola metal, while the formation of functional groups such as hydroxyl and aromatic structures during the carbonation process can react with sulfuric acid to form $\text{--SO}^3\text{H}$ groups. The catalyst prepared by sulfonating de-oiled canola metal carbonized at 300°C showed the best activity for the production of biodiesel due to the highest acid sites density and largest pores. The partial carbonization of de-oiled canola metal at 300°C retained more functional groups which can react with sulfuric acid to produce more acidic functionalities on the surface. Under optimization conditions, the maximum conversion up to 93.8% of waste oil was obtained in the presence of such catalysts.

Carbon-based solid acid catalysts were also used in Michael-type Friedel-Crafts reactions of indoles with α,β -unsaturated carbonyl compounds in water[239]. 85-96% yield of isolated product without by-products was achieved by using of 5% carbon-based solid acid in the reaction of indole and its derivatives with methyl vinyl ketone at ambient temperature. In the presence of carbon nanotube-based solid acid catalyst, 2-tert-butylhydroquinone, a widely used antioxidant, can be prepared by alkylation of hydroquinone with tert-butanol in a yield of 53.7% and conversion of 73.3%[240].

Carbon-based solid acid shows its advantages such as shorter reaction times, higher yield and simple workup over the aldol condensation reaction which is an important carbon-carbon bond-forming process in organic synthesis. Moreover,

carbon-based solid acid catalysts showed higher catalytic activity than the traditional solid acid catalysts such as zeolite and Amberlyst-15 in the oxathioketalization reaction[215, 241, 242]. Carbon-based solid acid catalysts prepared from C/Si composite showed high catalytic ability in the dimerization of methylstyrene[233, 243].

Carbon-based solid acid can also be applied in some applications such as the separation of special compounds, oxidation and electrochemical reactions. Sulfonated carbon-nanotube was used as an effective electrochemical catalyst for the oxidation of ethanol and ethylene glycol in alkaline medium[244, 245]. Carbon-based solid acid catalysts showed remarkable catalytic performance for the tetrahydropyranylation of alcohols and phenols in dichloromethane[246]. Moreover, the production of corresponding alcohols from 3,4-Dihydro-2H-pyran ethers can also be catalyzed by carbon-based solid acid in the presence of methanol.

2.4 Synthesis and applications of carbon-supported metal catalysts

Carbon materials such as active carbon, graphite, carbon black, carbon nanofibers/nanotubes and so on are widely used as supports to load the active sites i.e. metal, metal oxide and metal sulfide to stabilize the active phase and prepare carbon-supported metal catalyst. Because of the low cost and mass availability, active carbon and carbon black with high surface area are the most common carbon materials to be used for the preparation of carbon-supported catalysts. Prepared by pyrolysis of carbon precursor such as organic polymers and hydrocarbon at high temperature, carbon black is an amorphous carbon which is composed with roughly planar layers of sp² hybridized carbons[247]. Active carbon is also amorphous carbon with large surface area and pore volume, preparing by high temperature pyrolysis of carbon materials followed by physical or chemical activation. Along with the development and progress of carbon science and technology, people has synthesized various carbon materials such as

carbon nanoparticles, carbon nanotubes, graphene and mesoporous carbons. Carbon nanoparticles are usually prepared by the hydrothermal carbonization of biomass[248]. Carbon nanotubes and multiwall carbon nanotubes are the typical one-dimensional carbon materials, serving as ideal and unique templates for immobilization of metallic nanoparticles[249]. As a two-dimensional carbon material, graphene has remarkable surface area and unique physicochemical properties. It can be functionalized with metallic nanoparticles, polymers, doped with nitrogen and conjugated with various kinds of functional groups[250-256]. Three-dimensional carbon porous materials are usually prepared through template methods or sol-gel polycondensation of organic monomers[257-259].

Carbon materials are popular choice as support materials due to their remarkable physical and chemical properties such as mechanical strength, pore distribution, chemical and thermal stability. Wet-impregnation, incipient-wetness impregnation and ion adsorption are the most common methods to prepare carbon-supported metal catalysts. carbon support materials are put into large amount of the metal precursors solution, then the solvent was removed by evaporation, the final carbon supported metal catalysts are collected after optional calcination and reduction. During the evaporation process, the metal precursor in the solution out of the pores of the carbon support will deposit on the outer surface of the support, forming large particles. To overcome this disadvantages, incipient-wetness impregnation method was developed by using just enough amount of metal precursor solution to fill the pores of the carbon support to prevent the depositing of the metal precursor on the outer surface of the support. If the metal precursor ions can be adsorbed on the surface of the carbon support, the support material can be filtered out and dried, calcined and reduced to produce carbon-supported metal catalyst. This method can be called ion adsorption. The coulombic interaction between the support and the metal precursors is the factor which influences the distribution of the precursor over the

support. Generally, the negatively charged surface absorbs positively charged precursors and the positively charged surface attracts negatively charged precursors. Thus the surface properties of the carbon support play an important role in the formation of the carbon-supported metal catalysts[260]. During the preparation of carbon-supported Pt catalyst reported by Prado-Burguete, when heat-treated carbon black was used as the support, the Pt particle size was 5.1nm, this size can decrease to 2.4nm when the carbon black was treated with H_2O_2 to introduce oxygen groups and then used as the support[261].

The same phenomenon occurred when active carbon and carbon black were used to prepare carbon-supported Pd catalyst[262]. Results showed that the metal dispersion decrease with increasing content of surface oxygen groups. Zhu et al also reported the similar findings. 5.7 nm Ru particles were formed from RuCl_3 using untreated active carbon, while 51 nm particles could be obtained under the same synthesis conditions by using heat-treated active carbon as the support[263, 264]. What's more, reoxidation of the heat-treated carbon material resulted under the same synthesis conditions in 3.8nm particles. Furthermore, when the heated-treated carbon material was subsequently treated in CO_2 followed by nitric acid and then used as support, the smallest particles with size of 2.2nm were obtained. The size difference of the particles can be explained by the changes of the surface groups that the CO_2 treatment improved the mesoporous structure and the nitric acid treatment reduced the ash content which is beneficial for dispersion. Generally, the exist of oxygen groups on the surface of the carbon supports is conducive to the formation of small particles. But sometimes the results seem do not follow this principle completely, one of the reasons is that the amount of the oxygen groups such as carboxylic acid groups, might change during the impregnation procedure[265]. A typical example is that under a certain pH value, the carboxylic anhydride groups which can't absorb metal ions can hydrolyze to carboxylic groups which is available for adsorption. Gurrah et al., Van Dam and

Van Bakkum and Sepulveda-Escribano et al. further studied the adsorption of the metal precursors and the oxygen containing groups on the carbon supports and found that high dispersion was formed during the decomposition step but agglomeration occurred due to the decomposition of oxygen groups under high-temperature treatment[266-268]. It was reported by Fraga et al. that increasing amount of oxygen groups on the support could lead to higher metal loading[269]. This is because that water is the most commonly used solvent, the oxygen functionalities can enhance the wettability of the carbon support. In addition, the exist of other ions in the solution also affect the loading amount of the metal precursors[270, 271].

Another factor which influences the dispersion of the active phase is the pore structure of the carbon support. Two activated carbons with similar oxygen amount and pKa but different pore volumes are used as carbon supports to prepare carbon support Pt catalysts, resulting in 1 wt% loading amount with a dispersion of 35% on the high-pore-volume support and 0.7 wt% metal loading and a dispersion of 20 irrespective of the precursor[272]. Samant et al. claimed that Pt particles of 1-2 nm were successfully loaded on a highly mesoporous carbon with a surface area of 534 m²/g[273]. similarly, Ru particles of 2.2 nm were obtained using high-temperature CO₂ treated and HNO₃ oxidized mesoporous carbon as the support[273]. These work demonstrated that the high mesoporous area was a key factor to prepare highly dispersed and highly loaded carbon-supported metal catalyst.

Despite drying and adsorption, the deposition of metal precursors from the solution onto supports can also be done by chemical reactions, which is called deposition precipitation. Through increase of pH, change of valence of the metal ion and removal of a stabilizing ligand of the metal ion, the metal precursors can be deposited on the carbon support. Deposition precipitation method has been widely used to prepare carbon-supported metal catalyst due to its advantages such

as reproducibility, high metal dispersions at high metal loadings. The strong interaction between the metal hydroxide and the support is essential for the metal precursors to decompose on the surface of the support rather than in the bulk liquid phase[274, 275].

For most solution of metal precursors, the deposition starts when the pH of the solution increase to a certain value. Urea is widely used for the decomposition of metal hydroxide on the carbon support, in which the reactant was added at low temperature and the hydrolysis of urea takes place uniformly. It was claimed by Van Der Lee et al. that the carboxylic acid groups on the carbon support surface are the important nucleation sites for the deposition of nickel hydroxide[276]. Moreover, the change of metal valence can also promote the precipitation. The metal decomposition process can be controlled by the concentrations, temperature, and the support.[277-280] What is interesting is that bimetallic catalysts can be prepared using this reduction deposition precipitation method through the catalyzed redox reaction of the first metal to the second metal[281]. In some cases, carbon support can act as a reducing agent to reduce the metal precursors in the salt solution and facilitate the decomposition without external reductant[282, 283]. Highly oriented pyrolytic graphite can be used to reduce Pt and result in carbon-supported Pt catalyst. In addition, removal of the ligands such as ammonia and EDTA which are widely used to stabilize transition metal ions in water via evaporation or oxidation can trigger the deposition of metal precursors onto the carbon support[284, 285]. Bezemer et al. prepared highly loaded and highly dispersed Co/CNF through deposition of cobalt onto alumina starting from a cobalt amine complex by removing the ammonia slowly from the solution[286].

In order to further increase the loading amount of metal, researchers have developed some new methods. Different reductants were applied in the synthesis process and showed different effect on the control of the dispersions. For example, when formaldehyde was used to reduce Pt for the preparation of Pt/CNT, the

produced Pt particles have a size of 3.4nm with 10% loading amount, while when Pt was reduced using ethylene glycol, the resulted Pt particles had a size of 2.6nm with the same loading amount[287]. It was also found that the particle size increased with the increasing of the water amount in the solution. Chen et al. synthesized 20 wt% of spherical Pt particles by performing the drying step by microwave heating[288]. Yang et al. claimed that ultrasonic treatment can help in preparation of Pt-Ru particles with high level of metal dispersion on carbon black[289].

Carbon-supported catalysts are widely used in the catalytic transformation of biomass materials to value added chemicals. Carbon-supported Ru catalyst was applied in the hydrolysis of cellulose to glucose and hydrogenates glucose to sugar alcohols[290]. Tungsten carbide nanopowder supported on a three-dimensional mesoporous carbon enhances the ethylene glycol yield to 72.9% through direct conversion of cellulose[291]. Similarly, 80% yield of hexitol was obtained in the presence of a sea-urchin-like three-dimensional mesoporous carbon for the hydrolytic hydrogenation of cellulose[291]. Furfural yield of 67-69% and xylose conversion of 95-97% were obtained by graphene oxide or carbon black supported titanium dioxide nanoparticles catalyzing aqueous phase dehydration of xylose into furfural at 170°C[292]. Pt/RGO prepared by microwave-assisted reduction method was employed on the conversion of cellulose to sorbitol, resulting in sorbitol yield up to 58.9%[293]. Pt/C, Ru/C and Raney Ni catalysts were used in the hydrogenation of xylose to xylitol, among which Pt nanoparticles supported on MWCNTs showed higher activity than the other commercial catalysts with 100% xylose conversion and 99.3% selectivity to xylitol[294, 295]. Ru/C are used for the conversion of glucose to sugar alcohols by a two-step hydrolysis and hydrogenation reaction[290]. Carbohydrates can be converted to unsaturated compounds through hydrodeoxygenation in the presence of carbon-supported metal catalysts. Mo_2C is

an active catalyst for the hydrodeoxygenation of vegetable oil[296-299]. Tungsten carbide can catalyze the hydrodeoxygenation of propanal and propanol to propene[300]. Results showed that smaller particle size of the tungsten carbide favors the improvement of the reaction activity. Hydrodeoxygenation reactions catalyzed by carbon-supported metal are also needed in the upgradation of bio-oils which are derived from the pyrolysis of woody biomass. As a by-product of biodiesel production, glycerol can be transformed to value-added chemicals in the presences of carbon-supported catalysts such as Ru and Pt particles on activated carbon. Ru/C is more active than Pt/C at neutral pH for the conversion of glycerol to glycols, while Pt/C is more suitable for the formation of propylene glycol. Carbon-supported metal catalysts can also be used in the production of lactic acid which is usually produced through the biosynthesis by bacteria with glucose and sucrose as the substrates. Cu-graphene catalysts are applied in the conversion of glycerol, xylitol and sorbitol to lactic acid and showed good catalytic activity. Ru/C was found to be the most active catalyst for the hydrogenolysis of biomass-reived xylitol to ethylene glycol and propylene glycol[301]. Pt/C and Ni/C are also used in the aqueous phase reformation of xylitol[302, 303]. Carbon-supported noble metal catalysts are widely used in the selective oxidation of HMF which is an important intermediate in the utilization of carbohydrates[304-306].

2.5 Synthesis and applications of carbon sphere catalysts

Carbon materials have been the active research fields for a long time. Many different shape carbon materials have been synthesized and attracted a great deal of attention because of their excellent physical and chemical properties. The shaped carbon materials include tubes, fibers, spheres, horns, calabashes and flasks etc.[307-315]. In this chapter we mainly focus on the carbon materials with spherical shape. Carbon balls, carbon spheres, carbon onions and mesoporous microbeads are the names given to this type of spherically shaped carbon.

