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The effect of solvent addition on fructose dehydration to 5-hydroxymethylfurfural in biphasic system over zeolites

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ABSTRACT

The effect of organic solvent addition during dehydration of fructose over zeolites has been investigated as a way to enhance the 5-hydroxymethylfurfural (HMF) selectivity. The catalysts were characterized by chemical analysis, XRD, nitrogen adsorption–desorption and TPD NH_3. The selectivity of HMF formation during the addition of methyl isobutyl ketone (MIBK) is significantly increased, but its effect decreases in the order: MOR > ZSM-5 > BEA > amorphous aluminosilicate, which corresponds to the order of the decrease in the strength of the acid sites. An initial increase in the selectivity to HMF over zeolites after addition of organic solvent is attributed to the suppression of humins formation due to filling of the pores of zeolite with MIBK. Testing of silylated samples with deactivated surface acid sites indicates that in a biphasic system, the increase in the selectivity at higher conversions is induced by suppression by the solvent of the activity of external acid sites responsible for the unselective transformation of fructose.

1. Introduction

Over the last years, the dehydration of carbohydrates to 5-hydroxymethylfurfural has attracted increasing attention due to its possible application as a substitution for petroleum-based building blocks [1]. HMF and its derivatives can be applied as platform chemicals, precursor for polymers, fuel or solvent [2].

Different heterogeneous and homogeneous catalysts have been applied for this reaction, such as mineral acids [3,4], ion exchange resins [5–7], oxides [8,9], phosphates [10,11] and zeolites [12,13]. It was shown that water as a reaction medium promotes dehydration of HMF with the formation of acids and oligomeric products [14]. Román-Leshkov and Dumesic [15] investigated the water-immiscible organic solvent effect on the dehydration of fructose in a biphasic system. Addition of solvents like 2-butanol or MIBK extracting HMF from the reaction mixture was shown to increase the selectivity of HMF production. It was reported that 80% selectivity can be achieved over HCl in the presence of a organic solvent [15].

Heterogeneous catalysts offer several advantages over liquid acid catalysts like easy separation of product, reusability of catalyst and no corrosion of equipment, which makes them more suitable for an industrial application. Zeolites are among the most promising catalytic systems due to their high stability under hydrothermal conditions, easy regeneration and unique shape selective properties. Moreau et al. studied the dehydration of fructose in the presence of zeolites at 438 K in a solvent consisting of MIBK and water in the ratio of 5 [12]. The highest selectivity (90%) was observed over dealuminated mordenite, which was attributed to the bidimensional structure and absence of cavities [13]. However, explanations of the effect of organic solvent addition to zeolites are not represented in the papers. At the present time, different catalytic systems applied in fructose dehydration to HMF like zirconium and titanium phosphates [10], sulfated zirconia [16], niobic acid, niobium phosphate [11] and vanadyl phosphate [17] were tested only in aqueous solution without addition of organic solvent.

In this paper, we present the results of the investigation into the effect of organic solvent addition on the reaction of the fructose dehydration over zeolites. This effect was studied by catalytic testing of samples with deactivated external acid sites. External acid sites often work as catalytic sites for unselective reactions [18]. A valuable approach might be to deactivate the external acid sites of zeolites in order to improve the selectivity for HMF production. Several attempts on the deactivation of external acid sites of zeolites have been proposed in the literature, for example by chemical vapor and chemical liquid deposition to cover the external surface with silicon alkoxides [19,20], reaction with large amine molecules [21] or coking the external surface [22]. In this paper, we examine the silica modification of zeolite MOR, ZSM-5 and BEA by liquid deposition of TEOS and investigate the role of external and internal acid sites in the dehydration of fructose in the presence of organic solvent.

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2. Experimental

2.1. Catalysts

The powders of parent zeolites ZSM-5, MOR (Mordenite) and BEA (Beta) with Si/Al ratio 13, 12 and 16 were purchased from Zeolyst. The samples were converted into H-form from NH_4 by calcination in air at 823 K. Amorphous aluminosilicate Al_2O_3–SiO_2 with Si/Al ratio 11 was obtained from BASF. The surface-modified silylated samples were prepared by the chemical liquid deposition of silica, using TEOS as the silylation agent, following the procedures reported earlier by Weber et al. [19]. 10 g of dried zeolite in H-form was added to the solution of 20 ml of TEOS in 100 ml of *n*-hexane. The mixture was stirred at room temperature for 24 h. The sample was subsequently washed with water, dried and calcined at 823 K.

2.2. Characterization

The aluminum content of the samples was determined by ICP analysis. The powder and the deposited catalysts were analyzed by X-ray diffraction (XRD) in a Rigaku Geigerflex Max/B diffractometer, using Cu Kα radiation from a Cu X-ray tube at 40 kV and 40 mA. Texture properties of the parent and silylated catalysts were determined by N_2 adsorption at 77 K in a Micromeritics ASAP 2020 surface analyzer. The micropore volume and surface area of the zeolites were calculated by Dubinin–Radushkevich method.

