

Optimization for catalytic performances of $H\beta$ zeolite in the acylation of 2-methylfuran by surface modification and solvents effect

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Abstract The liquid phase acylation of 2-methylfuran with acetic anhydride over modified H β zeolite was first conducted in a continuous flow reactor. The deactivation of H β zeolites was attributed to strong adsorption of reactants or products and was verified by GC–MS and ¹³C MAS NMR. Deactivated zeolites can be regenerated to their original state by calcination. The acidic properties was adjusted by surface modification on H β , the maximum yield of 89.5 mol% and selectivity of 100 % were obtained over tartaric acid modified by H β . The deposition of tetraethoxysilane to silica on H β contributed to enhancing the catalytic stability. Combined with the results of NH₃-TPD and Py-FTIR, the amount of Broensted acids played a major role on catalytic activity. A close relationship between the catalytic stability and the ratio of the amount of strong to weak acids at 1:1 was highlighted here. The solvents' effect on the catalytic performances was examined, and 1,2-dichloroethane with moderate polarity exerted a positive effect on catalytic stability.

Keywords Acylation \cdot H β zeolite \cdot Surface modification \cdot Catalytic performances \cdot Solvents effect

Introduction

Friedel–Crafts acylation of aromatic substances is a well-renowned reaction in the fine chemical industry [1-4]. The obtained aromatic ketones are widely utilized as valuable intermediates in the fabrication of fine and special chemicals, such as

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drugs, pesticides, elasticizers, dyestuffs, and perfumes [5, 6]. As far as we know, Broensted acids (e.g., HCl, H₂SO₄) and Lewis acids (e.g., AlCl₃, BF₃) are often used as homogeneous catalysts for the conventional acylation synthesis. Unfortunately, the inherently encountered defects of such a manufacturing process basically cover the handling of toxic wastes, equipment corrosion, and products collection [7]. With increasing pressure on environmental and economic issues, the exploration of sustainable and available methodologies for the acquisition of high-valued products with no environmental pollution is a major challenge for our research community. Toward this purpose, some new and efficient heterogeneous catalysts such as zeolites [8–10], heteropolyacids [11], clays [12] and metal hydroxide fluorides [13] are sought to effectively figure out the problems mentioned above. Particularly, zeolites are extensively used due to their high activity, renewability and eco-friendly nature, which have been proven to be the most potential catalysts in the catalytic synthesis field [14]. The convenient applications of acidic zeolites for the Friedel-Crafts acylation of aromatic and heterocyclic aromatic compounds have been declared by several research groups [15-17]. For instance, Guignard et al. [18]recently announced the first commercial applications of zeolites for the acylation of veratrole and anisole. As it was published by Álvaro et al. [19], the high yields of 91 mol% of 2-acetylfuran were effectively synthesized over HB zeolite under mild reaction conditions. Nevertheless, zeolites are easily inclined to the fast deactivation when serving as catalysts for acylation. The deactivation phenomenon that results from strong adsorption of aromatic substrates or products has been witnessed by several reports [20, 21]. Therefore, the behavior of H β zeolite must be optimized further for dealing with both the problems of catalytic activity and stability, which are prerequisites for application in industrial production of aromatic ketones. It is deservedly noted that the Broensted acids on HB zeolite can account for its high activity in catalytic synthesis. Reddy et al. [22] reported that the liquid phase acylation reaction of pyrrole and furan were more positive on Broensted acids of $H\beta$ zeolite. Consequently, a connection between the catalytic performances and acid sites (both Broensted and Lewis acids) of zeolites should be emphasized. It was recently found by Zhao et al. [23] that an appropriate balance between the weaker and stronger acid amounts on the surface of H β zeolite can enhance the catalytic stability. There have been several approaches to the optimization of the Friedel-Crafts acylation reaction. An essential step in preparing the highly active and stable zeolite is the modification of its surface. From those results reported before [24–28], we have a solid foundation for believing that the surface modification using acid treatment and chemical liquid deposition can bring about many benefits, offering the possibility to tune the intensity and distribution of acid sites.

