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## Fructose Dehydration to 5-Hydroxymethylfurfural over Solid Acid Catalysts in a Biphasic System

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Different acidic heterogeneous catalysts like alumina, aluminosilicate, zirconium phosphate, niobic acid, ion-exchange resin Amberlyst-15, and zeolite MOR have been studied in fructose dehydration to 5-hydroxymethylfurfural (HMF). The acidity of these materials was characterized using temperature-programmed desorption of NH<sub>3</sub> and IR spectroscopy of adsorbed pyridine. The nature and strength of acid sites was shown to play a crucial role in the selectivity towards HMF. Brønsted acid sites in the case of zeolites and ion-exchange resin led to high selectivities in the dehydration of fructose with an increase in selectivity with the addition of an organic phase. Lewis acidity in the case of phosphate and oxides resulted in the intensive production of humins from fructose at the initial stages of the process, whereas organic phase addition did not affect selectivity.

## Introduction

Over the last few years the dehydration of carbohydrates to 5hydroxymethylfurfural (HMF) has attracted increasing attention due to its possible application as a substitute for petroleumbased building blocks.<sup>[1]</sup> HMF and its derivatives can be applied as platform chemicals, precursors for polymers, fuels, or solvents.<sup>[2]</sup>

Different heterogeneous and homogeneous catalysts have been applied for this reaction, such as mineral acids,<sup>[3,4]</sup> ion exchange resins,<sup>[5–7]</sup> oxides,<sup>[8,9]</sup> phosphates,<sup>[10,11]</sup> and zeolites.<sup>[12,13]</sup> It was shown that water as a reaction medium promotes the rehydration of HMF resulting in the formation of acids and polymeric products.<sup>[14]</sup> Dumesic and Roman-Leshkov<sup>[15]</sup> investigated the organic phase effect on the dehydration of fructose in a biphasic system. Addition of solvents like 2-butanol or methyl isobutyl ketone (MIBK), which extracted HMF from the reaction mixture, was shown to increase HMF selectivity. It was reported that 80% selectivity could be achieved over HCl in the presence of an organic phase.<sup>[15]</sup>

Heterogeneous catalysts offer several advantages over dissolved homogeneous acid catalysts, (e.g., easy separation of product, reusability of catalyst, and no corrosion of equipment), which makes them more suitable for industrial applications. Currently, several heterogeneous catalytic systems are described in the literature for sugar dehydration with the addition of an organic phase. Moreau et al. studied the dehydration of fructose in the presence of zeolites at 438 K in MIBK/water (5:1 v/v).<sup>[12]</sup> The highest selectivity (90%) is observed over dealuminated mordenite and is attributed to its 2D structure and absence of cavities.<sup>[13]</sup> Chheda and Dumesic<sup>[16]</sup> showed that good yields of HMF from fructose were achieved over Diaion PK216 in MIBK/water by modification of the aqueous phase with DMSO or N-methyl-2-pyrrolidone (NMP). Yang et al. studied sugar dehydration in the biphasic system water/butanol over niobium and tantalum hydroxides.[17,18] Synthesis of HMF from carbohydrates over tin-beta zeolite was reported in water/THF by the group of Davis.<sup>[19]</sup> However, explanations regarding the effect of organic phase addition to catalytic systems were not presented.

In our previous study the effect of organic phase addition during fructose dehydration over zeolites was due to the presence of strong Brønsted acid sites interacting with MIBK.<sup>[20]</sup> Herein, we present the results of a comprehensive study of different acidic heterogeneous systems in the dehydration of fructose with and without the presence of an organic phase.

## **Results and Discussion**

#### Physicochemical properties of catalysts

The acidity of solid catalysts was characterized by IR analysis of adsorbed pyridine (Py) and temperature-programmed desorption (TPD) of  $NH_3$ . IR spectra recorded before and after the adsorption of Py in the region of OH groups and the Py region are presented in Figure 1.

Zirconium phosphate exhibits an intense band at 3665 cm<sup>-1</sup> and a weak band at 3760 cm<sup>-1</sup>, which is attributed to PO–H and ZrO–H vibrations.<sup>[22]</sup> Py adsorption results in the disappearance of the 3760 cm<sup>-1</sup> band and a significant decrease of the band at 3665 cm<sup>-1</sup>. Chemically adsorbed Py is usually revealed by bands at 1545 and 1636 cm<sup>-1</sup> assigned to the pyridinium ion (PyH<sup>+</sup>), two bands at 1454 and 1622 cm<sup>-1</sup> related to coordinately adsorbed Py, and the superposition of signals of species adsorbed on Lewis and Brønsted acid sites at

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1



Figure 1. FTIR spectra of dehydrated catalysts observed before and after adsorption of pyridine.

