

CVD modified KL zeolite supported Pt for *n*-hexane aromatization

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Abstract

Modification of non-acidic KL zeolite by chemical vapor deposition (CVD) of $\text{Si}(\text{OEt})_4$ and $(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$ followed by Pt loading was used to study the influence of zeolite support on the aromatization of *n*-hexane. Deposited on the framework oxygen ions of the non-acidic zeolite, the silica layer effectively narrowed the pores of KL zeolite. But owing to the appearance of new basic sites, such as potassium oxide (K_2O), the interaction between Pt metal and zeolite support was strengthened, causing Pt particles to be more electron-excess. *n*-Hexane pulse-flow microreactions were carried out to study the effects on the aromatization reactivity and sulfur poisoning properties. © 1998 Elsevier Science B.V.

Keywords: Chemical vapor deposition; Pt supported KL zeolite; *n*-Hexane aromatization; Sulfur resistance

1. Introduction

The excellent Pt/KL catalyst for aromatization of linear hydrocarbons has attracted considerable interest in recent years [1,2]. Although the detailed mechanism of this catalyst is still not clear, the majority of studies have attributed the specific behavior to the unique channel structure of KL zeolite [3–5]. It has been observed that the properties of Pt particles are strongly dependent upon the surrounding zeolite and that the Pt particles in KL zeolite may be electron rich as a consequence of a charge transfer from the framework of KL zeolite to the small metal particles [6,7]. A variety of modified methods of synthesis have been inves-

tigated in order to improve the catalytic properties and/or to explain for the effectiveness of this catalyst [8–10].

Chemical vapor deposition (CVD) is widely used to control the pore size of zeolites and to improve the shape-selectivity of zeolite catalysts [11–14]. It has been pointed out that CVD, which is the chemical adsorption of deposition reagent on the surface hydroxyl groups of zeolites, terminal silanols and acidic hydroxyl groups, played an important role in the deposition process [11,14]. While most studies of this method focused on the H-type zeolite, we have recently reported results of CVD on basic metal ion exchanged (KX and NaY) zeolites [15]. We found that, differing from the mechanism of CVD on H-type zeolite, the framework oxygen ion is the deposition site on these non-acidic

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zeolites [15]. This kind of deposition might unavoidably cause the changes on both the geometric and electronic properties of the zeolite support. Therefore, it is our intention to study the effects of this deposition on the Pt particles supported and to make clear the nature of the excellent Pt/KL zeolite catalyst. In the present work, $\text{Si}(\text{OEt})_4$ and $(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$ were used to deposit on non-acidic KL zeolite. It was found that the pore size of KL zeolite was narrowed, some active sites in the KL zeolite for *n*-hexane 1,6-cyclization were destroyed. Meanwhile, the interaction between the Pt metal and zeolite support was strengthened, causing the Pt particles to be more electron-excess.

2. Experimental

2.1. Chemical vapor deposition

KL zeolite was obtained as described previously, the unit-cell composition of which was $\text{K}_{8.08}\text{Na}_{0.16}\text{Al}_{8.24}\text{Si}_{26.78}\text{O}_{72}$ [16]. Deposition was performed on a system with the aid of a home-built gravimetric apparatus. Before deposition, KL zeolite was evacuated at 413 K for 0.5 h and subsequently at 623 K for 2 h. After this treatment, the weight of dehydrated KL zeolite remained constant, meanwhile IR spectrum showed no H_2O stretching bands, indicating that all of the adsorbed water had been removed.

The vapor of $\text{Si}(\text{OEt})_4$ or $(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$ was introduced to the dehydrated samples at room temperature overnight, then samples were calcinated under the flow of oxygen at 673 K in situ to remove the carbonaceous residues. The extent of deposition was obtained by the weight increment of the SiO_2 deposited. For deposition with $\text{Si}(\text{OEt})_4$, the deposition increment was 1.84 wt% (labeled as SiKL-1), with $(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$ it was 4.86 wt% (labeled as SiKL-2).