The acidic properties were studied by temperature-programmed desorption of ammonia (NH_3 TPD) using an AUTOCHEM II (Micromeritics). Prior to adsorption, the samples were calcined *in situ* in a flow of dry air at 823 K for 1 h and, subsequently, in a flow of dry helium for 1 h and cooled down to ambient temperature. For NH_3 adsorption, a sample was subjected to a flow of diluted NH_3 for 30 min at 373 K. The 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 of 373–1100 K in a flow of dry He. The rate of heating was 9 K/min.

Adsorption of MIBK in the pores of zeolites and amorphous aluminosilicate was studied by addition of 1 g of catalyst to the mixture of 25 ml of MIBK and 25 ml of water. The mixture was stirred at room temperature for 0.5 h. The sample was subsequently filtered and washed with water. MIBK was extracted from the sample by an excess of butanol-1 and the quantity determined chromatographically.

2.3. Catalytic reactions

Experiments were carried out in a 2–1 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 catalysts was as follows: catalyst (4 g) and water (300 ml) were poured into the autoclave. Methyl isobutyl ketone (MIBK) was added in the autoclave in the biphasic experiments. The autoclave was purged with nitrogen. Fructose (20 g, 0.37 M) or HMF (5 g, 0.13 M) was poured into the autoclave after the temperature had been increased to 438 K, after which the catalytic experiment was started. The agitation speed was 500 rpm unless otherwise stated.

The stability of the catalysts in fructose dehydration was studied by reusing the catalysts in a subsequent catalytic cycle. The catalyst was removed from the reaction medium after 5 h of reaction by filtration. Then, it was washed with MIBK and water to remove the adsorbed reaction products and tested in the next catalytic cycle.

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%), products yield (mol%) and product selectivity (%) were defined as follows:

$$\text{Conversion (mol\%)} = (\text{moles of fructose or HMF reacted})/$$
$$(\text{moles of initial fructose or HMF}) \cdot 100\%$$
$$\text{Selectivity (\%)} = (\text{moles of HMF produced})/$$
$$(\text{moles of fructose reacted}) \cdot 100\%.$$

3. Results and discussion

3.1. Physicochemical properties of catalysts

The properties of the catalysts are shown in Table 1. The relative crystallinities of the samples after silylation show only a very minor change from the parent zeolites (Table 1). This implies that their structure was maintained after the modification.

Taking into account that the amount of aluminum in the samples after silylation remains the same, it is possible to calculate the weight gain after the deposition of TEOS from the aluminum content. The weight gain decreases in the order: MOR > ZSM-5 > BEA (Table 1).

The kinetic diameter of TEOS (8.9 Å) is larger than the pore mouth of all studied zeolites (5–7.5 Å), and only hydroxyl groups on the outer surface could react with the deposition agent to form Si–O–Si or Si–O–Al bonds [23]. Silica deposited on the external surface of zeolites might block pores, resulting in a decrease in the surface area and pore volume of the samples. Nitrogen adsorption (Table 1) shows no significant decrease in the surface area or micropore volume of the studied samples.

The acidity of materials was studied by NH_3 TPD (Fig. 1). All zeolites exhibit the ammonia desorption at two temperatures: a low-temperature peak at 400 K and a high-temperature peak at 600–800 K corresponding to the weak and strong acid sites of the samples. The amorphous aluminosilicate does not possess strong acid sites and has just broad peak at 500 K. The strength of acid sites decreases in the order: MOR > ZSM-5 > BEA. This result corresponds with the reported literature data for the acidity of zeolites

Table 1
Characterization results of catalysts.

Catalyst	Si/Al ratio	Al content (mmol/g)	Silylation weight gain (%)	Relative crystallinity (%)	S (m^2/g)	V_{mic} (cm^3/g)	TPD (NH_3) (μmol/g)	MIBK adsorbed (g/g)
Al_2O_3–SiO_2	10.8	1.54	–	–	327	0.0	225	0.11
H-MOR	11.7	1.42	–	100	461	0.21	1100	0.78
SiO_2/H-MOR	13.7	1.22	14.6	96	423	0.2	915	–
H-ZSM-5	13.0	1.28	–	100	442	0.18	966	0.24
SiO_2/H-ZSM-5	14.1	1.18	7.8	98	414	0.17	894	–
H-BEA	15.6	1.07	–	100	610	0.22	860	0.94
SiO_2/H-BEA	16.3	1.02	4.2	95	603	0.22	810	–

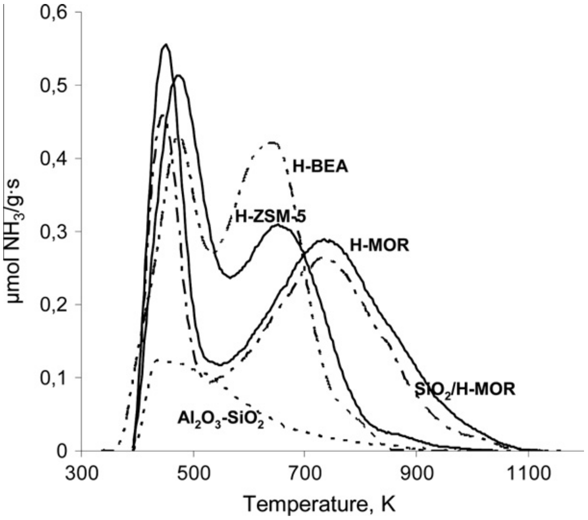


Fig. 1. TPD NH_3 profiles for zeolites H-MOR, H-ZSM-5, H-BEA, aluminosilicate Al_2O_3–SiO_2 and silylated sample SiO_2/H-MOR.

