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Article

Ceria-modified hierarchical H β zeolite as a robust solid acid catalyst for alkenylation of *p*-xylene with phenylacetylene

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ABSTRACT

A ceria-modified hierarchical H β zeolite was prepared by a desilication-dealumination procedure followed by ceria modification. The catalytic performance of the ceria-modified and unmodified hierarchical H β zeolite catalysts for alkenylation of *p*-xylene with phenylacetylene was investigated. Various characterization techniques, including X-ray diffraction, X-ray fluorescence, nitrogen adsorption-desorption, and NH₃ temperature-programmed desorption, were used to examine the structure-performance relationships. Our results show that the optimized ceria-modified hierarchical H β zeolite catalyst demonstrated higher catalytic activity, selectivity, and stability for alkenylation of *p*-xylene with phenylacetylene than those of pristine H β zeolite. This performance was attributed to more acidic sites and improved accessibility to active sites through larger pores, together with a higher mesoporous surface area and volume resulting from the hierarchical pore architecture and ceria modification. Thus, our 5 wt% CeO₂-H β -B_{0.2}A_{0.2} catalyst shows great potential for producing alkenyl aromatics through solid acid catalyzed alkenylation.

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1. Introduction

Alkenyl aromatics compounds are widely applied in many areas such as dyes, pharmaceuticals, natural products and agrochemicals [1,2]. The alkenylation of arenes with alkynes provides an environmentally friendly strategy for production of alkenyl aromatic with high efficiency and atom economy [3,4]. Homogeneous metal complex catalysts show prominent activity and selectivity for production of alkenyl aromatics [5–10]; however, these catalysts are expensive, have low recyclability as homogeneous catalysts, and feature difficulties in purification of the desired products. Hence, it would be desirable to develop a more clean and economical method. Heterogeneous

solid acid catalysts provide an easily recycled, separable, and environmentally friendly alternative approach [11–14]. Currently, only a few kinds of solid acid catalysts have been used for aromatic alkenylation reaction. Zeolites are a type of solid acid catalysts, which are widely used in various fields, having been first applied to the alkenylation of aromatic reactions by Sartori and coworkers. Unfortunately, the catalytic results with these materials have been far from satisfactory, and the yield of alkenyl aromatics compounds is quite low. Furthermore, the low catalytic efficiency cannot be overcome while HY is used as catalyst for the alkenylation. The reaction has been shown to take place on the external surface of the catalyst because the narrow channels of the zeolite limit diffusion of reactants and

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products [15–17]. Therefore, much attention has been paid to developing mesoporous solid acid catalysts.

Phosphotungstic acid (PTA) catalysts supported on MCM-41, modified activated carbon and mesoporous silica nanospheres have been developed as attractive mesoporous solid acid catalysts for alkenylation of a diverse range of aromatics [18–20]. However, the regeneration of supported PTA catalysts requires a large amount of organic solvent, which limits their cost effectiveness and contributes to environmental problems. Moreover, sulfated ZrO_2 , as a common solid super-acid, has been widely used in various reactions. A series of $\text{SO}_4^{2-}/\text{meso-La}_2\text{O}_3\text{-ZrO}_2$, as novel and efficient solid acid catalysts for alkenylation, have been developed [21–23]. Although the catalyst could be recovered by a calcination treatment, the simple low-cost preparation of well-ordered mesoporous $\text{La}_2\text{O}_3\text{-ZrO}_2$ remains challenging. Furthermore, Fe-containing mesoporous alumina-silicate exhibits a high activity for the alkenylation aromatic reaction under mild conditions. However, the selectivity of the reaction requires further improvements [24].

Hierarchical zeolites are solid acid catalysts that show excellent performance, owing to a combination of intrinsic zeolite and mesoporous properties, which improve mass transfer [25,26]. Thus, this material shows great promise as a hierarchical zeolite for solid acid catalysis for alkenylation. Various strategies have been developed to create hierarchical porous zeolites [25,27,28], and post-synthesis treatments by acid or alkali treatment through dealumination or desilication are considered to be simple and scalable approaches [29–31]. The modification of zeolites by metal oxides, such as alkaline earth and rare earth metal oxides has been demonstrated to be an efficient method for improving their catalytic performance in various transformations [32–38]; however, there have been few reports on promoted alkenylation.