The acylation of 2-methylfuran with acetic anhydride in liquid phase was used as a model reaction to study the effects of surface modification, and to examine the effect of the solvents polarity on the catalytic performances of H β zeolite. Although the fast deactivation was still observed by GC–MS and ¹³C MAS NMR after acylation reaction, we provided some efficient approach to optimize the catalytic stability. In our work, Py-FTIR and NH₃-TPD analysis were employed to investigate the relationship between acid sites and catalytic performance of H β zeolite. The objective of this study was to enhance the catalytic performance of H β

zeolite in an acylation reaction through surface modification and solvent effects. Our contribution to this vast field is that high yield and good catalytic stability were attained in the acylation of 2-methylfuran under mild conditions. With the catalytic result of modified H β zeolite, the modification of the mechanism concerning Broensted acids and the intensity distribution of acid sites of H β zeolite was discussed in detail, which is rarely found in other studies.

Experimental

Materials

2-Methylfuran (2-MF, >98 %) and Tetraethoxysilane (TEOS, >99 %) were purchased from Energy Chemical Technology Co., Ltd. Acetic acid (99.5 %), tartaric acid (99.5 %), and nitric acid (65–68 %) were supplied by Tianjin Guangfu Institute of Fine Chemistry. Hexane (98 %) and acetic anhydride (AA, 98.5 %) were supplied by Tianjin Jiangtian Chemical Technology Co., Ltd. 2-Acetyl-5methylfuran (2-AC-5-MF, >98.0 %) standard and tetraethylammonium hydroxide (TEAOH) were provided by Aladdin Reagent Co., Ltd. The commercial H β zeolite and aluminum oxide powder were procured from Nankai University Catalyst Co., Ltd. All chemical reagents were put to use without further purification.

Catalyst preparation and modification

Firstly, 50 g of H β zeolite powder with acid impregnations in an airtight container, was stirred with 500 mL of acetic acid (1 mol L⁻¹) at ambient temperature. After above mixture was stirred for 10 h, the zeolite sample was recovered by filtration and washed out with distilled water until the solution turned into neutral. Secondly, the acid-treated H β was prepared on the basis of the work of Matsukata et al. [29]. The mixture of 10 g zeolite powder, 3 g aluminum oxide and 4 g nitric acid solution (10 wt%) was agitated into homogeneity, squeezed, and trimmed into the shape of a short cylinder. Thirdly, the molded sample was dehydrated at 120 °C in dry air for 2 h, and calcination progress was made in a muffle furnace with temperature programmed to 550 °C for 4 h at a heating rate of 20–30 °C min⁻¹. The obtained catalyst was called AC-H β . Moreover, tartaric acid (1 mol L⁻¹) modified H β zeolites were prepared by the abovementioned method and designated as TA-H β .

Approximately 20 g of H β zeolite (named parent H β) was suspended in 50 mL of hexane, then 30 mL of tetraethoxysilane (TEOS) was added into this mixture. After stirring for 10 h, hexane was removed from its solution by evaporation, and the mixture was filtered further and dried at 120 °C. The H β zeolite supported with TEOS was roasted at 550 °C for 4 h. Thus, the SiO₂ chemical liquid deposition (SiO₂-CLD) modified H β zeolite was attained and labeled as Si-H β . The carbon deposits absorbed on the external surface and in the micropores of deactivated zeolites were recovered by the soxhlet extraction method. After acylation reaction, the deactivated catalyst was treated in a soxhlet extractor for 8 h using

dichloromethane as solvent. Then the dichloromethane was completely evaporated at 60 °C and the extracted organic compounds were obtained.

Catalyst characterization

The X-ray diffraction (XRD) powder patterns were obtained on a Bruker D8-S4 diffractometer operated at 50 mA and 40 kV with a Cu K α radiation source, scanning from 4° to 30° range with a scanning rate of 3.21°/min and steps = 2605. The framework Si/Al molar ratios of zeolites were analyzed by X-ray fluorescence (XRF) spectroscopy recorded on a Bruker S4 Pioneer spectrometer. The morphology of zeolites was characterized by a Hitachi S-4800 Scanning electron microscope (SEM) with high resolution. The pore diameter distribution and surface area were achieved on a Micrometrics ASAP 2020 volumetric instrument at -196 °C.

The acid nature of zeolites was detected on a Nicolet 750 infrared spectrometer through the pyridine adsorption–desorption method. A self-supported wafer was loaded into an infrared cell coupled with the conventional high vacuum system. Prior to pyridine adsorption, 25 mg of zeolites were pretreated at 450 °C for 2 h in the vacuum. When the self-supported wafer was cooled to ambient temperature, pyridine adsorption proceeded at 60 °C for 1 h. Then, the IR spectra were collected by the evacuation of adsorbed pyridine at 200 and 350 °C for 0.5 h, respectively. The information about the surface chemistry of zeolites was gained by FTIR techniques and recorded on a Bruker TENSOR 37 instrument with a resolution of 4 cm⁻¹.