2.2. Pt loading

0.6 wt% Pt/KL zeolite with and without CVD modification were prepared by dry impregnation of *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ at 353 K as described in our previous work [17]. After Pt loading, samples were calcined in a high flow of air at 2 K/min from room temperature to 573 K, followed by reduction in H_2 at 773 K for at least 2 h in order to obtain highly dispersed Pt particles [17].

2.3. Measurements

The adsorption of *m*-xylene on KL zeolites before and after deposition was carried out by gravimetric method. 0.4 g of the sample was evacuated at 623 K for 4 h and then used for adsorption at 393 K by keeping it in contact with 0.2 kPa of *m*-xylene vapor.

0.05 g sample for TPD measurement was activated in a quartz tube at 773 K for 2 h and exposed to ammonia for 5 min at room temperature, then maintained at 373 K under flowing N_2 . TPD measurement was done from 373 to 773 K at a heating rate of 10 K/min. Nitrogen of high purity was used as the carrier gas.

The surface area of the Pt supported samples were measured by means of N_2 adsorption in a Micromeritic ASAP 2000 instrument. IR experiments were carried out with self-supported zeolite wafers ($8 \text{ mg}/\text{cm}^2$). After reduction in H_2 , the samples were dehydrated at 623 K for 2 h. CO gas was admitted at a pressure of 4×10^4 Pa followed by evacuation. The CO-IR spectra were taken in a Nicolet 510P instrument at room temperature.

2.4. Catalytic studies

The isopropanol probe catalytic reaction was used to study the acid–basic properties of L zeolite with or without modification. In each run, 0.05 g of the zeolite catalyst on dry basis which was pelleted and screened between 20–40

mesh, was placed in a continuous microreactor. After in-situ activation at 773 K for 2 h under a N_2 flow, isopropanol decomposition reactions were carried out at atmospheric pressure with $W/F = 10.3 \text{ g/h} \cdot \text{mol}$.

n-Hexane pulse-flow microreaction was carried out to study the catalytic aromatization activity of Pt supported zeolites (0.05 g, 20–40 mesh). After the catalyst was reduced in-situ, $0.4 \mu\text{l}$ pure *n*-hexane or *n*-hexane containing 0.2 ppm thiophene was injected to the reactor at 773 K. The reaction products were analyzed by on-line gas chromatography. Results were reported as conversions calculated as the mole percent of *n*-hexane reacted, benzene yields and selectivities.

3. Results and discussion

3.1. Influence on the pore size and pore volume

Fig. 1 shows the adsorption profiles for *m*-xylene on KL and CVD modified ones. The amount of adsorption is quite large over the unmodified KL zeolite (Fig. 1a), showing that the pore size is big enough for an *m*-xylene molecule to enter. Whereas in the modified

SiKL zeolites (Fig. 1b and c), the ability for the adsorption of *m*-xylene decreases drastically.

In addition, the greater the weight increment of SiO_2 , the less amount adsorbed and thus the smaller the pore volume would be. It is clear that the pore size is narrowed and the pore volume is decreased by the SiO_2 deposited.

We also determined the surface area of Pt supported zeolites by means of N_2 adsorption. The internal and external surface areas of the Pt/KL zeolite are 190 and $70 \text{ m}^2/\text{g}$, respectively. After deposition with the $Si(OEt)_4$ molecule as deposition agent, there is little change both in the external ($157 \text{ m}^2/\text{g}$) and internal surface areas ($61 \text{ m}^2/\text{g}$) on the SiKL-1 zeolite. Whereas on the SiKL-2 zeolite, in which $(CH_3)_3Si-O-Si(CH_3)_3$ was the deposition agent, there is no change in the external ($70 \text{ m}^2/\text{g}$) but a great decrease in the internal surface area ($126 \text{ m}^2/\text{g}$). The molecule of $Si(OEt)_4$ (kinetic diameter [18], 1.1 nm) is larger than the pore size of the L zeolite (ca. 0.76 nm). Therefore, it seems that the deposition of this molecule would mainly occur on the external surface of the L zeolite. But the adsorption results of both *m*-xylene and N_2 show that it could also occur in the inner pore, which is similar to the CVD of NaY and KX zeolites [15]. In the case of the