In this work, CeO_2 modified hierarchical mesoporous H β zeolites were prepared by a desilication-dealumination procedure with subsequent cerium impregnation and then used to catalyze the alkenylation reaction. The effect of preparation parameters such as alkali concentration, acid concentration and CeO_2 loading on the nature and catalytic performance were investigated. The as-synthesized CeO_2 modified hierarchical H β demonstrated superior catalytic performance to that of pristine beta zeolite for alkenylation of aromatics, owing to more acidic sites and improved accessibility to the active sites through the interconnected mesopores and micropores of the hierarchical zeolites.

2. Experimental

2.1. Catalyst preparation

Commercially available H β zeolite calcined at 550 °C for 6 h, and is denoted as H β . The H β zeolite was treated with a NaOH aqueous solution with a range of concentrations (0.1, 0.2, 0.3 mol/L) and a liquid-to-solid ratio of 25 mL/g at 65 °C for 0.5 h. The resulting solids were filtered, washed with deionized water until the washings became neutral and then dried in the oven.

The as-prepared alkaline treated zeolites were labeled as H β -B $_x$, where x denotes the NaOH concentration. The alkaline-treated H β -B $_x$ zeolites were further treated by HNO_3 aqueous solution at certain concentrations (0.1, 0.2, and 0.3 mol/L) and a liquid-to-solid ratio of 15 mL/g at 65 °C for 5 h. The resulting solids were filtered, washed with deionized water until the washings were neutral and then dried in an oven. These samples are denoted as H β -B $_xA_y$, where y indicates the HNO_3 concentration. Ceria-modified hierarchical H β -B $_{0.2}$ A $_{0.2}$ zeolites were prepared by an impregnation method with a series of $\text{Ce}(\text{NO}_3)_3$ concentration solutions at 65 °C for 5 h, and then dried in an oven and calcined at 550 °C. The obtained catalysts are denoted as $z\%$ H β -B $_{0.2}$ A $_{0.2}$, where z indicates the mass ratio of ceria to zeolites.

2.2. Catalyst characterization

XRD data of the samples were collected in the 2θ range of 5°–80° with a step of 0.02° on a Rigaku D/max-2400 apparatus with Cu K_α radiation. Ratios of Si/Al in the samples were determined by X-ray fluorescence (XRF) conducted on a Bruker SRS3400 instrument. Nitrogen adsorption experiments at –196 °C were measured on samples previously evacuated at 150 °C overnight with the use of a Beishide 3H-2000PS1. Micropore volumes were determined from t -plots. The specific surface areas were determined with the Brunauer-Emmett-Teller (BET) model. Pore size calculations were performed from the sorption isotherms based on the BJH method. NH_3 temperature-programmed desorption (NH_3 -TPD) data were acquired on a Builder Chemisorption (PCA-1200) instrument with a thermal conductivity detector (TCD) to measure the desorbed NH_3 . A 50-mg sample was loaded into a quartz reactor between two quartz wool plugs, and then pretreated under an Ar atmosphere at 500 °C (a ramp rate of 10 °C/min) for 1 h, followed by cooling to room temperature. The pretreated sample was saturated with ammonia at 100 °C via pulse injection of ammonia. The ammonia desorption process was performed from 100 °C to 600 °C at a heating rate of 10 °C/min under an Ar flow. TGA analysis was conducted to study the coking behavior of spent H β , H β -B $_{0.2}$ A $_{0.2}$ and 5 wt% CeO_2 H β -B $_{0.2}$ A $_{0.2}$ catalysts for 6 h time on stream with the use of a Perkin-Elmer STA 6000 instrument at a heating rate of 10 °C/min from 25 to 800 °C under an air flow (60 mL/min).

2.3. Catalyst performance testing

The alkenylation of *p*-xylene with phenylacetylene was performed in a stainless steel fixed-bed continuous-flow reactor at 140 °C. A 1.0-g portion of catalyst with 20–60 mesh was loaded into the reactor for all performance tests. The residual space in the reactor was filled with 20–60 mesh quartz granules. The catalyst was pre-activated in situ for 1 h under an N_2 flow at 30 mL/min, and then input into the fixed-bed reactor by a syringe measuring pump. N_2 (99.999% purity) was used to maintain the reaction system pressure. The product was analyzed on FULI 9790 II GC with FID detector using HP-5 column (30 m $\times$ 0.32 mm $\times$ 0.25 μm). The GC chromatogram of the products

was found and the molecular structure of alpha-(2,5-dimethylphenyl) styrene (I) was further identified by ^1H NMR, as described in our previous report [18]. As evaluation criterion of the alkenylation reaction, the conversion of phenylacetylene was calculated as the weight percentage of converted phenylacetylene in the total amount of introduced phenylacetylene in the feed. The main product alpha-arylstyrene were labeled as (I), together with a series of side products, including acetophenone (II), (2,5-dimethylphenyl) ethylbenzene (III), beta-(2,5-dimethylphenyl) styrene (IV), and oligomers (V). Moreover, the stability of the developed ceria-modified and unmodified hierarchical beta zeolites as well as that of the pristine beta zeolite was investigated.