The ammonia temperature-programmed desorption (NH₃-TPD) for the acids amount and intensity of zeolites was carried out on a TP-5080 instrument with a combined thermal conductivity cell detector. First, around 10 mg of zeolite catalyst was pretreated in situ at 200 °C for 1 h in a flow of helium (50 mL min⁻¹), and then the NH₃ was adsorbed at 60 °C for 0.5 h. The NH₃ desorption was taken at the range of 120–800 °C with a heating rate of 10 °C min⁻¹. The ¹³C NMR spectra were acquired on a Varian Infinity plus NMR spectrometer to study the types of carbon deposits. The scanning frequency and pulse delay were 75.4 MHz and 5.0 s, respectively. The chemical shifts (δ) of spectra with units of ppm stood for the types of carbon deposits.

Catalytic tests

Continuous acylation reactions of 2-methylfuran (2-MF) by acetic anhydride (AA) over parent H β , AC-H β , TA-H β , Si-H β zeolite were conducted on a fixed-bed reactor (Fig. 1) under atmospheric pressure, consisting of a glass tube (inner diameter 10 mm) with an electrical heater. Before the acylation reaction, the same amounts of zeolites were activated at 200 °C in a drying oven for 2 h. The zeolites were transferred immediately into the reactor to prevent exposure to the atmosphere. For a standard experiment, acylation temperature was controlled at 60 °C by water bath heating at the first step. Then, 5.9 g of zeolite catalyst was fixed in the central section of a fixed-bed reactor. The mixture of 2-MF and AA (molar ratio 1:2.5 or 1:4) was fed to the catalytic column by a metering pump with a given flow rate



Fig. 1 Apparatus diagram of a fixed-bed reactor used for continuous liquid phase acylation of 2-methylfuran

(0.07 mL min⁻¹). The liquid acylated products were periodically collected from the reactor outlet, and quantitatively analyzed on a gas chromatograph (GC, Agilent 7890A) equipped with the flame ionization detector (FID) and DB-FFAP capillary column (length 30 m, phase thickness 0.25 μ m, diameter 0.25 mm). The target acylated product 2-acetyl-5-methylfuran (2-AC-5-MF) was obtained from acylation reaction, and identified by a mass spectrometer (MS, Agilent 5975C) with the mass selective detector.

The molar yield (mol%) of 2-acetyl-methylfuran ($Y_{2-AC-5-MF}$) was calculated as follows:

$$Y_{2-\text{AC-5-MF}} = \frac{\% \text{mol} (2-\text{AC-5-MF at time} = t)}{\% \text{mol} (2-\text{MF at time} = 0)} \times 100.$$
(1)

Results and discussion

Characterization of zeolites

XRD patterns (in Fig. 2) of the parent H β , AC-H β , TA-H β , and Si-H β are given. The characteristic diffraction peaks of all zeolite samples were at about 7.8° and 22.5°, indicating that the acid treatment and SiO₂-CLD modification had not changed the basic structure of H β zeolite, and there are very few visible impurity peaks. However, the XRD peaks at 7.8° and 22.5° of AC-H β , TA-H β and Si-H β were weaker than that of the parent H β and attributed to surface modification. According to the results of XRF as recorded in Table 1, the framework Si/Al of parent H β , AC-H β , TA-H β , Si-H β zeolites used in this work was 27.6, 28.2, 62.9, and 86.8 respectively, implying that the dealumination occurred obviously on zeolites in the acid treatment. However, the increase of Si/Al molar ratios in



Fig. 2 XRD patterns of parent and modified HB zeolites

SiO₂-CLD is mainly ascribed to the deposition of TEOS modifier on the surface of zeolite. The result in Table 1 presents the specific surface areas (including external and micropore) and average pore diameter of zeolites. The BET method was used to determine the specific surface area, and the BJH approach was used to calculate the pore diameter distribution. In comparison with H β zeolite, there are certain increases both in the outer surface area and average pore diameter for acid-modified H β zeolites. Particularly, the largest surface area and average pore diameter was observed on TA-H β . As a consequence of modification, the acid treatment can remove the non-framework impurities existing in H β zeolite micropores, resulting in increase in specific area. This suggests that the dealuminzation through the acid treatment can be in favor of the transfer of target products (2-AC-5-MF). However, SiO₂-CLD modification of H β zeolite led to a small decline in its average pore