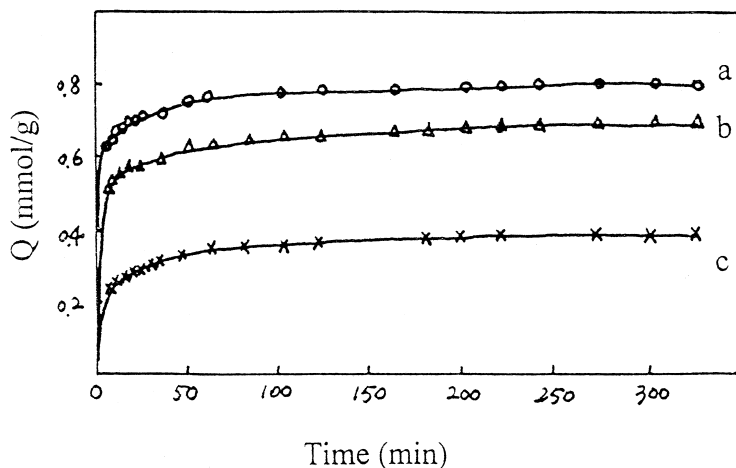
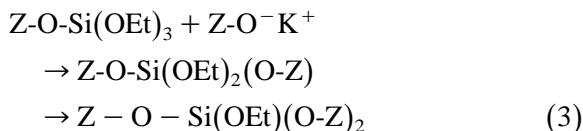
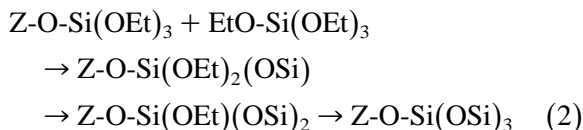
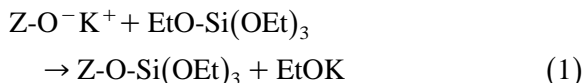


Fig. 1. *m*-Xylene adsorption profiles of (a) KL zeolite, (b) SiKL-1 zeolite (deposition increment 1.84 wt%) and (c) SiKL-2 zeolite (deposition increment 4.86 wt%). Adsorption temperature, 393 K; partial pressure of *m*-xylene, 0.2 kPa.

SiKL-2 zeolite, the molecule of $(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$ has a kinetic diameter of 0.64 nm, therefore, almost all of the deposition occurs in the internal surface of the L zeolite.

3.2. Influence on the electronic field

We studied previously the chemical vapor deposition of the same molecules on non-acidic NaY and KX zeolites [15]. Differing from the CVD on acidic zeolites, where the surface hydroxyl groups play important roles in the deposition process [11–14], the FTIR band of the non-acidic terminal hydroxyl group on NaY and KX zeolites is very small or even absent, not to mention the acidic hydroxyl group, whereas the weight increment of SiO_2 deposited on NaY and KX samples is similar to or even higher than that on H-type zeolites [15]. Therefore, the hydroxyl groups may not be the deposition sites on basic zeolites. Meanwhile, the adsorbed water on these basic zeolites is removed after dehydration. Therefore, we believe that the framework oxygen is the site for deposition. The deposition mechanism accordingly is suggested as follows [15]:



With this mechanism, some exchangeable K^+ cation (known as Lewis acidic sites) might be converted to EtOK, which would result in the decrease of exchangeable cations in zeolite. We used the TPD of the ammonia technique to determine the variation of the amount of exchangeable K^+ . From Fig. 2, we find that only one peak at 473 K existed on both KL and SiKL-2 zeolites, which is attributed to the ad-