1491 cm<sup>-1</sup>. Scheme 1 depicts the presence of a reasonable amount of geminal P(OH)<sub>2</sub> groups which are responsible for



Scheme 1. Acid sites of zirco-

nium phosphate.

2

Brønsted acidity in the sample.<sup>[23]</sup> Zirconium atoms in the structure of zirconium phosphate form Lewis acid sites for Py adsorption (Figure 1).

Free niobic acid has the composition  $H_8Nb_6O_{19}$  with eight protons above eight faces of the octahedron formed by six Nb atoms.[24]

Heating niobic acid at 573 K leads to partial dehydration of the catalyst with the removal of the intense bands at 3400 and

1600 cm<sup>-1</sup> assigned to water (Figure 1).<sup>[24]</sup> molecules After evacuation at 573 K niobic acid gives only a weak band at 3710 cm<sup>-1</sup>, which might be assigned to surface hydroxyl groups on partially decomposed niobic acid.<sup>[25]</sup> Py adsorption leads to neutralization of the band at 3710 cm<sup>-1</sup> with the appearance of the broad band of the pyridinium ion at 1545 cm<sup>-1</sup> intense and an band at 1454 cm<sup>-1</sup>. Tanabe<sup>[24]</sup> showed

Table 1. Properties of catalysts. Surface area TPD NH<sub>3</sub> Py adsorption Adsorption Sample Pore  $[\mu mol g^{-1}]^{[a]}$  $[m^2 g^{-1}]$ size [Å]  $[\mu mol g^{-1}]$  $[mmol g^{-1}]$ В HMF L/B Fructose L SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> 2 0.100 327 95 12 28 56 0.052 Al<sub>2</sub>O<sub>3</sub> 262 98 72 135 0.44 0.012 2 ZrPO, 85 45 0.010 93 111 92 0.17 108 27 0.005 Nb<sub>2</sub>O<sub>5</sub> 80 242 11 2.4 0.58 5-7.5 MOR 420 1100 229 42 0.2 0.008 0.05 53<sup>[b]</sup> 4700<sup>[b]</sup> Amberlyst-15 300<sup>[b]</sup> 0.013 0.19 [a] B: Brønsted acidity, L: Lewis acidity. [b] Parameters are taken from the technical data of the product.

that the Brønsted and Lewis acid bands turn into each other during dehydration or saturation of the sample with water.<sup>[24]</sup> Dehydration of alumina leads to the appearance of the usual set of bands at 3770, 3752, 3730, and 3675 cm<sup>-1</sup>

(Figure 1). According to the literature these hydroxyl bands are associated with hydroxyl groups of Al atoms with different coordination numbers.<sup>[26]</sup> Py adsorption does not significantly change the intensity of hydroxyl peaks due to their weak creases in the order:  $MOR > ZrPO_4 \approx SiO_2 - Al_2O_3 > Nb_2O_5 > Al_2O_3$ . Amberlyst-15 should have the highest contribution of Brønsted acidity due to the absence of Lewis acid sites in sulfated polystyrene.

The strength of acid sites might be determined by analysis of spectra of NH<sub>3</sub> TPD (Figure 2). MOR zeolite has the highest strength of acid sites with desorption of NH<sub>3</sub> up to 1000 K. Results of Py adsorption indicate that desorption proceeds

Brønsted acidity. An intense band at 1622 cm<sup>-1</sup> and a broad band at 1450 cm<sup>-1</sup> indicate Lewis acid sites with different acid strengths on the surface of the catalyst.[27]

The spectrum of activated amorphous aluminosilicate (Figure 1) shows an intense line of SiOH groups at 3740 cm<sup>-1</sup> and a broad band of hydrogen-bonded hydroxyl groups at 3600 cm<sup>-1</sup>. However, there is no band attributed to isolated bridging Al(OH)Si groups. Py adsorption leads to a small decrease of the band of silanol groups with the appearance of the weak band of PyH<sup>+</sup>. This was explained earlier by an inductive effect of the Al atom in the structure of amorphous aluminosilicate leading to an increase in the acidity of silanol groups.[28] Lewis acidity in the sample stems from octahedral and tetrahedral Al<sup>3+</sup> sites.

Mordenite (MOR) zeolite demonstrates five different bands of hydroxyl group vibrations (Figure 1). Bands at 3745 and 3730 cm<sup>-1</sup> correspond to external and internal silanol groups, respectively.<sup>[29]</sup> The band at 3606 cm<sup>-1</sup> is due to bridging hydroxyl groups.

