

HY Zeolite Modified by Liquid Silane Deposition and Its Catalytic Activity in Selective *tert*-Butylation of Naphthalene

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Abstract: HY zeolites were modified by chemical liquid deposition with $i\text{-C}_4\text{H}_9\text{Si}(\text{OC}_2\text{H}_5)_3$, followed by hydrothermal treatment. The samples were characterized by X-ray diffraction, N_2 adsorption and pulse mass analysis to investigate the influence on framework structure, specific surface area, pore diameter and adsorption behaviors. The catalytic performances of HY zeolite and the modified samples in the alkylation of naphthalene with *tert*-butyl alcohol were also evaluated. The results showed the modification of HY zeolite did not change framework structure but increased specific surface area, decreased average pore diameter, and reduced the size of pore opening. Catalytic activity of the modified HY zeolite catalyst for *tert*-butylation of naphthalene was decreased compared with that of HY zeolite catalyst while shape-selectivity of 2,6-di-*tert*-butylnaphthalene (2,6-DTBN) was increased obviously, the highest 2,6-DTBN/2,7-DTBN ratio of 6.62 obtained.

Key words: chemical liquid deposition; HY zeolite; naphthalene; *tert*-butyl alcohol; 2,6-di-*tert*-butylnaphthalene

Chemical liquid deposition (CLD) has been used to deactivate the external surface acid sites and control the pore opening size of zeolites [1–5] and has found wide applications in shape-selective catalysis [6–8]. In a typical CLD process, the added modification reagent reacts with hydroxyl groups on the surface and pore opening of the zeolite. It is then decomposed to deposit an oxide coating on the surface and pore opening of the zeolite by calcination.

The shape-selective alkylation of naphthalene to 2,6-dialkyl-naphthalene (2,6-DAN) has a high commercial value [9]. Previous studies showed that in the alkylation of naphthalene, besides a suitable surface acidity, the pore structure and pore opening size of the zeolite should match the molecular size of the target product, which is more important to improve the selectivity to 2,6-DAN [10–13].

In this paper, the HY zeolite was modified by CLD using $i\text{-C}_4\text{H}_9\text{Si}(\text{OC}_2\text{H}_5)_3$, which was followed by a hydrothermal treatment. The influence of this modification on the framework structure, specific surface area, and pore structure of the zeolite was investigated. The different adsorption behavior of various adsorbents with different kinetic diameters was characterized over HY and modified HY. The catalytic activity of HY and modified HY in the alkylation of naphthalene with *tert*-butyl

alcohol was investigated. The relationship between the narrowing of the pore opening size and shape-selectivity was established.

1 Experimental

1.1 Catalyst preparation

HY zeolite ($n(\text{Si})/n(\text{Al}) = 5.20$) was purchased from Wenzhou Huahua Group Co., Ltd, China. It was used after calcination at 550 °C for 4 h. $i\text{-C}_4\text{H}_9\text{Si}(\text{OC}_2\text{H}_5)_3$ was supplied by Shanghai Xingta Chemical Plant, China. Analytical grade cyclohexane, naphthalene, and *tert*-butyl alcohol were purchased from Tianjin Chemical Reagent Co., Ltd, China.

The calcined HY was mixed with cyclohexane using a liquid to solid mass ratio of 5:1. Then a fixed amount of $i\text{-C}_4\text{H}_9\text{Si}(\text{OCH}_2\text{CH}_3)_3$ was added into the mixture and stirred for 5 h at room temperature. After this was dried at 80 °C and calcined at 550 °C for 4 h, silica-deposited HY catalysts were obtained and designated as SiY(*c*). The letter “*c*” in the sample code represented the volume of $i\text{-C}_4\text{H}_9\text{Si}(\text{OCH}_2\text{CH}_3)_3$ added per gram of zeolite (ml/g). Then, SiY(0.3) was exposed to a steam atmosphere at 600 °C for 4 h to prepare sample SiY(0.3)-ST.