3. Results and discussion

3.1. Preparation and characterization of SHMS carrier and supported PTA catalyst

Fig. 1 shows the XRD patterns of H β and H β -B $_x$ A $_{0.2}$ processed with a range of NaOH concentrations, which featured the typical diffraction pattern of a beta zeolite. These results indicated that sequential alkali and acid treatments led to a gradual reduction in crystallinity, as seen by the decreasing diffraction intensity relative to that of pristine H β . The decrease in crystallinity of the as-prepared H β -B $_x$ A $_{0.2}$ zeolites can be clearly seen as the concentration of the NaOH solution was increased.

Fig. 2(a) shows that the N $_2$ adsorption-desorption isotherms measured for the pristine H β zeolite were type I isotherms of a purely microporous material [39]. From Fig. 2(b) and Table 1, the parent H β zeolite exhibited a minor mesoporous surface area and pore volume with pore size in the range of 5–30 nm, owing to the contributions of inter-particle voids originating from the disordered agglomeration of small crystals of the H β zeolite [30,31]. Processed H β zeolites with alkali-acid solution resulted in a clear hysteresis loop and a greater uptake of N $_2$ adsorption-desorption isotherms at high relative pressures, giving a relatively regular mesoporous distribution in the major peak profile compared with that of pristine H β . The N $_2$ adsorp-

Fig. 1. XRD patterns of H β -B $_x$ A $_{0.2}$ prepared under diverse alkaline concentrations and pristine H β .

tion-desorption isotherms of processed H β -B $_x$ A $_{0.2}$ zeolites contained type I and IV features, indicating a typical hierarchical structure [40]. The values of V_{micro} and S_{micro} decreased as the NaOH concentration was increased from 0.1 to 0.3 mol/L. In addition, the values of V_{meso} and S_{meso} increased as NaOH concentration was increased from 0.1 to 0.2 mol/L. Conversely, the S_{meso} value of H β -B $_{0.3}$ A $_{0.2}$ decreased as the NaOH concentration was increased up to 0.3 mol/L, attributed to the resulting framework of the zeolites collapsing at the higher alkali concentration [36]. From Table 1, while the HNO $_3$ concentration was fixed with 0.2 mol/L, the Si/Al ratio increased as the alkali

Table 1

Properties of the H β -B $_x$ A $_{0.2}$ processed with diverse alkaline concentrations and pristine H β .

Catalyst	Si/Al ^a	$n(\text{acid})$ ($\mu\text{mol/g}$)	V_{micro}^b (mL/g)	V_{meso}^c (mL/g)	S_{meso}^d (m ² /g)	S_{micro}^b (m ² /g)
H β	51	722	0.18	0.27	78.1	340.8
H β -B $_{0.1}$ A $_{0.2}$	79	561	0.17	0.27	99.7	324.1
H β -B $_{0.2}$ A $_{0.2}$	49	840	0.14	0.36	107.5	275.8
H β -B $_{0.3}$ A $_{0.2}$	38	632	0.12	0.40	99.0	245.1

^a XRF. ^b t -plot method. ^c BJH method from desorption branch.

^d $S_{\text{meso}} = S_{\text{BET}} - S_{t\text{-plot}}$.

Fig. 2. N $_2$ adsorption-desorption isotherms (a) and pore size distribution from adsorption branch (b) of the H β -B $_x$ A $_{0.2}$ processed with diverse alkaline concentrations and pristine H β .

Fig. 3. NH_3 -TPD profiles of $\text{H}\beta$ and the as-prepared $\text{H}\beta\text{-B}_x\text{A}_{0.2}$.

concentration was increased, and reached a maximum of 79 at 0.1 mol/L NaOH. Further increase of the concentration from 0.1 to 0.3 mol/L led to a continuous decrease of the Si/Al ratio. This result could be mainly attributed to the strengthened dealumination as the alkali concentration was increased [32].

