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Acetalization of furfural with zeolites under benign reaction conditions

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ABSTRACT

Acetalization is a viable method to protect carbonyl functionalities in organic compounds and offers a potential synthetic strategy for synthesizing derived chemicals. In this work, several families of commercial zeolites have been employed as solid acid catalysts in the acetalization of furfural to form furfural diethyl acetal at room temperature using ethanol as a renewable solvent. Among the tested catalysts, H-USY (6) provided the highest catalytic activity (79% acetal yield), excellent selectivity and reusability in five consecutive reaction runs. Process parameters such as, e.g. reaction time, catalyst loading and applicability of different lower alcohols were evaluated and optimized.

1. Introduction

Production of fuels, energy and chemicals from renewable feedstocks are attracting worldwide attention in order to minimize the large dependence on fossil reserves. Development of alternative technology based on sustainable resources will counteract increased fossil energy prices resulting from the depletion as well as environmental concerns caused by global warming. Lignocellulose, the second most abundant component of biomass, is positioned as the most feasible renewable source of organic non-fossil carbon, available for the production of valued-added chemicals and fuels [1–3].

Furfural (FUR) can be derived from lignocellulosic biomass and is a versatile industrial chemical with a wide range of applications [4]. Accordingly, it has been considered a platform molecule for the production of fuels (methyltetrahydrofuran – a gasoline additive), as well as important chemicals such as, e.g. furfuryl alcohol and tetrahydrofuran [2]. FUR is comprised of a heteroaromatic furan ring with an aldehyde group which is a useful handle for further chemical synthesis. In this connection, acid catalyzed acetalization of the formyl functionality (to make acetals) can be a versatile synthetic tool to make new chemicals, integrated in the so-called biorefinery concept, or may serve as a convenient method of protection. The stability of acetals under basic conditions and in the presence of oxidizing and reducing agents, make acetals suitable intermediates in multistep organic synthesis [5–7]. Dimethyl, diethyl and cyclic acetals are the most frequent acetals obtained through acetalization. Moreover, acetals also present industrial applications in pharmaceutical, polymer, fragrance and flavour industries, and they have been used as additive in ethanol fuel to decrease the autoignition temperature [8].

Acetalization is traditionally carried out with homogeneous catalysis using strong Brønsted mineral acids such as, e.g. H_2SO_4 or HCl, which lead to a series of problems associated to product separation, catalyst recovery and equipment corrosion. To overcome these drawbacks focus has recently shifted to the development of renewable and environmentally benign heterogeneous catalyst system instead [9–12]. Many solid catalysts have been used in the acetalization of carbonyl groups, such as lanthanum (III) nitrate hexahydrate [13], bismuth oxynitrate [14], anhydrous cerium(III) chloride [15], phosphotungstic acid [16], sulfated zirconia and titania [17], Ce-exchanged montmorillonite or mesoporous silica [18], Filtrol-24, Amberlyst-15, dodecatungstophosphoric acid (DTPA) supported on both ZSM-5 and K-10 clay [19] and melamine-formaldehyde based polymer [20]. Bhaskar et al. have further reported the use of zeolites as efficient catalysts for the protection of active groups in the synthesis of o-isopropylidene acetals

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from monosaccharides [21]. Application of zeolites takes advantage of their lack of toxicity, non-corrosiveness, easy recovery and possibility of reuse. Furthermore, their regular pore size as well as pore architecture provides them with shape-selective properties. An important advantage lies further in their tunable acid strength, which can be controlled by modification of the Si/Al ratio, that along with their thermal and chemical stability make them largely versatile as catalysts for a wide variety of organic reactions [22] in both the petrochemical industry and in biomass conversion.

In connection with our continuous work on biomass valorization, we have recently shown that commercially available Y and beta zeolites are very promising solid acid catalysts for the isomerization of glucose to fructose and for the direct conversion of glucose to alkyl levulinates in lower alcohols [23,24]. In the present work, we have explored the use of the commercial Y, beta, ZSM-5, and mordenite zeolites for the benign conversion of FUR to furfural diethyl acetal (FDA) by acetalization in ethanol at room temperature. The hydrolysis of FDA to yield FUR was further studied with the catalyst H-USY (6) by water addition as a mean of deprotection of the acetal.