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1.2 Catalyst characterization

Powder X-ray diffraction (XRD) was performed on a Rigaku D/MAX- γ B powder diffractometer with Cu K_{α} radiation. N_2 sorption analysis was performed on a Micromeritics ASAP 2000 autosorb instrument at $-196\text{ }^{\circ}\text{C}$ to measure the specific surface area and pore volume. Adsorption measurements were carried out on a TEOM 1500 PMA highly sensitive quartz microbalance at $30\text{ }^{\circ}\text{C}$, using a flow rate of $30\text{ cm}^3/\text{min}$ air, N_2 , and helium as the activation gas, purge gas, and carrier gas, respectively. The adsorbents were *m*-xylene and 1,3,5-trimethylbenzene (TMB).

1.3 Catalyst testing

Alkylation was carried out in a 75 ml stirred micro-autoclave reactor. For a typical run, 0.29 g (2.25 mmol) naphthalene and 16.62 g (200 mmol) cyclohexane as solvent were mixed together in the autoclave. Then 0.50 g freshly calcined catalyst and 0.50 g (6.75 mmol) of *tert*-butyl alcohol were added sequentially. The autoclave was sealed, purged with N_2 several times and filled with N_2 to 2.0 MPa. The reaction was carried out at $160\text{ }^{\circ}\text{C}$ for 2 h. Then, the reactor was quenched in cold water, and the catalyst was removed by centrifuging. The products in the liquid solution were analyzed quantitatively on a Varian 3800 gas chromatograph equipped with a Varian cp-sil-19 column. GC-MS (HP 5970) was used for the identification of the products.

2 Results and discussion

2.1 XRD results

Fig. 1 is the XRD patterns of HY zeolite and modified HY. The XRD pattern of HY zeolite showed the typical diffraction peaks of the FAU structure. Compared with the XRD pattern of HY zeolite, the same diffraction peak locations and no new diffraction peak were observed in the XRD patterns of SiY(0.1) and SiY(0.3). This shows that the HY zeolite framework remained unchanged and the deposited SiO_2 was amorphous and highly dispersed on the zeolite surface in the silanization modification by CLD. After silanization and hydrothermal treatment, the number and locations of the diffraction peaks remained unchanged in the XRD pattern of SiY(0.3)-ST, while

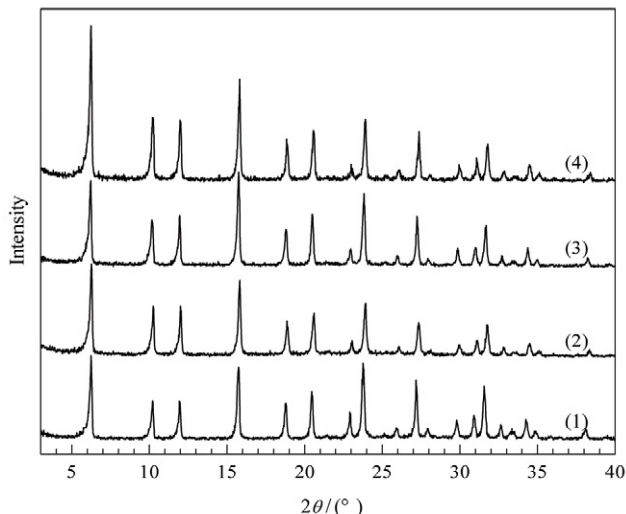


Fig. 1. XRD patterns of HY zeolite and the modified samples. (1) HY; (2) SiY(0.1); (3) SiY(0.3); (4) SiY(0.3)-ST.

the relative intensity of the low angle diffraction peaks at $2\theta = 5^{\circ}$ – 18° increased.

Taking HY zeolite as a reference standard, the relative crystallinity of modified HY was determined according to the ASTM D3906-2003 method. After the silanization modification by CLD, the calculated relative crystallinities of SiY(0.1) and SiY(0.3) were 95.14% and 98.12%, respectively. This shows that the deposited SiO_2 was highly dispersed on the zeolite surface and had minimal influence on the zeolite framework structure. After silanization and hydrothermal treatment, the calculated relative crystallinity of SiY(0.3)-ST was increased to 114.15%. This can be explained by the migration of the deposited SiO_2 into zeolite lattice defects [14], which would modify the HY zeolite framework structure and increase the relative crystallinity.

