DOI: 10.1002/cssc.201400119



Three-Phase Catalytic System of H₂O, Ionic Liquid, and VOPO₄–SiO₂ Solid Acid for Conversion of Fructose to 5-Hydroxymethylfurfural

Chengcheng Tian,^[a, b] Xiang Zhu,^[a, b] Song-Hai Chai,^{*[b]} Zili Wu,^[b] Andrew Binder,^[c] Suree Brown,^[c] Lin Li,^[c, d] Huimin Luo,^[e] Yanglong Guo,^{*[a]} and Sheng Dai^{*[b, c]}

Efficient transformation of biomass-derived feedstocks to chemicals and fuels remains a daunting challenge in utilizing biomass as alternatives to fossil resources. A three-phase catalytic system, consisting of an aqueous phase, a hydrophobic ionic-liquid phase, and a solid-acid catalyst phase of nanostructured vanadium phosphate and mesostructured cellular foam (VPO–MCF), is developed for efficient conversion of biomass-derived fructose to 5-hydroxymethylfurfural (HMF). HMF is a promising, versatile building block for production of value-added chemicals and transportation fuels. The essence of this three-phase system lies in enabling the isolation of the solid-

acid catalyst from the aqueous phase and regulation of its local environment by using a hydrophobic ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM]-[Tf₂N]). This system significantly inhibits the side reactions of HMF with H₂O and leads to 91 mol% selectivity to HMF at 89% of fructose conversion. The unique three-phase catalytic system opens up an alternative avenue for making solid-acid catalyst systems with controlled and locally regulated microenvironment near catalytically active sites by using a hydrophobic ionic liquid

Introduction

The utilization of abundant, renewable biomass resources for production of carbon-based fuels and chemicals provides a solution for mitigating the growing shortage of fossil resources and environmental pollution, and promotes the development of chemical industry in a sustainable manner. Furan derivatives,

[a]	C. Tian, ⁺ X. Zhu, ⁺ Dr. Y. Guo Key Laboratory for Advanced Materials Research Institute of Industrial Catalysis East China University of Science and Technology Shanghai 200237 (China) E-mail: ylguo@ecust.edu.cn
[b]	C. Tian, ⁺ X. Zhu, ⁺ Dr. SH. Chai, Dr. Z. Wu, Dr. S. Dai Chemical Sciences Division, Oak Ridge National Laboratory Oak Ridge, TN 37831 (USA) E-mail: chais@ornl.gov dais@ornl.gov
[c]	A. Binder, Dr. S. Brown, Dr. L. Li, Dr. S. Dai Department of Chemistry University of Tennessee Knoxville, TN 37996 (USA)
[d]	Dr. L. Li Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education College of Chemistry and Materials Science South-Central University for Nationalities Wuhan, Hubei 430074 (China)
[e]	Dr. H. Luo Energy and Transportation Science Division Oak Ridge National Laboratory Oak Ridge, TN 37831 (USA)
[†]	These authors contributed equally to this work. Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201400119.

such as 5-hydroxymethylfurfural (HMF), are biomass-derived platform molecules that have been identified as versatile intermediates for the production of fine chemicals, pharmaceuticals, plastic resins, and transportation fuels. However, they are not yet produced at an industrial scale due to their high production cost.^[1] The acid-catalyzed dehydration of hexoses such as fructose to produce HMF (Scheme 1) has been extensively studied by using various catalytic systems. The catalytic activity and selectivity for HMF formation depends strongly on the choice of catalysts, reaction media (i.e., solvents), and conditions.

Two categories of catalysts have been explored for the selective dehydration of fructose: (a) homogeneous acids such as mineral acids and soluble metal halides,^[2] and (b) heterogeneous solid acids such as ion-exchange resins,^[3] zeolites,^[3a,4] transition-metal phosphates,^[5] acid-functionalized silica and propylene fibers,^[3b,6] and modified tantalum hydroxide.^[7]. Although the homogeneous acids are inexpensive and highly active catalysts for the dehydration reaction at high temperatures, the large-scale application of this process is complicated due to the high cost of the catalyst recycling, reactor corrosion, and neutralization of the waste. From an environmental and economic point of view, solid-acid catalysts such as H-form zeolites and transition-metal phosphates are more desirable because they are less corrosive and easier to separate and recycle.