Carbon spheres are known to have a wide range of diameters from several nanometers to many micrometers. This will hold for the surface areas of the carbon spheres. The surface areas of carbon spheres vary from less than $1\text{m}^2/\text{g}$ to around $1000\text{m}^2/\text{g}$ [316]. The carbon chains/layers/flakes staggerly weaved together to form the carbon sphere with different chemical and physical properties. Moreover, hollow carbon spheres can be synthesized by various strategies. The most common method is the templating process which coat the carbon materials on spherical template material such as metal complex, silica sphere followed by the removal of the core[317, 318].

According to the reaction temperature, the synthesis methods of carbon spheres can be divided into two types. The first one is based on the decomposition of carbon containing materials under high temperature in inert atmosphere. The second method usually consist of low temperature pyrolysis and catalytic decomposition of organic compounds by heat treatment of polymers or other materials in autoclaves. The synthesis conditions such as carbon sources, oxygen, catalysts, temperature and pressure influence the properties of the prepared carbon spheres significantly.

Arc-discharge process which was used to prepare carbon nanotube can also produce carbon spheres. He et al claimed the synthesis of carbon spheres though DC arc-discharge method by using acetylene and coke powder as carbon source[319]. Polyethylene terephthalate resin was used for the synthesis of carbon spheres at 1100°C through non-classical arc-discharge method[320]. Thermal plasma treatment is another method which can be used for the synthesis of both carbon tubes and carbon spheres. During the process, the carbon precursor was vaporized in the high temperature reactor and then carbon particles formed after the condense of the vaporized carbon precursors[321]. Hollow carbon spheres were synthesized by Yang et al. using methane/hydrogen as the carbon source and silica supported MgO and Ni nanoparticles as the catalyst

through radio frequency plasma enhanced CVD[322]. Carbon spheres were also reported to be produced by use of a high pressure shock compression technique. Chemical vapor deposition which is an important method for the synthesis of shaped carbon materials, is a process in which carbon materials are developed from volatile carbon precursors. Toluene was reported by Qian et al. can be used to prepare carbon spheres. During the process, toluene was first vaporized at 200°C in the first furnace, then the vapors decomposed over the template at 1100°C[323]. Similarly, acetylene/toluene was used as the carbon precursors for the preparation of carbon spheres at 1000°C[324]. Other carbon substrate such as styrene, benzene, hexane, cyclohexane and ethane are also used in the large scale production of carbon spheres by a double furnace[325]. The feedstock was vaporized in the low temperature furnace at 250°C and then introduced to the high temperature reactor at range of 900-1200°C. The size of the synthesized carbon spheres is affected by the feed rate, temperature and reaction time. Not only carbon source contains only carbon and hydrogen can be used for the synthesis of carbon spheres, corn starch, tetrahydrofuran etc. which contain other elements such as oxygen can also be used to produce good quality of carbon spheres[326-328]. The above described procedures are non-catalytic CVD synthesis methods. In fact, metal catalysts are widely used in the production of shaped carbon materials such as carbon nanotube and graphene. These catalysts are also applicable for the synthesis of carbon spheres, acting as a template providing the nucleation sites for the formation of hollow sphere. By using toluene as the carbon source and ZnSe nanoparticles as the template, hollow carbon spheres were produced with diameters of 40-120nm at 1200°C after 60min[329]. Similar procedures were applied for the synthesis of nitrogen doped carbon spheres using fumed silica as hard template and melamine-formaldehyde resin as carbon precursor[330]. Moreover, using silica spheres as template, smooth single shell, deformed single shell and double shell carbon spheres can be

produced[331]. Large scale synthesis of carbon spheres was reported by Miao et al. using Kaolin supported transition metal salts as catalysts[332, 333]. Monodisperse 150nm carbon spheres with a foam-like macroscopic structure were synthesized by CVD methods in which acetylene was used as the carbon source and nickel metal clusters acted as catalyst. Hollow carbon nanospheres were synthesized from CH₄ using a sol-gel procedure in the presence of Ni/Al₂O₃ in which the Ni is supposed to act as catalyst/template for the growth of the carbon spheres[334]. For the catalytic chemical vapor deposition method, the separation of the encapsulated catalyst and the carbon spheres is a problem need to consider[335]. Thus mixed valence oxide catalysts were used for the synthesis of carbon sphere in the hope that this would make the separation process easier. Wang and Kang prepared various carbon microspheres using CH₄ as carbon source and transition or rare earth metal oxides with mixed valences as catalysts at 1100°C[336].

The carbon sphere synthesis method described above are all carried out at very high temperature which is energy intensive and procedures insecure. In order to overcome these disadvantages, autoclave methodologies were developed to synthesize carbon spheres under mild temperature condition. Pressure build up in the enclosed environment during the reaction process and the final reaction products will be affected by this pressure. A range of common organic reagents were used for the synthesis of carbon spheres in autoclaves[337, 338]. A perfect spherical morphology of non-graphitic carbon was produced by using mesitylene as carbon source[337]. The polymer polyethylene terephthalate has also been used as carbon source to prepare carbon spheres in a stainless steel reactor at 700°C[339]. Further studies on the synthesis of carbon spheres in water using carbohydrates as carbon source greatly reduced the reaction temperature to around 160-200°C[340]. Hollow carbon spheres can be generated by the combination of hydrothermal carbonization of glucose, polystyrene and P123 and

microwave treatment of the carbonization products[341]. Silica particles can be used as template during the hydrothermal carbonization of sucrose followed by calcination and HF etching to produce hollow carbon spheres. High quality and uniform size carbon spheres were reported to be synthesized at 65°C in the presence of CaC_2 and oxalic acid[342]. In fact, catalysts and reducing agents are also widely used for the preparation of carbon spheres in an autoclave. 30-580nm both filled and hollow carbon spheres were synthesized by the catalytic pyrolysis of C_2Cl_4 in the presence of ferrocene[343]. Similar procedures were carried out by Jia et al. to prepare hollow carbon spheres using ferrocene and ammonium chloride as starting material in argon atmosphere at 700°C[344]. Neckless-like hollow carbon spheres with size of 50-100nm were synthesized from hexachlorocyclopentadiene and ferrocene at 500°C in a stainless steel autoclave under an argon atmosphere[345]. Adding NaCl into the reaction during the carbonization of hexachlorobenzene can facilitate the formation of hollow carbon spheres because NaCl can act as a template for the synthesis of core-shell structure[346]. 400-600nm hollow carbon spheres were synthesized from CCl_4 in the presence of NaNH_2 with Co/Ni alloy as the catalyst[347]. Mg powder and Na_2CO_3 can also be used as catalysts for the carbonization of CCl_4 to make hollow carbon spheres[348]. Acetone was used to synthesize uniform carbon microspheres in a titanium alloy autoclave by a substrate assisted route in the presence of Ni foil[349, 350]. Ni catalyst was also applied in the synthesis of coral-like accreted hollow carbon microspheres from cyclohexane[351]. Recently, various mixtures of ferrocene and anthracene were used as starting materials for the synthesis of carbon spheres in evacuated quartz tubes placed in a furnace[352].

Carbon spheres can be used as catalyst supports as most carbon materials. Carbon sphere-supported metal nanoparticles has been widely used in a number of different catalytic reactions. Carbon spheres embedded with iron oxide

particles showed good activity in the Fischer-Tropsch synthesis[353]. Magnetic Fe_3O_4 /carbon sphere/cobalt composites were synthesized and applied for the catalytic oxidation of phenol solutions with sulfate radicals[354]. Carbon spheres supported visible-light-driven CuO-BiVO_4 heterojunction was prepared by hydrothermal process and impregnation technique[355]. The catalyst is an excellent photocatalyst for the degradation of organic pollutants. Liu et al. claimed that carbon spheres supported Pd catalyst can be used for the removal of trace amount of ethylene in agribusiness environments[356].

Carbon spheres are also widely used in electrochemical cells and batteries. Small Pt particles supported on carbon spheres were used for the methanol oxidation in direct methanol fuel cells[357]. High surface area hollow carbon spheres loaded with Pd particles were used for ethanol oxidation in an electrochemical cell[341]. PtRu supported on hollow carbon spheres were made into an electrode in a proton exchange membrane fuel cell[358]. Recently, carbon spheres supported Ag particles was mixed with Nafion and supported on a glassy carbon electrode for the oxidation of hydrazine[359]. For these applications, the well separated and stable metal particles which provide easy access for the reactant to contact with the active sites is the foundation of the successful electrochemical activity.

Chapter 3 Techniques of Characterization, Synthesis, and Catalytic Reactions

Many characterization technologies have been developing for the study of the chemical and physical properties of carbon materials. X-ray diffraction is used to study the composition and the molecular structure of a crystal. Raman spectroscopy is usually used to examine the extent of graphitization of the carbon materials. Fourier transform infrared spectroscopy can provide information on the surface groups of the carbon materials. Element analysis can help to study the elemental composition of the catalysts. X-ray absorption near edge structure is an important technology for the study of the phase, geometrical structures and electronical properties of the catalysts especially for the metal complexes. The structure of a certain compounds can be determined through the peaks of nuclear magnetic resonance spectra. Scanning electron microscope is widely used for the study of the morphologies of catalysts. Thermo gravimetric analyzer is used to study the weight change of the catalyst as temperature changes, it can also be used to determine the loading amount of metal on carbon supports. Brunauer-Emmett-Teller method is commonly used to study the surface area, pore size and pore volume of the catalysts. Through these characterization information, we can now better on the nature and arrangement of the building blocks of the catalysts, the morphologies and porosity, which is helpful for the further investigation on the catalytic mechanism and can provide necessary theory support for the catalysts design.

3.1 Characterization techniques

3.1.1 Characterization of catalyst morphologies

Field emission scanning electron microscopy (FESEM) is widely used for morphological studies which can also give the diameters, shape and chemical compositions of carbon spheres by providing topographical and elemental information at magnifications of 10x to 300,000x, with virtually unlimited depth

of field. Here, the morphology and structure of the catalysts were investigated using a field emission scanning electron microscope (FESEM, JOEL JSM 6701F). Before measurements, the samples were loaded on a sample holder with adhesive carbon double-sided tape and subsequently deposited with atomic Pt via sputtering.

3.1.2 Characterization of catalyst structures

X-ray diffraction (XRD) is a powerful tool for the determination of the crystallinity, inter-layer spacing, structural strain and impurities or supported-metal particles in carbon spheres[360]. It is a very effective and destructive technology which need little amount of sample for the measurement. For the amorphous carbon, there are usually two broad peaks at around 25° and 45° shown on the patterns, in which the width of the peaks gives information on carbon sphere crystallinity[361, 362]. XRD can also be used to study the supported metal nanoparticles. The average size of crystalline particles can be estimated based on the width at half maximum of specific peaks according to the Scherrer's equation[363]. Here, powder X-ray diffraction patterns were recorded on a Bruker Advance 8 X-ray diffractometer using a Ni filtered Cu K α radiation ($\lambda=0.154\text{nm}$), operated at 40 kV and 40 mA. XRD data were collected between 10 and 90° (2 θ) with a resolution of 0.02°.

Raman spectroscopy is an old but useful technology for the characterization of various carbon materials including carbon black, carbon nanotube, graphite, glassy carbon, coal and sputtered carbon. The Raman spectroscopy can reflect the size, strength and arrangement of chemical bonds. The most famous peaks for carbon materials are the so called D band which is around 1350cm⁻¹ and attributed to residual disorganized graphite, and G band which is around 1580-1600cm⁻¹ and assigned to graphite carbon[364-366]. The intensity ratio of D band and G band is a key factor to evaluate the proportion of graphitic and disordered carbon[367]. Here, Raman tests were carried out on a Renishaw 1000

Raman spectrometer equipped with a 514/633 nm excitation from HeNe laser, of which the detection depth is about 150 nm.

Physical adsorption of nitrogen is a typical technique to measure the surface area, pore size, pore volume and pore sized distribution of carbon materials from the adsorption and desorption isotherms[368, 369]. Here, the BET surface areas were measured on Autosorb-6B (Quantachrome instruments) using the liquid nitrogen adsorption method. Samples were degassed at 150°C over night before the measurement.

3.1.3 Characterization of catalyst active sites

FTIR spectroscopy has been used to study the chemical composition of carbon materials, especially for the determination of surface functional groups on the carbon supports. Usually, bands at 1630cm⁻¹ and 2850-2920cm⁻¹ are the two major sets of bands for carbon spheres, the former is attributed to C=C groups and the latter is assigned to C-H groups present on the surface of carbon spheres[370]. Other functional groups such as acidic groups, hydroxylic groups, carboxylic groups can also be detected by FTIR. Thus, FTIR can be used to study the changes of the groups on the surface of carbon spheres after the reactions. Also it can provide information on whether a certain function group is successfully grafted on the carbon sphere. In this thesis, one of the work is the dehydration of fructose to HMF by carbon-based solid acid. FTIR can provide evidence for the successful introduction of sulfuric acid groups[371]. Here, FTIR spectra were obtained on Digilab FTS 3100 FTIR with a 4 cm⁻¹ resolution in the range of 400-4000 cm⁻¹ using a standard KBr disk technique.