[24]. The results show that silica deposition over MOR leads to a 16% decrease in the amount of acid sites in comparison with the parent zeolite with preservation of the strength of acid sites (Fig. 1, Table 1). Other samples also show a decrease in acidity (Table 1). The effect decreases in the order MOR > ZSM-5 > BEA in accordance with decrease in the weight gain during silylation. A possible explanation for the highest weight gain and decrease in acidity in the case of zeolite H-MOR might be the highest acid strength of this zeolite. It should lead to the more intensive interaction and hydrolysis of TEOS with surface acid sites and higher amount of deposited silica.

3.2. Dehydration of fructose

3.2.1. Dehydration of fructose over catalysts in aqueous phase

The conversion of fructose versus time and selectivity in HMF versus conversion during dehydration of fructose without an addition of organic solvent over parent catalysts is shown in Fig. 2. The only detected by-product in the reaction system in all experiments was furfural and small amounts of levulinic and formic acids. The appearance of furfural was explained earlier by fast reverse-aldol cleavage of carbohydrates [25]. The selectivity in furfural and acids, however, did not exceed 3 mol.%, and therefore it has not been taken into account. Thus, the main by-product in the reaction is humins, which do not show up during the HPLC analysis.

H-ZSM-5 zeolite shows the highest activity among all studied zeolites. Almost full conversion of fructose was reached in 2 h. Zeolite H-BEA has the lowest conversion with an S-shape curve. The low amount of deposited silica indicates a low surface acidity of zeolite BEA (Table 1). This means that fructose transformation should occur inside of the pores of zeolite. The inductive period on the curve might be explained by initial diffusion limitations of fructose molecules in the pores of zeolite. The selectivity in HMF for zeolite ZSM-5 decreased from 30% to 1% when conversion of fructose exceeded 80%. The highest selectivity was observed for zeolite H-MOR (Fig. 2b). It increases with fructose conversion at the beginning of the experiment to 45% and then smoothly decreased at high conversion of fructose to 40%. It is interesting to note that the selectivity of zeolite H-BEA and amorphous aluminosilicate was similar and slightly decreased during the experiment from about 30%.

The low selectivity from the beginning of the reaction over all zeolites indicates the parallel transformation of fructose in the pores of catalyst to the oligomeric by-products or a fast secondary reaction of the adsorbed HMF molecules inside of the zeolite pores. Studies of the mechanism of hexoses dehydration performed by Antal et al. [26] showed that the dehydration of fructose goes through cyclic intermediates, which might also be very reactive and take part in the transformation into humins as well. In the case of the dehydration of fructose, with the formation and desorption of HMF and its subsequent transformation into the oligomeric products, the selectivity should continually decrease from the beginning of the experiment. The initial selectivity in all experiments, however, already was not higher than 50%. This means that HMF or its precursor transforms into oligomeric compounds very fast on the surface of the catalyst by oligomerization with other fructose or HMF molecules without intermediate desorption of HMF as shown by reaction 1 in the overall reaction scheme on Fig. 3. HMF formed by dehydration of fructose desorbs from the surface acid site and distributes between aqueous and organic phases (Reaction 2). HMF can then react with itself to form humins (Reaction 3). Secondary transformation of HMF is observed with a high rate over H-ZSM-5 and a lower rate over H-MOR (Fig. 2). Similar reaction scheme was described earlier for fructose and xylose dehydration using HCl and heterogeneous catalysts [27–29].

The catalytic behavior of the samples indicates that the structural properties and acidity might have great importance. Possible external mass transfer limitations on the process were checked by variation in stirring rate of the reaction mixture from 500 to 800 rpm. Increasing of the stirring rate did not show any change in catalytic activity or selectivity of the reaction (not shown). The high rate of secondary HMF transformation over H-ZSM-5 might be explained by fast secondary oligomerization of HMF on the outer surface of zeolite crystal [12]. The pore size of H-ZSM-5 zeolite is

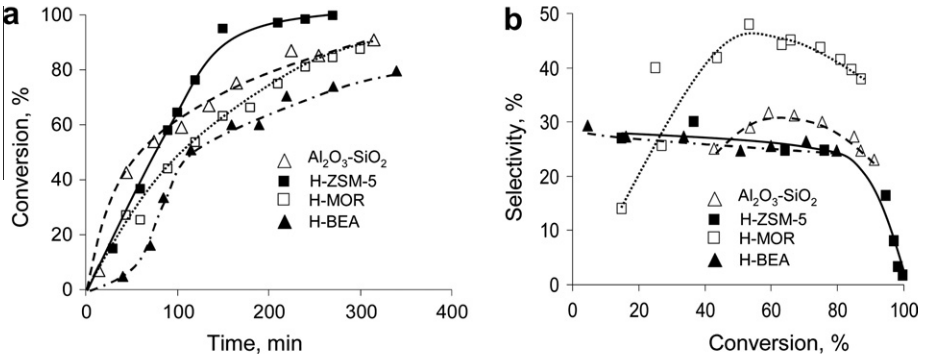


Fig. 2. Fructose conversion versus time (a) and selectivity to HMF versus fructose conversion (b) over zeolites H-MOR, H-ZSM-5, H-BEA and aluminosilicate Al_2O_3–SiO_2 without solvent. Catalysts: Al_2O_3–SiO_2 (Δ), H-ZSM-5 (■), H-MOR (□), H-BEA (▲).