Unfortunately, previously reported heterogeneous acidic catalysts suffer from a low HMF yield in aqueous media, resulting from rehydration of HMF with H_2O to form levulinic acid (LA) and formic acid, self-polymerization of HMF, and/or cross-poly-

CHEMSUSCHEM FULL PAPERS



Scheme 1. Reaction Scheme for conversion of fructose to HMF.

merization between HMF and fructose to form insoluble polymers and humins (Scheme 1).^[1a] To enhance the HMF yield, a biphasic solvent system consisting of water and a water-immiscible organic solvent (e.g., primary and secondary alcohols, ketones, cyclic ethers in the C_3 – C_6 range) has been investigated.^[1b] The organic solvent continuously extracts the formed HMF from the aqueous phase in which the catalytic dehydration of fructose proceeds. Consequently, the undesired rehydration of HMF is suppressed to a large extent, increasing the HMF selectivity and yield. Dumesic et al. reported a yield of approximately 70% of HMF from fructose in a biphasic system catalyzed by either hydrochloric acid^[1b] or heterogeneous silica-supported alkylsulfonic acids^[3b].

lonic liquids (ILs) as neoteric solvents have generated much interest in recent years because of their unique properties such as negligible vapor pressure, nonflammability, high thermal and chemical stability, and adjustable solvent power for organic and inorganic substances.^[8] Hydrophilic, water-miscible ILs containing imidazolium-based cations and halogen anions are often used in order to facilitate the dissolution of hexoses and metal halide catalysts.^[2c,9] For example, Zhao et al. studied the catalytic conversion of fructose and glucose into HMF in 1ethyl-3-methylimidazolium chloride ([EMIM]Cl) with various

metal chlorides as catalysts. CrCl₃ appeared to be the most efficient catalyst, leading to a HMF yield of 69% from fructose dehydration at 80 °C after a 3 h reaction.^[2c] Zhang et al. found that the HMF yield was strongly affected by the aggregation of the cations of the ILs (e.g., the imidazolium cations with an alkyl group of less than four carbons) and the hydrogen bonds between the anions of the ILs (e.g., Cl⁻ anion) and fructose.^[9b] However, the use of hydrophilic ILs would lead inevitably to the accumulation of water (either produced during the dehydration reaction or introduced along with the reactants) in the reaction media. The excessive H_2O could lower the HMF selectivity by promoting the secondary reactions of HMF and decrease the overall activity by competitive adsorption with the reactants on the acid sites. This would require an additional operation to remove H_2O from the reaction media, making it less attractive for the practical application of hydrophilic ILs.

Herein, we report a new efficient three-phase catalytic

system (Scheme 2), consisting of aqueous and ionic liquid (IL) phases and solid acid catalyst phase of nanostructured vanadium phosphate and mesostructured cellular foam silica (VPO-MCF), and we apply the system for the production of HMF from fructose. The first key feature of this system is the choice of a hydrophobic ionic liquid, i.e., 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf₂N]), which is denser than water and thus isolates the top aqueous phase from the bottom solid-acid catalyst. Fructose dissolved in the aqueous phase transports continuously into the IL phase through equilibrium partition and subsequently reacts at the IL-catalyst interface. The isolation of the aqueous phase from the solid catalyst significantly enhances the selectivity and yield of HMF, as compared to a typical biphasic system of organic solvent and H₂O in which the catalyst is well dispersed in the aqueous phase and the catalytic dehydration of fructose consequently proceeds at the H₂O-catalyst interface. The enhanced performance due to the use of the H₂O-IL solvent system is attributed, to a large extent, to the inhibition of secondary reactions of HMF with H₂O. To our knowledge, this is the first report that a H₂O-IL biphasic system can act as an efficient solvent system for the selective dehydration of fructose to HMF. The second key feature is the development of the



Scheme 2. Schematic illustration for the synthesis of hybrid VPO–MCF solid acid catalyst and catalytic dehydration of fructose in water–IL–(VPO–MCF) three-phase system.

VPO-MCF hybrid material as a promising heterogeneous solidacid catalyst which can be utilized repeatedly without obvious activity loss for HMF production in the three-phase catalytic system. The VPO-MCF hybrid material, possessing nanosized vanadium phosphate (VPO) crystals coated on the surface of mesostructured cellular foam silica (MCF), was synthesized by an in situ growth method that we developed recently for synthesis of nanoscopic lanthanide phosphates and barium sulfate.^[10] As shown in Scheme 2, vanadium pentoxide (V₂O₅) was incorporated into the mesoporous host of MCF through an impregnation method, followed by phosphatation of V₂O₅ using an organic amphiphilic n-octadecylphosphonic acid as the phosphate source. The phosphate head forms a strong interaction with vanadium ions while the alkyl chain caps on the V₂O₅ surface to prevent the growth and/or sintering of VPO nanocrystals during subsequent calcination. Highly uniform VPO nanocrystals formed during the subsequent high-temperature calcination (550 °C in air) along with decomposition and oxidation of the organic phosphonic acid.