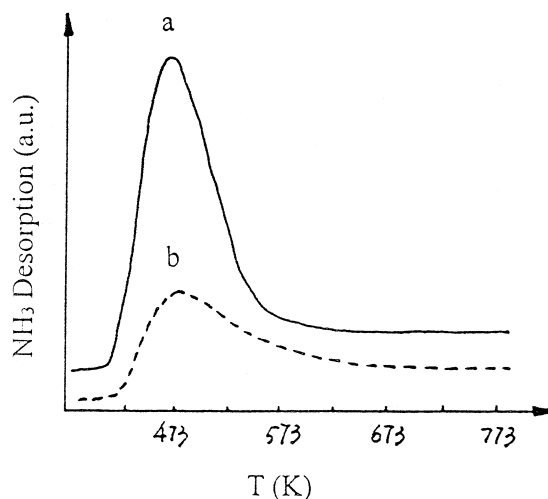


Fig. 2. NH_3 -TPD results of (a) KL zeolite and (b) SiKL-2.

sorption of ammonia on the exchangeable alkali metal cations [19]. After deposition of $(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$, the area of this peak decreases sharply. This result is consistent with the above mechanism.

It is well known that the framework oxygen ion is the basic site on the basic zeolites. Therefore, the deposition of a silica-containing molecule on KL zeolite will accordingly affect its basicity. In order to study this influence, we selected the decomposition of isopropanol as a probe reaction. In general, the dehydrogenation of isopropanol to acetone occurs over basic sites or acid–basic pair sites [20]. Fig. 3 shows the reaction results of isopropanol over KL and SiKL-2 zeolites. The yield of acetone on both samples increases with increasing reaction temperature. However, it is a little larger for the SiKL-2 zeolite whether the temperature increases or decreases. This result shows that after CVD modification, the KL zeolite becomes more basic. We consider that the reason for this phenomena may be the appearance of new basic sites, e.g. the potassium oxide formed from EtOK which was proposed in Eq. (1) of the above mechanism. The appearance of these new basic sites would compensate for the loss on basicity because of the deposition of a few framework oxygen ions.

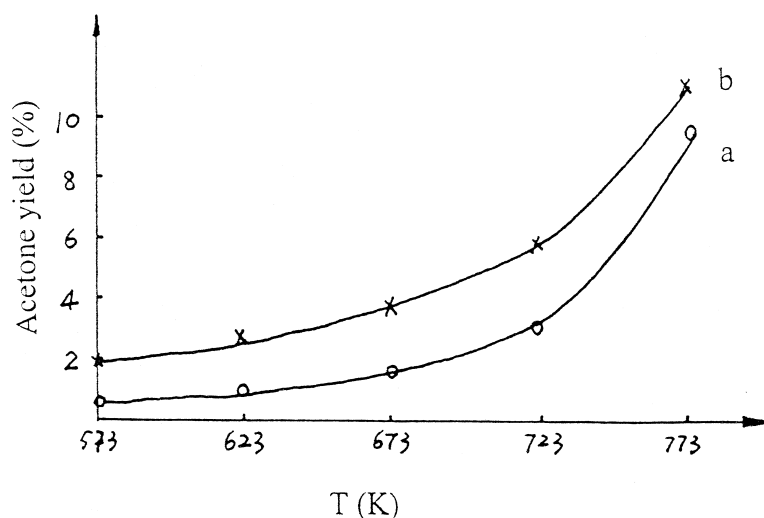


Fig. 3. Dehydrogenation of isopropanol on (a) KL zeolite and (b) SiKL-2. Atmospheric pressure, $W/F = 10.3 \text{ g/h} \cdot \text{mol}$.

Infrared spectroscopy of the adsorbed CO is frequently used as a useful method to determine the electronic state and also the particle size effect of Pt metal supported on zeolites [6]. It has been suggested that Pt particles supported on the KL zeolite may be electron-rich compared with Pt/NaY as a consequence of a charge transfer from the L zeolite to the small metal particles. The increase in the basicity of the L zeolite caused the infrared band of the CO to shift to a higher frequency [6]. We also carried out CO-adsorbed IR as seen in Fig. 4. The wavenumber of the CO IR band on the KL zeolite is 2035 cm^{-1} , which is electron-rich

compared with that on the HL zeolite as we studied previously [21]. There is a shift of this band to a higher frequency on Pt supported SiKL-2 zeolite, showing that Pt particles on the CVD modified zeolite are still more electron-rich than on the non-modified one. This result further confirms that CVD modification on the KL zeolite does not reduce the basicity, but strengthens the interaction of the zeolite and Pt particles.