The NH_3 -TPD technique was used to study the acidic properties of the series of $\text{H}\beta\text{-B}_x\text{A}_{0.2}$, and pristine $\text{H}\beta$ was examined for comparison. The NH_3 -TPD profiles are presented in Fig. 3. On the basis of previous reports [18–23], the NH_3 -TPD profiles could be divided into three regions, which can be respectively assigned as weak (150–300 °C), medium (300–450 °C), and strong (450–600 °C) acid sites. The amount of acid sites of the pristine $\text{H}\beta$ zeolite was 722 $\mu\text{mol/g}$. However, a lower amount of 561 $\mu\text{mol/g}$ acid sites was observed on $\text{H}\beta\text{-B}_{0.1}\text{A}_{0.2}$, which was attributed to the loss of Al^{3+} . Owing to the decrease of the Si/Al ratio through desilication at higher alkali concentrations, the amount of acid sites increased from 561 to 840 $\mu\text{mol/g}$ as the alkali concentration was increased from 0.1 to 0.2 mol/L. Although the Si/Al ratio decreased, a further increase in the alkali concentration from 0.2 to 0.3 mol/L resulted in a decrease in the amount of acid sites, mainly because of the collapsed framework of the zeolite owing to the excessively high NaOH concentration.

From Table 2, unlike pristine $\text{H}\beta$ zeolite, hierarchical zeolites prepared with different alkali concentrations exhibited much higher catalytic activity for alkenylation, attributed to the increase in the amount of acid sites and the strengthened mass transfer of the as-formed mesopores. The $\text{H}\beta\text{-B}_{0.2}\text{A}_{0.2}$ sample

Table 2

Reaction results of alkenylation of *p*-xylene with phenylacetylene over $\text{H}\beta$ and $\text{H}\beta\text{-B}_x\text{A}_{0.2}$.

Catalyst	Con. (%)	Product distribution (%)				
		I	II	III	IV	V
$\text{H}\beta$	82.9	85.3	0.2	0.1	13.8	0.6
$\text{H}\beta\text{-B}_{0.1}\text{A}_{0.2}$	91.0	85.7	0.2	0.8	12.5	0.8
$\text{H}\beta\text{-B}_{0.2}\text{A}_{0.2}$	95.8	95.1	0.2	1.0	2.9	0.8
$\text{H}\beta\text{-B}_{0.3}\text{A}_{0.2}$	91.8	94.1	0.1	0.8	2.8	2.2

Reaction conditions: $m_{\text{cat}} = 1.0$ g, $n_{p\text{-xylene/Phen}} = 25:1$, $T_r = 140$ °C, $P_s = 1.0$ MPa, TOS = 4 h, VHSV = 6 mL/h/g_{cat}.

showed the highest conversion. Owing to the lower amount of acid sites and collapsed framework resulting from an excessively high alkaline concentration, the $\text{H}\beta\text{-B}_{0.3}\text{A}_{0.2}$ catalyst also showed a lower conversion compared with $\text{H}\beta\text{-B}_{0.2}\text{A}_{0.2}$ prepared at an optimum alkali concentration. Moreover, narrow micropores are beneficial for producing the beta-(2,5-dimethylphenyl) styrene (IV) because of the thermodynamic stability compared with the main production. As a result, both $\text{H}\beta\text{-B}_{0.2}\text{A}_{0.2}$ and $\text{H}\beta\text{-B}_{0.3}\text{A}_{0.2}$ demonstrated a lower percentage of the product IV. Furthermore, the collapsed framework of $\text{H}\beta\text{-B}_{0.3}\text{A}_{0.2}$ limited mass transport, which led to formation of more oligomers [41]. Thus, the hierarchical $\text{H}\beta\text{-B}_{0.2}\text{A}_{0.2}$ zeolite treated by alkali and acid at 0.2 mol/L of alkali demonstrated a much higher catalytic activity and selectivity than both pristine $\text{H}\beta$ and the hierarchical zeolites prepared under other alkali concentrations, attributed to more acidic sites and greater accessibility to acidic sites.

