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ARTICLE

Zeolite Nanofiber Assembles as Acid Catalyst with High Activity in the Acetalization of Carbonyl Compounds with Alcohols

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Zeolite nanofiber assembles (HNB-MOR) as an efficient heterogeneous catalyst for the formation of a range of acetals in good yields. The mesoporousity in the HNB-MOR benefit the mass transfer and the strong acidic sites on the HNB-MOR facilitate the acetalization activity. The catalyst can be reused for 10 times without loss of the activity.

Introduction

Acetals are imperative class of fine chemicals.[1] In multi-stage synthesis, acetalization is also an important protection strategy for carbonyl groups.[2] Generally, the acetalization can be catalyzed efficiently by conventional mineral acids with high activity. However, these acid catalysts are toxic, corrosive and difficult to be removed from the reaction medium, which strongly limit their practical applications in industry. One solution to these problems is to replace mineral acids with high active solid acid catalysts with the advantages that isolation and purification of intermediates are not required.

Different kinds of solid catalysts such as heteropoly acids,[3] imidazolium salts,[4] sulfated zirconia,[5] montmorillonite,[6] envirocat EPZG,[7] alumina/KSF[8] and natural kaolinitic clay[9] have been employed for the acetalization of carbonyl compounds. However, these solid acid catalysts show lower activity due to their relatively small surface area. Other solid acids like cationic exchange resins[10] and metal organic frameworks[11] show better activity towards the acetalization reactions, but the activity of such catalysts cannot be regenerated by calcinations after the catalyst deactivation due to their relatively lower thermostability.

Great attention has been dedicated on the uses of acidic aluminosilicate zeolites to achieve the acetalization reaction.[12] However, one disadvantage of the conventional micropore zeolites is that the pore sizes are too small to allow bulky molecules to access. Ordered mesopore molecular sieves such as Al-MCM-41[13] and Al-SBA-15[14] could overcome the pore size limitation, but higher activity was not achieved over these catalysts for acetal formation. This is attributed to the lower acidity of ordered mesoporous materials due to the amorphous nature of mesoporous walls.[15,16] Therefore, the development of economic, greener and sustainable catalytic system for this fundamental transformation is highly desired.

Recently, we reported a facile method to synthesize nanofiber assembles of mordenite (NB-MOR).[17] The material has parallel-mesopore channels in the nanofiber assembles of the microporous mordenite. After ion-exchange of NH_4^+ and calcination, the H-form of the NB-MOR (HNB-MOR) was obtained. The HNB-MOR catalyst with strong acidity shows high activity in the acetalization of various carbonyl compounds with series alcohols involving the bulky organic substrates under mild reaction temperature (50 °C) compared with HAlMCM-41 and msopore-free HMOR catalysts.

Experimental

Materials synthesis

Mordenite nanofiber assembles (NB-MOR) as well as msopore-free mordenite (MOR) were synthesized similar to previous work.[16] The mesoporous aluminosilicate (Al-MCM-41) was synthesized according to the literature.[15] The H-form of samples were obtained by ion-exchanging twice with NH4NO3 solution (1M) at 80 °C for 4 h, followed by calcination at 550 °C for 4 h.

Catalyst characterization

Nitrogen adsorption-desorption isotherms were obtained using a Micromeritics ASAP 2020M apparatus at liquid nitrogen temperature (-196 °C). Specific surface areas were calculated from the adsorption data, using the Brunauer-Emmett-Teller (BET) equation. The mesopore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) model. Acidities of the materials were determined by the stepwise temperature-programmed desorption of ammonia (NH_3-STPD)

Table 1 Textural parameters of catalyst samples.

Samples	$S_{BET}{}^{a}$ (m²/g)	$S_{exter}{}^{b}$ (m²/g)	$V_{meso}{}^{c}$ (cm³/g)	$V_{micro}{}^{d}$ (cm³/g)
HMOR	346	12	0.002	0.13
HNB-MOR	474	158	0.50	0.13
HAlMCM-41	876	824	0.67	0.01

[a] BET surface area. [b] External surface area that including mesoporous surface area. [c] Mesoporous volume. [d] Microporous volume.
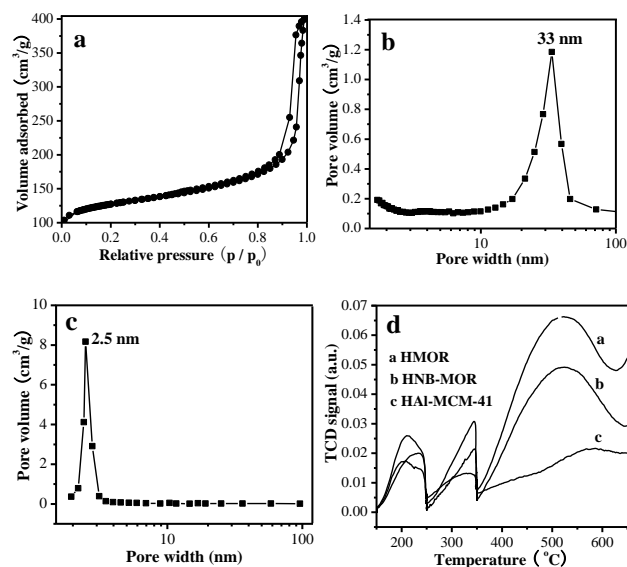