Sample	Surface a	rea^{a} (m ² /g)	Average pore	Si/Al molar	
	Total	Micropore	External	diameter ^b (nm)	ratios ^c
Parent	365	237	128	0.55	27.6
АС-Нβ	376	235	142	0.61	28.2
ΤΑ-Ηβ	427	222	205	0.76	62.9
Si-Hβ	351	232	118	0.52	86.8

Table 1 The framework Si/Al molar ratios, BET surface area, micropore volume, and average pore diameter of parent H β and modified H β zeolites

^a Surface area calculated by the BET and t-plot method

^b Average pore diameter determined by the Horvath-Kawazoe method

^c Si/Al molar ratios measured by XRF

diameter and external surface area, which can adjust the acidic intensity distribution of zeolites, similar to the previous report [30].

In order to explore the modification mechanism regarding the acid sites with the amount and distribution of H β zeolite, some analytical methods were done in this study. IR was widely applied to detect the properties of zeolite hydroxyls. Py-FTIR was also adopted to study the effect of acid treatment and SiO₂-CLD modification on the acid properties. As released by Emeis [31], the concentration of surface acid sites can be calculated by the integrated peak area of adsorbed pyridine. The integrated molar extinction coefficients of Broensted acid sites and Lewis acid sites bands were 1.67 and 2.22 cm/µmol, respectively. The information of Lewis and Broensted acid sites on H β zeolite was gained by Py-FTIR through the pyridine adsorption–desorption method, summarized in Table 2. In a typical NH₃-TPD run, the quantity of desorbed NH₃ can be regarded as the acidic quantity of zeolites, and the acidic intensity was classified by desorption temperature. The results from NH₃-TPD analysis for different zeolites are listed in Table 3.

Effect of acids modification on catalyst properties

From the catalytic point of view, the activity of zeolite can be connected with the amount of both Broensted and Lewis acid sites in Friedel–Crafts acylation. As already been pointed out, the total number and nature of acid sites should have a direct effect on the activity and stability of catalyst [32, 33]. Acid treatments are utilized to remove the extra-framework Al sites to increase the external surface of zeolite crystals, which may contribute to improve the adsorption capacity of reactants. To study the effect of the acid modification, the catalytic performances of different acid-modified H β were tested in the acylation of 2-MF. 2-AC-5-MF was the only product observed in this acylation, so the selectivity for 2-AC-5-MF was almost 100 %. As shown in Fig. 3, the highest activity and stability are obtained on TA-H β catalyst, the yield of 2-AC-5-MF at the beginning is 89.5 mol%, and TA-H β can maintain a high yield plateau (\geq 70 mol%) for 45 h in the acylation of 2-MF. Nevertheless, AC-H β exhibited the lower initial yield of 82.3 mol%, besides the yield of 2-AC-5-MF only can remain at about 70 mol% after 12.5 h on stream,

Samples	200 °C			350 °C			
	L acid site	B acid site	B/L ^a	L acid site	B acid site	B/L ^a	
Parent	4.863	0.663	0.136	4.263	0.589	0.138	
АС-Нβ	4.531	0.547	0.121	3.984	0.506	0.127	
ΤΑ-Ηβ	3.668	0.836	0.228	3.152	0.673	0.214	
Si-Hβ	2.928	0.605	0.207	2.475	0.498	0.201	

Table 2 Acid site properties and amounts determined by Py-FTIR spectra for parent and modified H β zeolites at desorption temperatures of 200 and 350 °C

^a B/L: the ratio of Broensted to Lewis acid site amounts, measured by the ratio of the integrated area of FTIR peaks to sample weight

Samples	Weak acidic sites		Strong acidi	c sites	Acid distribution	
	L T-peak ^a (°C)	Weak acid (mmol/g)	H T-peak ^b (°C)	Strong acid (mmol/g)	Total acid (mmol/g)	S/W ^c
Parent	206	0.630	300	0.413	1.043	0.656
ΤΑ-Ηβ	203	0.553	315	0.567	1.120	1.025
АС-Нβ	195	0.658	302	0.371	1.029	0.564
Si-Hβ	202	0.294	320	0.308	0.742	1.048
Deactivated	190	0.532	298	0.210	0.602	0.395