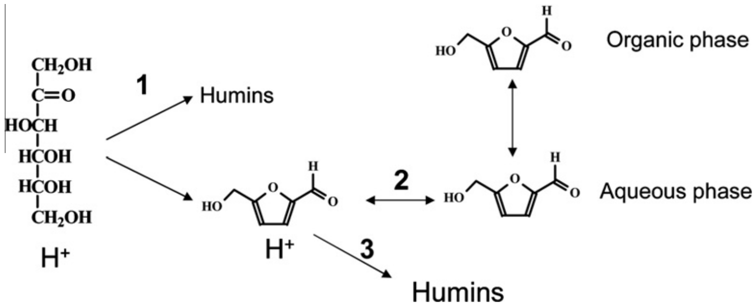


Fig. 3. Fructose dehydration reaction scheme.

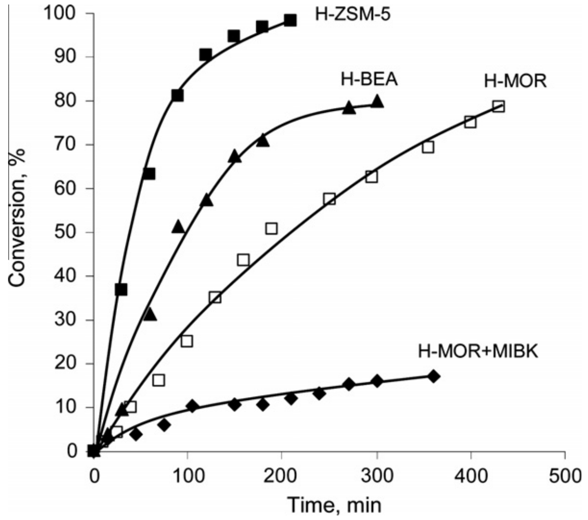


Fig. 4. HMF conversion over zeolites H-MOR, H-ZSM-5, H-BEA in aqueous phase and zeolite H-MOR with addition of MIBK with MIBK/water = 3/1 vol.

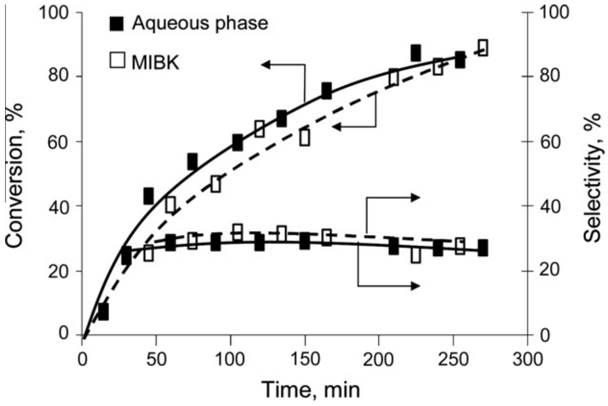


Fig. 5. Influence of addition of MIBK on fructose conversion and selectivity to HMF over amorphous aluminosilicate in aqueous phase (■) and with MIBK/water = 3/1 vol. (□).

about 5 Å, and therefore diffusion of fructose and HMF inside the pores should be very limited. Moreau [12] explained the highest selectivity to HMF during fructose dehydration over H-MOR (>90–95%) in the presence of MIBK by the shape selective properties due to the large channels (6.5–7 Å) and the absence of cavities. However, the difference in the pore diameters between zeolite H-BEA (5.6–7.5 Å) and H-MOR (6.5–7 Å) is not so high that one can expect a significant change in selectivity. It is more likely that the difference in catalytic properties is due to the higher strength of acid sites of zeolite H-MOR in comparison with H-BEA (Fig. 1). The low acidity of amorphous aluminosilicate and the similar catalytic behavior to zeolite BEA support this hypothesis.

Investigation into pure HMF transformation in aqueous phase over zeolites shows a correlation of the rate of HMF oligomerization over zeolites (Fig. 4) with the HMF selectivity during the fructose dehydration (Fig. 2). The rate of HMF consumption over zeolite ZSM-5 is the highest among all studied zeolites. It corresponds to the fast decrease in HMF selectivity with increase in fructose conversion (Fig. 2). The rate of HMF oligomerization is higher over zeolite BEA in comparison with MOR (Fig. 4). This means that HMF oligomerization does not need strong Brönsted acidity and that the nature of secondary HMF oligomerization and primary fructose transformation into humins is similar. There are many possible ways described in the literature of HMF oligomerization over different catalysts [30]. In spite of the high rate of HMF oligomerization over zeolites, the curve of HMF selectivity during fructose dehydration does not decrease immediately from the beginning of experiment. It might be explained by occupation of acid sites by fructose molecules. At high conversions of fructose, processes of secondary HMF oligomerization accelerate over zeolites (Fig. 2).