2. Experimental

2.1. Materials

All chemicals in the study were of analytical grade and used without further purification. 2-furaldehyde diethyl acetal (97%), furfural (99%), naphthalene (99%, internal standard), ethanol (99.9%) were purchased from Sigma–Aldrich. All the commercially zeolites used were provided from Zeolyst International and obtained in pure NH_4^+-forms without added binder material. Prior to use, the zeolites were calcined at 550 °C for 6 h with a heating rate of 1 °C min^{-1} in static air in order to convert them to their H-forms.

2.2. Catalytic reactions

The catalytic acetalizations were carried out at room temperature (25 °C) in 15 ml Ace vials equipped with magnetic stirring. In a typical procedure, 80 mg (0.8 mmol) of furfural (2 wt.% with respect to ethanol), 75 mg of zeolite, 25 mg (0.2 mmol) of naphthalene (internal standard) and 4 g (87 mmol) of anhydrous ethanol were charged into a reactor and treated under vigorous stirring for 1 h, where after the reaction mixtures were analyzed.

In recycling experiments the same experimental conditions as above were applied. The reaction time for each run was 1 h (when the maximum FDA yield was achieved). To perform consecutive acetalizations, the reaction mixture along with the catalyst were initially dried for a few hours in order to remove adsorbed/entrapped compounds, where after the catalyst was calcined overnight at 550 °C with a ramp of 1 °C min^{-1} in air. Finally, the catalyst was collected and placed into a fresh test tube and the reaction started.

2.3. Product analysis

Aliquots of the reaction mixtures were subjected to GC-FID analysis (Agilent 6890N instrument, HP-5 capillary column 30.0 m × 320 μm × 0.25 μm) after filtering off the catalyst. A GC–MS system (Agilent 6850 GC system coupled with an Agilent 5975C mass detector) was used for qualitative analysis. Authentic samples of FUR and FDA were used as standards to obtain quantitative calibration curves. The following formulae were employed to calculate FUR conversion and FDA yield:

$$\text{FUR Conversion} = \frac{\text{mol of FUR}_{\text{initial}} - \text{mol of FUR}_{\text{final}}}{\text{mol of FUR}_{\text{initial}}} \times 100$$

$$\text{FDA Yield} = \frac{\text{mol of FDA}_{\text{produced}}}{\text{mol FUR}_{\text{initial}}} \times 100$$

3. Results and discussion

The acetalization of FUR to FDA was performed in ethanol at room temperature and the results are presented in Table 1. In the absence of catalyst, no reaction was observed (Table 1, entry 13). Moreover, no conversion to FDA was observed when Na-mordenite was used as catalyst (Table 1, entry 12), implying that an acid catalyst was indeed required to perform the reaction as expected. Next, experiments were carried out over H-forms of commercial beta, ZSM-5 and mordenite zeolites with different Si/Al ratios. The results demonstrate that in all cases, FDA was essentially the only reaction product formed (>95% selectivity). All Y and beta large-pore zeolites yielded between 71 and 79% of FDA (Table 1, entries 1–6) with H-USY (6) giving the highest yield (79%) among the employed zeolites. The total number of acid sites for the H-zeolites was estimated by using NH_3-TPD and reported in our previous work [23,24] and the results are given in Table 1. Interestingly, H-beta (150) – having a relatively low number of acid sites (Table 1) – gave also a good FDA yield of 75%. On the other hand, H-ZSM-5 (medium-pore size) gave FDA yields below 50% (Table 1, entries 9–12). When comparing the same zeolite structure with different Si/Al molar ratios, the only appreciable differences were observed for H-ZSM-5 with Si/Al ratios of 40 and 140, respectively. Moreover, the formation of FDA did not depend on the number of acid sites present in the zeolites, but pore size of the zeolites played a major role. However, H-mordenite (large-pore size) gave only 33% FDA.