3.2. Effects of acid concentration

On the basis of the optimized alkali concentration for the alkali/acid treatment for synthesizing hierarchical beta zeolite, the effect of the acid concentration on the nature and catalytic performance of the as-synthesized hierarchical beta zeolites was investigated by adjusting the acid concentration from 0 to 0.3 mol/L. The as-synthesized hierarchical beta zeolite catalysts are listed as $\text{H}\beta\text{-B}_{0.2}$, $\text{H}\beta\text{-B}_{0.2}\text{A}_{0.2}$ and $\text{H}\beta\text{-B}_{0.2}\text{A}_{0.3}$. Powder XRD patterns of the $\text{H}\beta\text{-B}_{0.2}$, $\text{H}\beta\text{-B}_{0.2}\text{A}_{0.2}$, and $\text{H}\beta\text{-B}_{0.2}\text{A}_{0.3}$ are shown in Fig. 4. All the samples featured typical XRD patterns corresponding to beta zeolite. Moreover, the $\text{H}\beta\text{-B}_{0.2}$ and $\text{H}\beta\text{-B}_{0.2}\text{A}_{0.2}$ featured a lower crystallinity than that of $\text{H}\beta\text{-B}_{0.2}\text{A}_{0.3}$, which can be attributed to the residual amorphous aluminosilicate species produced by alkali treatment of beta zeolite in the framework. The acid treatment can efficiently remove the as-formed aluminosilicate species from the hierarchical zeolite framework.

Fig. 5(a) depicts the N_2 adsorption–desorption isotherms of the $\text{H}\beta\text{-B}_{0.2}$, $\text{H}\beta\text{-B}_{0.2}\text{A}_{0.2}$ and $\text{H}\beta\text{-B}_{0.2}\text{A}_{0.3}$ samples, and the mesoporous size distribution is shown in the Fig. 5(b). The textural properties are listed in Table 3. From Fig. 5(a), no sharp rise on

Fig. 4. XRD patterns of $\text{H}\beta$ and the as-prepared $\text{H}\beta\text{-B}_{0.2}\text{A}_y$.

Fig. 5. N₂ adsorption-desorption isotherms (a) and pore size distribution from adsorption branch (b) of the Hβ and the as-prepared Hβ-B_{0.2}A_y.

the isotherm of Hβ-B_{0.2} at lower P/P_0 could be observed, suggesting that no micropores were present in this sample. This could be attributed to the blockage of inherent micropores in the beta zeolite by the as-formed amorphous aluminosilicate species in the process of the alkali treatment. From Table 3, both the surface area and the pore volume of the micropores were close to 0. From Fig. 5(a), the isotherms of the three samples showed type IV characteristic with a hysteresis loop, implying that mesopores were induced in the as-prepared hierarchical zeolites by the alkali/acid treatment. Fig. 5(b) featured mesopores with sizes in the range of 2–30 nm for all three samples. From Table 3, after the alkali-treated beta zeolites were subjected to the acid treatment, the samples featured a greatly increased specific surface area together with an increase in the pore volumes of the micropore and mesopore regimes in the as-prepared hierarchical zeolites. This result can be attributed to the role of the acid treatment in removing amorphous aluminosilicate and the further dealumination, which leads to formation of additional mesopores. The considerable increase in surface area and pore volume, of mesopores in particular, is of great importance for enhancing the alkenylation by improving accessibility to acidic sites.

From Fig. 6 and Table 3, owing to the as-formed amorphous aluminosilicate having been cleaned up through the acid treatment, both the Hβ-B_{0.2}A_{0.2} and Hβ-B_{0.2}A_{0.3} catalysts showed a greater increase in the number of acidic sites than that of the alkali treated Hβ-B_{0.2} without the acid treatment procedure; those catalysts also showed a much higher Si/Al ratio than Hβ-B_{0.2}. As the concentration was increased, the acid treatment led to a considerable decrease in the Si/Al ratio through dealumination, which markedly affected the acidic properties

[42]. Hβ-B_{0.2}A_{0.2} zeolite prepared by alkali and acid treatment in sequence with a 0.2 mol/L of alkali and acid concentration showed a much higher amount of acidic sites than those of the other two samples, which suggests that it might be a highly active alkenylation catalyst.

Table 4 presents the catalytic results of the alkenylation of *p*-xylene with phenylacetylene over a series of Hβ-B_{0.2}A_y zeolites treated with acid over a range of concentrations. From Table 4, Hβ-B_{0.2} showed lower activity and selectivity for alkenylation than those behaviors of the acid treated hierarchical Hβ-B_{0.2} zeolites. This result was attributed to the lower surface area and pore volume, and the blockage of acidic sites resulting by residual amorphous aluminosilicate formed in the alkali treatment process. As the acid concentration was increased from 0 to 0.2 mol/L, an increase in catalytic activity was found, which could be attributed to more acidic sites generated by the clean-up of blockages in the amorphous aluminosilicate. However, further increasing the acid concentration up to 0.3 mol/L led to a decrease in catalytic activity, attributed to a decrease in the amount of acidic sites caused by dealumination in the acid treatment. Hβ-B_{0.2}A_{0.2} featured the highest catalytic activity and selectivity among the four catalysts, which

Table 3

Properties of Hβ-B_{0.2}A_y processed with a range of acid concentrations.