The possible reason for the higher selectivity of HMF formation over strong acid sites might be high rate of fructose dehydration with the formation of HMF. Transformation of fructose over weak acid sites should proceed with the formation of intermediate products, which might oligomerize further by reaction with fructose or HMF (Fig. 3).

3.2.2. Dehydration of fructose over zeolites in biphasic system

The effect of MIBK addition on the conversion of fructose and selectivity of HMF formation over the amorphous aluminosilicate Al_2O_3–SiO_2 is shown in Fig. 5. The partition ratio for HMF between water and MIBK at reaction temperature is about 0.8. This means that at the volume ratio of MIBK to water 3, the amount of HMF present in the organic phase is 2.5 times higher than the amount in water. This should lead to decrease in the rate of HMF condensation in aqueous phase. Fig. 4 shows the suppression of pure HMF condensation over zeolite MOR in the presence of MIBK. Addition of organic solvent in the presence of aluminosilicate only results in a small decrease in the conversion and does not change selectivity of the reaction at all. This corresponds to the previous assumption about transformation of HMF on the surface of the catalyst without it desorbing into the solution. Addition of organic solvent in this case will only lead just to redistribution of HMF between the aqueous and the organic phase without influencing the selectivity of HMF formation (Fig. 3). Preservation of the catalytic activity of Al_2O_3–SiO_2 after addition of MIBK means that the surface of the catalyst during the reaction does not have contact with

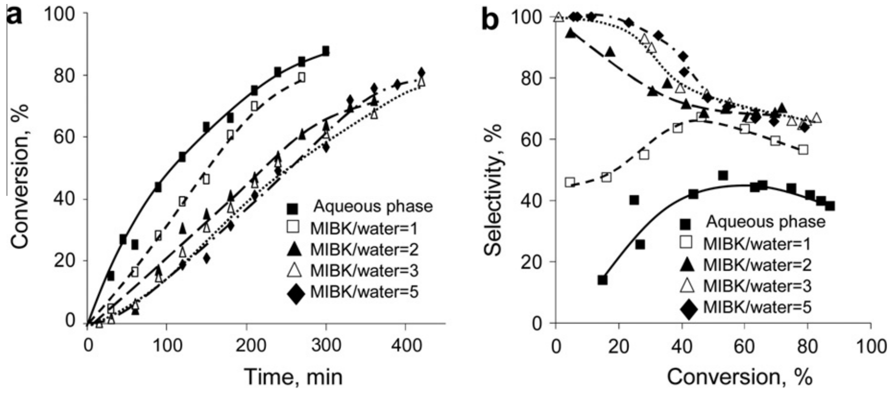


Fig. 6. Influence of MIBK to water volume ratios on fructose conversion versus time (a) and selectivity to HMF versus fructose conversion (b) over zeolite H-MOR: aqueous phase (■), MIBK/water = 1 (□), MIBK/water = 2 (▲), MIBK/water = 3 (△), MIBK/water = 5 (♦).

the organic solvent. An aqueous layer should coat the catalyst even when the particle is in the organic solvent.

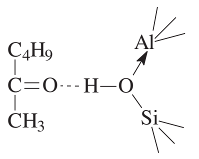
According to literature, the selectivity in fructose dehydration over zeolites should be higher in the presence of extracting solvent [12,13]. Fig. 6 shows conversion in time and selectivity of HMF formation as a function of conversion depending on the amount of added MIBK in the fructose dehydration over H-MOR. This result indicates a different mechanism of fructose dehydration over zeolites in the presence of organic solvent in comparison with the amorphous aluminosilicate (Table 1). The selectivity curve of HMF can be separated in two parts: an initial period and a period of stable selectivity (Fig. 6).

The low selectivity during the initial period of HMF formation without addition of MIBK over H-MOR might be attributed to the formation of intermediate products or adsorption of HMF over acid sites of zeolite [11]. Increasing the amount of MIBK leads to a significant increase in the HMF selectivity for an initial period of time at low conversions (Fig. 6). It is also interesting that the initial period of higher selectivity increases in time for a higher amount of MIBK with saturation at the ratio of MIBK to water 3. Addition of a higher amount of MIBK does not lead to an increase in the selectivity. At the ratio of MIBK to water 3–1, the selectivity is almost 100% until the conversion of fructose reaches 20% (Fig. 6).

Full transformation of fructose into HMF during the initial period at high amount of organic solvent results in the suppression of the formation of the oligomeric compounds. The main reason for this might be intensive interaction of MIBK with catalyst.

The hydrophobic properties of the zeolites in comparison with amorphous aluminosilicate should promote adsorption of organic solvent in the pores [31]. The amounts of adsorbed MIBK in the pores of zeolites at room temperature in the mixture of MIBK with water are shown in Table 1. Indeed, amorphous aluminosilicate adsorbs just small amount of MIBK, whereas adsorption of MIBK in zeolites BEA, MOR and ZSM-5 corresponds to the total pore volume of these zeolites.