2.2 N_2 adsorption

Table 1 shows the specific surface area and pore volume analysis results of HY zeolite and modified HY. HY zeolite had a large mesopore surface area and mesopore volume, indicating that a large number of mesopore structure was distributed in the HY zeolite framework. There was a decrease in the mesopore surface area and mesopore volume with SiY(0.1), while the total surface area, micropore surface area, and mi-

Table 1 Specific surface area and pore volume analysis of HY zeolite and the modified samples

Sample	Surface area (m^2/g)			Pore volume (cm^3/g)			Average pore diameter (nm)
	Total	Micropore	Mesopore	Total	Micropore	Mesopore	
HY	317.6	239.2	74.1	0.23	0.12	0.10	2.85
SiY(0.1)	329.2	293.2	39.9	0.21	0.14	0.07	2.60
SiY(0.3)	374.4	342.7	38.0	0.23	0.17	0.07	2.49
SiY(0.3)-ST	474.4	438.6	42.4	0.30	0.21	0.08	2.49

cropore volume were increased. The result shows that in the silanization modification by CLD, SiO₂ deposition occurred not only on the external surface but also in the mesopore of the HY zeolite. The mesopore structure was partly blocked by the deposited SiO₂ to form a new micropore structure. After some silanization reagent had diffused into a mesopore, the probability was limited for more silanization reagent to enter the mesopore, and then the remaining silanization reagent had to be deposited on the external surface. Thus, the mesopore volume of SiY(0.3) was similar to that of SiY(0.1) despite the increased amount of deposited SiO₂. However, the micropore volume of SiY(0.3) was increased. This was possibly due to the formation of a new micropore structure on the external surface from SiO₂ in the calcination. After silanization and hydro-

thermal treatment, SiY(0.3)-ST exhibited an increase in mesopore volume, micropore surface area, and micropore volume, which was possibly due to Al extraction from the zeolite framework and the migration of the deposited SiO₂ under the steaming condition [14].

2.3 Adsorption curves

In order to know the effective pore opening size of the HY zeolite after the modification [15], adsorption experiments were carried out over HY and modified HY using *m*-xylene (0.71 nm) and 1,3,5-TMB (0.76 nm) as adsorbates.

Fig. 2 is the adsorption characteristics of *m*-xylene and 1,3,5-TMB on HY zeolite and modified HY. The amount of *m*-xylene (Q_m) adsorbed at equilibrium was almost similar to that of 1,3,5-TMB (Q_t) on HY zeolite. After the modification, different Q_m and Q_t were observed on SiY(0.1), SiY(0.3), and SiY(0.3)-ST, and Q_t was less than Q_m . A possible reason is that the pore opening was narrowed by the modification, and this would more affect the larger molecule 1,3,5-TMB.

The equilibrium time of adsorption of *m*-xylene and 1,3,5-TMB was designated as t_m and t_t , respectively. As shown in Fig. 2, the values of t_m and t_t were increased over SiY(0.1) and SiY(0.3) as compared with that over HY zeolite. Less adsorption and slower diffusion of *m*-xylene and 1,3,5-TMB were observed after the silanization modification by CLD. This may be due to the narrowing of the pore opening and partial blocking of the mesopore structure. After silanization and hydrothermal treatment, SiY(0.3)-ST exhibited the largest values of t_m and t_t . This indicates that adsorption suppression was enhanced further. Because of the migration of the deposited SiO₂ during steaming, a modification of the zeolite framework structure, narrowing of the pore opening, and formation of a fresh micropore structure were observed on SiY(0.3)-ST, which caused the adsorption suppression to be at its maximum.