A broad shoulder at about 3690 cm<sup>-1</sup> is usually ascribed to OH groups attached to extraframework AI species.<sup>[30]</sup> A very broad band at about 3510 cm<sup>-1</sup> is assigned to SiOH groups interacting through hydrogen bonds with bridging hydroxyl groups or other silanol groups.<sup>[30]</sup> Adsorption of Py results in the disappearance of the band of bridging hydroxyl groups and the appearance of the intense bands assigned to the pyridinium ion. Lewis acidity in MOR zeolite appears due to the partial destruction of the zeolite structure.

The concentration of Brønsted (B) and Lewis (L) acid sites are calculated based on published extinction coefficients for the bands at 1545 and 1454 cm<sup>-1.[31]</sup> The results given in Table 1 suggest that the contribution of Brønsted acidity de-

ChemSusChem 0000, 00, 1-9



Figure 2. TPD NH<sub>3</sub> profiles for catalysts.

from the Brønsted acid sites. The amount of desorbed NH<sub>3</sub> (Table 1) and the strength of acid sites (Figure 2) decrease for oxides and phosphate in the order: Nb<sub>2</sub>O<sub>5</sub> > ZrPO<sub>4</sub> > Al<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. This order corresponds to the decrease of electronegativity of the metals and of the acidity of the oxides.<sup>[32]</sup> The strength of Brønsted and Lewis acidity should simultaneously decrease in this order.

The chosen catalysts possess different acidic properties, a fact which allows us to study the influence of acidity on fructose dehydration.

#### Dehydration of fructose

Figure 3 and 4 show the conversion of fructose and the selectivity for HMF and acids versus fructose conversion during the dehydration of fructose in an aqueous solution over different heterogeneous catalysts. The only products detected in all experiments were formic acid, levulinic acid, and furfural. The selectivity towards furfural did not exceed 1 mol% and therefore we did not investigate its formation further. The appearance of furfural was explained previously by a fast reverse aldol cleavage of carbohydrates.<sup>[33]</sup> Formic and levulinic acids were the products of HMF rehydration over acidic catalysts.<sup>[34]</sup> The main byproducts in the reaction were polymeric humins, which were not observed in HPLC analyses.

Catalytic activity in the dehydration of fructose (over heterogeneous catalysts) at 408 K decreases in the order: Nb<sub>2</sub>O<sub>5</sub> > ZrPO<sub>4</sub> > Amberlyst-15 > Al<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> > MOR. The high activity over catalysts having mainly Lewis acid sites (Figure 1) indicates that the reaction proceeds over Brønsted and Lewis acid sites of these heterogeneous catalysts. Notably, activity in the transformation of fructose correlates with the strength of the Lewis acid sites of the heterogeneous catalysts as follows: Nb<sub>2</sub>O<sub>5</sub> > ZrPO<sub>4</sub> > Al<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (Figure 2). The activity of Amberlyst-15 is comparable with the activity of Lewis acid catalysts, whereas MOR zeolite demonstrates the lowest fructose



**Figure 3.** a) Fructose conversion versus time; b) selectivity to HMF versus fructose conversion over catalysts. Reaction conditions: catalyst (4 g), fructose (20 g), water (300 mL), 408 K.



Figure 4. Selectivity for acids versus fructose conversion over catalysts. Reaction conditions: catalyst (4 g), fructose (20 g), water (300 mL), 408 K.

conversion, in spite of the high amount of acid sites (Figure 1, Table 1). This fact may be explained by serious diffusion limitations for fructose inside the zeolite's narrow pores (Table 1). Zeolite activity was high at 438 K.<sup>[12]</sup> All other catalytic systems have pores larger than 8 nm.

HMF selectivity (about 60%) is highest for catalysts with Brønsted acid sites such as Amberlyst-15 and MOR zeolite. Catalytic systems containing both Lewis and Brønsted acid sites like aluminosilicate, niobic acid, and zirconium phosphate show selectivity in the range 25–30%. The lowest selectivity (2–17%) was observed over alumina. Results indicate a decrease in selectivity towards HMF with an increase in Lewis acidity contribution and high selectivity over catalysts with Brønsted acidity. The strength of Brønsted acid sites also plays an important role in the dehydration reaction. Thus, the use of amorphous aluminosilicate with weak Brønsted acidity does

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not lead to high selectivities for HMF (Figure 3). Testing of zeolites with different strengths of acid sites also showed that the highest selectivity was observed over MOR zeolite with acid sites of the highest strength.<sup>[20]</sup> Those acid sites which are able to interact with Py influence HMF selectivity. Figure 5 shows

60 Amberlyst-15 MOR 50 Selectivity to HMF / % 40 30 0,-AI,0 20 ZrPO, Nb,O, 10 0 5 10 15 Bronsted/Lewis

Figure 5. Selectivity towards HMF at fructose conversion of 10% versus Brønsted/Lewis ratio determined by Py adsorption.

a strong correlation between selectivity for HMF at the same levels of fructose conversion and Brønsted/Lewis ratios (determined by Py adsorption).