Brönsted acid sites of zeolites strongly interact with ketone group of adsorbed MIBK by formation of hydrogen bond [32]:



Molecules of MIBK inside of the pores should suppress oligomerization of HMF by displacement of HMF from the acid sites into the reaction medium and by dilution of fructose and HMF inside of the pores by organic solvent molecules. Absorption of HMF by MIBK prevents the return of HMF molecules in the pores of zeolite (Fig. 3).

Interaction of organic solvent with hydrophilic amorphous aluminosilicate without micropores does not allow the removal of HMF from the surface and an increase in the selectivity of the reaction (Fig. 5). The decrease in the conversion of fructose over H-MOR with the addition of MIBK indicates an intensive interaction of this solvent with the acid sites of the catalyst. Increasing the amount of organic solvent in the system will lead to an increase in the residence time of a zeolite crystal in the organic solvent and a more important role of the MIBK in the interaction with the acid sites. The same selectivity curve at high ratios of MIBK to water (Fig. 6) indicates that the pores are saturated by MIBK, and an additional amount of solvent does not improve the selectivity of the process.

Fig. 7 shows a comparison of the selectivities of HMF formation over zeolites at the ratio of MIBK to water 3. The effect of MIBK addition is the highest for zeolite H-MOR. The high initial selectivity of HMF formation over zeolites H-BEA and H-ZSM-5 decreases almost immediately after the start of the reaction to the stable selectivity levels. The maximal effect of MIBK addition over H-MOR should be attributed to the highest strength of acid sites in H-MOR, which also leads to the highest selectivity over H-MOR without the addition of MIBK. Interaction of organic solvent with the strong acid sites of H-MOR should be more intensive and lead to a higher retention time of solvent in the pores of zeolite in comparison with H-BEA and H-ZSM-5.

After the initial period, the selectivity starts to decrease and comes to a stable value (Figs. 6 and 7). This might imply that the amount of HMF in the reaction medium is already high enough to start to displace molecules of organic solvent inside of zeolite pores over acid sites and take part in oligomerization reactions. The selectivity of HMF formation at this stable level should be similar to that which was observed before MIBK addition (Fig. 2). The level of stable selectivity for H-MOR increases to 56% from 41% with the addition of an equal volume of MIBK to water and it reaches the 68% for the ratios of MIBK/water 2, 3 and 5 (Fig. 6). In the case of H-BEA, the stable value is at 40% after addition of MIBK in comparison with 30% without organic solvent (Fig. 2 and 7). Addition of MIBK leads to a suppression of the reaction of the secondary oligomerization of HMF over H-ZSM-5 (Fig. 2) with a stable selectivity at 60% (Fig. 7).

These are unusual effects of the addition of extracting solvent. If we will take into account that the water-immiscible organic solvent in this stage of reaction should be an inert compound that just absorbs formed HMF and prevents it transformation into oligomeric compounds, then the addition of organic solvent should just

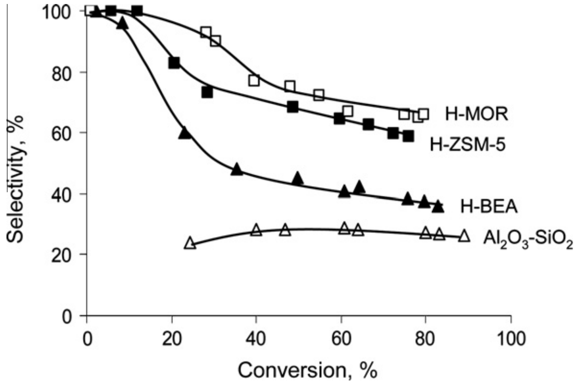


Fig. 7. Selectivity of HMF formation versus fructose conversion over H-MOR, H-ZSM-5, H-BEA and aluminosilicate Al_2O_3–SiO_2 with addition of MIBK with MIBK/water = 3/1 vol.

decrease the rate of HMF consumption. Our experimental observations indicate that MIBK continues to interact with catalyst. Such an interaction should proceed especially intensive with acid sites with a higher accessibility like on the surface of the zeolite crystal. Indeed, these acid sites should be the most unselective in the transformation of fructose. Catalytic testing of the silylated samples was used to verify this hypothesis.