Table 3 NH₃-TPD data of parent and modified Hβ zeolites

^a L T-peak: low-temperature peak

^b H T-peak: high-temperature peak

^c S/W: the ration of strong acid to weak acid number



Fig. 3 Catalytic performances tests for acylation of 2-methylfuran with acetic anhydride over parent H β , TA-H β and AC-H β zeolites in a fixed bed reactor (experimental conditions: 60 °C, 2-methylfuran/acetic anhydride molar ratio = 1:2.5, flow rate: 0.07 mL/min, 5.9 g of zeolites)

which is similar to that of the parent H β with 13.5 h. This indicates that a serious catalyst deactivation occurred on AC-H β and the parent H β .

Table 2 shows that a decrease in the concentration L acid sites because of the removal of extra-framework aluminum through the acid treatment. However, tartaric acids as a special chelating agent can further react with the removed aluminum, converting into the more stable B acid sites. Meanwhile, the more stable B acid sites were replenished into the framework structures of H β zeolite, thus leading to the increase in B acid sites. What is interesting is that TA-H β exhibited higher catalytic stability with the greater amount of Broensted but with less Lewis acid sites. AC-H β with the lower activity in acylation can be ascribed to the lower amounts of Broensted acids (Table 2, line 2) in comparison with parent

H β . It seems that Broensted acids amounts are of great importance in accounting for their behaviors in acylation reactions. NH₃-TPD tests were carried out to measure the amounts and types of acid sites of zeolites. The amount of acid sites was determined on the basis of the peak areas of TPD, and listed in Table 3. The peak at the range of about 150–200 °C was ascribed to the weaker acids and the peak approximately at 300–400 °C to the stronger acids announced by Ghiaci et al. [34]. As shown in Fig. 4, by contrast, there was a decrease both in the weaker acid and stronger acid amounts in TA-H β and AC-H β . Nevertheless, TA-H β shows the better behavior with the strong to weak acids ratio of nearly 1:1 (Table 3, line 3), and more appropriate distribution of acid intensity. It implies that the catalytic stability primarily depended on acid intensity distribution not at large acid amounts.

Effect of SiO₂-CLD modification on catalyst properties

For purpose of gaining better performance, some available modification methods have been utilized to optimize catalysts. Considering some benefits of chemical liquid deposition (CLD) [35, 36], the deposition of tetraethoxysilane to silica on its external surface can increase the hydrophobic properties of zeolite, and enhance the adsorption capacity of organic reactants. It is worthy to study the effect of CLD of silicates on catalytic performances in our work. The deposition of TEOS modifier to SiO₂ over H β zeolite was also done in our study. IR technique was put to use to distinguish the features of zeolite hydroxyls. In line with the previous publication [37], the framework bridging Al(OH)Si was assigned to the band at 3600–3610 cm⁻¹, Al(OH) of extra-framework was assigned to the band at about 3660 cm⁻¹, while silanol Si(OH) of zeolites was assigned to the band approximately at 3740 cm⁻¹. As depicted in Fig. 9, the acidic hydroxyls of H β consist of the framework bridging Al(OH)Si, extra-framework Al(OH) and silanol group Si(OH). The silanol group Si(OH) initiates dropping without calcination in SiO₂-



Fig. 4 NH₃-TPD profiles of the parent H β and acid modified H β zeolites

CLD treatment. Whereas, the amount of Si(OH) at 3740 cm⁻¹ diminished merely after calcination. Thus, it can be concluded that TEOS reacted with the hydroxyls of zeolite during the chemical liquid deposition, and thus covered the external surface of H β . Besides, the band at about 2965–3070 cm⁻¹ is related to the C-H bond of the modifier TEOS deposited on surface of H β zeolite. In contrast to the parent H β (Fig. 5), it reveals that the C-H bond can disappear after calcination treatment, suggesting that TEOS can decompose into silica completely in the SiO₂-CLD.

