Modified beta zeolite as catalyst for Fries rearrangement reaction

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Modified beta zeolites were applied as catalysts for the Fries rearrangement reaction. The properties of the modified zeolites were characterized by NH_3-TPD, *n*-hexane and 1,2,4-trimethylbenzene adsorption. Modification with SiO_2 did not block the pores of the beta zeolite but reduced the number of acid sites on the surface. However, when the beta zeolite was modified with Ce_2O_3, the number of acid sites determined by NH_3-TPD increased, which indicated that new acid sites are created by the interaction of cerium oxide and zeolite. Modified beta zeolites and H-beta were applied as catalysts for the Fries rearrangement of phenol acetate. Reaction over H-beta has low selectivity and the catalyst is easily deactivated. SiO_2 modification of the catalyst increases the selectivity of the reaction but decreases the conversion. Ce_2O_3-modified beta zeolites show higher catalytic activity and rearrangement selectivity in the reaction than other catalysts. The stability of the catalyst is also improved after Ce_2O_3 modification. About 70% selectivity and 60–80% conversion can be achieved over 16 wt% Ce_2O_3-modified beta zeolite.

KEY WORDS: beta zeolite; zeolite modification; Fries rearrangement reaction.

1. Introduction

Zeolites as solid acid catalysts have attracted much attention in recent years because the traditional acid-catalyzed synthesis processes of fine chemicals produce large amount of pollutants and need to be replaced by environmentally friendly processes. Aluminum silicate zeolites as the solid acid are non-corrosive and reusable, hence catalytic processes using zeolites for organic chemicals synthesis are being developed as green technology.

Aromatic acylation is of importance in various areas of the fine chemical industry and substituted acetophenones are essential intermediates for many chemicals. Current industrial practice involves over-stoichiometric amounts of metal halides (e.g. $AlCl_3$, $FeCl_3$) as catalysts, which results in a substantial amount of by-products and corrosion problems. The use of zeolite catalysts in aromatic acylation and Fries rearrangement reactions is a promising research direction to solve the above problems. There have been many reports about acylation and Fries rearrangement reactions catalyzed by CeNa-Y [1], beta zeolite, ZSM-5, and Y [2–6].

In general, gas–solid phase Fries rearrangement reactions over zeolites have low selectivity and the catalysts are deactivated after a few hours of reaction [6]. Modified ZSM-5 with Ga improves the selectivity for Fries rearrangement products [7]. When zeolite-catalyzed Fries rearrangement reactions are carried out in polar solvents, relatively high selectivity can be achieved [4]. The selectivity and reactivity of zeolite catalysts need to be improved and rapid deactivation of catalysts needs to be overcome before these catalytic reactions can be applied in industrial processes.

In this work, beta zeolite was modified by surface deposition of SiO_2 and impregnation with cerium oxide. The sorption and acidic properties of modified beta zeolite samples were tested. The catalytic properties of modified beta zeolite for gas-phase rearrangement of phenyl acetate were also studied. Beta zeolites modified with large amounts of Ce_2O_3 show improved reactivity and stability in the reaction.

2. Experimental

2.1. Catalyst preparation

Beta zeolite was provided by Nankai University (synthesized according to a patent [8]). The SiO_2/Al_2O_3 ratio of the beta zeolite was 88 and the spherical crystals had an average size of about 0.4 μm.

H-form beta zeolite was prepared through ion exchange of the above sample with 0.5 N NH_4OH solution at 80 °C for 2 h. The ion-exchange process was repeated twice and the resulting product was calcined at 540 °C for 3 h.

Beta zeolite was modified with SiO_2 through a chemical liquid deposition (CLD) process. The calculated amount of $Si(OC_2H_5)_4$ was dissolved in cyclohexane. H-form beta zeolite was added to the solution and treated at 40 °C for 12 h. The solution was distilled and the solid was dried at 110 °C and calcined at 540 °C for 5 h.

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Table 1
Adsorption properties and NH_3-TPD data for beta zeolite modified with SiO_2

Sample	Amount of SiO_2 (wt%)	Adsorption capicity (wt%)		TPD acidic sites (mmol/g cat.)		
		n-Hexane	1,2,4-TMB	Weak[a]	Strong	Total
Hβ	–	16.5	18.8	0.164	0.167	0.331
S1	3.0	16.3	18.6	0.159	0.122	0.281
S2	5.0	15.8	18.1	0.152	0.107	0.259
S3	12.0	15.3	17.6	0.144	0.091	0.235

[a] Weak acid, <350 °C; strong acid, >350 °C.