Results and Discussion

The characteristic structure of as-synthesized VPO–MCF was analyzed by a variety of techniques including powder X-ray diffraction (XRD), solid-state ³¹P magic-angle-spinning nuclear magnetic resonance (³¹P MAS-NMR), and Raman and Fourier transform infrared (FTIR) spectroscopies. Figure 1 a shows the XRD patterns of VPO–MCF, VPO, and MCF samples. The broad XRD peak in the range of $2\theta = 18-36^{\circ}$ is attributed to the



Figure 1. (a) Powder XRD patterns of VPO, MCF, and VPO–MCF; (b) solid-state ³¹P MAS-NMR spectrum of VPO–MCF.

amorphous silica. For the VPO–MCF sample, the broad peaks at $2\theta = 12.1$ and 29.0° are indexed to be (001) and (200) planes of lamellar VOPO₄ phase (VOPO₄·2H₂O),^[11] respectively, indicating the presence of nanocrystalline VPO with an average diameter of 5–7 nm as estimated by the X-ray line broadening method. The other peaks of VPO phase in the range of $2\theta = 18-25^{\circ}$ are completely covered by the very broad peak of amorphous silica and thus cannot be observed. The chemical state of phosphate groups in VPO–MCF was probed by solid-state ³¹P MAS-NMR (Figure 1b). The NMR spectrum shows a peak at about -12 ppm and a shoulder at about -22 ppm, corresponding to the phosphorus species in P–O–V bonds.

The broad signal around -38 ppm could be related to phosphorus species bound to silicon atoms of the MCF support through oxygen bridges (P–O–Si).^[12] Further characterization of the synthesized VPO-MCF was performed by Raman and FTIR spectroscopies. From Figure S1, VPO-MCF shows the same well-resolved Raman bands as pure VPO. The major band at 955 cm⁻¹ can be attributed to ν (as) P–O–P in the PO₄^{3–} unit of VOPO₄ phase, the bands at 992 and 1034 cm⁻¹ further indicate the presence of V⁵⁺-containing species in large proportion.^[13] Figure S2 shows the FTIR spectra of VPO, MCF, and VPO-MCF. For the VPO sample, the bands between 990 and 940 cm⁻¹ correspond to ν (V=O) or ν (V–OH), and the band at 670 cm⁻¹ is assigned to δ (V–OH) or δ (P-OH).^[14] The spectrum of VPO-MCF sample shows a clear vibration peak at 670 cm⁻¹ attributed to δ (V–OH) or δ (P–OH) of the VOPO₄ phase and a Si-OH band of MCF at around 970 cm⁻¹. This indicates the coexistence of VOPO₄ and SiO₂ phases, in agreement with the XRD result shown in Figure 1a.

The textural properties of as-synthesized VPO–MCF were characterized by nitrogen sorption at -196 °C. Figure 2 shows the adsorption–desorption isotherms and the pore-size distribution of MCF and VPO–MCF. Both MCF and VPO–MCF samples show type IV isotherms, and the hysteresis loop of the sorption isotherms suggests "ink-bottle" pores with narrower windows (bottle necks) and larger spherical cells (bottles).^[10] The VPO–MCF retains the characteristic mesopore structure of the MCF support, although the pore diameter of VPO–MCF (window size of ≈ 8 nm and cell size of ≈ 21 nm, Figure 2b) decreased by approximately 2 nm due to the coating of VPO

on the MCF surface. The results indicate that no bulk VPO crystals were formed to block the pores of MCF, and VPO nanocrystals were well dispersed on the surfaces of MCF. The use of the organic ODPA surfactant as the phosphate source is the key to controlling the nanocrystal size of VPO and ensuring the conformal growth of VPO on the wall of MCF. The alkane phosphonate can react with vanadium species highly dispersed on the surface of MCF to form vanadium phosphonate micelles

through a strong electrostatic interaction, as demonstrated in the previous study for synthesis of nanoscopic $BaSO_4\text{-}MCF$ hybrid materials. $^{[10b]}$

Microscopic investigation by scanning transmission electron microscopy (STEM) offers a direct visual evidence for the conformal formation of VPO nanocrystals on the MCF support, and a high-angle annular dark-field detector coupled with STEM can provide a higher contrast for heavy elements in a low atomic number matrix as compared to conventional brightfield images. Figure 3 presents representative STEM images of VPO–MCF sample under bright and dark fields. The dark-field image (Figure 3 b) shows a uniform distribution of VPO as