The catalytic performances of Si-H β and parent H β were compared in the acylation of 2-MF with AA. In fact, we can see that SiO₂ mainly covered the external surface of H β during the chemical liquid deposition, but it is interesting to find that Si-H β showed the better behavior. Thus, we might declare that the acylation of 2-MF with AA primarily took place in the micropores of H β zeolite. As shown in Fig. 6, the average lifetime (yield of 70 mol% as benchmark) and yield of Si-H β increased by 10 h, and 10 mol%, respectively, compared to the parent H β . Moreover, the NH₃-TPD profile (Fig. 7) indicates that the strong acids amount of Si-H β is far less than that of parent H β . It should be the coverage of silica on the outer surface of H β that results in the reduction of acid amounts and silanol hydroxyls. The SiO₂-CLD modification on H β led to a decrease of acid sites, but also a more reasonable acid intensity distribution with the nearly equal amounts of strong and weak acid (Table 3, line 4). In terms of such results, it may be speculated that the appropriate acid intensity distribution is the key to maintaining the catalytic stability.



Fig. 5 IR spectra of parent H β and modified H β zeolites in SiO_2-CLD before and after calcination treatment



Fig. 6 Acylation results of 2-methylfuran by acetic anhydride in a fixed bed reactor over the parent H β , modified H β with SiO₂-CLD (experimental conditions: 60 °C, 2-methylfuran/acetic anhydride molar ratio = 1:4, flow rate: 0.07 mL/min, 5.9 g of zeolites)



Fig. 7 NH₃-TPD profiles of the parent Hβ and Si-Hβ zeolites

Catalytic performances

To illustrate the effects of surface modification on the catalytic performances, we herein compared the catalytic results of modified and parent H β zeolites. Concerning acid treatment effects, TA-H β exhibited the more stable catalytic performances shown in Table 1, it was found that the total BET surface areas and average pore diameters of TA-H β were larger than those of AC-H β and parent H β . These results might be explained by the dealumination effect due to acid

modification, which also is confirmed by the increase in Si/Al ratio. With regard to the SiO₂-CLD modification, the increase of Si/Al molar ratios in SiO₂-CLD is mainly ascribed to the deposition of TEOS modifier on the surface of zeolite. It should be noticed that the catalytic performances improved with the increasing molar ratios of Si/Al to some extent.

The modifications on the acid properties of HB zeolites were caused the different behavior involving in he acylation process. Such a close correlation between the catalytic performance and the amount of Broensted acids on zeolites was highly stressed. Unfortunately, a relation was not observed concerning the Lewis acids in the acylation of 2-methylfuran. In this way, the amount of Broensted acids should be the restrictive factor, and there are much less Broensted than Lewis acids on each zeolite catalyst. NH₃-TPD results for all zeolites were given in Table 3, and clearly explain that the higher catalytic stability is well associated with the more appropriate distribution of acid intensity. Indeed, the strong to weak acids ratio of TA-H β , and Si-H β was almost 1:1, while parent H β , AC-H β were not. Consequently, we have reason to believe that larger numbers of total acid sites of zeolites would not contribute to the higher catalytic performance, which was verified by AC-H^β with terrible catalytic stability in acylation of 2-MF. The desired zeolite catalysts do not have a larger number of acid sites but must with the appropriate acid intensity distribution, similar to the results published by Zhao et al. [23].

Informed by the previous report [29], the reusability of zeolites is also a sign of catalytic stability of zeolites. The reusability of parent H β , AC-H β , TA-H β , and Si-H β were investigated in the same acylation of 2-MF with AA, and the results are given in Table 4. As can be seen, the regenerated zeolites almost exhibited the identical stability with the same reaction time, and activity with the maximum yields as their origins. It also shows that zeolites can be recycled by high temperature calcination. As expected, the parent and modified H β still remained at the same time on stream before the deactivated point (yields below 70 mol%), and catalytic activity (yields of 2-MF). After the eight cyclic regenerations, the average lifetimes of TA-H β and Si-H β were still longer than that of the parent H β and AC-H β .

Origin of deactivation of zeolites

As can be seen from the SEM image (Fig. 11), there are severe carbon deposits existing on the surface of the deactivated H β zeolites (the yields of 2-AC-5-MF below 70 mol%), which might block the acidic sites of the catalyst, leading to the decrease of the reaction rate. Moreover, the H β zeolite became dark brown at the end of the acylation reaction. Figure 7 shows that the yield of 2-AC-5-MF decreased obviously with increasing time on stream, which means the fast catalyst decay mainly occur in the acylation of 2-MF. The ¹³C MAS NMR spectrum of the deactivated H β is given in Fig. 8. The spectral feature of deactivated H β is associated with the species of carbon deposits, composed of fat carbon, olefin carbon, aromatic carbon and poly aromatic carbon, etc. [38]. The fat carbon corresponds to the band at 10–40 ppm, the aromatic carbon is assigned to a band at