The V K-edge X-ray absorption near edge structure (XANES) is a very sensitive and powerful technique to study the metal oxide encapsulated in the carbon spheres[372]. When only a small amount of metal oxide was loaded on the carbon support with homogenous dispersion, it is difficult to see the signal of the metal oxide on the XRD patterns, and X-ray photoelectron spectroscopy is

not available due to the limitation of its depths of detection. This will be the time for XANES to show its advantages. It can determine the chemical state of elements which are present in bulk in minute quantities. Here, XANES spectra was recorded at XAFCA beamline of Singapore Synchrotron Light Source (SSLS).

3.1.4 Characterization of chemical properties of catalysts

As the same suggests Elemental Analysis is a technique for the determination of the mass fraction of carbon, hydrogen, nitrogen and sulfur of the tested samples, which can help to ascertain the structure and purity of a synthesized compound. In this thesis, carbon materials are prepared by different methods and after treated with different conditions. Element analysis was used to study the influence of various reaction conditions on the chemical composition of the synthesized carbon spheres as well as the stability of the functional groups and the carbon supports. Here, the element composition of the catalyst was estimated by Vario EL III CHNS Elemental Analyzer.

Thermo gravimetric analysis is a technique that has been widely used for the characterization of carbon spheres, in which changes in physical and chemical properties of materials are measured as a function of increasing temperature. These data provide basis for the further thermal treatment of the catalyst in order to modify the physicochemical properties of the carbon materials. Beside the study of the thermostability of the catalysts, TGA can also be used to determine the organic or inorganic content in the carbon sphere supported catalysts[373]. In this thesis, carbon sphere encapsulated metal oxide catalysts were synthesized and their TGA tests were run in air under high temperatures to remove the carbon support. Thus the remaining items will be the metal oxide. Here, the TGA test was conducted on an SDT Q600 instrument and alundum pans under air atmosphere.

Nuclear Magnetic Resonance (NMR) is a widely used and selective technique for the determination of the topology, dynamics and three-dimensional structure of molecules in solid or solution state. Carbon-13 NMR and proton NMR are the most commonly used NMR measurements. NMR can also be used for purity determination[374]. In this thesis, ^1H -NMR spectra was measured to analysis the separated product on a Bruker Avance II 300 MHz spectrometer with CDCl_3 as the solvent.

Temperature-programmed desorption (TPD) is a widely used method for the observation of desorbed molecules from the surface of the catalysts when the surface temperature is increasing. Small molecules or atoms always absorb onto the surface of the catalysts by forming a bond with the surface to minimized their energy. When the surface temperature increases, the energy transferred to the adsorbed molecules or atoms will cause them to desorb. Then the desorbed species can be identified and quantified by a mass spectrometer to give information on the surface attached functional groups. In addition, NH_3 can absorb on the surface of the samples as probe molecules under room temperature and desorb during the temperature programmed increasing. Generally, the adsorption force between NH_3 and acidity of the surface of the catalysts has a positive linear relation. High temperature is essential when the force of attraction is so strong that the adsorption cannot be reversed easily. Thus NH_3 -TPD can provide information on the acidity distribution of the catalysts[375]. Here, TPD was performed on a Micromeritics AutoChem II 2920 instrument. Typically, the pretreatment of the sample was conducted in a quartz reactor by high-purity Ar at $200\text{ }^\circ\text{C}$ for 2 h. Then after the temperature cooled down to $100\text{ }^\circ\text{C}$, it was set to rise to $1020\text{ }^\circ\text{C}$ at a rate of $5\text{ }^\circ\text{C}/\text{min}$. A mass spectrometer (ThermoStar GSD 301 T2) was used to detect the desorbed CO and CO_2 . The ammonia temperature-programmed desorption (NH_3 -TPD) was carried out on a Micromeritics Auto

Chem 2920 chemisorption analyzer equipped with a quadrupole mass spectrometer to study the acidity of the catalyst.

3.2 Synthesis methodologies

3.2.1 Materials

Concentrated nitric acid (69%, Sigma-Aldrich), alpha-D (+)-glucose (Sigma, 99.5%, anhydrous), chloric acid HCl (36-38 wt.%), potassium hydroxide KOH (90%, Sigma-Aldrich), sodium hydroxide NaOH (>98%, Sigma-Aldrich), toluene anhydrous (>99.8%, Sigma-Aldrich), ethanol (>99.5%, Sigma-Aldrich), oxalic acid (OXA, 98%), ethyl acetate (EA, >99.8%, Sigma-Aldrich), Fructose ($\geq 99\%$, Sigma-Aldrich), HMF (99%, Sigma-Aldrich), DFF(99, Sigma-Aldrich), HMFCa (99%, Sigma-Aldrich), FDA (99%, Sigma-Aldrich), sulfuric acid (98% purity), DMSO (99%, Sigma-Aldrich), phosphomolybdic acid (99%, Sigma-Aldrich), NH_4VO_3 (99%, Sigma-Aldrich). These commercial chemicals were used as received without further purification.

3.2.2 Preparation of sulfonated carbon sphere solid acid catalysts

The CS was prepared by hydrothermal carbonization of glucose. In the typical synthesis, 5 g of glucose was dissolved in 30 ml of deionized water to form a clear solution under stirring. The solution was then transferred into a 40 ml capacity teflon-lined autoclave and maintained at 180 °C for 10 h. The resulting solid products were filtered and washed with deionized water and ethyl alcohol, followed by vacuum drying for 4 h at 60 °C to afford CS.

The as-synthesized CS was dispersed in a sulfuric acid solution under stirring. The suspension was placed in a 40 ml teflon-sealed autoclave and maintained at 180 °C for 4 h. The black products were filtered, washed and then dried following the same procedures in CS preparation. Sulfuric acid solutions with different concentrations were employed in the sulfonation processes. The sulfonated CS solid acid catalysts were labeled as CS-1, CS-2, CS-3 and CS-4 according to the sulfuric acid and water volumetric ratios of 1:5, 1:2, 1:1 and 2:1, respectively.

For comparison purposes, sulfonated CS was also prepared in one-step following the procedures as reported by Liu et al[376]. Equal amounts of glucose dissolved in sulfuric acid solutions of different sulfuric acid and water ratios (1:5, 1:2, 1:1, 2:1); the solutions were placed in teflon-sealed autoclaves and heated at 180 °C for 4 h. The products were labeled as C-1, C-2, C-3 and C-4.

3.2.3 Preparation of V-embedded mesoporous carbon microspheres

The V-embedded mesoporous carbon microspheres were prepared by one step hydrothermal method of glucose and NH_4VO_3 solution followed by calcination. Typically, NH_4VO_3 and oxalic acid (molar ratio 1:2) were dissolved in 30 mL DI water and kept stirring to form dark green solution. Then 4g glucose was added into the solution and stirred for 3 h. Afterward, the solution was transferred to a Teflon-lined autoclave (40 mL in volume) and hydrothermally treated in an electric oven at 180°C for 4 h, and naturally cooled to room temperature, the dark product precipitate was collected by filtering and washing thoroughly with water and ethanol and then dried at 60°C overnight. This as-synthesized sample was denoted as V-CS. The V-CS sample was then transferred into a crucible with a lid and calcined at different temperatures (600, 700, 800, 900 °C) for 1h in a muffle furnace connected to the outside atmosphere or in a tube furnace under Ar at 900°C. These obtained black powders were marked as V-CS-600, V-CS-700, V-CS-800, V-CS-900 and V-CS-900-Ar.

3.2.4 Preparation of molybdenum trioxide supported on carbon spheres

The Mo-carbon microspheres were prepared by a classical hydrothermal carbonization procedure, in which glucose and phosphomolybdic acid were used and the carbon and Mo sources respectively. Typically, glucose and phosphomolybdic acid were dissolved in 30 mL DI water with molar ratio of carbohydrate to metal was 8:1. and kept stirring to 6h until the color of the solution turn from yellow to green. Afterward, the solution was transferred to a Teflon-lined autoclave (40 mL in volume) and put into a constant temperature

oven of 180°C for 12h. Then brown or dark product was collected by filtering and washing thoroughly with water and ethanol after the autoclave naturally cooled to room temperature and then dried in vacuum overnight. This as-synthesized sample was denoted as Mo-CS. The Mo-CS sample was then transferred into a muffle furnace which was connected to the outside atmosphere and calcined at 275°C for 3h, the resulted sample was marked as Mo-CS-275. The Mo-CS sample was also annealing under nitrogen in a tube furnace at 750°C for 3h, the resultant sample was donated as Mo-CS-N2.

3.3 Catalytic reactions

3.3.1 Dehydration of fructose to HMF

The catalytic reaction was performed in a 25 ml capacity flask equipped with a condenser. In a typical catalytic run, a DMSO solution of fructose (0.5 g of fructose in 10 ml of DMSO) was added into the flask along with 100 mg of CS solid acid catalysts. The reaction mixture was heated to the reaction temperature in oil bath with a thermostat and an electronically controlled magnetic stirrer. The reaction samples were removed periodically and analyzed by liquid chromatography (HPLC, Agilent 1100 series, Bio-Rad Aminex HPX-87H, 300mm×7.8mm pre-packed column). Reactant conversion (mol %), HMF yield (mol %) and product selectivity (%) were defined as follows:

$$\text{Conversion (mol\%)} = \frac{\text{moles of fructose reacted}}{\text{moles of initial fructose}} \times 100\%$$

$$\text{Yield (mol\%)} = \frac{\text{moles of HMF produced}}{\text{moles of initial fructose}} \times 100\%$$

$$\text{Selectivity (\%)} = \frac{\text{moles of HMF produced}}{\text{moles of fructose reacted}} \times 100\%$$

3.3.2 Selective oxidation of HMF to DFF

Typically, HMF (63mg, 0.5mmol) was firstly dissolved into 5 mL solvent with a magnetic stirring at room temperature. Then the catalyst was added and oxygen was bubbled through the reaction mixture at a flow rate of 20 mL/min. The reaction was conducted at different temperatures (i.e., 100, 120, 140, 160°C).

The reactor was equipped with a condenser to prevent the evaporation of the solvent. After reaction, the catalyst was separated from the reaction mixture by filtration and products were analyzed by HPLC.

3.3.3 One-pot and One-step synthesis of DFF from fructose

Dehydration of fructose to HMF

In a typical reaction, the procedure for fructose dehydration into HMF was as follows:

Fructose (200mg), Mo-carbon catalyst (30mg), and DMSO (5mL) were added into a 25mL three-necked, round-bottomed flask equipped with a reflux condenser. The reaction was heated in oil bath with magnetic stirring. After the reaction, the mixture was filtered and diluted with water before analyzed by HPLC.

Aerobic oxidation of HMF to DFF

In a typical run, the procedure for aerobic oxidation of HMF was as follows: HMF (63mg, 0.5mmol), Mo-carbon catalyst (30mg), and DMSO (5mL) were added to a 25 three-necked round-bottomed flask equipped with a reflux condenser and magnetic stirring. The reaction was heated in oil bath to target temperature and bubbled with O₂ at a flow rate of 20mL/min. After the reaction, the mixture was filtered and diluted with water and then analyzed by HPLC.

Direct conversion of fructose to DFF

Typically, fructose (200mg) was firstly dissolved into 5 mL DMSO with a magnetic stirring at room temperature. Then the catalyst was added and oxygen was bubbled through the reaction mixture at a flow rate of 20 mL/min. The reaction was conducted at different temperatures (i.e., 100, 120, 140, 160°C). The reactor was equipped with a condenser to prevent the evaporation of the solvent. After reaction, the catalyst was separated from the reaction mixture by filtration and products were diluted with water before analyzed by HPLC.

3.3.4 Analytical Methods

Analyses of fructose, HMF and DFF were conducted on an Agilent 1260 HPLC system with a Bio-rad aminex 87H column (300mm×7.8mm pre-packed column) for the separation of the samples components[133, 377]. The reaction products were diluted in water and filtered through a syringe filter (VWR, 0.22 μ m PTFE) prior to analysis. The mobile phase was constituted of 5mM H₂SO₄ solution at 0.6mL/min. The column oven temperature was kept at 60°C. The amount of each compound was quantified by external standard calibration curve method, which were constructed based on the pure compound.

Chapter 4 Efficient Dehydration of Fructose to 5-hydroxymethylfurfural over Sulfonated Carbon Sphere Solid Acid Catalysts

In this work, a modified preparation of carbon-based solid acid under mild conditions was developed. The CS was prepared by hydrothermal carbonization of glucose at 180 °C which was remarkably lower than the temperature in other CS synthetic routes. The resulted CS was sulfonated by sulfuric acid aqueous solutions instead of concentrated H₂SO₄ or fuming sulfuric acid. Catalytic results showed that the catalysts afforded high activity for the dehydration of fructose to HMF. The effects of acid site density, reaction time, solvents, catalyst amount, temperature and mole ratio of catalyst to substrate were investigated. Under an optimized condition, fructose was converted into HMF with 90% yield at 160 °C after reaction duration of 1.5 h.