Formation of formic and levulinic acids as byproducts was observed mainly over Amberlyst-15 and MOR zeolite (Figure 4). In those reactions, the selectivity for acids increased with an increase in fructose conversion. Catalysts with a high contribution of Lewis acidity formed small amounts of acids. Thus, fructose mainly transformed into humins over those catalysts. The important role of Lewis acid sites in the conversion of xylose into humins was also shown by Weingarten et al.<sup>[35]</sup>

The selectivity of all studied heterogeneous catalysts is low at the beginning of the reaction with a subsequent increase to 17-60%. The low initial selectivity might be explained by a strong adsorption of HMF on the surface of the catalyst at the beginning of the reaction. A study of HMF adsorption over the catalysts (Table 1) shows that significant adsorption of HMF is observed only in the case of aluminosilicate and Amberlyst-15. It indicates an important role of Brønsted acid sites in the interaction with HMF. Brønsted acid sites should strongly interact with the carbonyl group of HMF.[36] Low adsorption of HMF over MOR zeolite may be the result of diffusion limitations. The presence of strong Lewis acidity in the case of zirconium phosphate, niobic acid, and alumina does not lead to HMF adsorption on the surface of the catalyst. As a result, aluminosilicate and Amberlyst-15 show an initial increase in selectivity for HMF at low conversions due to a gradual desorption of HMF from the surface. The low linear increase in HMF selectivity with time, in the case of other catalysts, can be explained by the deactivation of strong Lewis acid sites with the increase in selectivity for HMF (Figure 3).

Fructose dehydration characteristics indicate a parallel transformation of fructose over the catalyst to polymeric byproducts or a fast secondary reaction of adsorbed HMF. An earlier study of xylose dehydration using heterogeneous catalysts



showed similar results (low selectivity at the beginning of the reaction).<sup>[32]</sup> This was explained by a xylose reaction with furfu-

ral, which gave humins. Accordingly, fructose might undergo

a dehydration over an acid site to form HMF (Figure 6, reac-

Figure 6. Fructose dehydration reaction scheme.

fructose to form humins (Figure 6, reaction 1). HMF could also desorb from the acid site and be extracted in an organic solvent (in a biphasic system) (Figure 6, reaction 3) or it may react with itself to form humins, or rehydrate into acids (Figure 6, reaction 4). To investigate the conversion of fructose into by-products, the HMF reaction was studied over different catalysts.

#### **HMF transformation**

Consumption of HMF over Amberlyst-15 is much faster relative to niobic acid and alumina. Conversion of HMF over both these catalysts was not higher than 10% in 6 h. The main products over Amberlyst-15 were formic and levulinic acid with a selectivity of about 80%. Alumina and niobic acid showed a selectivity of 50 and 30%, respectively (Figure 7). These results indicated that catalysts with Lewis acid sites were not highly efficient. The low adsorption of HMF on these catalysts correlated with catalytic results (Table 1).

Thus, low selectivity during fructose transformation over alumina, aluminosilicate, niobic acid, and zirconium phosphate cannot be explained by secondary HMF reactions (Figure 3). A more plausible explanation is the fast oligomerization of fructose over the surface of these catalysts without an intermediate desorption of HMF. Fructose adsorption experiments support this hypothesis. Catalysts with strong Lewis acid sites like niobic acid and alumina show a strong adsorption of fructose. Conversely, Amberlyst-15 shows significant adsorption of HMF, but not fructose. This difference might be explained by the presence of an aromatic ring on HMF. Interaction of the carbonyl group on HMF with a Lewis acid site leads to migration of the positive charge to the aromatic ring with repulsion of HMF from a neighboring Lewis acid site. Lewis acidity is more effective in the adsorption of fructose by multiple surface interactions of carbonyl and hydroxyl groups with Lewis acid sites. This results in surface condensation of fructose molecules and in turn the formation of humins.

Although Amberlyst-15 shows a high activity in the secondary transformation of HMF with a high selectivity for acids



**Figure 7.** a) HMF conversion; b) selectivity towards acids over  $Al_2O_2$ ,  $Nb_2O_5$ , and Amberlyst-15. MIBK was added (MIBK/water = 3:1 v/v in the case of Amberlyst-15) after 5 h. Reaction conditions: catalyst (4 g), fructose (20 g), water (300 mL), 408 K.