Catalyst	Regeneration time	Calcination temperature (°C)	Deactivated point (%)	Catalyst dosage (g)	Catalytic lifetime (h)	Maximum yield of (mol%)
Parent Hβ	0	550	70.0	5.92	13.5	84.5
	1	550	70.0	5.92	13.5	84.1
	2	550	70.0	5.92	13.5	83.8
	3	550	70.0	5.92	13.5	83.8
	4	550	70.0	5.92	13.5	83.8
	5	550	70.0	5.92	13.5	83.4
	6	550	70.0	5.92	13.4	83.4
	7	550	70.0	5.92	13.4	83.4
	8	550	70.0	5.92	13.4	83.4
Average/total					13.5	83.7
ΤΑ-Ηβ	0	550	70.0	5.93	45.0	89.5
	1	550	70.0	5.93	45.0	89.5
	2	550	70.0	5.93	45.0	89.5
	3	550	70.0	5.93	45.0	89.4
	4	550	70.0	5.93	45.0	89.3
	5	550	70.0	5.93	45.0	89.3
	6	550	70.0	5.93	44.5	89.3
	7	550	70.0	5.93	44.5	89.2
	8	550	70.0	5.93	44.5	89.2
Average/total					44.8	89.3
АС-Нβ	0	550	70.0	5.95	12.5	81.4
	1	550	70.0	5.95	12.5	81.4
	2	550	70.0	5.95	12.5	81.4
	3	550	70.0	5.95	12.5	81.1
	4	550	70.0	5.95	12.4	81.1
	5	550	70.0	5.95	12.4	80.9
	6	550	70.0	5.95	12.3	80.9
	7	550	70.0	5.95	12.3	80.7
	8	550	70.0	5.95	12.3	80.5
Average/total		550			12.4	81.0
Si-Hβ	0	550	70.0	5.91	23.5	87.6
	1	550	70.0	5.91	23.5	87.6
	2	550	70.0	5.91	23.5	87.6
	3	550	70.0	5.91	23.5	87.4
	4	550	70.0	5.91	23.5	87.3
	5	550	70.0	5.91	23.5	87.3
	6	550	70.0	5.91	23.2	87.3
	7	550	70.0	5.91	23.2	87.2
	8	550	70.0	5.91	23.2	87.1
Average/total					23.4	87.3

Table 4 Results of the regeneration capacity of the parent and modified $H\beta$ zeolites



Fig. 8 The ¹³C MAS NMR patterns of the parent and deactivated Hβ zeolites

125–170 ppm, while the band at 170–200 ppm belongs to poly aromatics. In contrast to parent H β , the apparent deactivation phenomenon was evidenced by the strong characteristic signal of carbon deposits in this acylation. Nevertheless, it is not easy to determine the specific coke content by ¹³C MAS NMR spectra.

The carbon deposits absorbed on the external surface and in the micropores of deactivated zeolites were analyzed by GC–MS. It was found acetic acid, 2-AC-5-MF, and some minor compounds, basically oligomers (Fig. 9), derived from the consecutive acylation of monoacylated products. In our work reported here, we can summarize that the prominent deactivation on H β zeolite exists in the acylation of 2-MF, which matches well with a recent report [39]. The acylated products were easily adsorbed on the acid sites related to its strong polarity, so the adsorption of the 2-MF on the channel of zeolites was limited. Therefore, the acid sites on H β were covered, which contributes to the reduction of reaction rate. Moreover, the adsorbed 2-AC-5-MF might react further again, giving by-products of larger molecular dimensions, i.e., carbon deposits, caused the diffusion problems of reactants within the channels of the zeolites.