Beta zeolite was also modified with cerium oxide. The calculated amount of $Ce(NO_3)_3$ was dissolved in distilled water and H-form beta zeolite was added to the solution and treated at room temperature for 12 h. The mixture was heated to dryness at 110 °C and calcined at 540 °C for 5 h.

2.2. Characterization

XRD analyses of zeolite samples were carried out on a Shimadzu XD-3A X-ray diffractometer with Cu Kα radiation. Adsorption of *n*-hexane and 1,2,4-trimethylbenzene on the zeolite samples was carried out at 25 ± 0.2 °C in a thermostated bath. The adsorbates ($P/P_s = 0.5$, where P_s is the saturated pressure of the adsorbate) were carried by a nitrogen flow through the sample and the amount of adsorbed material was calculated from TCD signal.

NH_3-TPD experiments were carried out as follows: 0.2000 g of sample was heated at 500 °C for 2 h. The temperature was decreased to 120 °C, the sample contacted with NH_3, vacuumized for 30 min, then the temperature was increased at a rate of 32 °C/min to 600 °C in a 40 ml/min helium flow. The desorbed NH_3 was analyzed by GC using the external standard method. The number of acid sites on the samples was calculated from the amount of NH_3 desorbed.

2.3. Catalytic experiments

Continuous gas-phase reactions were carried out in a fixed-bed reactor at ambient pressure. The 0.6–2 mm fraction of the binder-free catalyst was packed into an 8 mm i.d. stainless-steel reactor and activated in dry nitrogen at 500 °C for 1 h. Phenyl acetate was charged through a pump and carried by nitrogen. The WHSV of phenyl acetate was 6.5 h^{-1}. The reaction products were collected periodically in an ice trap and analyzed off-line by GC using a cross-linked methylsilicone capillary column (30 m × 0.2 mm i.d. SE-52 column). The conversion and selectivity (to Fries rearrangement products) of the reaction were calculated as follows: conversion = mol% of starting material converted, yield = mol% of product obtained, selectivity (%) = 100 × (sum of the yield of *p*- and *o*-hydroxyacetophenone and *p*-acetoxyacetophenone)/conversion.

3. Results and discussion

3.1. Surface deposition of SiO_2

Tetraethyl orthosilicate (TEOS) has a molecular size larger than the pore size of beta zeolite and ZSM-5, so it is a suitable agent for surface modification of these zeolites. Surface deposition of SiO_2 can eliminate acid sites on the outer surface of the zeolite, so the shape-selective catalytic properties of the modified zeolite are improved. H-beta was modified with TEOS through a chemical liquid deposition (CLD) process. The adsorption properties and NH_3-TPD data for the modified beta zeolite are summarized in table 1. NH_3-TPD profiles of SiO_2 modified beta zeolite samples are illustrated in figure 1.

The number of acid sites on beta zeolite decreases with increase in the amount of SiO_2 deposited on its surface. The SiO_2 modification has more influence on strong acid sites and the number of strong acid sites decreased drastically after modification, which indicates that

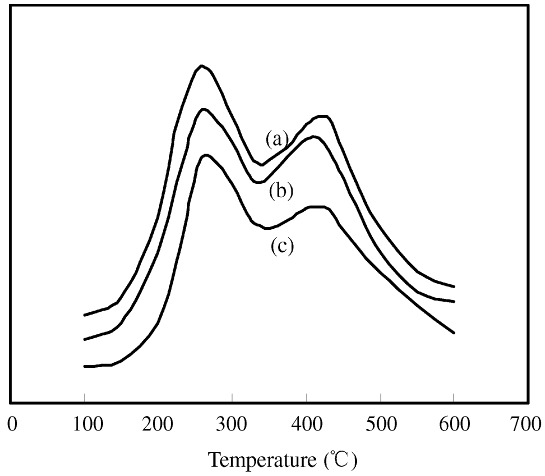

Figure 1. NH_3-TPD profiles of H-beta (a), 3 wt% SiO_2-modified beta zeolite (b), and 12 wt% SiO_2-modified beta zeolite (c).