(Figure 7), the dehydration of fructose proceeds with the formation of HMF in a maximum yield of 60%, with a further decrease in HMF selectivity due to its secondary reaction. This indicates that direct fructose or intermediate product conversion into humins (Figure 6, reaction 1) might also take place over catalysts with Brønsted acid sites. A comparison with fructose dehydration over homogeneous HCl supports this hypothesis (Figure 8). The selectivity for HMF over HCl at low conversions is 75% with the formation of 5% acids. During the reaction it decreases to 45% with an increase in selectivity for acids to 40%. Thus, acids are the main products of the HMF secondary reaction over HCI. This means that 80% is the maximum HMF selectivity over Brønsted acid sites before the secondary consumption of HMF. The lower selectivity of HMF formation over Amberyst-15 is the result of partial direct formation of humins (Figure 6, reaction 1).

#### Effect of organic solvent addition

The addition of a water-immiscible solvent may suppress secondary transformation of HME.<sup>[15]</sup> Indeed, Figure 8 shows that the addition of excess MIBK (MIBK/water = 3:1 v/v) to an aqueous solution of HCI leads to a stabilization of selectivity for HMF at 75%. The addition of MIBK does not lead to a significant change in catalytic activity because HCI remains in the aqueous phase. The amount of HMF extracted by MIBK exceeds the amount of HMF in water more than three-fold, therefore significantly inhibiting HMF rehydration over HCI. The decrease in HMF selectivity only starts at higher conversions of fructose (Figure 8) and agrees with the initial thought that the addition of organic solvent would decrease the rate of HMF transformation by extraction of HMF by the solvent.<sup>[15]</sup>



**Figure 8.** a) Influence of addition of MIBK on fructose conversion versus time; b) selectivity for HMF versus fructose conversion over HCl. Reaction conditions: HCl (1.6 g, 36%), fructose (20 g), water (300 mL), MIBK (900 mL), 408 K.  $\blacksquare$ ,  $\blacktriangle$ : water;  $\Box$ ,  $\triangle$ : MIBK/water = 3.

The effect of MIBK addition to the aqueous solution of fructose with niobic acid as a heterogeneous catalyst is shown in Figure 9. Results suggest that organic phase addition does not result in any significant changes in the conversion of fructose or selectivity for HMF. Similarly, solvent addition had no signifi-



**Figure 9.** a) Influence of addition of MIBK on fructose conversion versus time; b) selectivity for HMF versus fructose conversion over  $Nb_2O_5$ . Reaction conditions: catalyst (4 g), fructose (20 g), water (300 mL), MIBK (900 mL), 408 K.  $\blacksquare$ : water;  $\Box$ : MIBK/water = 3.

cant effect for zirconium phosphate, alumina, and amorphous aluminosilicate catalysts (not shown). This agrees with the previous assumption regarding the transformation of fructose on the surface of the catalyst directly to humins without intermediate HMF formation (Figure 6). The addition of MIBK leads just to a redistribution of HMF between the aqueous and the organic phase without influencing selectivity for HMF (Figure 9). The partition ratio for HMF between water and MIBK at the reaction temperature is about 0.9. This means that at this MIBK/water ratio (3:1 v/v), the amount of HMF present in the organic phase is 2.7 times higher than the amount in water. The preservation of the activity of the catalysts after the addition of MIBK means that the acid sites of the catalyst during the reaction do not have contact with the organic phase (Figure 9). An aqueous layer coats the acidic oxides and zirconium phosphate even when the particles are in the organic solvent.

Figure 10 shows the effect of MIBK addition during fructose dehydration over Amberlyst-15. Relative to a catalyst contain-



**Figure 10.** a) Influence of MIBK/water ratio (*v*/*v*) on fructose conversion versus time; b) selectivity for HMF versus fructose conversion over Amberlyst-15. Reaction conditions: catalyst (4 g), fructose (20 g), water (300 mL), 408 K.  $\blacksquare$ : water;  $\Box$ : MIBK/water = 1;  $\triangle$ : MIBK/water = 3;  $\bigcirc$ : MIBK/water = 5.

ing Lewis acid sites, the addition of a water-immiscible solvent causes an increase in selectivity for HMF. The higher the amount of added MIBK, the higher the selectivity. Addition of MIBK to water (1:1 v/v) results in an increase in selectivity for HMF on the order of 53–66% with fructose conversion at 35%. At a MIBK/water ratio of 3:1 v/v, the selectivity is already 74%, but a further increase in the amount of organic phase does not significantly influence selectivity (77% at MIBK/water=5:1 v/v). Furthermore, the addition of MIBK does not lead to any considerable change in the conversion of fructose. A high amount of added organic solvent results only in a decrease of

the curve in the initial time period. It suggests an absence of any interaction of the catalyst with MIBK as it was observed in the case of zeolites.<sup>[17]</sup> Thus, the enhanced selectivity in the presence of MIBK for Amberlyst-15 might only be explained by the extraction of HMF by water-immiscible solvent.