4.1 Characterization of CS catalysts

Fig. 4.1 (a) XRD patterns of CS, CS-1, CS-2, CS-3 and CS-4, (b) Raman spectra of CS, CS-1, CS-2, CS-3 and CS-4, (c) FTIR spectra of CS, CS-1, CS-2, CS-3 and CS-4

The XRD patterns of synthesized CS solid acids are shown in Fig. 4.1(a). The weak diffraction peaks at 2θ angles of 10-30° and 35-50° are attributed to the (002) and (101) planes of amorphous carbon, respectively, indicating the carbonization of the glucose precursors [204, 216]. All the samples display two broad signals D-band (1390 cm⁻¹, A_{1g} D breathing mode) and G-band (1590 cm⁻¹, E_{2g} G mode)

in the Raman spectra as shown in Fig. 4.1(b). The peak intensity ratios of D- to G-band of these CS materials are nearly the same, implying the similar average graphene sizes of these CSs [378]. The FTIR spectra of these CS samples are shown in Fig. 4.1(3). The absorption band at 1037 cm^{-1} is assigned to $-\text{SO}_3\text{H}$ groups, showing that the $-\text{SO}_3\text{H}$ groups are successfully linked onto the CS surfaces. The bands attributed to $-\text{OH}$ group at 3420 cm^{-1} , $\text{C}=\text{O}$ group at 1720 cm^{-1} and $\text{C}-\text{O}$ group at 1203 cm^{-1} suggest the presence of $-\text{COOH}$ groups. The peaks at 1620 and 1380 cm^{-1} are attributed to $\text{C}=\text{C}$ groups.

Fig. 4.2 TPD profiles for carbon spheres. A-C CO_2 desorption profiles, D-F CO desorption profiles. A and D are carbon spheres before sulfonation, B and E are carbon spheres after sulfonation, C and F are sulfonated carbon spheres recycled after dehydration reaction.

The oxygen-containing functional groups on the surfaces are further studied by TPD and the relative concentrations of various functional groups including carboxyl, anhydride, ester, phenol and carbonyl/quinone are shown in Fig.4.2,

and summarized in Table 4.1. The sequence of temperatures for decomposition of the oxygen-containing groups to produce CO₂ and CO upon heating is carboxyl < anhydride < ester and anhydride < phenol < carbonyl/quinone. The relative concentrations of different functional groups are estimated by means of overlapping peak deconvolution.

Table 4.1 Relative concentration of functional groups over the CS catalysts^a

Functional groups	CS	CS acid	CS acid ^b
CO ₂ desorption peak			
Carboxyl	17	73	100
Anhydride	97	56	100
Ester	77	100	53
CO desorption peak			
Anhydride	45	18	100
Phenol	32	100	34
Carbonyl/quinone	100	3	30

^aEstimated from the desorbed CO and CO₂ peaks in TPD spectra, the concentration of the strongest peak for each functional groups among the three samples has been normalized to 100. ^bThe catalyst sample was collected after reaction.

As seen in Table 4.1, for the CS after sulfonation, the relative concentrations of carboxyl, ester and phenol groups increase while those of anhydride and carbonyl/quinone decrease. After reaction, the concentrations of carbonyl/quinone and carboxyl groups increase due to the hydrolysis of ester groups and the loss of phenol groups. However, the catalytic reaction results and recycle experiments suggest that the catalytic activities remain the same although the type and quantity of these functional groups change.

Fig.4.3 FESEM images of: (a) CS, (b) CS-1, (c) CS-2, (d) CS-3, (e) CS-4, (f) C-1, (g) C-2, (h) C-3, (i) C-4.

SEM images shown in Fig. 4.3 reveal that the CSs prepared by the two-step method possess narrow distributed granular diameters of approximately 400-500 nm regardless the concentration of sulfuric acid solutions. On the other hand, those CSs prepared by the one-step method show irregular shapes with wide size distributions. Furthermore, particle agglomeration occurs significantly on the CSs prepared by the one-step method. The products C-1, C-2, C-3 and C-4 prepared by the one-step hydrothermal method show different morphological features depending on the concentration of the sulfonating solution. The diameter of C-1 sphere is in the range of 5-8 μm while it decreases to 1-4 μm as the concentration of the sulfonating solution is doubled (C-2). C-3 and C-4 are

primarily formed by the aggregation of fine particles and the particle sizes of C-4 are remarkably smaller than those of C-3.

Table 4.2 The physicochemical properties of the catalysts

	Surface area(m ² /g)	SO ₃ H amount(mmol/g)	Acid density(mmol/g)
CS-1	26.70	0.09	8.53
CS-2	40.17	0.17	7.90
CS-3	153.75	0.32	7.89
CS-4	357.43	0.71	7.79

The strength and density of acid sites of carbon-based solid acid is a vital factor closely related to the catalytic activity [379]. The total number of acid sites on the catalyst surfaces were determined by a well-established acid-base back neutralization titration method [380]. The CS catalyst (30 mg) was suspended in a sodium hydroxide aqueous solution (0.1 M, 20 ml). The mixture was stirred using a magnetic stirrer for 4 h, followed by ultrasonication for 1 h at room temperature. The concentration of the OH⁻ ions in the supernatant solution was calibrated by oxalic acid standard solution. The content of -SO₃H groups on the surfaces of the CSs were determined by neutralization titration with sodium hydroxide. A sodium chloride aqueous solution (0.2 M, 20 ml) was added to the catalyst (30 mg). The mixture was stirred using a magnetic stirrer for 4 h, followed by ultrasonication for 1 h at room temperature. The supernatant solution was titrated using a sodium hydroxide (0.01 M) solution. The sulfonated CSs have both strong and weak acid sites on the surfaces. As shown in Table 2, the total acid density on the surface is almost the same for CS-1, CS-2, CS-3 and CS-4 regardless the concentration of sulfonating solution, while the amount of -SO₃H increases from CS-1 to CS-4 with increasing the concentration of the sulfuric acid solutions.

The BET surface areas of CSs also show correlation with the concentrations of the sulfonating solutions as shown in Table 4.2; the areas increase from 26.7 to 357.4 m²/g as the sulfuric acid concentrations increase. The BET surface areas of the CSs synthesized by one-step hydrothermal carbonization are remarkably smaller compared to those of prepared by the two-step method [376].

4.2 Catalytic performance of catalysts

4.2.1 Effect of solvent

Solvents usually play a significant role in liquid phase catalytic reactions and in this study the solvent effects on the dehydration of fructose to HMF are shown in Fig. 4.4. Among the solvents tested, DMSO is the best for fructose dehydration to HMF, showing superior catalytic performances. Amarasekara et al. [381] suggested that DMSO acted as the catalyst in the process of fructose dehydration. To verify the solvent effect of DMSO, a blank experiment in the absence of catalyst is conducted in DMSO. Fructose conversion of 56.4% and HMF selectivity of 22.4% can be achieved in 0.5 h at 140 °C. Furthermore, by using DMSO and DMF mixture (volume ratio of 1:4) as solvent, 93.1% of fructose conversion and 52.2% of HMF yield are obtained in the presence of CS-2 catalyst, while these two values are only 29.3% and less than 2%, respectively without catalysts. Reactions in toluene and ethylene glycol show extremely high fructose conversion (99.1% and 82.7%, respectively). Nonetheless, the HMF selectivity is less than 2% after 2 h reaction duration, implying the presence of significant side reactions. Caratzoulas and Vlachos [382] studied the solvent effects using hybrid Quantum Mechanics/Molecular Mechanics Molecular Dynamics simulations and found that the activation energy for the hydride transfer in fructose dehydration was closely related with the polar solvent environment. According to the further study by Vlachos et al. [383], DMSO solvents arranged themselves in the immediate vicinity of hydrogen atoms of the hydroxyl groups in fructose, helped prevent fructose from forming reversion and polymerization

products. On the other hand, DMSO molecules around C1 atom of HMF hindered the rehydration of HMF and humins formation.

Fig.4.4 Dehydration of fructose in different solvents. Reaction conditions: fructose (500 mg), catalyst (100 mg), solvent (10 mL), 140 °C for 2 h.

4.2.2 Effect of the acid site density over the catalyst

CS catalysts with different amounts of $\text{-SO}_3\text{H}$ groups on surfaces are attempted in the dehydration of fructose to HMF, and the results are shown in Fig. 4.5. Amberlyst-15 and SBA- SO_3H have been reported as solid acid catalysts to catalyze fructose dehydration to HMF [384], and sulfonic acid groups were suggested as the active sites in this particular reaction. Nonetheless, it can be seen from Fig. 4.5, CS catalyst in the absence of any sulfonic acid groups shows a reasonably good catalytic performance with fructose conversion of 64.3% and HMF yield of 36.7% in 0.5 h reaction duration, implying that other surface acid groups such as -COOH also show catalytic activity in this reaction [69]. Introducing sulfonic acid groups significantly improves the catalytic activity. The fructose conversion and HMF yield are above 97% and 75%, respectively over

CS-2 and CS-3. CS-2 affords the highest HMF selectivity of 77%. Under the same reaction conditions, a fructose conversion of only 9% and HMF yield of 3% are obtained when the reaction is catalyzed by CS-Na which is prepared by ion-exchange H^+ by Na^+ over CS-2, indicating the important role of protonic acid in the dehydration of fructose to HMF. Generally, the more the sulfonic groups on CS catalyst surfaces, the higher the conversion and yield of catalytic performances, as shown in Fig. 4.5 over catalysts from CS-1 to CS-3. As for CS-4, the yield of HMF decreases slightly because HMF proceeds further decomposition due to the remarkably high sulfonic acid site density over CS-4 surfaces, the amounts of sulfonic acid groups of CS-4 is two times higher than that of CS-3 [385]. Furthermore, the conversion of sucrose to HMF is also conducted using the CS solid acid as catalyst and 91.1% HMF yield can be reached in 6 h in DMSO at 140 °C, indicating the superior catalytic activity of CS solid acid catalysts.

Fig.4.5 Dehydration of fructose by different catalysts. Reaction conditions: fructose (500 mg), catalyst (100 mg), DMSO (10 mL), 140 °C for 0.5 h.

4.2.3 Catalytic role of the S=O group

Table 4.3 The catalytic reaction results for the dehydration of fructose to HMF with different acid catalysts and salts

Entry	Catalyst	Salt	T(°C)	Time(min)	Fructose conv. (%)	HMF sel. (%)	HMF yield (%)
1	H ₂ SO ₄	-	125	30	85.34	79.05	67.46
2	H ₂ SO ₄	Na ₂ SO ₄	125	30	76.91	68.50	52.68
3 ^a	H ₂ SO ₄	Na ₂ SO ₄	125	30	65.05	63.98	41.62
4	CS-2	-	125	30	86.30	71.94	62.08
5	CS-2	Na ₂ SO ₄	125	30	63.63	67.36	42.86
6	CS-2	C ₈ H ₇ S O ₃ Na	125	30	93.09	70.03	65.19
7	-	Na ₂ SO ₄	125	30	3.04	-	-
8	-	C ₈ H ₇ S O ₃ Na	125	30	34.59	35.36	12.23

^a the amount of Na₂SO₄ of entry is two times of entry 2.

DMSO acted as both solvent and catalyst in the dehydration of fructose to HMF and S=O group in DMSO was proposed to be the catalytic active site [381]. In this study, different type and quantity of salts in which there are S=O structures are added into the reaction system as the control experiments to further verify the role of sulfonic groups on the catalytic reactions (Table 4.3). When adding H₂SO₄ as the catalyst, fructose conversion of 85.34% and HMF yield of 67.46% are achieved (Table 4.3, Entry 1), while adding Na₂SO₄ results in the decrease both in fructose conversion and HMF selectivity (Table 4.3, Entry 2), and the further decrease occurs when more Na₂SO₄ is added (Table 4.3, Entry 3). Similar results are observed when using CS as the catalyst instead of H₂SO₄. Fructose conversion decreases from 86.3% to 63.63% and the yield of HMF decreases from 62.08% to 42.86% due to the addition of Na₂SO₄ (Table 4.3, Entry 4, 5). These results suggest that the S=O structure in -SO₄²⁻ shows negative effect in

converting fructose to HMF, resulting in the production of humins and levulinic acid. However, the addition of styrene-4-sulfonic acid sodium salt in the reaction system catalyzed by CS solid acid enhances the catalytic efficiency (Table 4.3, Entry 6). Contrast experiments (Table 4.3, Entry 7, 8) show that styrene-4-sulfonic acid sodium has more remarkable catalytic effects than Na_2SO_4 . Therefore, the S=O structure in $-\text{SO}_3^-$ acts as a co-catalyst in the reaction, and the $-\text{SO}_3^-$ group on the surface of the CS acid promotes the reaction to certain extent.

4.2.4 Effect of catalyst/substrate ratio

A series of experiments are conducted at different catalyst/substrate ratios (5%, 10%, 20%, 30%, and 40%) at 140 °C in DMSO using CS-2 as a representative catalyst, and the results are presented in Fig. 4.6. Gradually, the conversion increases from 86.5% to 100% as the CS-2/fructose ratio increases from 5% to 40%, while the HMF yield firstly increases from 60.7% (catalyst/substrate ratios 5%) to 75.4% (catalyst/substrate ratios 20%), followed by slightly decreasing to 70.8% (catalyst/substrate ratios 40%). This decrease in yield is attributed to the increasing amounts of catalyst which causes abundant acid sites in the reaction environment, and the side-reactions such as converting HMF to levulinic acid occurs under such conditions [385].

Fig.4.6 The influence of ratio of catalyst/substrate on the conversion and HMF selectivity. Reaction conditions: fructose (500 mg), catalyst (following the ratio), DMSO (10 mL), 140 °C for 0.5 h.

4.2.5 Effect of temperature

The reaction is carried out at different temperatures from 100 to 160 °C and the results are summarized in Fig. 4.7. The conversion of fructose is only 12.8% at 100 °C after 0.5 h. The conversion reaches 100% within the same reaction time duration at 160 °C. The selectivity of HMF also increases from 40.5 to 76.3% as the temperature increases from 100 to 160 °C. When the temperature is higher than 140 °C, the reaction finishes (100% conversion) in 1.5 h. Longer reaction time leads to the slight decrease in HMF yield because HMF is unstable under high temperatures [386].