Fig. 9 Second acylation oligomers (E)-1,2-bis(5-methylfuran-2-yl)ethane

Solvent effects

The solvents are generally employed for accelerating reactions rate, and the stability and selectivity in the organic synthesis of functional chemicals [40]. As it is known, Dimroth et al. [41]. considered solvents as structured isotropic continuum, mainly composed of the individual solvent molecule with itself having interactions called solvent/solvent, and the special solute/solvent interactions like hydrogen-bond, EPD/EPA and so on. The solvent polarity is represented by experience parameters, such as $E_{\rm T}$ (30) and normalized values $E_{\rm T}^{\rm N}$. To delay the deactivation of the catalyst further, nitromethane and 1,2- dichloroethane were used as solvents in this acylation reaction. The solvent effects experiments were carried out at 60 °C with the same flow rate (0.07 mL min⁻¹) in a fixed bed, the equal amount of solvent (20 wt% of total reactants) was mixed into the mixture of 2-MF and AA (molar ratio 1:2.5), then was introduced into the catalytic column by a metering pump. After 45 h of reaction, what is interesting is that 1,2-dichloroethane $(E_T^{N} = 0.327)$ was found to be effective with good activity and stability in the acylation of 2-MF. However, the other important result is that the yield of 2-AC-5-MF decreases when 1,2dichloroethane is substituted by nitromethane ($E_{\rm T}^{\rm N} = 0.481$). Indeed, the initial yield of 2-AC-5-MF, which is around 93 mol% in 1,2-dichloroethane, becomes less than 75 mol% in nitromethane shown in Fig. 10 compared to the solvent free.

In this work, SEM was employed to characterize the morphologies of the parent and deactivated H β (after reaction of 45 h) with different solvents. As depicted in Fig. 11, the particle size of the parent and deactivated H β mainly distribute in the range of 0.2–0.5 and 0.5–1 µm, respectively. In general, fresh parent H β mainly consists of loose aggregates of tiny crystals 30–100 nm in size and uniformly distributed. The aggregation level of zeolite particles reflects the amounts of carbon



Fig. 10 2-Acetyl-5-methylfuran yield (mol%) versus time on stream in the presence and absence of solvent in the continuous acylation of 2-methylfuran with acetic anhydride (experimental conditions: 60 °C, 2-methylfuran/acetic anhydride molar ratio = 1:2.5, flow rate: 0.07 mL/min, 5.9 g of parent H β zeolite)



Fig. 11 SEM images of the parent and deactivated ${\rm H}\beta$ zeolites after acylation with different solvent conditions

deposits. With nitromethane as solvent in acylation of 2-MF, there were serious carbon deposits remaining on the zeolites, resulting in reaction rate decreases. However, the lower carbon deposits on catalysts were observed using 1,2-dichloroethane, indicating that 1,2-dichloroethane of medium polarity could exert a significant effect to minimize catalyst decay. The solvent with moderate polarity can favor the generation of acyl cations and desorption of 2-acetyl-5-methylfuran, thus promoting the acylation process, similar to report from Kim et al. [42]. However, the stronger polar solvents such as nitromethane ($E_T^N = 0.481$) will weaken the desorption process, and impede the formation of the acyl cation. It is critical to note that an increasing solvent polarity may lead to the competitive adsorption with reactants on acid sites of zeolites.

Conclusions

The catalytic performance of all modified H β zeolites were first tested in continuous liquid-phase acylation of 2-methylfuran. Among these zeolites, TA-H β and Si-H β showed the more stable catalytic activity, while AC-H β and parent H β were easily deactivated. What's more, the high yield of 89.5 mol% was achieved on TA-H β

with 100 % selectivity in our research. In a solvent effect study, 1,2-dichloroethane as a solvent of intermediate polarity can enhance the catalytic stability in acylation reaction. The analysis results from GC–MS and ¹³C MAS NMR clearly elucidate that H β zeolite is sensitive to the deactivation, owing to the coke deposits powerfully adsorbed on its surface. Whereas, deactivated H β zeolites can be regenerated to its original status through the high temperature calcination.

Based on the characterization (IR, Py-FTIR, and NH₃-TPD) of the acid properties and catalytic results for the acylation of 2-methylfuran, the proposed modification mechanism involved in the properties and distribution of the acids intensity on H β was discussed. It was clearly found that there was the possibility of adjusting the distribution of the acid intensity using surface modifications. The acid treatment and SiO₂-CLD modification can be successfully applied for coordinating the distribution of acid intensity. The best catalytic performances can be achieved as long as the strong acids were not as intense as possible but with an appropriate acid intensity distribution, especially, the strong and weak acid amounts were equational (ratio of 1:1). Heterogeneous catalysts in acylation reactions require such a catalytic flexibility and stability to enlarge the opportunities for the synthesis of other aromatic ketones. Our work highly supports the potential of surface modification on H β zeolite, which could tune acidity of zeolites to meet the requirements.

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