Table 1
Acetalization of FUR to FDA over various zeolites.[a]

Entry	Pore size	Zeolite	Si/Al ratio	Acid sites[b] (μmol/g)	Conversion (%)	FDA yield (%)
1	Large	H-USY	6	835	79	79
2		H-USY	30	347	75	74
3		H-beta	12.5	855	76	72
4		H-beta	19	806	75	72
5		H-beta	25	n.a	71	71
6		H-beta	150	147	79	75
7		H-mordenite	10	1656	33	33
8		Na-mordenite	6.5	n.a	<1	<1
9	Medium	H-ZSM-5	11.5	1394	40	37
10		H-ZSM-5	25	n.a	35	35
11		H-ZSM-5	40	451	29	28
12		H-ZSM-5	140	n.a	8	8
13		–	–	–	<1	<1

[a] Reaction conditions: 80 mg (0.8 mmol) FUR, 75 mg zeolite, 25 mg (0.2 mmol) naphthalene (internal standard), 4 g (87 mmol) ethanol, 25 °C, 1 h.
[b] n.a = not available.

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From the data of Table 1, it can be inferred that the pore size of the zeolites had a stronger influence on the acetalization reaction than the concentration of acid sites. Climent et al. [25] and Thomas et al. [18] have observed a similar effect in the acetalization of aldehydes and ketones employing zeolites as catalysts. Since the most active and selective catalyst was H-USY (6), exhibited a yield of 79% FDA, this catalyst was chosen for further study and optimization of other reaction conditions, such as, e.g. reaction time, catalyst amount and catalyst reusability.

Methanol is the lower alcohol most commonly employed as solvent in acetalization of aldehydes and ketones due to its high reactivity [9,17,26,27]. However, to make the process more environmentally sustainable, ethanol was here used instead of methanol since it can be easily produced from renewable agricultural feedstocks. Moreover, it was found that reactions with higher alcohols such as, e.g. 1-propanol or 1-butanol, resulted in lower conversion to the respective acetals (70 and 25%, respectively) when using H-USY (6) as catalyst under identical reaction conditions. Probably, this decrease in catalytic activity can be attributed to diffusional limitations in the zeolite, which hinders the larger molecular sized acetals to readily diffuse out of the micropores when formed.

The acetalization of FUR is accomplished through the reaction mechanism shown in Scheme 1. The first step is the formation of a protonated intermediate (2) via protonation of the carbonyl group of FUR (1) by a Brønsted acid site of the zeolite. Then, ethanol reacts with the intermediate (2) forming the hemiacetal (3) after removal of a proton, which then re-protonates and dehydrates to the intermediate (4). Afterwards, the intermediate (4) reacts with another ethanol molecule giving the intermediate (5), which upon deprotonation forms the acetal FDA (6) and regenerates the acid site. Although the synthesis of FDA requires initial formation of the corresponding hemiacetal (3), this was not detected as intermediate in any of the examined reactions. This suggests that the acetal formation was fast compared to hemiacetal formation, as also previously reported for other systems.

It is noteworthy that acetalization is a reversible reaction and Moreau et al. have shown that the hydrolysis of acetals and thioacetals of FUR can be carried out in water in the presence of strong Brønsted acids, through a pseudo-first order mechanism [28]. Therefore, water produced in the acetalization process together with the Brønsted acid sites present on the H-USY (6) zeolite could potentially hydrolyze FDA to reform FUR during the reaction (Scheme 1). To suppress the concurrent hydrolysis reaction and obtain high FUR conversion, a large excess of alcohol in comparison to the stoichiometric amount (i.e. EtOH:FUR molar ratio = 100:1) was accordingly used for the acetalization reactions. The hydrolysis reaction was, however, facile in the presence of the same zeolites with added water resulting in complete hydrolysis of FDA to FUR after 1 h of reaction at room-temperature with a H_2O:EtOH weight ratio of 1:2 or larger.

The influence of the concentration of FUR in ethanol was also studied with 2–10 wt.% FUR with H-USY (6) under identical conditions as shown in Table 1. The yield to FDA decreased from 79 to 74% when the concentration of FUR was increased from 2 to 5 wt.%. However, as the amount of FUR increased to 10 wt.% the FDA yield (73%) remained almost unchanged, implying that a high yield of FDA could also be achieved at a higher concentration of FUR.