^{© 2014} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 2. Nitrogen adsorption-desorption isotherms and pore size distributions of MCF and VPO-MCF.



providing general information about the amount and strength distribution of acid sites, and FTIR spectroscopy of pyridine adsorption, probing the nature (Brønsted- or Lewis-type) of acid sites. Figure 4 shows NH₃-TPD profiles of MCF and VPO-MCF in the temperature range of 100-500 °C. According to the temperature regions of NH₃ desorption, the strength of solid acid sites are formally classified as weak moderate (<250°C), (250 -400 °C), and strong (>400 °C).^[15] As expected, the MCF (SiO₂) sup-

Figure 3. STEM images of VPO–MCF under (a) bright and (b) dark fields. VPO nanocrystals are indicated by black arrows.

a bright coating on the silica wall. The wall of VPO-MCF exhibits a much higher contrast (indicated by the black arrows in Figure 3b) which can be attributed to the much heavier atomic weight of V compared to that of Si. No isolated large nanoparticles of VPO were observed inside the pores, which was consistent with XRD analysis (Figure 3 a). The above results suggest that VPO nanocrystals grow in the form of thin layered nanostructures along the wall of MCF. This is the reason why the pore size of VPO-MCF is slightly smaller than that of the MCF support after the formation of the VPO conformal nanoparticle coating. An energy dispersive X-ray (EDX) element mapping of VPO-MCF (Figure S3) measurement shows uniform X-ray intensities of V, P, and Si signals throughout the mesoporous particles, revealing the existence of a homogeneous distribution of multiple components. As measured by EDX analysis, the V-loading of VPO–MCF is \sim 11.3 wt%, and the atomic ratio of V to P is close to 1:1. The above structural characterizations by a couple of combined techniques indicate that VPO-MCF is composed of uniform vanadium phosphate nanocrystals coated conformably on the mesoporous MCF support.

The acid property of VPO-MCF sample was investigated by temperature-programmed desorption of ammonia (NH₃-TPD),

port exhibits a negligible peak of NH_3 desorption due to its extremely weak acidity. The NH_3 -TPD profile of VPO-MCF features a main desorption peak at 160 °C, corresponding to the weak acid sites, and a shoulder peak between 300-350 °C, corresponding to the moderate acid sites. The total acid amount of VPO-MCF, estimated from the amount of desorbed NH_3 , is



Figure 4. NH₃-TPD profiles of MCF and VPO–MCF.

ChemSusChem 0000, 00, 1-8

^{© 2014} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 5. (a) FTIR spectra of pyridine adsorbed on MCF and VPO–MCF catalysts after thermal treatment of the pyridine-adsorbed samples at elevated temperatures; (b) variation in the integrated areas of IR bands at 1448 (Lewis acid sites) and 1548 cm⁻¹ (Brønsted acid sites) as a function of the temperature of thermal treatment.

0.65 mmolg⁻¹, most of which is contributed by the acid sites of weak and moderate strength. There is a minor amount of NH_3 desorbed from VPO-MCF above 400 °C (Figure 4), implying the presence of strong acid sites.

The IR spectra (Figure 5) of pyridine adsorbed on MCF and VPO-MCF were recorded at room temperature (22°C) after thermal desorption of adsorbed pyridine- at different temperatures (up to 400 $^{\circ}$ C) in a helium flow. Consistent with the NH₃-TPD analysis, the featureless IR spectrum of pyridine adsorption on MCF indicates the poor acidity of the MCF support. Two types of adsorbed pyridine species were observed on the VPO-MCF catalyst: a pyridine protonated on Brønsted acid sites (the band at 1548 cm⁻¹) and a covalently bound species on Lewis acid sites (the band at 1448 cm⁻¹).^[14] The individual amount of Brønsted and Lewis acid sites can be quasi-quantitatively estimated by the integrated area of their corresponding IR bands. As shown in Figure 5b, the band area related to Brønsted acid sites (1548 cm⁻¹) decreases continuously on increasing the treatment temperature of the pyridine-adsorbed VPO-MCF from 22 to 400 °C, due to the desorption of pyridine adsorbed on the acid sites of weak and moderate strength as defined in the NH₃-TPD measurement (Figure 4). The IR band at 1548 cm⁻¹ is still discernible after the thermal treatment at 400 °C, suggesting the presence of strong Brønsted acid sites. In contrast, the area of the band corresponding to Lewis acid sites (1448 cm⁻¹) was less than 20% the area of the band corresponding to Brønsted acid sites when the sample was thermally treated at the same temperature, and completely disappeared after the treatment at 350 °C. This indicates that the Brønsted acidity of VPO-MCF is much larger in quantity and stronger in strength than its Lewis acidity. The above acidity characterization by of pyridine adsorption by means of NH₃-TPD and IR suggests that the VPO-MCF mesoporous material is dominated by Brønsted acid sites of weak and moderate strength along with a small fraction of strong Brønsted and weak/moderate Lewis acid sites. As observed on other acidic metal phosphates such as ZrPO₄ and NbOPO₄, surface hydrogen phosphate species (e.g., P-OH groups) are presumably responsible for the Brønsted acidity of VPO-MCF, while the Lewis acidity is related to the vanadium ions that are attached to phosphate groups (–V–O–P–) and/or coordinatively unsaturated.^[5b,14] The characteristic acidity of VPO–MCF makes it a promising heterogeneous acid catalyst for the fructose dehydration to HMF, given that Brønsted acid sites have been widely accepted as catalytically active sites for the dehydration reaction.^[16]