HMF transformation over this resin shows that the addition of an organic phase leads to a suppression of HMF conversion (Figure 7). The main products of HMF transformation over Amberlyst-15 are formic and levulinic acid (Figure 7), and addition of MIBK during fructose dehydration results in a decrease in the rate of acid formation (Figure 10). The selectivity for acids without MIBK is 13%, whereas after addition of MIBK (MIBK/ water = 5:1 v/v) only 2% of converted fructose is in the form of acids. However, it is difficult to explain the effect of organic solvent addition only by the suppression of secondary HMF consumption. HMF selectivity in this case should not decrease (remaining at around 60%) similarly to the HCl reaction (Figure 8). An increase in selectivity is due to the decrease in the amount of humins formed after the addition of MIBK. There are several possible reasons for this: the formation of humins might be accompanied by its depolymerization over acid sites. In this case, the addition of organic solvent at a high conversion of fructose should lead to a fast increase in selectivity due to the shift of equilibrium in the direction of humin depolymerization. However, no increase in selectivity was observed in this experiment (not shown). The other possible explanation might be a decrease in the rate of formation of humins directly from fructose and HMF (Figure 6, reaction 1).

To check this possible reaction pathway, the dehydration of fructose over Amberlyst-15 was studied in the presence of HMF. Figure 11 shows a comparison of fructose conversion and



**Figure 11.** a) Comparison of fructose conversion versus time; b) selectivity for humins versus fructose conversion over Amberlyst-15 with fructose exclusively and with addition of HMF. Reaction conditions: catalyst (4 g), fructose (20 g), HMF (2.5 g), water (300 mL), 408 K. **•**: fructose;  $\Box$ : fructose se + HMF.

■6 www.chemsuschem.org © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 下下 These are not the final page numbers! humin selectivity for a standard experiment and one in which HMF (20 mmol) is added besides fructose. The presence of HMF in the reaction mixture leads to a significant increase in fructose conversion (Figure 11). This might be due to a reaction with HMF. The decrease in fructose conversion after addition of MIBK might be explained by a decrease in the rate of the fructose reaction with HMF towards humins due to HMF extraction (Figure 10). The selectivity for humins due to the primary fructose transformation (Figure 6, reaction 1) was calculated by taking into account the difference between the amount of fructose and HMF before and after the reaction by subtraction of formed acids multiplied by a coefficient of 1.25. This coefficient reflects the formation of humins in addition to acids in the secondary transformation of HMF (Figure 7). As a result, Figure 11 shows the selectivity towards humins from the reaction of fructose with other fructose molecules or HMF. The selectivity for humins without addition of HMF slightly decreases from 40 to 30% with an increase in fructose conversion. Addition of HMF leads to an increase in humin selectivity to 70%. Thus, the results show that fructose condensation with HMF takes place during fructose dehydration over Amberlyst-15. Addition of MIBK leads to a reaction-rate decrease by HMF extraction.

Extraction of HMF by MIBK in the reaction medium results in an increase in HMF selectivity from 60 to almost 80% at a fructose conversion of 20% (Figure 10). Thus, approximately 20% of humins are formed by fructose condensation, which is equivalent to MIBK addition. At the same time, the selectivity towards humins during fructose dehydration is 30%, which means that about 10% of humins are produced by fructose condensation with HMF. Addition of MIBK leads to the suppression of this reaction.

## Conclusions

A series of well-characterized acid catalysts were tested in the aqueous-phase dehydration of fructose to HMF. The concentration of Brønsted and Lewis acid sites was determined by Py adsorption. The contribution of Brønsted acidity of the samples decreases in the order: Amberlyst-15 > MOR > ZrPO<sub>4</sub> > SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> > Nb<sub>2</sub>O<sub>5</sub> > Al<sub>2</sub>O<sub>3</sub>.

The HMF selectivity correlates with the contribution of Brønsted acid sites with the highest selectivity over Amberslyst-15 and MOR. Lewis acidity is responsible for the decrease in HMF selectivity due to the fast initial condensation of fructose into humins over Lewis acid sites.

The addition of water-immiscible MIBK to the reaction mixture with oxides and phosphates does not have any effect on selectivity. Amberlyst-15 has an improved selectivity for HMF with the addition of organic solvents. This effect was ascribed to extraction of HMF by MIBK with suppression of the rehydration reaction of formed HMF and primary fructose condensation with HMF.