Table 2
Adsorption properties and NH_3-TPD data for beta zeolite modified with Ce_2O_3

Sample	Amount of Ce_2O_3 (wt%)	Adsorption capacity (wt%)		TPD acidic sites (mmol/g cat.)		
		n-Hexane	1,2,4-TMB	Weak [a]	Strong	Total
H*β*	–	16.5	18.8	0.164	0.167	0.331
Ce1	4.0	15.1	17.7	0.229	0.132	0.361
Ce2	8.0	13.9	16.9	0.214	0.138	0.352
Ce3	16.0	12.3	15.9	0.192	0.146	0.338

[a] Weak acid, <350 °C; strong acid, >350 °C.

there are more strong acid sites on the zeolite surface. SiO_2 modification just slightly reduces the adsorption ability of beta zeolite, which means there is no severe pore blocking after SiO_2 deposition.

3.2. Impregnation with cerium oxide

Rare earth impregnation has been proved to be an effective method for modifying zeolite catalysts. Rare earth-modified HY zeolites have been successfully applied in the FCC process. The properties of Ce_2O_3-modified beta zeolite are summarized in table 2. NH_3-TPD profiles of Ce_2O_3 modified beta zeolite samples are illustrated in figure 2 and XRD patterns of the Ce_2O_3-modified beta zeolite are shown in figure 3.

The adsorption capacity of beta zeolite is decreased after modification with Ce_2O_3, which indicates that part of the cerium oxide is deposited in the channels of the zeolite crystal and block the porous system. The number of NH_3-TPD acid sites in Ce_2O_3-modified samples is higher than that in unmodified beta zeolite. Ce_2O_3 modification creates new acidic sites on the zeolite surface. Weak acid sites increased more than the strong acidic sites, which means that the new acidic sites created by interaction of cerium oxide and zeolite surface are virtually weak acid sites. There is a strong XRD peak of the Ce_2O_3 crystal in the XRD pattern of the 16 wt% Ce_2O_3-modified sample, which means that part of the Ce_2O_3 exists in crystalline form. The XRD peak of Ce_2O_3 in the pattern of the 4 wt% Ce_2O_3-modified sample is very small, which indicates that when the Ce_2O_3 content is lower than 4 wt%, Ce_2O_3 is amorphous. The 4 wt% Ce_2O_3-modified beta zeolite contains more acid sites than the 16 wt% Ce_2O_3-modified sample, which is explained by part of the original acid sites being covered by the Ce_2O_3 crystalline phase in the 16 wt% Ce_2O_3-modified sample.

3.3. Catalytic Fries rearrangement

When unmodified H-beta is applied as the catalyst and the catalytic reaction is carried out at 573, 623, and 673 K the conversion and selectivity of the reaction were as summarized in figure 4. With increase in temperature the conversion is increased but the selectivity is decreased. Reaction at 623 K has a relatively high conversion and selectivity and thus a relatively high yield of Fries rearrangement products. After a few hours of reaction, the catalyst is drastically deactivated.

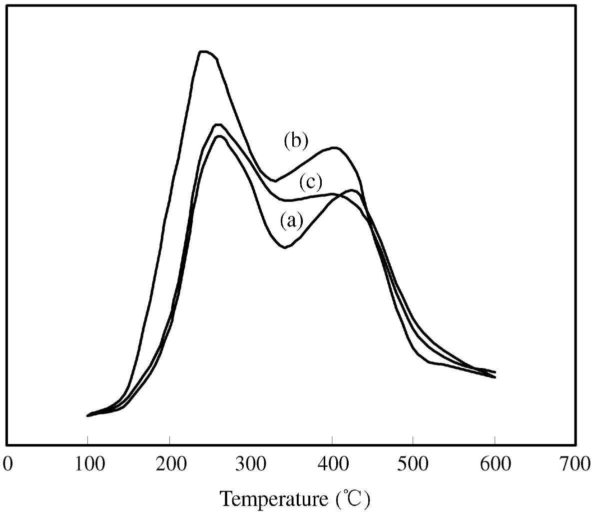

Figure 2. NH_3-TPD profiles of H-beta (a), 4 wt% Ce_2O_3-modified beta zeolite (b), and 16 wt% Ce_2O_3-modified beta zeolite (c).