Catalyst	Si/Al ^a	<i>n</i> (acid) (μmol/g)	<i>V</i> _{micro} ^b (mL/g)	<i>V</i> _{meso} ^c (mL/g)	<i>S</i> _{meso} ^d (m ² /g)	<i>S</i> _{micro} ^b (m ² /g)
Hβ-B _{0.2}	37	200	0	0.28	49.5	0
Hβ-B _{0.2} A _{0.2}	49	840	0.14	0.36	107.5	275.8
Hβ-B _{0.2} A _{0.3}	68	593	0.12	0.40	106.7	245.1

^a XRF. ^b *t*-plot method. ^c BJH method from desorption branch.

^d *S*_{meso} = *S*_{BET} - *S*_{*t*-plot}.

Fig. 6. NH₃-TPD profiles of the as-prepared Hβ-B_{0.2}A_y.

Table 4

Reaction results of the alkenylation of *p*-xylene with phenylacetylene over H β -B $_{0.2}$ A $_{0.2}$.

Catalyst	Con. (%)	Product distribution (%)				
		I	II	III	IV	V
H β -B $_{0.2}$	6.8	70.7	3.3	0.0	6.0	20.0
H β -B $_{0.2}$ A $_{0.1}$	82.7	92.3	0.6	1.1	3.7	2.3
H β -B $_{0.2}$ A $_{0.2}$	95.8	95.1	0.2	1.0	2.9	0.8
H β -B $_{0.2}$ A $_{0.3}$	92.6	94.8	0.1	1.0	2.5	1.6

Reaction conditions: $m_{\text{cat}} = 1.0$ g, $n_{p\text{-xylene/Phen}} = 25:1$, $T_r = 140$ °C, $P_s = 1.0$ MPa, TOS = 4 h, VHSV = 6 mL/h/ g_{cat} .

was attributed to this sample having the largest amount of acidic sites and the highest specific surface area and pore volume. The 0.2 mol/L acid concentration treatment was found to be the optimum acid concentration for achieving excellent catalytic performance for the alkenylation reaction.

3.3. Stability to alkenylation

Fig. 7 demonstrates the catalytic stability of the as-prepared H β -B $_{0.2}$ A $_{0.2}$ zeolite solid acid catalyst for alkenylation of *p*-xylene with phenylacetylene. The performance of pristine H β is also included for comparison.

From Fig. 7, unlike the pristine H β solid acid catalyst, the as-prepared hierarchical H β zeolite featured superior stability for alkenylation of *p*-xylene with phenylacetylene. However, the catalytic stability of the hierarchical H β zeolite was unsatisfactory. A further increase of the stability would be highly desirable. From previous reports, the modification of zeolites by metal oxides, such as alkaline earth and rare earth metal oxides has been demonstrated to be an efficient method for improving their catalytic performance and stability for various transformations [32–38]. However, there have been few reports on the promotion of alkenylation through metal oxide modification. Herein, CeO $_2$ modified hierarchical H β zeolites with a range of loadings were prepared by impregnation, and the catalytic stability of the ceria-modified hierarchical H β zeolites for alkenylation was investigated. As shown in Fig. 7, the 5 wt% CeO $_2$ modified hierarchical H β zeolite showed higher stability for alkenylation than the unmodified H β -B $_{0.2}$ A $_{0.2}$ zeolite

Fig. 8. NH $_3$ -TPD profiles of H β , H β -B $_{0.2}$ A $_{0.2}$ and the 5 wt% CeO $_2$ H β -B $_{0.2}$ A $_{0.2}$.

and the pristine H β zeolite. Both hierarchical zeolites show higher selectivity than that of the pristine zeolite, owing to enhanced mass transfer from the as-formed hierarchical pores. The ceria-modified H β -B $_{0.2}$ A $_{0.2}$ zeolite showed a slightly lower selectivity than that of the unmodified H β -B $_{0.2}$ A $_{0.2}$ zeolite, which may be attributed to the partial blockage of hierarchical pores by the introduced ceria.