3.2.3. Dehydration of fructose over silylated catalysts

Silylation of zeolites should inactivate the external surface and help to determine the reason of the change of the selectivity of HMF formation. Fig. 8 shows the comparison of the fructose conversion and HMF selectivity for the parent and silylated zeolite H-MOR. In comparison with the parent zeolite, H-MOR silylation leads to a decrease in the rate of the conversion of fructose. The selectivity curve preserves its form with a low selectivity during the initial period of time and a decrease in the selectivity at higher conversion but it was shifted to the higher values. The volcano form of the curve is the result of the same processes in the pores of silylated zeolite H-MOR: adsorption of HMF during the initial period of time and secondary transformation of HMF in the oligomeric products at high conversions. Inactivation of the external surface of H-MOR leads to an increase in the selectivity of HMF formation to 62%, close to the selectivity in the presence of MIBK over parent H-MOR (Fig. 6). However, dehydration of fructose in HMF is still not complete. This means that condensation processes with formation of small chain oligomers during fructose dehydration take place also inside the pores of the zeolite. The higher selectivity of fructose dehydration after deactivation of external acid sites is due to the space constraints inside of the pores of zeolite. Addition of MIBK to the silylated sample leads to a decrease in the rate of HMF transformation without a change in the level of the maximum HMF selectivity (Fig. 8). The effect of the addition of higher amounts of MIBK to the silylated sample does not differ from the addition of MIBK to the parent H-MOR (not shown).

Silica deposition over zeolite H-ZSM-5 leads to a suppression of HMF consumption and a stable selectivity (37%) in HMF formation similar to the effect observed after addition of small amount of MIBK (Fig. 9). Silylation of H-ZSM-5 gives lower increase in the selectivity in comparison with addition of high amount of organic solvent (Fig. 9). It might be explained by an incomplete deactivation of the external acid sites and larger role of even weak acidity in fructose transformation over H-ZSM-5 due to narrow pores of this zeolite.

Silica deposition over zeolite H-BEA leads to small increase in the selectivity to 30% (not shown). It agrees with the weak effect after addition of MIBK to zeolite BEA (Fig. 7). Deactivation of the external surface acid sites by silylation or organic solvent in this case is not effective due to the low strength of the acid sites.

Catalytic testing of the samples with deactivated external acidity strongly indicates that the main effect of organic solvent at high fructose conversion is attributed to the suppression of external acidity of zeolites. In that case with addition of high amount of MIBK, we should observe true selectivity of HMF formation inside of zeolite pores. Fig. 10 summarizes the above results and gives the selectivity of HMF formation over stable level for the catalysts (Fig. 7) versus peak maximum temperature of TPD ammonia curves (Fig. 1). The results obtained show that selectivity to HMF is almost proportional to the strength of the acid sites of the catalysts. Thus, the main factor for the selective dehydration of fructose to HMF over zeolites is the strength of acid sites.

Deactivation of heterogeneous catalysts during fructose dehydration was shown to be important problem due to the deposition of insoluble humins on the catalyst surface [11]. Addition of organic solvent, besides increasing the selectivity to HMF, should have an effect in increasing the stability of the catalysts by suppressing humins formation. This was examined by testing of zeolite MOR after filtration in an additional catalytic cycle (Fig. 11). Aqueous phase catalytic testing leads to the formation of a high amount of black insoluble humins in the mixture with the catalyst. Testing of this catalyst shows a significant decrease in fructose conversion and selectivity in comparison with initial results (Fig. 11). At the same time, the zeolite after reaction in the biphasic system almost does not show any significant decrease in activity and selectivity (Fig. 11). This indicates that the effect of organic solvent in the suppression of the formation of insoluble humins compounds over the catalyst increases the catalyst stability.

Comparison of the yields of HMF during fructose dehydration over zeolites with other heterogeneous systems shows that zeolite

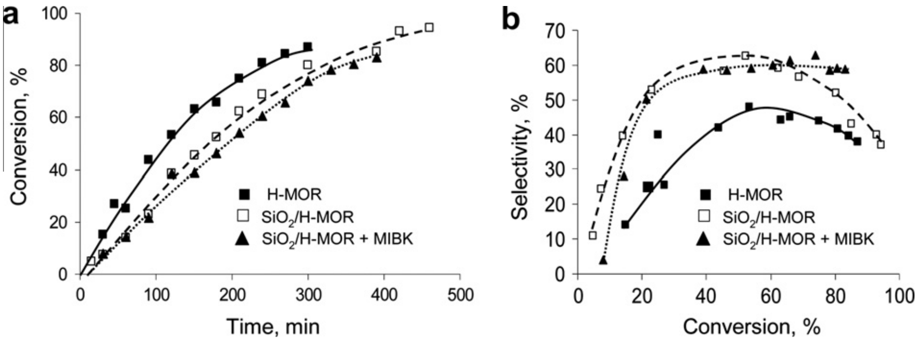


Fig. 8. Comparison of the fructose conversion versus time (a) and selectivity to HMF versus fructose conversion (b) over parent zeolite H-MOR in aqueous phase (■) and zeolite H-MOR after silylation in aqueous phase (□) and with addition of equivalent volume of MIBK to water (▲).