In order to understand quantitatively the different adsorption properties over the various samples, k_m/k_t was designated as a parameter of the relative adsorption rate, where k_m and k_t denote the average adsorption rate of *m*-xylene and 1,3,5-TMB, respectively. k_m/k_t increased in the order HY < SiY(0.1) < SiY(0.3) < SiY(0.3)-ST as shown in Table 2. Therefore, it can be concluded that owing to the narrowing of pore opening and

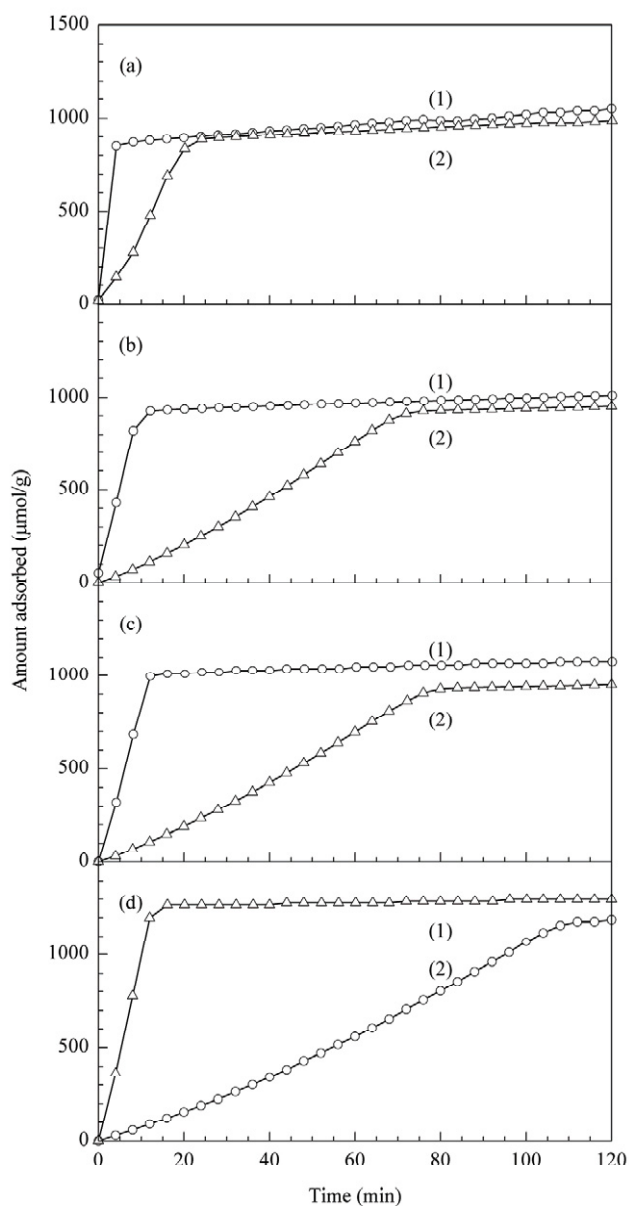


Fig. 2. Adsorption curves of *m*-xylene and 1,3,5-TMB over HY zeolite and the modified samples. (a) HY; (b) SiY(0.1); (c) SiY(0.3); (d) SiY(0.3)-ST. (1) *m*-xylene; (2) 1,3,5-trimethylbenzene.

Table 2 Adsorption properties over HY zeolite and the modified samples

Sample	$k_m/(\mu\text{mol}/(\text{g}\cdot\text{min}))$	$k_t/(\mu\text{mol}/(\text{g}\cdot\text{min}))$	k_m/k_t
HY	224.72	41.98	5.35
SiY(0.1)	94.14	13.25	7.10
SiY(0.3)	89.23	12.31	7.25
SiY(0.3)-ST	102.54	10.98	9.34

k_m : adsorption rate of *m*-xylene.

k_t : adsorption rate of 1,3,5-trimethylbenzene.

Table 3 Reaction results over HY zeolites and the modified samples

Sample	Naphthalene conversion (%)	Product distribution (%)			Selectivity (%)		2,6-DTBN/2,7-DTBN
		TBN	DTBN	Others ^a	2, 6-DTBN	2, 7-DTBN	
HY	83.4	37.7	53.6	8.7	80.6	19.4	4.16
SiY(0.1)	58.6	55.6	42.6	1.8	85.5	14.5	5.91
SiY(0.3)	51.0	57.2	41.4	1.4	86.1	13.9	6.21
SiY(0.3)-ST	63.4	47.6	52.4	—	86.9	13.1	6.62

Reaction conditions: reaction temperature = 160 °C, reaction pressure = 2.0 MPa, reaction time = 2.0 h, naphthalene:*tert*-butyl alcohol:cyclohexane = 1:3:90.