The catalytic performance of as-synthesized VPO–MCF solid acid catalyst for fructose dehydration to HMF was explored at 120°C in a specifically designed three-phase system consisting of H₂O, ionic liquid, and solid acid

catalyst (Scheme 2), in which a water-immiscible phase of imidazolium-based ionic liquid ($[BMIM][Tf_2N]$) lies between the top aqueous phase and the bottom solid-acid catalyst to fully isolate them from each other. As demonstrated in Figure 6,



Figure 6. Catalytic performance of VPO–MCF for fructose dehydration as a function of reaction time. Reaction conditions: 0.10 g catalyst, 0.23 g fructose, 3.5 g $H_2O/[BMIM][Tf_2N]$ (wt/wt of 1:6), 120 °C.

both fructose conversion and HMF yield over VPO-MCF increase continuously with the reaction time, while HMF selectivity increases in the initial 8 h from 67 to 88 mol% and then becomes stable. After reaction for 20 h, fructose conversion of 89 mol% was obtained along with HMF selectivity of 91 mol%. In Table S1, the VPO-MCF catalyst in the H₂O-IL system for fructose dehydration to HMF is compared under similar reaction conditions (80-200 °C, 1.9-10 wt% fructose, and 0.2-3.8 wt% catalysts) with other representative catalytic systems reported previously. At similar conversion levels (75-100%), our H₂O-IL-(VPO-MCF) three-phase system exhibits the best HMF selectivity (~90 mol%) among those reported for both homogeneous (e.g., mineral acids and metal chlorides) and heterogeneous acid catalysts (e.g., ion-exchange resins, zeolites, acid-functionalized metal oxides, and transition-metal phosphates) dissolved/dispersed in single-phase (e.g., H₂O, hydrophilic ILs, and DMSO) and/or biphasic (e.g., MIBK-H₂O and (MIBK/2-BuOH)-H₂O) solvents.

www.chemsuschem.org

^{© 2014} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1. Catalytic performance of VPO–MCF for fructose dehydration. ^[a]									
Solvent	X [%] ^[b]	S [ma HMF	l %] ^[c] LA	Y [mol %] ^[d]	Rate $[mmol h^{-1} g_{cat}^{-1}]^{[e]}$				
H ₂ O-[BMIM][Tf ₂ N] H ₂ O [BMIM][Tf ₂ N]	76 76 33	88 13 38	8.9 33 16	67 10 13	1.07 0.16 0.20				
[a] Reaction conditions: 0.10 g catalyst, 0.23 g fructose, 3.5 g solvent ($H_2O/[BMIM][Tf_2N] = 1:6$ wt/wt), 120 °C, and reaction time of 8 h. [b] Fructose conversion. [c] Product selectivity. [d] HMF yield. [e] Formation rate of HMF.									

For comparison with the H₂O-[BMIM][Tf₂N] system, VPO-MCF was tested for the dehydration reaction of fructose in individual H₂O and [BMIM][Tf₂N] solvents. As shown in Table 1, the use of H₂O as solvent has little effect on the fructose conversion, but significantly reduces the HMF selectivity to only 13 mol %. The undesired LA was produced in the H₂O solvent system with a much higher selectivity (33 vs. 8.9 mol%) in comparison with the H₂O-IL system. The HMF yield (67 mol%) and formation rate (1.07 mmol $h^{-1}g_{cat}^{-1}$) in the H₂O–IL system after 8 h reaction are almost seven times of those obtained in H₂O, indicating that isolation of the solid-acid catalyst from the aqueous phase is the key to achieving high activity for the selective production of HMF from fructose. The catalytic activity of VPO-MCF in the [BMIM][Tf₂N] solvent is approximately 43% of that in the H₂O and H₂O-IL systems, along with medium selectivities for HMF (38 mol%) and LA (16 mol%). In addition, there was a considerable amount of insoluble humin-like heavy products observed in the reaction media and on the catalvst surface.