Fig. 8 shows that the hierarchical H β -B $_{0.2}$ A $_{0.2}$ zeolite featured more acidic sites than did the pristine H β , which allowed H β -B $_{0.2}$ A $_{0.2}$ to exhibit a higher initial catalytic activity. The higher stability of H β -B $_{0.2}$ A $_{0.2}$ could be ascribed to its hierarchical pore structure. Furthermore, owing to possible blockage of Bronsted acidic sites by the ceria modification [38], the 5 wt% CeO $_2$ H β -B $_{0.2}$ A $_{0.2}$ zeolite featured fewer weak, medium and strong acidic sites compared with those of the unmodified H β -B $_{0.2}$ A $_{0.2}$ zeolite. The loss of Bronsted acidic sites of ceria-modified H β -B $_{0.2}$ A $_{0.2}$ zeolite might have reduced polymerization and oligomerization, which in turn reduced the formation of carbonaceous deposits. As a result, the 5 wt% CeO $_2$ H β -B $_{0.2}$ A $_{0.2}$ zeolite demonstrated much higher catalytic stability for alkenylation than that of the unmodified H β -B $_{0.2}$ A $_{0.2}$ zeolite.

Fig. 7. Catalytic stability of H β , H β -B $_{0.2}$ A $_{0.2}$ and 5 wt% CeO $_2$ H β -B $_{0.2}$ A $_{0.2}$ for the alkenylation of *p*-xylene with phenylacetylene.

Fig. 9. TGA curves of H β , H β -B_{0.2}A_{0.2} and 5 wt% CeO₂ H β -B_{0.2}A_{0.2}.

Moreover, some of the acidic sites on H β -B_{0.2}A_{0.2} could become covered by carbonaceous species that rapidly formed owing to the higher concentration of strong acidic sites. This effect in turn led to a decrease in catalytic activity. As a result, from Fig. 7, the lower amount of acidic sites on the 5 wt% CeO₂ H β -B_{0.2}A_{0.2} zeolite did not result in a decrease of its catalytic activity over the investigated time range on stream (from 240 to 480 min).

TGA was used to reveal the possible mechanism for the remarkably improved catalytic stability of our optimized catalyst compared with those of the unmodified H β -B_{0.2}A_{0.2} zeolite and the pristine H β zeolite. From Fig. 9, the ceria-modified and unmodified H β -B_{0.2}A_{0.2} zeolites featured similar total weight losses, which was less than that of the pristine H β zeolite. This result was attributed to the hierarchical pore structure of the former. As a result, both hierarchical zeolites featured superior stability to that of the pristine H β zeolite. Furthermore, the spent ceria-modified H β -B_{0.2}A_{0.2} zeolite showed lower oligomer content (weight loss at low temperature) and more eupolymer (weight loss at high temperature) content compared with those features of the spent unmodified H β -B_{0.2}A_{0.2} zeolite catalyst. The reason for this effect is unclear and will be further investigated in our future work. Moreover, the temperature of carbon

combustion of the ceria zeolite was clearly lower than that of the unmodified H β -B_{0.2}A_{0.2} zeolite and the pristine H β , which might be the main reason for its higher catalytic stability. Hence, the developed 5 wt% CeO₂ H β -B_{0.2}A_{0.2} zeolite shows great potential as a solid acid catalyst for producing alkenyl aromatics through alkenylation.

4. Conclusions

Ceria-modified hierarchical H β zeolites were prepared by a desilication-dealumination procedure with subsequent cerium impregnation. Our results show that the ceria-modified hierarchical H β zeolite catalyst prepared with optimized parameters demonstrated high catalytic activity, selectivity, and stability for alkenylation of *p*-xylene with phenylacetylene, attributed to the more acidic sites and the improved accessibility to active sites owing to enlarged pores, a higher mesoporous surface area, and a mesoporous volume resulting from the hierarchical pore architecture and ceria modification. The combination of excellent catalytic performance and the easy recovery of the spent catalyst by calcination, make the 5 wt% CeO₂-H β -B_{0.2}A_{0.2} catalyst with a hierarchical pore architecture attractive for producing alkenyl aromatics through acid catalyzed alkenylation of aromatics.

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Graphical Abstract

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Ceria-modified hierarchical H β zeolite as a robust solid acid catalyst for alkenylation of *p*-xylene with phenylacetylene

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Aceria-modified hierarchical pore H β zeolite was prepared by a desilication-dealumination procedure with subsequent ceria modification and demonstrated good catalytic performance for alkenylation of *p*-xylene with phenylacetylene.