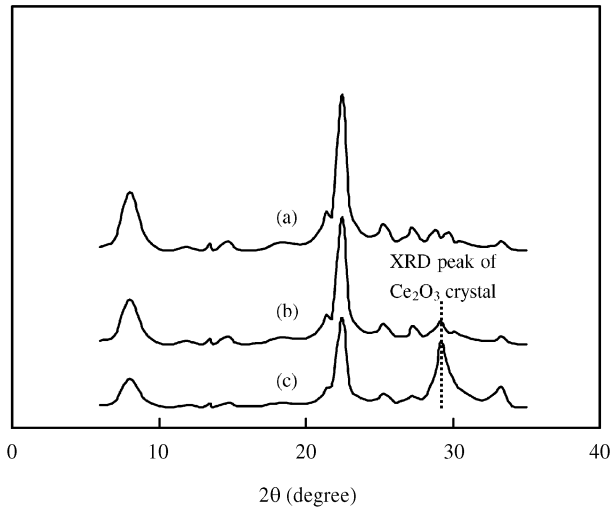

Figure 3. XRD patterns of H-beta (a), 4 wt% Ce_2O_3-modified beta zeolite (b), and 16 wt% Ce_2O_3-modified beta zeolite (c).

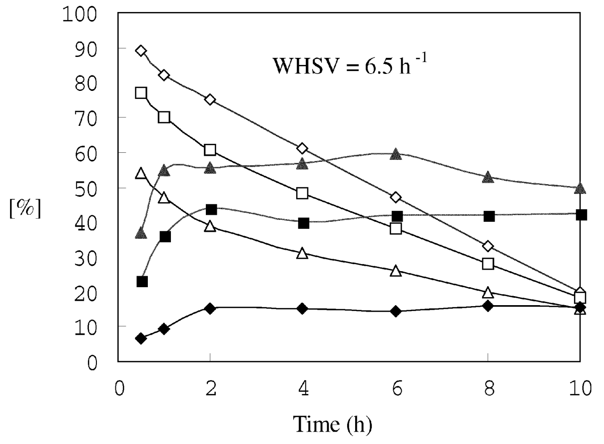

Figure 4. Fries rearrangement of phenyl avetate over H-beta at different temperatures: (△) conversion at 573 K; (▲) selectivity at 573 K; (□) conversion at 623 K; (■) selectivity at 673 K; (◇) conversion at 673 K; (◆) selectivity at 673 K.

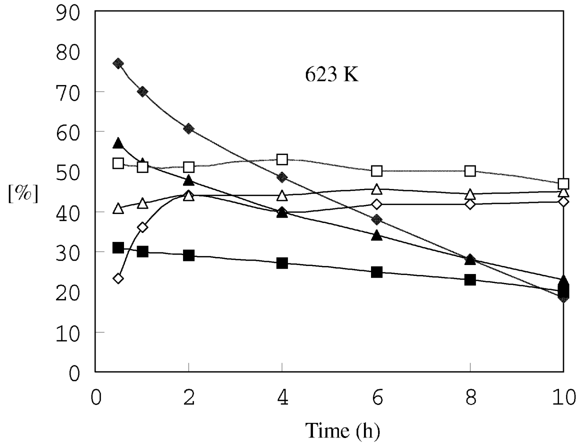

Figure 6. Fries rearrangement of phenyl acetate over SiO_2-modified beta zeolites: (◆) conversion over H-beta; (◇) selectivity over H-beta; (▲) conversion over 3 wt% SiO_2-modified beta zeolite, at 573 K; (△) selectivity over 3 wt% SiO_2-modified beta zeolite; (■) conversion over 12 wt% SiO_2-modified beta zeolite; (□) selectivity over 12 wt% SiO_2-modified beta zeolite.

The organic base 2,6-dimethylpyridine can deactivate the Brønsted acid sites, but because of the blocking of the methyl group it has little effect on Lewis acid sites [9]. We used 2,6-dimethylpyridine (DMP) to detect the active catalytic centers. DMP is carried into the reactor by N_2 and adsorbed by the H-beta catalyst. After the treatment, the conversion of the reaction decreased. The results of the poisoning experiments are shown in figure 5. When the amount of DMP is increased to 40 μl, the catalyst is completely deactivated. This experiment indicates the effective catalytic centers for this reaction are the Brønsted acid sites.