## **Experimental Section**

### Catalysts

 $\gamma$ -Alumina (Al<sub>2</sub>O<sub>3</sub>) was purchased from Aldrich. Amorphous aluminosilicate (SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) was obtained from BASF with a Si/Al ratio of 11:1. MOR Zeolite with a Si/Al ratio of 12:1 was purchased from Zeolyst. Niobic acid (Nb<sub>2</sub>O<sub>5</sub>) was obtained from CBMM (Brazil). Amberlyst-15 (wet) was purchased from Rohm and Haas. Zirconium phosphate (ZrPO<sub>4</sub>) was prepared in a similar manner as reported in the literature<sup>[21]</sup> by precipitation of ZrOCl<sub>2</sub>·8 H<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub> at a P/Zr molar ratio equal to 2:1. The precipitate was filtered, washed with water, and dried at 373 K. The catalyst was calcined at 673 K in air. All catalysts were dried at 373 K and pulverized before reaction.

#### Characterization

Acidic properties were studied by means of  $NH_3$  TPD using an AU-TOCHEM II (Micromeritics). Prior to adsorption, samples were calcined in situ in a flow of dry air at 573 K for 1 h, and subsequently in a flow of dry He for 1 h, and cooled to ambient temperature. For  $NH_3$  adsorption, a sample was subjected to a flow of diluted  $NH_3$  for 30 min at 373 K. Physisorbed  $NH_3$  was removed in a flow of dry He at 373 K for 1 h. Typical TPD experiments were carried out in the temperature range 373–1100 K in a flow of dry He. The rate of heating was 9 K min<sup>-1</sup>.

IR spectra were recorded with a Nicolet Protégé 460 FTIR spectrometer at an optical resolution of  $4 \text{ cm}^{-1}$ . Prior to measurements, catalysts were pressed in self-supporting discs and activated in the IR cell attached to a vacuum line at 573 K for 4 h. Adsorption of Py was performed at 423 K for 30 min. Excess Py was further evacuated at 423 K for 1 h. Adsorption–evacuation was repeated several times until no changes in spectra were observed.

Adsorption of HMF or fructose over the catalysts was studied by addition of catalyst (0.5 g) to a solution of HMF or fructose (3 mmol) in water (25 mL). The mixture was stirred for 1 h at 298 K. The amount of adsorbed HMF or fructose was determined chromatographically by determining the concentration of fructose remaining in water.

### Catalysis

Experiments were carried out in a 2 L stirred autoclave working in a batch mode and equipped with two valves for sampling liquid from the aqueous and organic phases. The procedure for testing the catalysts was as follows: heterogeneous catalyst (4 g) or HCl (1.6 g of 36%) and water (250 mL) were poured into the autoclave. MIBK was added to the autoclave for experiments with organic solvents. The autoclave was purged with nitrogen. Fructose (20 g, 0.37 m) or HMF (5 g, 0.13 m) or fructose with HMF (20 g fructose, 2.5 g HMF) dissolved in 50 mL of water was poured into the autoclave after the temperature had been increased to 408 K, at which point the catalytic experiment was started. The agitation speed was 500 rpm.

Periodically liquid samples were taken from the autoclave, which were analyzed using HPLC (Shimadzu) equipped with refractive index and UV-Vis detectors with a BIO-RAD Aminex HPX-87H column.

Reactant conversion (mol%) and product selectivity (mol%) were defined as follows:

Conversion (mol%) = (moles of fructose reacted)/(moles of initial fructose)  $\times 100\,\%$ 

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7

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Selectivity (%) = (moles of HMF or formic acid produced)/(moles of fructose reacted)  $\times$  100 %.

Selectivity for humins in the experiment with  $\mathsf{HMF}$  addition was calculated as follows:

[(moles of HMF + moles of fructose)<sub>before reaction</sub>-(moles of HMF + moles of fructose)<sub>after reaction</sub>-formic acid produced × 1.25]/(moles of fructose reacted) × 100 %.

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- [1] X. Tong, Y. Ma, Y. Li, Appl. Catal. A 2010, 385, 1.
- [2] A. Corma, S. Iborra, A. Velty, Chem. Rev. 2007, 107, 2411.
- [3] B. F. M. Kuster, Starch/Staerke 1990, 42, 314.
- [4] K. Hamada, H. Yoshihara, G. Suzukamo, Chem. Lett. 1982, 617.
- [5] T. El Hajj, A. Masroua, J.-C. Martin, G. Descotes, Bull. Soc. Chim. Fr. 1987, 85.
- [6] P. Vinke, H. van Bekkum, Starch/Staerke 1992, 44, 90.
- [7] L. Rigal, A. Gaset, Biomass 1985, 8, 267.
- [8] M. Watanabe, Y. Aizawa, T. Iida, R. Nishimura, H. Inomata, Appl. Catal. A 2005, 295, 150.
- [9] H. Yan, Y. Yang, D. Tong, X. Xiang, C. Hu, Catal. Commun. 2009, 10, 1558.
- [10] F. Benvenuti, C. Carlini, P. Patrono, A. M. R. Galletti, G. Sbrana, M. A. Massucci, P. Galli, Appl. Catal. A 2000, 193, 147.
- [11] P. Carniti, A. Gervasini, S. Biella, A. Auroux, Catal. Today 2006, 118, 373.
- [12] C. Moreau, R. Durand, C. Pourcheron, S. Razigade, Ind. Crops Prod. 1994, 3, 85.