Fig.4.7 Influence of reaction time and temperature on the dehydration of fructose to HMF. Reaction conditions: fructose(500 mg), catalyst(100 mg), DMSO(10 mL), (a)100 °C, (b)120 °C,(c) 140 °C, (d) 160 °C.

4.2.6 Effect of reaction time

The effect of reaction time duration on the reaction is also investigated and the results are shown in Fig. 4.7. The fructose conversion, HMF selectivity and yield keep increasing along with the reaction time as far as the reaction temperature is below 140 °C though there is a little decrease in the growth rate. When conducting the reaction at the temperature higher than 140 °C, the conversion of fructose quickly reaches almost 100%, indicating the superior catalytic activity, while the selectivity of HMF firstly increases then decreases, e.g., Fig. 7(d) shows the reaction conducted at 160 °C, the HMF selectivity increases from 76.3% (0.5 h) to 90.1% (1.5 h) then decreases to 75.6% (2 h). This decrease in selectivity suggests that the long reaction time leads to the further condensation of HMF into byproducts especially at high reaction temperature [387, 388].

4.3 The adsorption properties test

The adsorption of fructose and HMF by CS is studied in DMSO solution at room temperature. A certain amount of CS is added into 5ml DMSO solution containing 480 mg of fructose or 100 mg of HMF. The suspension is filtered and analyzed by HPLC after stirring for 6 h under room temperature. As shown in Table 4.4, the catalyst adsorbs fructose in the solution but hardly adsorbs HMF. The adsorption amount of fructose is remarkably higher compared with Amberlyst-15 [229]. The strong adsorption of reactant and quick desorption of product play an important role in affording the high catalytic activity and good selectivity toward desired product.

Table 4.4 The adsorption properties of fructose or HMF by CS

Catalyst	Adsorption of HMF		Adsorption of fructose		R
	Initial	Equilibrium	Initial	Equilibrium	
	concentration (mg)	concentration (mg)	concentration (mg)	concentration (mg)	
Blank	100	100	480	446	-
CS	100	100	480	308	3 27

R represents the adsorption quantity of HMF or fructose per gram of catalyst (mg/g)

4.4 Reusability of the catalyst

The results of stability and reusability of the catalyst are shown in Fig. 4.8. After each reaction run, the catalyst is separated from the reaction mixture and washed with hot water and ethanol, then dried under vacuum at 80 °C for 4 h. There is a slight decrease in both fructose conversion and HMF selectivity after the first run. The conversion and selectivity remain constant during the following cycles. Fructose conversion of 96.2% and HMF selectivity of 73.9% can be maintained even after the 5th run, indicating a good recyclability of the catalyst.

To further study the stability of $\text{-SO}_3\text{H}$ groups, a leaching test was conducted. 100 mg catalyst was dissolved in 10 mL DMSO, heated at 140°C and stirring for 2 h. Then the solution was filtered and the filtrate was used to conduct the dehydration experiment. Results showed in Fig. S1 that the fructose conversion and HMF yield was similar to that of a blank experiment, indicating the high stability of $\text{-SO}_3\text{H}$. It was confirmed by element analysis in Table S1 that the S content in the catalyst was almost constant. In addition, Fig. S2 showed that the morphology of the catalyst didn't change after the reaction indicating its fairly stable structure.

Fig.4.8 Fructose conversions and selectivity towards HMF in the recycling runs. Reaction conditions: fructose (500 mg), catalyst (100 mg), DMSO (10 mL), 140°C , 1 h

4.5 Discussion

The dehydration of fructose to HMF is an acid-catalyzed reaction consisting of several steps such as protonation, dehydration and deprotonation. Sulfonated

CS catalyst, as a strong protonic acid, is suitable for the conversion of fructose to HMF and usually a higher acid density affords better catalytic performances. Carbon-based solid acids are commonly prepared by the sulfonation of different carbon precursors. Konwar et al. [203] studied the influence of different carbon precursors in the preparation of carbon-based solid acid and found that highly carbonized materials were difficult to be sulfonated. In this study, the CSs prepared from the aromatization and carbonization of glucose under hydrothermal conditions were incomplete carbonation materials [389], and they were easy to be sulfonated with high density $\text{-SO}_3\text{H}$ groups on surfaces, showing superior catalytic performances. Different from the CSs prepared by one-step method, the size and morphology of CSs prepared by the two-step method did not change with the concentrations of sulfuric acid solutions, indicating its stable structure and possibility of tuning the acid density on surfaces without changing the carbon-based support. Furthermore, the large surface areas due to the low degree of agglomeration afforded surfaces for $\text{-SO}_3\text{H}$ groups grafting in the sulfonation step and enhanced the contact between fructose and $\text{-SO}_3\text{H}$ groups in the reaction, which contributed to the high catalytic efficiency. Moreover, the strong fructose adsorption and quick HMF desorption capabilities of the CS contributed to the catalytic performances.

In addition to the catalyst, selection of solvent also played an important role in fructose dehydration. Different reaction pathways existed in the dehydration of fructose to HMF in the presence of DMSO solvent. Amarasekara et al. [381] demonstrated that DMSO catalyzed the dehydration of fructose to HMF due to the S=O bond in DMSO that acted as the catalyst. Similarly, the S=O structure in the $\text{-SO}_3\text{H}$ groups on CS solid acid surfaces can play the similar role. Therefore, in the presence of CS solid acid, both protonic acid-catalysis (Bronsted acid catalysis) and S=O -catalysis synergistically worked in the reaction system. In addition, the DMSO solvent prevented fructose from side reactions such as the

rehydration of HMF to levulinic acid, formic acid and humins because the cleavage of C1 carbon in HMF led to the hydration of HMF to levulinic acid and formic acid. DMSO preferred stay in coordination with the hydroxyl group and C1 carbon in HMF, which effectively provided a shielding effect to the HMF molecule [390].

4.6 Summary

In summary, a sulfonated CS solid acid catalyst bearing $-\text{SO}_3\text{H}$, $-\text{OH}$ and $-\text{COOH}$ groups was synthesized by a two-step hydrothermal method. Aqueous sulfuric acid solution replaced the concentrated or fumed sulfuric in the sulfonation step. The acid density and BET surface area of these CS solid acid catalysts increased with the concentrations of the sulfonation solution. The catalyst showed good performances in the dehydration of fructose to HMF under mild conditions, e.g., 100% fructose conversion can be obtained in 0.5h and HMF yield can reach 90% in 1.5h at 160°C. High acid density and reaction temperature accelerated the reaction and improved the selectivity. Nonetheless, excessive amounts of acid sites and high temperature resulted in slight decrease in HMF selectivity due to the further condensation of HMF into byproducts. Besides, high purity HMF can be obtained through extraction by tetrahydrofuran[391](Fig. S3) and there was no significant loss in activity after five catalytic cycles, indicating the high stability and reusability of the catalyst.

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Appendix: Supporting Information

Fig. S1. Leaching test of sulfonic acid groups on CS acid.

Table S1 Element analysis of CS catalyst before and after reaction.

Samples	C%	H%	O%	S%
CS-2	63.00	3.87	32.52	0.55
CS-2 ^a	61.75	4.09	33.63	0.53

^a the catalyst was recycled after reaction.

Fig. S2. FESEM pictures of CS-2 before and after reaction.

Fig. S3. ¹H-NMR spectra of HMF isolated from the reaction mixture.

¹H-NMR for HMF (300MHz, CDCl₃): δ 9.58 (s, 1H, CHO), δ 7.23 (d, 1H, furan ring CH), δ 6.53 (d, 1H, furan ring CH), δ 4.71 (s, 2H, CH₂).

Chapter 5 Selective Aerobic Oxidation of 5-hydroxymethyl-2-furfural into 2, 5-diformylfuran over V-embedded Mesoporous Carbon Microspheres

In this chapter, V-embedded mesoporous carbon microspheres were synthesized and applied in the aerobic oxidation of HMF to DFF. The catalytic performance of the catalysts prepared under different conditions were studied and the changes in the morphology of the catalysts were studied with characterization methods such as XRD, SEM, BET, FTIR, Raman spectroscopy and elemental analysis. The catalysts showed high activity in the oxidation of HMF to DFF. Under optimized reaction conditions, HMF conversion of 100% and DFF yield of more than 99% were obtained in DMSO at 120°C with oxygen bubbling at a flow rate of 20mL/min after 9h.

5.1 Catalyst characterization of V-embedded mesoporous carbon microspheres

Fig. 5.1 XRD analysis of V-CS before and after thermal treatment

In Fig.5.1, the XRD patterns of the as prepared catalysts exhibit a broad peak in the 2 theta range 10-30° which was attributed to C (0 0 2) interlayer reflection among irregularly oriented polycyclic aromatic carbon sheets[392]. This peak shifts toward higher degrees and become relatively sharper after calcination, indicating a decrease in the interlayer space[393]. Another broad peak in the 2 theta range 35-50° corresponding to the C (1 0 0) diffraction peak becomes more

evident with increasing calcination temperature, which is a sign of the increasing degree of ordered structure in the catalysts[394]. These two broad peaks suggest that the carbon material of the catalysts are amorphous. No other peaks exist for the catalysts except V-CS-900, indicating the homogeneous distribution of vanadium in the carbon spheres. The typical diffraction peaks of V-CS-900 can be perfectly indexed to the VO₂ (M)[395], demonstrating that the aggregation of the highly dispersed VO₂ (M) in the carbon spheres occurred during the calcination process because of the high temperature and the decomposition of the unstable carbon layer.

Fig. 5.2 XANES spectra of V-CS before and after thermal treatment

Since XRD was not able to provide enough information on V because of its low loading and low aggregation state, XANES measurements of these catalysts were performed to characterize the coordination and oxidation state of the vanadium species. Also reference substances with different vanadium coordination and oxidation states were measured. It can be seen that there is an obvious change in the XANES spectra for the catalysts before and after calcination in Fig.5.2. The spectra of V-CS calcined at 600°C, 700°C, 800°C and

900°C are comparable, indicating a similar local environment of V. Due to the high sensibility of the XANES region to the geometric structure and the specific bonding situation around the absorber atom it is concluded that the VO_x embedded in the carbon sphere after calcination is similar to VO_2 , suggesting that the calcination can promote the VO_x species evolve to form VO_2 [396]. It is worth noting that the oscillation magnitudes of the samples are weaker than VO_2 because the samples are amorphous state.

Fig.5.3 Raman spectra of V-CS before and after thermal treatment

Fig.5.3 shows the Raman spectra of the as-prepared catalysts. Two typical peaks attributed to the D and G bands can be seen for each catalyst. The peaks at around 1340 cm^{-1} is associated to the disordered structure of the carbon microspheres while the peaks at 1600 cm^{-1} corresponds to the presence of crystalline graphitic carbon. The I_D/I_G values of the catalysts are all larger than 0.5, indicating that the amorphous carbon structure has a high content of defects in the graphite sheets[393]. The value of I_D/I_G for V-CS is 0.58 and this value increase dramatically to 1.41 after calcination at 600 $^{\circ}\text{C}$. And, the I_D/I_G ratios increase from 1.41 to 1.86 as the calcination temperature increase from 600 $^{\circ}\text{C}$ to 900 $^{\circ}\text{C}$, which can be attributed to the change of the microstructure of carbon sheets in carbon spheres. Though calcined at same temperature, the I_D/I_G of V-CS-900-Ar is lower than V-CS-900 because of the different atmosphere during the calcination.

Fig. 5.4 FTIR spectra of V-CS before and after thermal treatment

FTIR spectroscopy was utilized to study V-embedded mesoporous carbon microspheres. In Fig. 5.4, the broad band around 3426 cm^{-1} is attributed O-H stretching vibration. The peaks at 2922 and 1388 cm^{-1} can be assigned to stretching and bending mode of C-H bond. The C=O vibration of aldehydes, ketones, carboxylic acids or esters and the C=C bond of alkenes or aromatic rings appears at 1702 cm^{-1} and around 1569 cm^{-1} respectively[395].

Fig.5.5 FESEM images of (A) V-CS, (B) V-CS-600, (C) V-CS-700, (D) V-CS-800, (E) V-CS-900, (F) V-CS-900-Ar

Fig.5.5 shows general morphology of the as-synthesized catalysts. As can be seen, these carbon spheres are almost monodispersed and the particle size ranges from 3 to 10 μm (Fig. 5.5 A). After the calcination, the spherical morphology remains unchanged. The size of the vanadium-embedded carbon microspheres

does not reduce significantly, indicating the high stability of the carbon structure even at temperature up to 900°C.