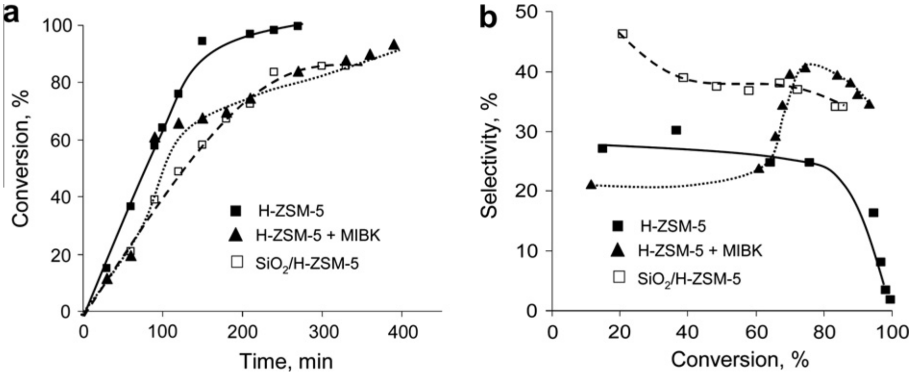


Fig. 9. Comparison of the fructose conversion versus time (a) and selectivity to HMF versus fructose conversion (b) over parent zeolite H-ZSM-5 in aqueous phase (■) and with addition of equivalent volume of MIBK to water (▲) and zeolite H-ZSM-5 after silylation in aqueous phase (□).

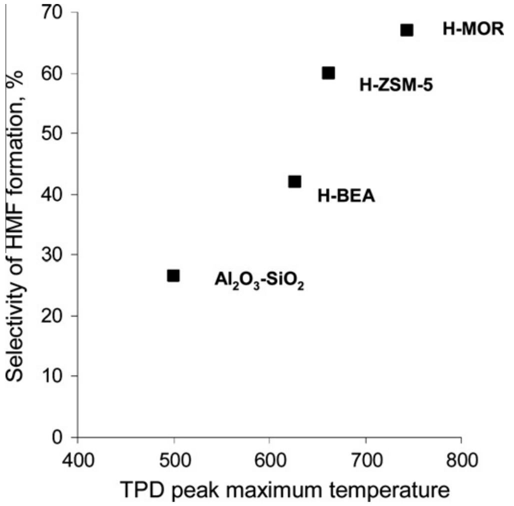


Fig. 10. Selectivity of HMF formation over H-MOR, H-ZSM-5, H-BEA and aluminosilicate Al_2O_3–SiO_2 versus peak maximum temperature of TPD ammonia curves.

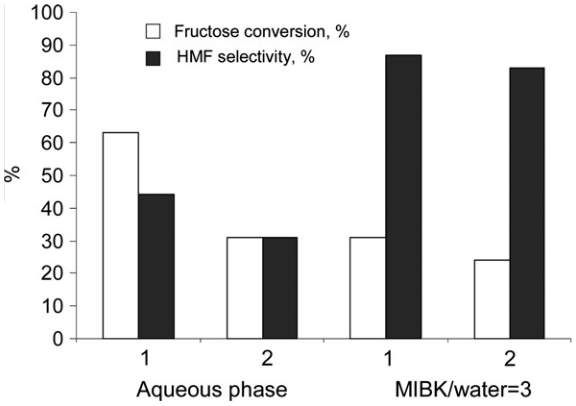


Fig. 11. Fructose conversion and selectivity to HMF in aqueous phase and with addition of MIBK with MIBK/water = 3 measured after 150 min over zeolite MOR in two subsequent cycles.

MOR is an effective catalyst in this reaction. Fructose dehydration in aqueous phase over zeolite MOR gives a yield of HMF 33 mol.%. Fructose dehydration over other heterogeneous catalysts like vanadyl phosphate [17], niobium phosphates [11] and zirconium phosphates [10] in the aqueous phase gives similar yields in the range 20–44 mol.%. Addition of an organic solvent leads to increase in the HMF yield over zeolite MOR to 53 mol.% at the conversion of fructose 85%. This yield of HMF is lower than those reported for fructose dehydration over ion exchange resins in ionic liquids or high boiling organic solvents (73–82 mol.%) [33,34]. However, it provides an opportunity to work with an aqueous phase solution without an energy demanding isolation procedures of HMF.

4. Conclusions

On the basis of the obtained results, it appears that HMF formation in zeolites is not highly selective due to parallel fructose transformations to oligomeric by-products. Addition of organic solvent to zeolites leads to an increase in the selectivity of HMF formation, although amorphous aluminosilicate does not give any increase in the selectivity. The organic solvent in the biphasic system with zeolite as catalyst not just fulfills the function of absorbent of HMF but also intensively interacts with acid sites of the zeolite. This interaction leads to the high initial selectivity of HMF formation due to desorption of HMF from the acid sites by filling of zeolites pores with organic solvent. An increase in the amount of solvent extends the period of high selectivity in fructose dehydration.

Deactivation of external acid sites by silylation procedure has shown that the external surface is involved in the reaction of fructose dehydration for different zeolites to a variable degree, which depends on the pore size and acid strength. Organic solvent allows to suppress the activity of external acid sites with increase in the selectivity to HMF at high fructose conversions. Effect of the organic solvent addition in increase in the selectivity of fructose dehydration to HMF decreases in the row: MOR > ZSM-5 > BEA > aluminosilicate. This order corresponds to the row of the decrease in the strength of acid sites. High selectivity of fructose dehydration over strong acid sites might be explained by fast dehydration of fructose without intermediate product formation, which might take part in further oligomerization reactions. Suppression of humins formation by addition of organic solvent leads to increase in the stability of zeolite in the reaction of fructose dehydration.

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