Fig. 1. (a) N_2 adsorption isotherm, (b) pore size distribution of HNB-MOR, (c) pore size distribution of HAlMCM-41, (d) NH_3-STPD curves of the samples.

on a Micromeritics ASAP 2920 instrument. The detailed operating procedure and conditions were described in a previous work.[18]

Reaction and analysis

In a typical experimental procedure for the acetalization reaction in the presence of catalyst (30 mg), the carbonyl compound (0.2 mmol) and alcohol (2.0 mL) were placed in a 10 mL glass vessel. Then the reaction was allowed to proceed at 50 °C for 12 h. After the reaction was finished, the catalyst was separated by centrifugation and after passing the liquid phase through a filter paper. The liquid were analyzed with an Agilent 7890A GC equipped with a FID detector and mass spectrometer. The products were obtained by flash chromatography(hexane:EtOAc). ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) were recorded with spectrometers at 20 °C using CDCl₃ as the solvent. Chemical shifts are given in parts per million relative to TMS as the internal standard at room temperature.

Results and discussion

Fig.1 shows the nitrogen adsorption isotherm, pore size distribution and NH_3-STPD profiles of the samples. The

Table 2 Acetal formation of aldehydes with methanol over HNB-MOR, HMOR and HAlMCM-41 catalysts.

Entry	Product	Yields [%] a/b/c
1		100(94)/100/100
2		100(91)/100/99
3		100(93)/100/100
4		100(92)/100/100
5		100(89)/95/90
6		100(87)/97/94
7		100(95)/93/58
8		97(91)/48/14

Reaction condition: aldehyde (0.2 mmol), methanol (2 mL), catalyst (30 mg), 50 °C, 12 h. The yields were obtained by GC analysis (isolated yields in parenthesis). **a**: HNB-MOR as catalyst, **b**: HMOR as catalyst, **c**: HAlMCM-41 as catalyst.

nitrogen sorption isotherm of HNB-MOR exhibits a hysteresis loop at a relative pressure of 0.85-0.95, which is typically assigned to the presence of mesopore structure (Fig. 1a). The mesopore-size distributions of the HNB-MOR and HAlMCM-41 are mainly centered at 33 and 2.5 nm (Fig. 1b and c), respectively. Sample textural parameters are presented in Table 1. The NH_3-STPD profiles of the samples were shown in Fig. 1d. For the characterization of acidity by NH_3-STPD, the acidic strength can be differentiated as weak, middle and strong according to the desorption temperature.[19] Clearly, the concentrations of relatively strong (250~350 °C) and strong

Table 3 Acetal formation of p-nitrobenzaldehyde with various alcohols over HNB-MOR, HMOR and HAlMCM-41 catalysts.

Entry	Product	Time (h)	Yields [%] a/b/c
1		12	100(93)/98/84
2		12	100(91)/83/72
3		18	100(89)/77/65
4 [d]		12	87(81)/37/11
5 [e]		12	99(90)/70/53

Reaction condition: p-nitrobenzaldehyde (0.2 mmol), HNB-MOR (30 mg), alcohol (2 mL), 50 °C, 12 h. The yields were obtained by GC analysis (isolated yields in parenthesis). a: HNB-MOR as catalyst, b: HMOR as catalyst, c: HAlMCM-41 as catalyst.d: benzyl alcohol (1.2 mmoL), CH_3CN (1.5 mL), e: ethanediol (0.6 mmoL), CH_3CN (1.5 mL).

(>350 °C) acidic sites of HNB-MOR and HMOR catalysts are much higher than those of HAlMCM-41.

The activity and the scope of the acetalization of various aldehydes with series alcohols over HNB-MOR, HMOR and HAlMCM-41 catalysts are shown in Table 2-5. The blank experiment showed that no product was obtained when the reaction was carried out in the absence of catalyst. Table 2 shows the reaction activity of the acetal formation of various aldehydes with methanol over HNB-MOR, HMOR and HAlMCM-41 catalysts. Clearly, the HNB-MOR, HMOR and HAlMCM-41 catalysts gave high yields for the aldehydes not only with electron-withdrawing group as halogens (entries 1-3) but also with electron-donating group as -CH_3 and -CH_2CH_3 (entries 4-6). However, when the aldehyde with an electron-withdrawing group of nitro substituent was used as substrate, the product yields over HNB-MOR reach to 97-100%, the yields over HMOR and HAlMCM-41 catalysts are only 48 and 14% (entries 7,8). Meanwhile, the activity of zeolite HNB-

Table 4 HNB-MOR-catalyzed acetal formation of ketone with series alcohols.

| Entry	Product	Yield [%] a/b/c
1 [d]		91/53/38
2		98/97/94
3		82/75/64
4		69/65/25
5 [e]		42/27/5

Reaction condition: Cyclohexanone (0.2 mmol), HNB-MOR (30 mg), alcohol (2 mL), 50 °C, 12 h. The yields were obtained by GC analysis. And the products were detected by GC-MS. a: HNB-MOR as catalyst, b: HMOR as catalyst, c: HAlMCM-41 as catalyst. d: ethanediol (0.6 mmoL), CH_3CN (1.5 mL), e: benzyl alcohol (1.2 mmoL), CH_3CN (1.5 mL).