Both the VPO–MCF catalyst and [BMIM][Tf₂N] (HMF dissolved in the IL phase was removed by extraction using ethyl acetate^[9b]) were recycled for the fructose dehydration reaction at 120 °C in order to test the stability of this catalytic system (Table 2). The HMF yield after 4 h reaction is maintained at approximately 48% after the catalyst is recycled five times, suggesting an excellent stability of the VPO–MCF catalyst for HMF production. This indicates that the environmental friendly H₂O–ionic liquid–(VPO–MCF) three-phase catalytic system is catalytically active and stable. The use of this unique system could open up a new possibility for efficient HMF production.

Table 2. Catalytic performance of VPO–MCF catalyst during recycling for HMF production from fructose. ^[a]								
	X [%] ^[b]	S [mol%] ^[c]	Y [mol%] ^[d]					
Run 1	68	74	50					
Run 2	64	72	46					
Run 3	66	74	49					
Run 4	65	74	48					
Run 5	66	73	48					
[a] Reaction conditions: 0.10 g catalyst, 0.23 g fructose, 3.5 g solvent $(H_2O/[BMIM][Tf_2N] = 1:6 \text{ wt/wt})$, 120 °C, and reaction time of 4 h. [b] Fructose conversion. [c] HMF selectivity. [d] HMF yield.								

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Note that fructose has very poor solubility in the hydrophobic IL ([BMIM][Tf₂N]), and the undissolved fructose was melted at the reaction temperature (120°C) and suspended as small liquid droplets in the IL phase. A large amount of insoluble humin-like heavy products were produced, darkening the catalyst and reaction media when only pre-dried IL was used (see Table 1). This was probably caused by reaction of the fructose liquid droplets over the VPO-MCF catalyst. Those heavy products deposited on the catalyst surface could result in the catalyst deactivation by blocking the active sites, consequently leading to much lower fructose conversion and HMF yield compared to the H₂O-IL biphasic solvent system as shown in Table 1. When using H₂O-IL (wt/wt of 1:6) system, the reaction media was visibly clear without any insoluble reactant or reaction products observed. It is interesting that an appreciable amount of H_2O (\approx 1.1 wt%, measured by Carl Fischer titration method) was found in the IL phase, which greatly improved the dissolution of fructose. The initial concentration of fructose in the IL phase was measured to be 0.045 g g⁻¹IL $(0.19 \text{ gg}^{-1}\text{H}_2\text{O} \text{ in the aqueous phase})$ when adding 0.23 g fructose in 3.5 g H₂O–IL solvent (H₂O/IL = 1:6 wt/wt). We also investigated H₂O-saturated IL as a single-phase solvent for fructose dehydration under the same reaction conditions, but the reactant could still not be fully dissolved. Therefore, to convert fructose efficiently to HMF, the solvents of H₂O and IL need to work in a synergistic way that so the aqueous phase is responsible for the dissolution of fructose and subsequent partitioning of reactant to the IL phase in which fructose undergoes a dehydration reaction on the surface of solid acid catalyst. The isolation of solid acid catalyst from the aqueous phase can reduce, to a great extent, the negative effect of excessive H₂O on the selectivity and yield to HMF.

Conclusions

A novel three-phase catalytic system, consisting of an aqueous phase, a hydrophobic ionic-liquid phase, and a solid-acid catalyst phase of nanostructured vanadium phosphate and mesostructured cellular foam (VPO-MCF) was developed for efficient conversion of biomass-derived fructose to HMF. The essence of this three-phase system lies in enabling the isolation and the solid-acid catalyst from the aqueous phase and the regulation of its local environment by using a hydrophobic ionic liquid ([BMIM][Tf₂N]). This system significantly inhibits the side reactions of HMF with H₂O and leading to 91 mol% selectivity to HMF at 89% of fructose conversion. The VPO-MCF hybrid material, prepared by an in situ growth method using an organic alkane phosphonic acid (n-octadecylphosphonic acid, ODPA) as the phosphate source, is characterized by Brønsted acidity of weak and moderate strength endowed by VPO nanocrystals coated on a high-surface-area mesoporous silica support. The unique three-phase catalytic system opens up an alternative avenue for making solid-acid catalyst systems with controlled and locally regulated microenvironment near catalytically active sites by using a hydrophobic ionic liquid, and provides insights for developing efficient heterogeneous catalysts for the HMF production.