Table 5.1. Elemental composition of V-CS before and after thermal treatment

Catalyst	Carbon ^a	Hydrogen ^a	Oxygen ^a	Nitrogen ^a _b	Vanadium
V-CS	56	4.09	38.17	0.79	0.95
V-CS-600	67.1	2.83	27.39	1.15	1.53
V-CS-700	67.55	2.57	25.74	1.1	3.04
V-CS-800	56.66	2.47	36.41	0.98	3.48
V-CS-900	61.28	2.44	30.66	0.5	5.12
V-CS-900-Ar	79.94	1.65	16.17	0.41	1.83

^a Determined by elemental analysis

^b Determined by TGA[397]

Table 5.1 lists the chemical composition of the as-synthesized catalysts. The carbon content of V-CS is 56%, this value increases significantly after the calcination due to the decomposition of the carbon sphere. Comparing with V-CS, the hydrogen and oxygen content decreases dramatically as a result of the falling of groups such as hydroxyl, aldehyde and carboxyl group at high calcination temperature. The vanadium content is determined by thermogravimetric analysis under air atmosphere. It can be seen that the vanadium content increases along with the rising of the calcination temperature. The vanadium content increases from 0.95 % (V-CS) to 5.12 % (V-CS-900), which is caused by the loss of carbon during the calcination by the reaction

between the carbon atoms or fragments and oxygen in limited air atmosphere. This explanation can also be confirmed by the comparison of vanadium content between V-CS-900 and V-CS-900-Ar, the vanadium content of V-CS-900-Ar is much lower than V-CS-900 since there is no oxygen to react with carbon atoms to reduce the carbon amount under argon atmosphere.

Table 5.2. Textual properties of V-CS before and after thermal treatment

Catalyst	S_{BET} (m^2/g)	V_{micro} (m^3/g)	$V_{\text{macro\&meso}}$ (m^3/g)	V_{total} (m^3/g)	D ($\text{\AA}$)
V-CS	60	-	-	-	-
V-CS-600	559	0.189	0.081	0.27	19.3
V-CS-700	613	0.208	0.089	0.297	19.4
V-CS-800	765	0.23	0.16	0.39	20.4
V-CS-900	934	0.252	0.276	0.528	22.6
V-CS-900-Ar	515	0.197	0.047	0.244	18.9

In order to investigate the physical properties of the as-synthesized catalysts, the samples were further characterized by BET. Shown in Table 5.2, the BET surface area for V-CS is very low, and no significant porosity is detected. However, the BET surface area increases from $60\text{m}^2/\text{g}$ to $550\text{m}^2/\text{g}$ after calcination at 600°C in air and up to $936\text{m}^2/\text{g}$ at 900°C . In addition, the pore volume and pore size increase from $0.27\text{m}^3/\text{g}$ and $19.3\text{ \AA}$ to $0.528\text{m}^3/\text{g}$ and $22.6\text{ \AA}$ respectively as the calcination temperature raise from 600°C to 900°C . It deserved to note that the pore volume and BET surface area of V-CS-900-Ar are even smaller than V-CS-600 though the latter is calcined at a 300°C lower temperature. Therefore, the oxygen plays an important role in making pores during the calcination process, which is consistent with the results of element analysis.

5.2 Catalytic performance of catalysts

5.2.1 Catalytic oxidation of HMF over V-embedded carbon spheres

The catalytic activity of the as-prepared catalysts was evaluated by the oxidation of HMF in DMSO by bubbling oxygen under atmospheric pressure at 120°C. Since VO₂ was supposed to be the active site and its weight percent was different for every catalyst, the dosage of each catalyst was different in order to ensure the amount of VO₂ is equal in the reaction system. Fig.5.6 shows the results of HMF oxidation using various catalysts. Low HMF conversion of 0.77% was obtained when using V-CS as the catalyst. After calcination at 600-900 °C, the activity of the catalyst increase significantly. It can be seen that the HMF conversion of 34.13% and DFF yield of 30.93% can be observed in the presence of V-CS-600. In addition, the HMF conversion and DFF yield increased with the enhancement of the calcination temperature. These results demonstrate that the VO₂ was encapsulated by the carbon sphere, leading to few contact chance between the reactants and active sites when V-CS was used as catalyst. For the catalysts such as V-CS-600, V-CS-700 and V-CS-800, the porous structure and high interface improved the contact efficiency between HMF and VO₂. Thus the HMF conversion and DFF yield increase from 34.13% and 30.93% to 63.00% and 62.95% respectively as the calcination temperature raise from 600°C to 800°C resulting in increasing surface area and pore volume. However, though the surface area and pore volume of V-CS-900 are much larger than V-CS-800, the HMF conversion and DFF yield of V-CS-900 are lower than those of V-CS-800. It is because the aggregation of VO₂ in V-CS-900 which is confirmed by the XRD results affects the contact efficiency between HMF and VO₂. In addition, due to the lack of oxygen in the calcination process, the surface area and pore volume of V-CS-900-Ar are much smaller than the catalysts calcined in air, so its activity is much lower than the other catalysts. Therefore, V-CS-800 was the most efficient one for the catalytic oxidation of HMF to DFF.

Fig. 5.6 Comparison of HMF oxidation over V-CS thermal treated at different temperatures. Reaction conditions: DMSO(5mL), HMF(0.05mol), catalyst (V 1.2mg), 120°C, O₂(20mL/min),4h.

5.2.2 Effect of solvents on the catalytic oxidation of HMF to DFF

To optimize the product selectivity, the oxidation of HMF was conducted in various solvents. It can be seen in Table 5.3 that the HMF conversion and DFF yield were greatly affected by the reaction solvents. With strong polarity and high boiling point, DMSO and DMF were found to be effective for the HMF conversion. This can be attributed to the high oxygen solubility in the polar solvents compared to that in nonpolar solvents. However, DFF yield of 62.95% obtained from DMSO was much higher than that of 30.34% observed in DMF under the same reaction conditions. High HMF conversions were also achieved in aromatic solvents such as toluene and dimethylbenzene, but there was a large range between the selectivities of DFF. HMF conversions were lower in other solvents such as Isoamyl alcohol and N-Methyl-2-pyrrolidone, which might be the result of strong interactions between the solvent and the catalytic active sites

since the heteroatoms N, O in the solvent molecules can work as the electron donor. Notably, toluene (nonpolar solvent) afforded HMF conversion of 99% which is higher than that for DMSO and DMF under the investigated conditions. This result could be possibly attributed to the following reason. The active sites (VO_2) were located in the organic carbon layer, which make it easier for the aromatic solvents with low polarity to bring the HMF to the activity sites, leading to high reaction efficiency. Therefore, according to the above results, it is difficult to get a direct correlation between the polarity of the solvent and the performance of the catalysts, which is consistent with the conclusion reported by Riisager et al[398] and Chen et al[393]. However, considering the HMF conversion and DFF yield together, DMSO was the optimal solvent for the aerobic oxidation of HMF to DFF.

Table 5.3 Effects of solvents on the aerobic oxidation of HMF to DFF

Entr y	solvent	HMF	DFF	DFF
		Conversion (%)	Yield (%)	Selectivity (%)
1	DMSO	63.00	62.95	99.91
2	DMF	88.19	30.34	34.40
3	Toluene	99.00	43.89	44.33
4	Isoamyl alcohol	10.12	5.11	50.51
5	N-Methyl-2- pyrrolidone	16.27	3.09	19.02
6	Dimethylbenzene	55.83	1.51	2.69

Reaction conditions: Solvent(5mL), HMF(0.05mol), V-CS-800 (35mg), 120°C, O_2 (20mL/min), 4h.

5.2.3 Effect of temperature and time on the catalytic oxidation of HMF to DFF

Fig.5.7 shows the influence of the reaction temperature and time on the HMF oxidation to DFF over V-CS-800 in DMSO. The reactions were conducted at

100°C, 120°C, 140°C and 160°C spanning a 30-hour time period. The HMF conversion and DFF yield were obtained in 12.85% and 11.39% respectively when the reaction was carried out at the reaction temperature of 100°C after 2h. Further increasing the reaction temperature to 120°C, HMF conversion increase to 42.78% at the same reaction time. Moreover, the DFF yield sharply increased from 11.39% at 100°C to 74.82% at 160°C in 2h. As expected, the increase of the reaction temperature dramatically promoted the aerobic oxidation of HMF to DFF, because the increase of the reaction temperature accelerated the movement and contact of the reactant molecules.

In addition to the effects of the reaction temperature on HMF conversion to DFF, the influence of reaction time on the aerobic oxidation of HMF was also investigated under different reaction temperature. It can be seen in Fig.5.7 that the time-changing trend of HMF conversion and DFF yield is greatly affected by the reaction temperature. When the reaction was carried out at 100°C, the HMF conversion and DFF yield increase over time—specifically, HMF conversion and DFF yield were 12.5% and 11.39% respectively after 2h while these values increased to 81.74 % and 79.85% after 30h. Similar phenomenon occurred when the reaction temperature rise to 120°C. HMF conversion and DFF yield reached 86.34% and 85.79% respectively in 8h, then the growth trend slowed dramatically. However, when the reaction temperature was higher than 140°C, there would be a turning point in the curve of DFF yield versus time though the HMF conversion kept growing as the time went by. A DFF yield of 76.80% was achieved in 8h at 140°C, then the DFF yield started to decrease. Further raising the reaction temperature to 160°C, the inflection point for the growth of DFF yield appeared earlier and subsequently declined by up to 17 percent after 30h. The above results about the influences of reaction temperature and time therefore demonstrated that the optimal temperature for selective oxidation of HMF to DFF

is 120°C, as higher reaction temperature could cause the over oxidation of HMF to by-products such as FFCA and FDA after a long time reaction[399].

Fig.5.7 Effect of temperature and time on the catalytic oxidation of HMF to DFF. Reaction conditions: DMSO(5mL), HMF(0.05mol), V-CS-800(35mg), O₂(20mL/min), reaction temperature (A) 100 °C, (B) 120 °C, (C) 140 °C,(D) 160°C.

5.2.4 Effect of catalyst to substrate ratio on the catalytic oxidation of HMF to DFF

The dosage of catalyst was also a crucial factor for optimization of the reaction. Fig.5.8 shows the relations among HMF conversion, DFF yield and ratio of metal to substrate. It can be seen that the HMF conversion and DFF yield increased significantly with increasing the catalyst concentrate. Under the optimal reaction conditions, the HMF conversion and DFF yield reached 100% and 99% respectively with the increase of ratio of vanadium to HMF as only 2 wt.%, indicating the high catalytic efficiency of the catalyst.

Fig.5.8 Effect of catalyst to substrate ratio on the catalytic oxidation of HMF to DFF. Reaction conditions: DMSO(5mL), HMF(0.05mol), 120°C, O₂(20mL/min),9h.

5.3 Catalyst recycling experiments

The reusability of the V-CS-800 catalyst was investigated by conducting five consecutive runs in DMSO. Before each reuse, the catalyst was washed thoroughly with the corresponding solvent and ethanol and dried overnight at 80°C. It can be seen from the results showed in Fig. 5.9 that the yield of DFF almost remained unchanged even after being used 5 times. Recently, PVP-1/VO (Vanadyl-pyridine complexes immobilized on a polymeric mesoporous support) was developed by Navarro et al. for HMF oxidation[393]. The performance of the catalyst decreased significantly due to the vanadium leaching. Vanadium phosphate oxide, synthesized by Dumeignil et al. , also showed a decrease in catalyst activity for oxidation of HMF to DFF during the recycling test owing to the change in catalyst structure which reduced to number of accessible reactive vanadium centers[400]. Moreover, Riisager et al. reported the loss of activity of the zeolite-supported vanadium catalyst in the stability test as a result of the vanadium leaching and site blocking phenomena[398]. However, TGA results

showed that the vanadium amount of V-CS-800 remained about the same after the reusability test, suggesting the strong interaction between the vanadium species and the carbon support.

Fig. 5.9 Catalyst V-CS-800 recycling. Reaction conditions: Solvent (5mL), HMF (0.05mmol), V-CS-800(65mg), 120°C, O₂ (20mL/min), 9h.

5.4 Summary

In summary, vanadium-embedded mesoporous carbon microspheres were synthesized by a facile hydrothermal method. The nonporous V-CS catalyst was activated by thermal treatment to introduce micro- and mesoporous structure, leading to the increase in specific surface from 60 to 934 m²/g. Under appropriate conditions, the vanadium catalyst (V-CS-800) showed homogeneously dispersed VO₂ nanoparticles within the mesoporous carbon matrixes. The as-prepared vanadium catalyst was highly selective for catalytic aerobic oxidation of HMF to DFF using molecular oxygen as oxidant. The high activity was attributed to the mesoporous structure of the catalyst which allowed the free movements of reactants and products and enhanced the contact chances between reactants and active sites. Different reaction conditions were investigated to increase the yield

of DFF. The effects of solvents, reaction time, temperature and ratio of catalyst to substrate were studied. The choice of solvent also had a very important effect on the reusability and stability of the catalyst though the reason behind is remaining not clear. Under optimized reaction conditions, HMF conversion of 100% and DFF yield of more than 99% were achieved when the 2 wt.% (V/HMF) V-CS-800 was applied as the catalyst in DMSO at 120°C and oxygen bubbling at a flow rate of 20mL/min after 9h. In addition, there was little decline in the catalytic performance in the recycling experiments, indicating the excellent stability and reusability of V-CS-800. In short, this novel step-economic synthetic strategy can facilely produce efficient catalyst for biomass-based conversion.

Chapter 6 Molybdenum Trioxide Supported on Carbon Sphere for One-Step Approach to 2,5-Diformylfuran from Fructose

In this chapter, a series of molybdenum oxide species supported on carbon spheres (Mo-CS) were developed and used catalysts in the direct synthesis of 2,5-diformylfuran (DFF) from fructose with molecular oxygen as the oxidant and dimethylsulfoxide as solvent. Different aftertreatment methods were applied to the solid Mo-CS precursor to strengthen the sphere structure, generate micro- and mesopores within the catalyst and change the oxidation states of encapsulated molybdenum in order to enhance the performance in the one-step conversion of fructose to DFF. The structure and properties of the resultant catalysts were characterized by X-ray diffraction (XRD), element analysis, Raman spectroscopy, Field emission scanning electron microscopy (FESEM), Fourier transform infrared (FTIR) spectra, Brunauer-Emmett-Teller (BET) Surface Area Analysis, and ammonia temperature-programmed desorption (NH₃-TPD). The as-synthesized catalysts showed high activity and selectivity towards direct transformation from fructose to DFF. A 100% conversion of fructose can be obtained within 2 h at 160 °C in DMSO and the corresponding DFF yield can reach as high as 77%, which is a very satisfying result. Moreover, the heterogenized catalysts could be recycled and reused for at least 5 runs without significant loss of activity.