The results of the rearrangement reaction over SiO_2-modified catalysts are compared with these of unmodified sample in figure 6. SiO_2 modification decreases the catalytic activity but slightly increases the selectivity, and the stability of the catalyst is also improved after modification.

The results of the rearrangement reaction over Ce_2O_3-modified catalysts are compared with those for the unmodified sample in figure 7. Ce_2O_3-modified zeolites show higher catalytic activity and selectivity than the unmodified sample. The best reaction results are obtained over 16 wt% Ce_2O_3-modified beta zeolite; the selectivity is increased to about 70% while the conversion remains at 60–80%. The catalyst is stable and the decrease in reactivity is only about 20% after 10 h of reaction. The stability of the catalyst is improved. The results are explained as follows: the new acid sites created by interaction of Ce_2O_3 and the zeolite surface are more selective and reactive for the Fries rearrangement reaction and these acid sites are less likely to be deactivated. On the 16 wt% Ce_2O_3-modified beta zeolite, the original acid sites of the zeolite are completely covered by cerium oxide, so the catalyst is stable, selective and reactive, although it contains fewer acid sites than the 4 wt% Ce_2O_3-modified sample.

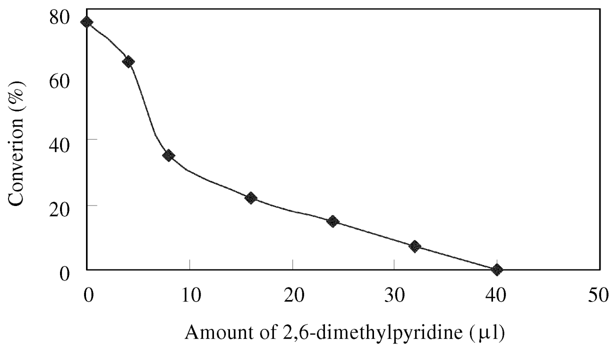

Figure 5. Catalytic activity of organic base-poisoned H-beta zeolite for the Fries rearrangement reaction of phenyl acetate.

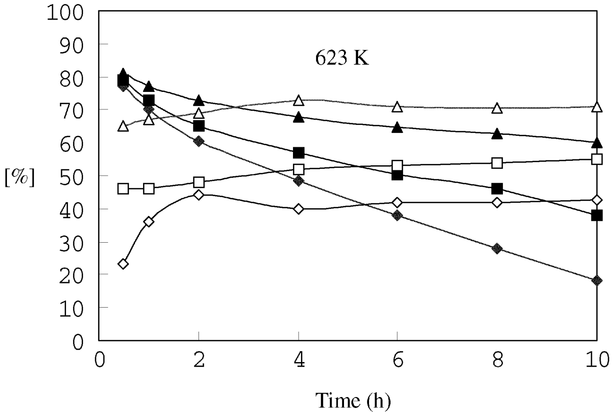

Figure 7. Fries rearrangement of phenyl acetate over Ce_2O_3-modified beta zeolites: (◆) conversion over H-beta; (◇) selectivity over H-beta; (■) conversion over 4 wt% Ce_2O_3-modified beta zeolite; (□) selectivity over 4 wt% Ce_2O_3-modified beta zeolite; (▲) conversion over 16 wt% Ce_2O_3-modified beta zeolite, at 573 K; (△) selectivity over 16 wt% Ce_2O_3-modified beta zeolite.

4. Conclusion

Surface and acidic properties of H-beta and SiO_2-modified and Ce_2O_3-modified beta zeolites were studied. SiO_2 modification decreases the number of acid sites and has more influence on strong acid sites. Ce_2O_3 modification increases the number of acid sites. New acid sites are created by interaction of cerium oxide and the zeolite surface.

Fries rearrangement of phenol acetate over H-beta has low selectivity and the catalyst is readily deactivated. SiO_2-modified beta zeolites are less reactive but more selective in the reaction than the unmodified sample. Ce_2O_3-modified beta zeolites are more reactive and selective in this reaction. The stability of the catalyst is also improved after Ce_2O_3 modification. Over the 16 wt% Ce_2O_3-modified sample, the selectivity is about 70% and the conversion is about 60–80%.

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