Experimental Section

The VPO-MCF hybrid materials were prepared by an in situ growth method.^[10] First, mesostructured cellular foam silica (MCF) was synthesized as described by Schmidt-Winkel and co-workers.^[17] NH₄VO₃ was selected as the vanadium precursor and incorporated into a MCF framework using a solvent evaporation method. Briefly, the prepared MCF (0.3 g) was added into deionized water containing the vanadium precursor (0.07 g). The mixture was stirred at 40 °C for 3 h, and then the temperature was increased to 80 °C to completely evaporate water in the vacuum. The product (V-MCF) was calcined at 350 °C for 3 h. Secondly, the prepared V-MCF (0.3 g) and a certain amount of *n*-octadecylphosphonic acid (V/P molar ratio = 1) as the phosphate source were refluxed in 20 mL ethanol for 16 h. The suspension was washed several times with ethanol and acetone by centrifugation, and the obtained precipitate was dried overnight at 80 °C and subsequently calcined in air at 550°C for 3 h to obtain VPO-MCF. The bulk VPO sample was prepared for a comparative purpose as described in the literature.^[18] Typically, V_2O_5 (5.0 g) and H_3PO_4 (30 mL, 85%) were refluxed in deionized water (120 mL) for 16 h. A yellow solid was recovered by centrifugation, washed with distilled water (100 mL) and acetone (100 mL), and dried in air at 80 °C overnight. Catalytic dehydration of fructose to HMF was conducted at 120 $^\circ\text{C}$ in a 25 mL round-bottom flask by using 0.1 g catalyst, 0.23 g fructose, and 3.5 g solvent consisting of deionized H₂O and ionic liquid ([BMIM]-[Tf₂N]) (H₂O/[BMIM][Tf₂N] = 1/6 in weight). Detailed procedures for catalyst characterization and catalytic dehydration of fructose are provided in the Supporting Information.

Acknowledgements

This work was funded from the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, US Department of Energy, under Contract No. De-AC05-000R22725 with Oak Ridge National Laboratory managed and operated by UT-Battelle, LLC. The DRIFTS experiment was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Science, US Department of Energy. CCT and YLG also gratefully acknowledge the National Basic Research Program of China (2010CB732300, 2013CB933201), Program for New Century Excellent Talents in University (NCET-09-0343), the Shu Guang Project (10SG30), and 111 Project (B08021).

Keywords: 5-hydroxymethylfurfural · biomass · fructose · ionic liquids · solid acid catalysts · vanadium phosphate