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氧化铈改性多级孔H β 分子筛催化对二甲苯与苯乙炔烯基化反应

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摘要: 烯基芳香化合物是重要的精细化学品及中间体, 在医药、染料、农药、香料、新型高分子材料和天然产品等化学工业领域得到广泛应用。传统工艺采用芳香化合物与烯基化合物的反应合成烯基芳香化合物。但是, 传统过程存在许多不足: (1)芳环需预活化, 如卤代等; (2)伴生氢卤酸等废物, 污染环境; (3)原子经济性差。因此, 研究烯基芳香化合物的清洁、高原子经济性合成备受关注。采用芳香化合物与烯基化合物的烯基化, 可以100%原子经济性地合成烯基芳香化合物, 且芳环无需预活化, 不产生废弃物。因此, 通过芳香化合物与烯的烯基化路线来合成烯基芳香化合物引起了人们的极大兴趣。尤其是固体酸催化烯基化, 工艺成本低, 清洁无污染, 颇具工业前景。然而, 固体酸催化烯基化不同于烷基化, 烯基阳离子稳定性很差, 比碳正离子易于聚合, 进而导致催化剂积碳失活。微孔沸石分子筛用于烯基化存在底物适用范围窄、催化效率低、选择性差和炔聚合严重的问题。本研究组开展了硫酸化的铜钨氧化物介孔固体超强酸、担载磷钨酸介孔固体酸催化烯基化。采用前者, 合成有序的介孔铜钨氧化物较为困难; 而采用后者, 催化剂的再生需要大量有机溶剂, 会造成环境污染。硅铝分子筛固体酸易于制备, 且可以通过简单的焙烧来再生。多级孔分子筛具有微孔分子筛和介孔分子筛的双重优势, 用于烯基化反应可望获得良好效果。

本文采用碱、酸对商业微孔 β 沸石分子筛进行处理, 通过脱硅、脱铝过程来合成多级孔 β 分子筛, 并进行稀土金属铈改性, 从而制备了氧化铈改性的多级孔 β 分子筛, 研究了其催化对二甲苯与苯乙炔的烯基化反应。通过改变碱浓度和酸浓度, 对所制备的多级孔 β 分子筛的组织性质和酸性质进行调控, 在优化的条件下获得了良好的烯基化催化性能, 得到95.8%的苯乙炔转化率和95.1%的目标产物 α -2,5-二甲苯基苯乙烯的选择性, 总的烯基化产物(α -和 β -烯基芳香化合物)的选择性达到

98%。相对于微孔 β 分子筛,所制备的多级孔 β 分子筛展示了显著增强的催化活性和稳定性,目标产物选择性也有所提高。显著提高的催化性能归因于多级孔分子筛的传质强化和酸性位的增多。氧化铈的改性使得多级孔 β 分子筛的弱、中等和强酸中心的数目减少,可能源于减少了表面暴露的B酸位,从而导致了催化稳定性的显著提高。可见,本文所制备的氧化铈改性多级孔 β 分子筛用于烯基化反应具有一定前景。

关键词: 多级孔分子筛; 烯基化; 清洁合成; 烯基芳香化合物; 多相催化

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《催化学报》进入中科院 JCR 期刊分区工程技术大类2区

近日,中国科学院文献情报中心发布 2016 年版中科院JCR期刊分区, *Chinese Journal of Catalysis* (《催化学报》) 在工程技术类 1845 种期刊中排名第 354 位, 居工程技术大类2区。中科院 JCR 期刊分区按照学术影响力作为划分方式, 将每个学科的所有期刊按照学术影响力 (3年平均JCR影响因子 (IF)) 由高到低降序排列, 依次划分为4个区, 使每个分区期刊影响力总和相同。由于学科内期刊的3年IF的偏态分布, 这使得1区期刊数量极少。为保证期刊1区期刊数量, 1区期刊取整个学科数量总数的5%, 即3年平均IF最高的5%的期刊为1区期刊。2–4区期刊使用3年平均IF总和相同的方式划分 (分区方法详见<https://www.fenqubiao.com>)。

近年,《催化学报》的学术质量及影响力不断提升,这是中国化学会催化委员会委员、《催化学报》编委、审稿专家、作者和读者长期不懈努力和共同支持的结果。衷心感谢各位老师、投稿原创性高质量稿件、学术质量把关以及组约优秀稿件、组办高水平专刊等方面所给予的持续的、巨大的支持!

(《催化学报》编辑部)