MOR and HMOR catalysts was much higher than HAlMCM-41 in the reaction entries of 5-8.

Table 3 shows the reaction activity of the acetal formation of p-nitrobenzaldehyde with various alcohols over HNB-MOR, HMOR and HAlMCM-41 catalysts. The reactions with ethanol, ethanediol, n-propanol, n-butanol and benzyl alcohol over HNB-MOR catalyst proceeded readily and gave the corresponding acetals in very high yields. In contrast, the products yields over HMOR and HAlMCM-41 catalysts are very low except for the reaction with ethanol as a substrate (entry 1). In addition, the products yields over HMOR catalyst were reduced with increasing of the molecule dimensions of alcohols. Particularly, when the aromatic alcohol was used as a substrate the yields were very low over HMOR and HAlMCM-41 catalysts. The results from Table 2 and Table 3 indicate that the HNB-MOR catalyst shows an excellent activity in the acetalization with aldehydes and alcohols including the bulky organic substrates.

It is worth mentioning that not only with aldehydes, but that ketone is good substrate in the HNB-MOR-catalyzed acetalization reaction relative to HMOR and HAlMCM-41 catalysts. Table 4 show clearly that the HNB-MOR catalyst gives the highest conversions in the acetalization of ketone with series alcohols. These results indicated that the HNB-MOR

Table 5. Recyclability experiments of the HNB-MOR system.
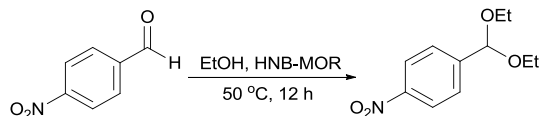
Entry	Recycle	Yield [%]
1	run 1	100
2	run 2	100
3	run 3	100
4	run 4	>99
5	run 5	100
6	run 6	100
7	run 7	100
8	run 8	100
9	run 9	100
10	run 10	>99

Reaction condition: p-nitrobenzaldehyde (0.2 mmol), HNB-MOR (30 mg), ethanol (2 mL), 50 °C, 12 h. The yields were obtained by GC analysis.

catalyst shows a good activity in the acetalization of ketone with alcohols. The reusable ability of HNB-MOR catalyst was also surveyed. After the reaction, the catalyst was simply separated by filtration and washed with ethanol, dried at 50 °C, and reused in 10 times without loss of the activity (Table 5). These results indicated that the HNB-MOR catalyst have a good catalyst life, which is one of the key features in applications of industrial catalysts.

Generally, the catalytic performance of zeolite in the acetalization could be co-influenced by acidities and pore structure. For the acetalization of the aldehydes with small dimensions of alcohols, the reactant as well as the product can diffuse into the micropores in HMOR so that HNB-MOR and HMOR have a comparable catalytic activity (entry 1-6, Table 2). However, when using substrate alcohol in large molecule dimensions, the conversion of aldehyde over HMOR are much lower than those of over HNB-MOR (entry 2-5, Table 3), which is due to the difference in the mesoporousity of both catalysts. The HNB-MOR shows mesopore surface area (158 m^2/g, Table 1) that could favour the mass-transfer, while the HMOR shows external surface area only 12 m^2/g. It is reasonable that HNB-MOR catalyst gives higher conversion compared with mesopore-free HMOR. Compared with HNB-MOR, although HAlMCM-41 have a relatively high mesopore volume (0.67 m^3/g) and mesopore surface area (876 m^2/g), it still showed a lower acetalization capability of the bulky substrate, which may be related to the difference in acidities between HNB- MOR and HAl-MCM-41catalysts. It has been reported that acidic sites on catalysts facilitate acetalization reaction,[20] and in this work HNB-MOR zeolite with strong and abundant acidic sites could give high product yield, compared with HAlMCM-41 with relatively weak acidities (Fig. 1d). Particularly, the acetalization reaction by using aldehyde with nitro substituent as substrate, the avtivity of the HAlMCM-41catalyst is even lower than HMOR (entry 7-8, Table 2 and entry 1-5, Table 3). These phenomena indicated that strong acidic catalyst was desired in the acetalization reaction, especially when the aldehyde with the electron-withdrawing group of nitro substituent. These results further demonstrate that the strong acidic sites on the catalyst play an important role in the acetal formation reactions.

Conclusions

In summary, we have developed an example of zeolite material (HNB-MOR) as an outstanding catalyst for the synthesis of acetals with excellent yields under mild conditions. The mesoporousity in the HNB-MOR benefit the mass transfer and the strong acidic sites on the HNB-MOR facilitate the acetalization activity.

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Notes and references

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