The effect of catalyst loading on the FUR acetalization was also studied over H-USY (6) under typical experimental conditions (see Section 2.2). In general, an increase in catalyst loading implies an increase of the number of acid active sites available for the catalytic process, and consequently the conversion (i.e. reaction rate) is expected to increase if the reaction is kinetically controlled. Nevertheless, the data displayed in Fig. 1 reflect that the FDA yield (and thus also the FUR conversion) only increased when the amount of added catalyst augmented from 2 to 5 mg. With higher catalyst loadings (12.5–75 mg) the FDA yield remained unchanged, indicating that excess of acid needed to facilitate the reaction was present. When using a low amount of catalyst (2 mg), the FDA yield attained a value of 65% after 2 h of reaction time and increased further to 77% after 3 h of reaction (Fig. 2). This confirmed that the catalysts remained active and longer reaction time was just required to produce almost the same FDA yield as found for higher amount of catalyst at shorter reaction time.

Catalyst reusability in the acetalization of FUR was also evaluated for H-USY (6) by performing five consecutive runs (see Section 2.2 for regeneration procedure applied after each run). Fig. 3 shows that the catalyst maintained a good performance providing a similar product distribution after each run with a FDA yield of 76–84%. These results corroborate that the H-USY (6) zeolite can be regenerated with the applied procedure without structural damage, since such structural alteration would be expected to result in loss of performance. Similarly, leaching of Al from the zeolite is not likely to occur as this also would be expected to alter the catalyst performance due to the associated loss of acid sites. Such a change in catalyst performance has already been reported by Thomas et al. in their study on acetalization of carbonyl compounds with cation exchanged montmorillonites [9].

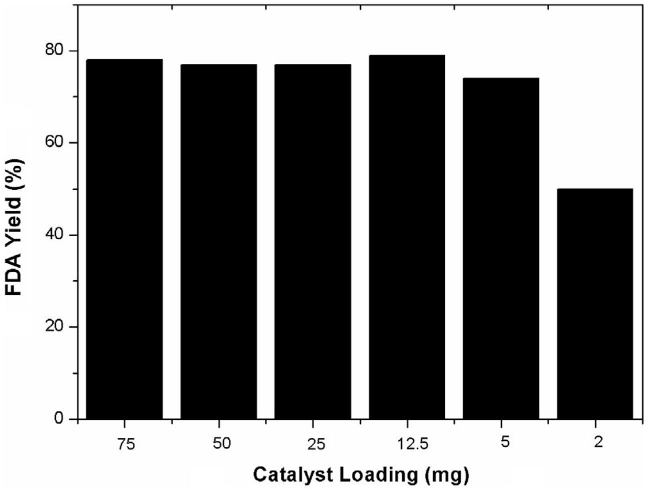

Fig. 1. The influence of H-USY (6) catalyst loading on the yield of FDA. Reaction conditions: 80 mg (0.8 mmol) FUR, 4 g (87 mmol) ethanol, 25 °C, 1 h.

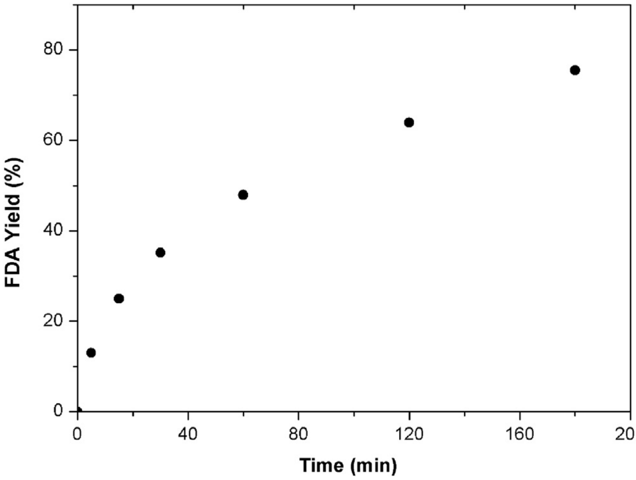

Fig. 2. The formation of FDA over H-USY (6) as a function of time. Reaction conditions: 80 mg (0.8 mmol) FUR, 4 g (87 mmol) ethanol, 2 mg catalyst, 25 °C.