- [13] C. Moreau, R. Durand, S. Razigade, J. Duhamet, P. Faugeras, P. Rivalier, P. Ross, G. Avignon, Appl. Catal. A 1996, 145, 211.
- [14] C. Moreau, Agro Food Ind. Hi-Tech 2002, 13, 17.
- [15] Y. Román-Leshkov, J. A. Dumesic, Top. Catal. 2009, 52, 297.
- [16] J. N. Chheda, J. A. Dumesic, Catal. Today 2007, 123, 59.
- [17] F. Yang, Q. Liu, X. Bai, Y. Du, Bioresour. Technol. 2011, 102, 3424.
- [18] F. Yang, Q. Liu, M. Yue, X. Bai, Y. Du, Chem. Commun. 2011, 47, 4469.
  [19] E. Nikolla, Y. Román-Leshkov, M. Moliner, M. E. Davis, ACS Catal. 2011, 1,
- [20] V. Ordomsky, J. van der Schaaf, J. C. Schouten, T. A. Nijhuis, J. Catal. 2012, 287, 68.
- [21] Y. Kamiya, S. Sakata, Y. Yoshinaga, R. Ohnishi, T. Okuhara, Catal. Lett. 2004, 94, 45.
- [22] M. Ziyad, M. Rouimi, J.-L. Portefaix, Appl. Catal. A 1999, 183, 93.
- [23] A. Corma, Chem. Rev. 1995, 95, 559.
- [24] K. Tanabe, Mater. Chem. Phys. 1987, 17, 217.
- [25] I. Ahmad, T. J. Dines, J. A. Anderson, C. H. Rochester, Spectrochim. Acta, Part A 1999, 55, 397.
- [26] C. Morterra, G. Magnacca, Catal. Today 1996, 27, 497.
- [27] X. Liu, J. Phys. Chem. C 2008, 112, 5066.
- [28] V. L. Zholobenko, D. Plant, A. J. Evans, S. M. Holmes, *Microporous Meso-porous Mater.* 2001, 44-45, 793.
- [29] N. S. Nesterenko, F. Thibault-Starzyk, V. Montouillout, V. V. Yuschenko, C. Fernandez, J.-P. Gilson, F. Fajula, I. I. Ivanova, *Microporous Mesoporous Mater.* 2004, 71, 157.
- [30] M. Maache, A. Janin, J. C. Lavalley, E. Benazzi, Zeolites 1995, 15, 507.
- [31] C. A. Emeis, J. Catal. 1993, 141, 347.
- [32] N. C. Jeong, J. S. Lee, E. L. Tae, Y. J. Lee, K. B. Yoon, Angew. Chem. 2008, 120, 10282; Angew. Chem. Int. Ed. 2008, 47, 10128.
- [33] D. A. Nelson, P. M. Molton, J. A. Russell, R. T. Hallon, Ind. Eng. Chem. Prod. Res. Dev. 1984, 23, 471.
- [34] B. F. M. Kuster, Carbohydr. Res. 1977, 54, 177.
- [35] R. Weingarten, G. A. Tompsett, W. C. Conner, Jr., G. W. Huber, J. Catal. 2011, 279, 174.
- [36] H. Fang, A. Zheng, Y. Chu, F. Deng, J. Phys. Chem. C 2010, 114, 12711.

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## **FULL PAPERS**



Fructose dehydration over heterogeneous acidic catalysts is studied. Lewis acidity leads to direct fructose condensation and humins are produced. Brønsted acidity results in selective 5hydroxymethylfurfural (HMF) formation with subsequent rehydration into acids. Organic solvent addition increases selectivity exclusively over Brønsted acid catalysts due to suppression of the rehydration reaction of HMF and primary fructose condensation with HMF (see figure). V. V. Ordomsky, J. van der Schaaf, J. C. Schouten, T. A. Nijhuis\*

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Fructose Dehydration to 5-Hydroxymethylfurfural over Solid Acid Catalysts in a Biphasic System