^a Derivatives of polynuclear aromatic hydrocarbons identified with MS.

the modification of the micropore structure by the modification, the difference in adsorption rates of the various adsorbates with different kinetic diameters became pronounced, and the decrease of the adsorption rate was more than the larger molecule, 1,3,5-TMB.

2.4 Catalytic performance

Kinetic diameters of 2,6-DTBN and 2,7-DTBN [16] are similar to that of *m*-xylene and 1,3,5-TMB, respectively. Due to the narrowing of pore opening and the modification of micropore structure, the slower diffusion and formation of 2,7-DTBN would be enhanced in HY zeolite channels. Therefore, 2,6-DTBN would be produced selectively over the modified catalysts in the *tert*-butylation of naphthalene.

Table 3 lists the reaction results over HY zeolite and the modified catalysts. Except for TBN, only two DTBNs were observed in *tert*-butylation of naphthalene in the products. These results show that a shape-selective effect has been achieved in the *tert*-butylation of naphthalene over the HY zeolite. HY zeolite showed the highest naphthalene conversion of 83.4% and a 2,6-DTBN/2,7-DTBN ratio of 4.16. After the silanization modification by CLD, naphthalene conversions of 58.6% and 51.0% were obtained over SiY(0.1) and SiY(0.3) catalysts, while 2,6-DTBN/2,7-DTBN ratios were increased to 5.91 and 6.21, respectively. After silanization and hydrothermal treatment, SiY(0.3)-ST exhibited a higher naphthalene conversion of 63.4% as well as the high 2,6-DTBN/2,7-DTBN ratio of 6.62.

The desorption and diffusion behavior of the reaction products are closely related to the activity of the zeolite catalyst. The reaction is faster with increased diffusion rate. Over the modified HY zeolite catalyst, the narrowing of pore opening and the blocking of mesopore structure would inhibit the formation and diffusion of the products, which resulted in a decrease in reaction activity over the SiY(0.1) and SiY(0.3) catalysts. However, the reaction activity was observed to recover over SiY(0.3)-ST, which was possibly due to acidity modification after silanization and hydrothermal treatment [6,17].

Shape selectivity in zeolite catalysts is also related to the diffusion behavior of the reaction products. The products with

higher diffusion rate will be produced preferentially to those with lower diffusion rate. The selectivity to 2,6-DTBN in the *tert*-butylation of naphthalene increased in the order HY < SiY(0.1) < SiY(0.3) < SiY(0.3)-ST, which was the same as that of k_m/k_t . It can be concluded that the diffusion rate of 2,6-DTBN and 2,7-DTBN was more different with increasing relative adsorption rate, which resulted in the improved selectivity to 2,6-DTBN over the modified catalyst. Therefore, the close relationships established for the narrowing of the pore opening, adsorption rate, and shape selectivity can provide the opportunity to improve catalytic properties by a modification by CLD.

3 Conclusions

HY zeolite was modified by liquid deposition with $i\text{-C}_4\text{H}_9\text{Si}(\text{OC}_2\text{H}_5)_3$ and a hydrothermal treatment. Deposited SiO_2 was coated on the external surface of the zeolite, and a small amount of SiO_2 diffused into the mesopore structure. The modification of HY zeolite did not change the framework structure but increased the specific surface area, decreased pore diameter, and narrowed pore openings. Due to the modification of the micropore structure and the narrowing of pore openings by the modification, the differences in the adsorption rate of adsorbates with different kinetic diameters were enhanced. The selectivity to 2,6-DTBN was improved in the *tert*-butylation of naphthalene, and a high 2,6-DTBN/2,7-DTBN ratio of 6.62 was obtained.

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