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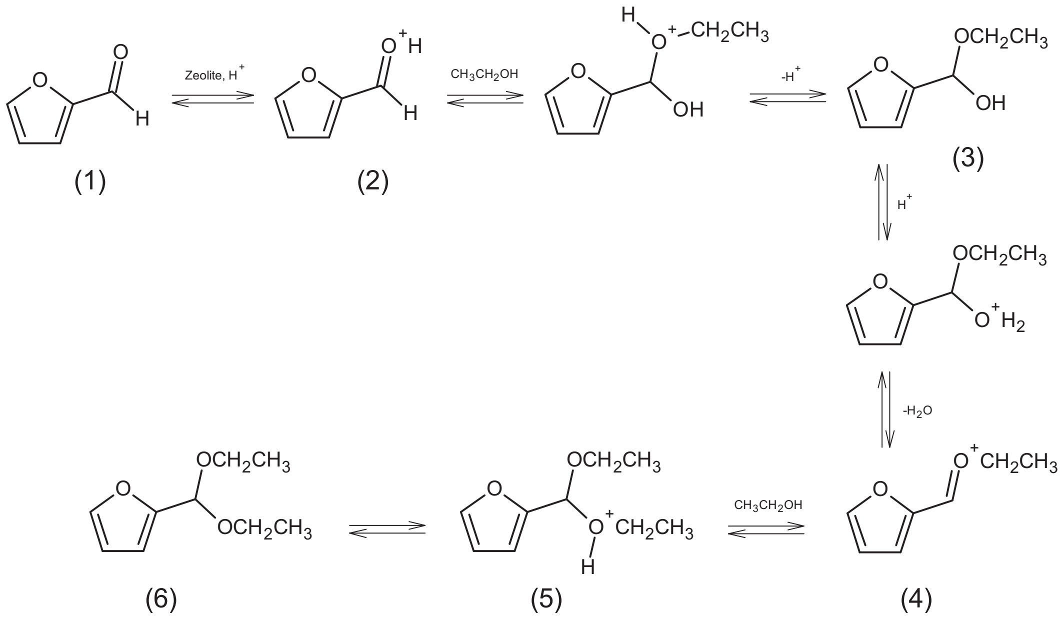

Scheme 1. The mechanism of the acid-catalyzed acetalization of FUR to FDA.

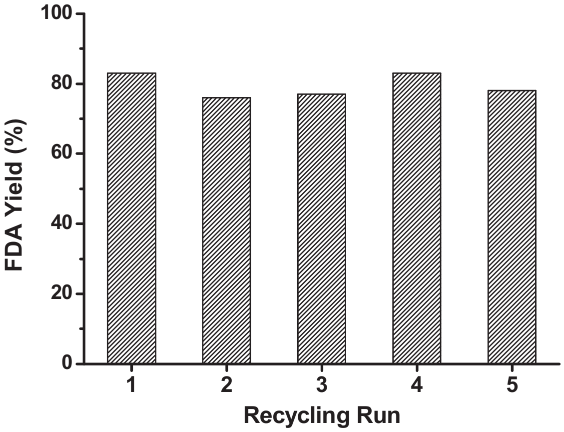

Fig. 3. Reusability of the H-USY (6) catalyst in the acetalization of FUR. Reaction conditions: Catalyst to FUR mass ratio = 5.9, 4.3 wt.% FUR in ethanol, 25 °C, 1 h.

4. Conclusions

A series of commercial microporous zeolites were applied for room-temperature acetalization of furfural with ethanol to form furfural diethyl acetal. The hemiacetal was not observed as reaction product with the catalysts under the applied conditions. The best acetal yield close to 80% was found using H-USY (6) zeolite catalyst. This yield was also obtained with low loading of the catalyst (2.5 wt.% with respect to the substrate) at prolonged reaction time. The H-USY (6) catalyst proved further reusable in five consecutive runs with unchanged performance, thus demonstrating it to be an excellent recyclable solid acid catalyst for acetalization with potential for industrial application.

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