- a) R. J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.* **2013**, *113*, 1499–1597; b) Y. Román-Leshkov, J. N. Chheda, J. A. Dumesic, *Science* **2006**, *312*, 1933–1937.
- [2] a) G. Yong, Y. Zhang, J. Y. Ying, Angew. Chem. Int. Ed. 2008, 47, 9345–9348; Angew. Chem. 2008, 120, 9485–9488; b) T. Thananatthanachon, T. B. Rauchfuss, Angew. Chem. Int. Ed. 2010, 49, 6616–6618; Angew. Chem. 2010, 122, 6766–6768; c) H. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, Science 2007, 316, 1597–1600; d) T. Deng, X. Cui, Y. Qi, Y. Wang, X. Hou, Y. Zhu, Chem. Commun. 2012, 48, 5494–5496; e) J. N. Chheda, Y. Roman-Leshkov, J. A. Dumesic, Green Chem. 2007, 9, 342–350.
- [3] a) K. Shimizu, R. Uozumi, A. Satsuma, *Catal. Commun.* 2009, *10*, 1849–1853; b) A. J. Crisci, M. H. Tucker, M.-Y. Lee, S. G. Jang, J. A. Dumesic, S. L. Scott, *ACS Catal.* 2011, *1*, 719–728.
- [4] a) V. V. Ordomsky, J. van der Schaaf, J. C. Schouten, T. A. Nijhuis, *J. Catal.* **2012**, 287, 68–75; b) E. Nikolla, Y. Roman-Leshkov, M. Moliner, M. E. Davis, ACS Catal. **2011**, *1*, 408–410.
- [5] a) F. Benvenuti, C. Carlini, P. Patrono, A. M. R. Galletti, G. Sbrana, M. A. Massucci, P. Galli, *Appl. Catal. A* **2000**, *193*, 147–153; b) V. V. Ordomsky, J. van der Schaaf, J. C. Schouten, T. A. Nijhuis, *ChemSusChem* **2012**, *5*, 1812–1819.
- [6] a) C. Tian, C. Bao, A. Binder, Z. Zhu, B. Hu, Y. Guo, B. Zhao, S. Dai, *Chem. Commun.* 2013, *49*, 8668–8670; b) C. Tian, Y. Oyola, K. M. Nelson, S.-H. Chai, X. Zhu, J. C. Bauer, C. J. Janke, S. Brown, Y. Guo, S. Dai, *RSC Adv.* 2013, *3*, 21242–21246.
- [7] F. Yang, Q. Liu, M. Yue, X. Bai, Y. Du, Chem. Commun. 2011, 47, 4469– 4471.
- [8] a) P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 2000, 39, 3772–3789;
 Angew. Chem. 2000, 112, 3926–3945; b) A. Riisagera, R. Fehrmanna, M. Haumannb, P. Wasserscheid, Top. Catal. 2006, 40, 91–102; c) X. Sun, H. Luo, S. Dai, Chem. Rev. 2012, 112, 2100–2128.
- [9] a) M. E. Zakrzewska, E. Bogel-Łukasik, R. Bogel-Łukasik, *Chem. Rev.* 2011, 111, 397–417; b) C. Shi, Y. Zhao, J. Xin, J. Wang, X. Lu, X. Zhang, S. Zhang, *Chem. Commun.* 2012, 48, 4103–4105.
- [10] a) C. Tian, S.-H. Chai, X. Zhu, Z. Wu, A. Binder, J. C. Bauer, S. Brwon, M. Chi, G. M. Veith, Y. Guo, S. Dai, *J. Mater. Chem.* **2012**, *22*, 25227–25235; b) C. Tian, S.-H. Chai, D. R. Mullins, X. Zhu, A. Binder, Y. Guo, S. Dai, *Chem. Commun.* **2013**, *49*, 3464–3466.
- [11] F. Wang, J. L. Dubois, W. Ueda, J. Catal. 2009, 268, 260-267.
- [12] J. Frey, C. Lieder, T. Schölkopf, T. Schleid, U. Nieken, E. Klemm, M. Hunger, J. Catal. 2010, 272, 131–139.
- [13] a) X.-K. Li, W.-J. Ji, J. Zhao, Z.-B. Zhang, C.-T. Au, *J. Catal.* 2006, *238*, 232–241; b) F. Ben Abdelouahab, R. Olier, N. Guilhaume, F. Lefebvre, J. C. Volta, *J. Catal.* 1992, *134*, 151–167.
- [14] V. V. Ordomsky, V. L. Sushkevich, J. C. Schouten, J. van der Schaaf, T. A. Nijhuis, J. Catal. 2013, 300, 37–46.
- [15] E. Dumitriu, V. Hulea, J. Catal. 2003, 218, 249-257.
- [16] V. Choudhary, S. H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N. S. Marinkovic, A. I. Frenkel, S. I. Sandler, D. G. Vlachos, J. Am. Chem. Soc. 2013, 135, 3997–4006.
- [17] a) P. Schmidt-Winkel, W. W. Lukens, D. Zhao, P. Yang, B. F. Chmelka, G. D. Stucky, J. Am. Chem. Soc. 1999, 121, 254–255; b) P. Schmidt-Winkel, W. W. Lukens, P. D. Yang, D. I. Margolese, J. S. Lettow, J. Y. Ying, G. D. Stucky, Chem. Mater. 2000, 12, 686–696.
- [18] G. C. Behera, K. M. Parida, D. P. Das, J. Catal. 2012, 289, 190-198.

Received: January 23, 2014 Published online on

FULL PAPERS

C. Tian, X. Zhu, S.-H. Chai,* Z. Wu, A. Binder, S. Brown, L. Li, H. Luo, Y. Guo,* S. Dai*

☐ Three-Phase Catalytic System of H₂O, Ionic Liquid, and VOPO₄-SiO₂ Solid Acid for Conversion of Fructose to 5-Hydroxymethylfurfural



Set phases to stun! A three-phase catalytic system, consisting of an aqueous phase, a hydrophobic ionic-liquid phase, and a solid-acid catalyst phase of nanostructured vanadium phosphate and mesostructured cellular foam is developed for efficient conversion of biomass-derived fructose to 5-hydroxymethylfurfural. This unique three-phase catalytic system opens up an alternative avenue for making solid-acid catalyst systems with controlled microenvironment.