6.1 Catalyst characterization

Uniform spherical carbon spheres could be prepared by hydrothermal method in the temperature range of 160–200 °C with carbohydrates as the carbon precursor, while the preparation of this type of metallic-carbon hybrids with homogeneously distributed metal species is still quite challenging [389]. Fig. 6.1 shows the morphology of as-synthesized carbon sphere supported molybdenum oxide catalysts prepared at 180 °C for 12 h under hydrothermal conditions and followed by different after-treatments. As can be seen, the spherical catalysts

have a uniform size distribution of around $1\ \mu\text{m}$ (Fig. 6.1a). after carbonization in nitrogen at 750°C or calcination in air at 275°C for 3h, the spherical morphology remains unchanged, but the size decrease to less than $1\ \mu\text{m}$, which is probably due to the gasification of carbon at high temperature especially when oxygen exists in the environment[394]. It is worth noting that the surface of Mo-CS was smooth and it remains smooth even after annealing in nitrogen at 750°C for 3h. However, Mo-CS-275, which was obtained from calcination of Mo-CS in air, has obviously rough and grainy surface. This is because of the remove of carbon component by the reaction between the carbon atoms or fragments and oxygen in air atmosphere leads to the explosion of molybdenum oxide species.

Fig.6.1 FESEM images of Mo-CS (a,b), Mo-CS-275 (c,d), Mo-CS-N2 (e,f).

X-ray powder diffraction was carried out to study the crystallographic structure of the as-synthesized catalysts. According to the study by Alexander Briceno, molybdenum was reduced by glucose from the oxidation state $+6$ in its precursor phosphomolybdic acid to the $+4$ in MoO_2 [401]. Due to the homogeneous distribution of molybdenum oxide species in carbon spheres, no obvious peaks of MoO_2 are observed in Fig. 6. 2 for the sample Mo-CS. For the same reason, similar behaviors are also found for the sample Mo-CS-N2, in which the molybdenum oxide species may be further reduced and carbonized to hexagonal molybdenum carbide after calcination at 750°C in nitrogen[402]. However, after calcination in air, the crystallinity of molybdenum oxide species was significantly improved. A considerable amount of carbon atoms or fragments were removed and the molybdenum oxide species were oxidized to orthorhombic molybdenum trioxide with major diffraction peaks as shown in Fig. 6. 2[403]. There are no graphitic carbon peaks observed, since the carbonaceous phase in these carbon spheres are amorphous which is confirmed by the broad peak between $20\text{-}30^\circ$. This peak attributed to 002 interlayer reflection in the carbon packing and might reflect the average separation distance between polycyclic aromatic carbon segments[404].

Fig. 6. 2 XRD analysis of Mo-CS, Mo-CS-275 and Mo-CS-N2.

Fig. 6.3 Raman spectrum of Mo-CS, Mo-CS-275, Mo-CS-N2.

The Raman spectrums of carbon sphere supported molybdenum oxide samples are shown in Fig. 6.3. Two typical peaks at $\sim 1300\text{ cm}^{-1}$ and $\sim 1600\text{ cm}^{-1}$ are observed for all the as-synthesized samples. The peak at $\sim 1300\text{ cm}^{-1}$ also known as D-band is attributed to the vibration of carbon atoms with dangling bonds, while the G-band ($\sim 1600\text{ cm}^{-1}$) corresponds to the in-plane E_{2g} zone-center mode[392]. The intensity ratios of the D- and G- bands are larger than 0.5,

reflecting the low degree of graphitization of the carbon sphere and the presence of high contents of lattice edges and defects in the disordered carbon[405, 406], which is consistent with the XRD results. Moreover, this ratio ID/IG increased after calcination, indicating that high temperature carbonization enhanced the degree of disorder.

Fig. 6.4 FTIR spectra of Mo-CS, Mo-CS-275 and Mo-CS-N2.

FTIR spectroscopy was utilized to study the assignment of surface functional groups of the as-synthesized catalysts (Fig. 6.4). Generally, all the peaks become less obvious after calcination at 750°C in nitrogen indicating the shedding of the functional groups due to high temperature. The broad band centered around 3400cm⁻¹ is attributed to the O-H groups. The peaks at 2920 and 1380 cm⁻¹ correspond to the stretching and bending modes of C-H groups. Compared with Mo-CS, the intensity of these peaks of Mo-CS-275 and Mo-CS-N2 decreased after the calcination. In contrast, the intensity of the peak corresponding to C-O groups (1000-1300cm⁻¹) increased after calcination in air. The peaks at 1702 cm⁻¹ and 1619 cm⁻¹ can be assigned to the C=O vibration of ketones, esters,

aldehydes or carboxylic acid and C=C bond of alkenes or aromatic rings respectively[407]. Element analysis were carried out to study the chemical components (i.e. carbon, hydrogen, oxygen) of the catalysts and the results were consistent with the FTIR analysis. It can be seen that there are great differences in chemical composition between different samples in Table 6.1. Mo-CS-N2 has a much higher percentage of carbon and less level of hydrogen and oxygen than the other two types of catalysts because of the loss of hydrocarbon group and carbon-oxygen groups under high temperature during the calcination in nitrogen. Meanwhile, when Mo-CS was annealing in air, the oxidation reaction between carbon atoms and oxygen lead to a higher oxygen-to-carbon ratio in Mo-CS-275 than Mo-CS and Mo-CS-N2. Moreover, the calcination also caused the increase of molybdenum content because of the consumption of carbon atoms in the process.

Table 6.1 Elemental composition and surface areas of Mo-CS, Mo-CS-275 and Mo-CS-N2.

Catalyst	Carbon ^a /%	Hydrogen ^a n ^a %	Oxygen ^a a%	Mo ^b / %	BET/m ² /g
Mo-CS	63.36	4.95	29.02	2.67	<1
Mo-CS-275	44.74	2.21	46.27	6.78	28
Mo-CS-N2	81.11	1.50	13.11	4.28	427

^a Determined by elemental analysis

^b Determined by TGA

Fig. 6.5 NH₃-TPD curves of Mo-CS, Mo-CS-275 and Mo-CS-N₂

Since the dehydration of fructose to HMF is an acid catalyzed reaction, the acidity of the catalysts should be one of the key factors which influence the catalytic activity. Thus, NH₃-TPD examination was carried out to study the acidity of the catalysts (Fig. 6.5). It can be seen that there is a big peak ranging from 250°C to 650°C for Mo-CS, indicating the rich Brønsted and Lewis acid sites on the surface, which are attributed to the various surface functional groups such as hydroxyl, carboxyl groups and the molybdenum oxide species [408]. This peak disappeared for the samples after calcination, while a new peak around 220°C was observed for Mo-CS-275 and Mo-CS-N₂. It should be noted that the peak intensity of Mo-CS-275 is much higher than that of Mo-CS-N₂. Generally, the high-temperature peak is related to medium acid sites and the low-temperature is associated with weak temperature. Therefore, the heat treatment of the Mo-CS leads to the loss of medium acid sites and the formation of weak

acid sites due to the change of the surface groups and the oxidation state of molybdenum, which is line with the analysis of FTIR results.

6.2 Catalytic performance of catalysts

6.2.1 Dehydration of fructose of HMF

A series of experiments were conducted to initially investigate the catalytic performance of the carbon sphere supported molybdenum oxide catalysts towards fructose dehydration. In Fig. 6.6, all the tested catalysts showed good activity and both the fructose conversion and HMF yield increased with reaction time. However, Mo-CS-275 obviously showed better performance than the other two types of catalysts especially at the early stage of the dehydration reaction. It can be seen that the yield of HMF can reach more than 70% in only 2h in the presence of Mo-CS-275, whereas this value was just 52.69% and 62.03% by using Mo-CS-N2 and Mo-CS respectively. The same goes for the fructose conversion rate, when the reaction was conducted in the presence of Mo-CS-275, the fructose conversion increased to 97.02% after 2h, while it took 4-6h for Mo-CS and Mo-CS-N2 to catalyze the reaction and get the comparable fructose conversion under the same condition. In general, Mo-CS-275 showed the best catalytic activity for the dehydration of fructose to HMF due to its relatively high acid concentration and large BET surface area comparing with Mo-CS-N2 whose acid amount is too little and Mo-CS who has a very small BET surface area which cannot provide enough contact chance for the active site and reactant.

Fig. 6.6 Dehydration of fructose to HMF over Mo-CS, Mo-CS-275 and Mo-CS-N2. Reaction conditions: fructose (200mg), catalyst (30mg), DMSO (5mL), 110°C.

6.2.2 Aerobic oxidation of HMF to DFF

After the investigation of the catalysis performance for fructose dehydration to HMF, aerobic oxidation of HMF to DFF was further explored in order to select the best catalyst for one-step approach transformation from fructose to DFF. It was found that the catalytic performances of the as-synthesized catalysts varied greatly with different after-treatments for the metallic sites and the carbon support as shown in Fig. 6.7. HMF conversion of 31.96% and DFF yield of 30.83% were obtained after 2h in DMSO at 140°C with oxygen bubbling rate as 20mL/min, whereas these values were less than 10% when Mo-CS or Mo-CS-N2 was used as the catalyst. Moreover, when the reaction time was further prolonged to 8h, the results gap between different catalysts became much more evident. The conversion of HMF and yield of DFF increased to 89.36% and 86.74% respectively after 8h in the presence of Mo-CS-275. In sharp contrast, HMF

conversion and DFF yield of 45.60% and 43.38% respectively were observed from Mo-CS-N2, and these values can be much less for Mo-CS. Above results indicate that the catalytic performance was influence dramatically by the molybdenum oxide species state and BET area. The catalytic effect of Mo-CS was limited by the low surface area, while the low valence state of Mo in Mo-CS-N2 is related to the low reaction activity towards the aerobic oxidation of HMF to DFF.

Fig. 6.7 Aerobic oxidation of HMF to DFF over Mo-CS, Mo-CS-275 and Mo-CS-N2. Reaction conditions: HMF (63mg, 0.5mmol), catalyst (30mg), O_2 (20mL/min), DMSO (5mL) 140°C.

6.2.3 One-pot conversion of fructose to DFF

Based on two separate studies on the catalytic performance of Mo-CS, Mo-CS-275 and Mo-CS-N2 in fructose dehydration to HMF and HMF oxidation to DFF, Mo-CS-275 was supposed to be the best choice for direct conversion of fructose to DFF. Thus one-pot synthesis of DFF from fructose was carried out by using the as-synthesized catalysts to further confirm the preliminary prediction. Unlike the one-pot but two-step reaction, in which the dehydration of fructose to

HMF was performed under inert gas and the aerobic oxidation of HMF to DFF was performed under oxygen, no inert gas was applied as the protection gas and the reaction system was bubbled with oxygen from beginning to end. Meanwhile, in order to eliminate the effect of molybdenum oxide species loading level, calculated amount of catalysts with equivalent molybdenum content were fed into the reaction. It can be seen in Fig. 6.8 that all the tested catalysts showed good catalytic activity as expected with fructose being 100% converted and HMF and DFF were detected as the main products. The exist of HMF affirmed the intermediate role of HMF during the transformation of fructose to DFF. In comparison, the yield of target product DFF presented by Mo-CS-275 was higher than that by Mo-CS and Mo-CS-N2 under the investigated conditions, suggesting that Mo-CS-275 was the best catalyst for one-step approach towards DFF from fructose because of its relatively high acid density and strong oxidative ability.

Fig. 6.8 Direct transformation of fructose to DFF catalyzed by Mo-CS, Mo-CS-275 and Mo-CS-N2. Reaction conditions: fructose (200mg), catalyst (Mo 2mg), DMSO (5mL), O₂ (20mL/min), 130°C, 8h

Specimens sampled at specified time intervals from the reaction mixture were analyzed to study the time course of the one-pot conversion of fructose to DFF. As shown in Fig. 6.9, fructose dehydrated to HMF quickly that HMF yield could reach nearly 80% after 1h with fructose conversion approaching 100%. As the reaction proceeding, the yield of HMF exhibited a declining tendency and became trace after 30h. Accordingly, the yield of DFF increased from 7.69% at 2h to 77.75 at 30h. Obviously, the reaction can be divided into two stages, namely the dehydration of fructose to HMF and the accumulation of DFF with destruction of HMF. During the process, the quick dehydration of fructose to HMF considerably reduced the contact time of fructose with oxygen and oxidative active centers which can avoid the large generation of by-products and force the reaction to move into the second stage. As to the second stage, the excellent activity of the catalyst and high selectivity towards DFF in aerobic oxidation of HMF has been proven. They are the reasons why Mo-CS-275 showed superior performance in the one-pot and one-step conversion of fructose to DFF.

Fig. 6.9 Conversion of fructose to HMF and DFF as a function of time. Reaction conditions: fructose (200mg), CS-Mo-275 (30mg), DMSO (5mL), O₂ (20mL/min), 130°C.

6.3 Optimizations of the reaction conditions over Mo-CS-275

In order to achieve a maximum possible DFF yield, reaction conditions such as temperature, time and ratio of reactant to catalyst were investigated. The effect of weight ratio of Mo to fructose was studied at the ratio of 0.4, 1%, 2% and 4% under similar conditions. Overall, the results showed the catalyst work steadily with a remarkable performance (Fig. 6.9). 57.78% DFF yield and 20.16% HMF yield were obtained after 18h under 130°C in DMSO even though the ratio of Mo to fructose was only 1%.

Fig. 6.10 Influence of ratio of Mo/fructose on the synthesis of HMF and DFF from fructose. Reaction conditions: CS-Mo-275 (30mg), DMSO (5mL), O₂ (20mL/min), 130°C, 18h

In terms of the final results, reaction temperature has a significant influence to the yield of the target product (Table 6.2). It has been proven that the dehydration of fructose to HMF ran very fast under the investigated temperature range and reached 100% conversion of fructose, turning the reaction into an

aerobic oxidation reaction of HMF. Thus the temperature affects the final yield of DFF by affecting the HMF oxidation rate. For instance, 95.98 fructose conversion and 69.60 HMF yield were attained in 2h at 110°C, while the DFF yield was only 1.44%. This is because the rate of HMF oxidation is far slower than fructose dehydration at rate 110°C, resulting in the accumulation of large amount of HMF in the reaction system. Nevertheless, when the reaction temperature raised to 150°C, HMF yield of 34.34 and DFF yield of 38.02 were achieved with fructose conversion of 100% after the same reaction time period. What deserves to be noticed is that when the reaction temperature further increased to 165°C, DFF yield could be as high as 77.85% in 2h with thimbleful HMF residues.

Table 6.2 Influence of temperature and time on the synthesis of HMF and DFF from fructose

Entry	Mo/fructose (wet.%)	Time (h)	Temperature (°C)	Fructose conv. (%)	HMF yield (%)	DFF yield (%)
1	1	2	110	95.98	69.60	1.44
2	1	72	110	100	10.31	50.81
3	1	18	130	100	20.16	57.78
4	1	2	150	100	34.34	38.0
					2	
5	1	5	150	100	4.33	66.83
6	1	2	165	100	0.8	77.85

Reaction conditions: fructose (200mg), CS-Mo-275 (30mg), DMSO (5mL), O₂ (20mL/min)

6.4 Reusability of the catalyst

Five-cycle experiments were conducted to study the reusability of Mo-CS-275. The used catalyst was separated from the reaction mixture by filtration, washed with ethanol and DI water, followed by drying under vacuum at 45°C and

calcining at 275°C for 3h before the next run. Generally, the catalyst can run for long time and be reused without significant decreased of catalytic performance as shown in Fig. 6.10. In details, DFF yield decreased from 61.67% to 53.85% after the first run, then the descending of DFF yield developed slowly and the content of HMF increased slightly, while the fructose conversion kept at 100%. XRD analysis shows that the XRD peaks of molybdenum trioxide species in the catalysis become very weak or disappear. According to the FESEM pictures in Fig. 6.11, the spherical morphology of the catalyst basically remained with slight scuffing and chipping. In addition, the TGA result showed that the molybdenum content of the catalyst dropped by 27% after the recycling test, suggesting the leaching of the active sites, which is the main reason for the changes of XRD pattern and catalytic activity.

Fig. 6.11 Reusability test of CS-Mo-275. Reaction conditions: fructose (200mg), CS-Mo-275 (30mg), DMSO (5mL), O₂ (20mL/min), 155°C, 2h.

Fig. 6.12 XRD and FESEM picture of recovered Mo-CS-275

6.5 Summary

For a long time, people have got the idea of preparing catalysts with both acid sites and oxidative sites to apply in the one-pot conversion of fructose to DFF. In fact, it is quite challenging to find such kinds of catalysts which can catalyze the reaction and achieve a satisfactory result-not because the catalysts are too difficult to design and prepare, but because the conflicts between the function of the two kinds of active sites are difficult to deal with. Generally, organic acids such as formic acid, levulinic acid and humic acid will appear in the reaction system as by-products of the dehydration of fructose to HMF. These acid products will always be the poisoning reason of the catalyst which are usually used in the aerobic oxidation of HMF to DFF[409]. This issue has led to the limitation on use of catalysts such as Pt/C, Pd/C, Pt/TiO₂/ZrO₂ and so on[386]. Later, a series of vanadium oxide catalysts were found to be efficient not only for the oxidation of pure HMF but also efficient for the in-situ oxidation of HMF generated from fructose. But new issue emerged during the application of vanadium oxide catalysts in transformation of fructose to DFF. Fructose was over oxidized and degraded to unwanted organic acid and insoluble polymeric furanic compounds due to the strong oxidative ability of the catalyst[410]. Therefore, the ideal catalyst should meet the following requirements: tolerance to all the organic by-products and water, mildly oxidize ability which can catalyze the aerobic

oxidation of HMF instead of leading to rapid decomposition of fructose. Fortunately, the as-synthesized catalyst is such a catalyst which meets all the above requirement, therefore it can be successfully applied in the one-pot and one-step synthesis of DFF from fructose. The excellent catalytic performance of the catalyst is exactly attributed to the relative high acidity and moderate oxidative ability. The former catalyzes the dehydration of fructose to HMF, while the later acts on the aerobic oxidation of HMF, thus when these two factors affect together DFF can be obtained as a product directly from fructose. Under optimized conditions, 77.85% yield of DFF was obtained from fructose with Mo-CS-275 as the catalyst and bubbling oxygen as the oxidant in only 2h at 165°C. In addition, the catalyst could be separated and reused at least five cycles without significant loss in activity.

Chapter 7 Conclusions and Future Work

7.1 Conclusions

In this study, series of carbon-based catalysts were synthesized and employed for the conversion of fructose to HMF and its derived chemicals. The investigated reactions have huge implication for the utilization of biomass materials. The catalysts were well characterized by advanced technologies in order to emerge the physical and chemical properties and their relationship with the catalytic performance. Reaction conditions were also optimized to achieve a highest possible yield of the target products.

Carbon materials have long been used as support materials because they can be chemically functionalized with various active groups and decorated with metallic nanoparticles. In this thesis, carbon spheres were chosen as the support materials and modified according to the requirements of the reactions. Compared with other carbon materials such as carbon nanotubes, graphene and active carbon, carbon spheres were prepared by a facile hydrothermal method at temperature lower than 200°C, which is a more economic and greener synthesis method. Carbon spheres bearing $-\text{SO}_3\text{H}$ groups can be prepared by functionalizing the carbon materials with sulfuric acid. The as-synthesized catalyst is an insoluble Bronsted acid and showed good performance in the dehydration of fructose to HMF under mild conditions. 90% yield of HMF can be achieved in only 1.5h at 160°C. It worth to note that solvent play an important role in the fructose dehydration. On one hand, the $\text{S}=\text{O}$ structure in DMSO can catalyze the dehydration of fructose to HMF as a catalyst and on the other hand, DMSO can stay in coordination with the hydroxyl group and C1 carbon of HMF which can prevent the side reactions such as the rehydration of HMF to formic acid and levulinic acid.

Carbon supported metal oxide catalysts have been widely used in the transformation of biomass to fuels and chemicals. In Chapter 5, we described the

synthesis of vanadium-embedded mesoporous carbon spheres and their application in the aerobic oxidation of HMF to DFF. As known to all, the surface area of hydrothermal synthesized carbon spheres is usually very small, which is not favorable for the fully contact between the reactant and active sites. To overcome this problem, the vanadium-embedded mesoporous carbon spheres were calcined under high temperature with limited oxygen to introduce porous structures into the solid carbon spheres. As a result, the surface area of the carbon spheres increased dramatically as well as the catalytic activity. Under optimized reaction conditions, HMF conversion of 100% and DFF yield of more than 99% were achieved when only 2 wt.% (V/HMF) catalyst was applied in the aerobic oxidation of HMF to DFF with DMSO as solvent at 120°C and oxygen bubbling at a flow rate of 20 mL/min after 9 h. The only weak point here is the little decline in the catalytic activity due to the leaching of the active sites during the recycling tests, which is a common problem for the vanadium oxide catalysts.

Since dehydration of fructose to HMF is an acid catalyzed reaction and the conversion of HMF to DFF is an aerobic oxidation reaction, people will naturally think it is very hopeful to synthesize DFF directly from fructose catalyzed by catalysts bearing both acid sites and oxidative sites. Actually, it is quite challenging to prepare such kinds of catalysts and exhibit satisfactory catalytic effect. One reason is that the by-products of the dehydration of fructose to HMF such as formic acid, levulinic acid and humic acid always deactivate the oxidative active sites, terminating the reaction at the first step. The other reason is that most of the oxidative catalysts which are efficient in the aerobic oxidation of HMF to DFF can also oxidize fructose, leading to rapid decomposition of fructose and poor yield of DFF. Fortunately, molybdenum trioxide supported on carbon sphere as described in chapter 6 is an excellent catalyst with high acidity and moderate oxidative ability. Thus the catalysts can facilitate the dehydration of fructose to HMF on one hand, and will not degrade fructose to unwanted products.

Under optimized conditions, 77.85% yield of DFF was obtained from fructose with Mo-CS-275 as the catalyst and bubbling oxygen as the oxidant in only 2h at 165°C. In addition, the catalyst could be separated and reused at least five cycles without significant loss in activity.

In conclusion, carbon materials based/supported catalysts are the one of the most achievable and economical catalysts for the conversion of biomass materials to value-added chemicals.

7.2 Future Work

Based upon the discoveries in the previous PhD work, we proposed some research topics which may be interesting and worthy of further work. In chapter 4, carbon sphere solid showed excellent catalytic performance in the dehydration of fructose to HMF. We noticed that the surface area of the carbon spheres is not very high and this may influence the fully utilization of the carbon materials. Therefore, mesoporous carbon sphere will be a better choice for the support of acid sites. While it is important to note, completely carbonized carbon materials are difficult to be sulfonated and grafted with high-density acid sites. Thus the processing temperature during the synthesis of mesoporous carbon spheres could not be too high. What is more, nitrogen doping is a common approach to change the physicochemical properties of carbon materials. Thus it deserves to be further investigated on the catalytic effect of nitrogen-doped mesoporous carbon spheres based solid acid for the dehydration of HMF.

In chapter 5, vanadium oxide was the active site for the aerobic oxidation of HMF to DFF. But its strong oxidizability can lead to the aerobic degradation of fructose to various by-products, which limited the use of it for the one-pot and one-step synthesis of DFF from fructose. However, bimetallic oxide consisting of vanadium and another metal with lower oxidizability maybe will help overcome this disadvantage. If the bimetallic oxide contains Lewis acid sites on its surface, then it could act as a bifunctional catalyst and will probably be active

in both the dehydration of fructose to HMF and oxidation of HMF to DFF. In this way, it can be used in the direct transformation of fructose to DFF.

In chapter 6, carbon spheres supported molybdenum trioxide has proved to be an efficient catalyst for the one-step approach conversion of fructose to DFF. Actually, phosphomolybdic acid is an ideal catalyst with strong Bronsted acid sites and appropriate oxidize ability, except the fact that it is soluble in the reaction solvents and form a homogeneous reaction system which cause trouble in the recycle of catalyst. A solution is immobilizing the POM (phosphomolybdic acid) by preparing MOF (metal organic framework) encapsulated Kegginpolyoxometalate catalyst. In this way, the hybrid material can be used in the direct conversion of fructose to DFF and is easy to be separated from the reaction solution.

The above work plans are more focused on the improvement of the performance of the catalysts. Actually, the mentioned reaction can be extended to use cheaper carbohydrates as the starting materials. To produce glucose by catalytic hydrolysis of cellulose using carbon-based solid acid catalysts has attracted much attention, because the heterogeneous reaction systems can avoid disadvantages such as product separation, reactor corrosion and poor catalyst recyclability. The strength and density of the acid sites, the micropores of the carbon catalysts are the key factors which affect the catalytic performance. In addition, the isomerization of glucose to fructose is another important reaction which convert the not very sweet glucose to fructose, the sweetest natural sugars. Glucose is the most abundant monosaccharide available in nature and is the cheapest one. The combination of glucose isomerization with fructose dehydration can make it possible to synthesis DFF from glucose in a one-pot reaction, which can further lower the production cost of DFF. It can be clearly seen that the isomerization of glucose to fructose is a bridge reaction which connects the synthesis of HMF derived chemicals to the conversion of glucose

and even cellulose. This progress is of great practical significance because it can greatly simplify the production process, reduce the energy consumption and lower the production cost.

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Appendix

Journal publications

[1] J. Zhao, Y. Dai, Y. Yan, C. He, Y. Yang*, Selective aerobic oxidation of 5-hydroxymethyl-2-furfural into 2, 5-diformylfuran over V-embedded mesoporous carbon microspheres, (2016-prepared).

[2] J. Zhao, L. Bai, J. Huang, Y. Yan, Y. Yang*, Molybdenum trioxide Supported on Carbon Sphere for One-Step Approach to 2,5-Diformylfuran from Fructose, (2016-prepared).

[3] Y. Yan, K. Li, L. Thia, Y. Dai, J. Zhao, X. Chen, Y. Yang, J.-M. Lee, hydrothermally driven three-dimensional evolution of mesoporous hierarchical europium oxide hydrangea microspheres for non-enzymatic sensors of hydrogen peroxide detection, *Environmental Science: Nano*, (2016).

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