3.3. Catalytic reactions

Table 1 lists the results of *n*-hexane aromatization. It was found that after CVD modification, Pt/SiKL zeolites show a lower activity

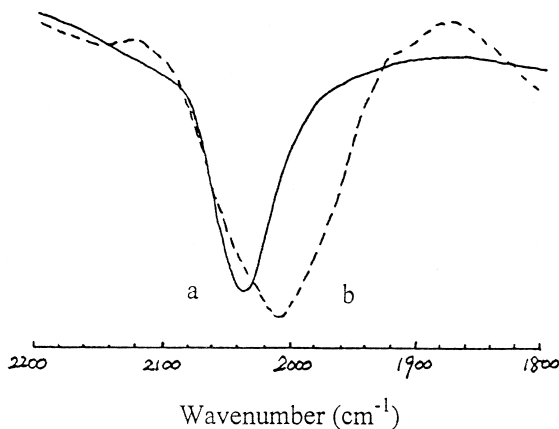


Fig. 4. CO adsorbed FTIR results of (a) Pt/KL and (b) Pt/SiKL-2.

Table 1
n-Hexane aromatization of different Pt/KL zeolites (pulse-flow microreaction, atmospheric pressure, temperature 773 K)

Samples ^a	Conversion (%)	Benzene selectivity (%)	Yield (%)
Pt/KL	90.4	77.2	69.8
Pt/SiKL-1	85.3	79.4	67.7
Pt/SiKL-2	76.8	87.7	67.3
Pt/KL-KCl	45.2	72.2	32.6

^aSiKL-1: chemical vapor deposited KL zeolite, silica increment 1.84 wt%, SiKL-2: chemical vapor deposited KL zeolite, silica increment 4.86 wt%, KL-KCl: KL zeolite impregnated with excess KCl solution.

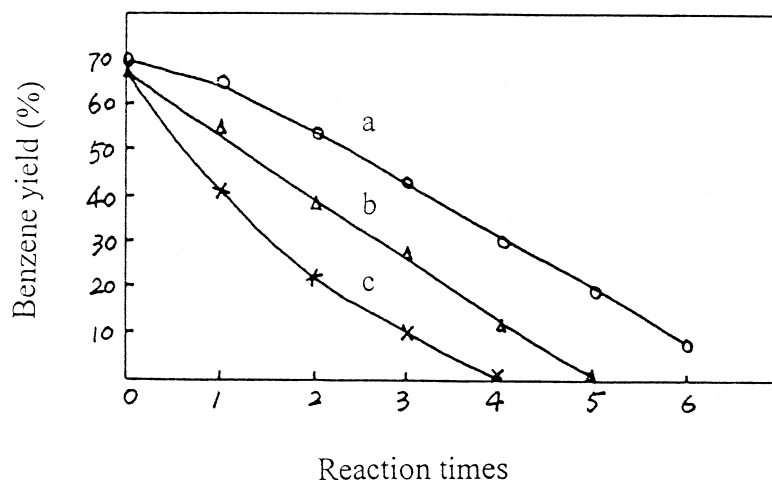


Fig. 5. Benzene yield as a function of sulfur-poisoning times. (a) Pt/KL, (b) Pt/SiKL-1 and (c) Pt/SiKL-2. Pulse-flow microreaction, atmospheric pressure, temperature 773 K.

than that of the Pt/KL zeolite. We have shown above that the effective pore size and pore volume of KL zeolite have been reduced by means of CVD. This kind of modification might cause the destruction of a few sites which is especially suitable for *n*-hexane 1,6-cyclization as proposed by Derouane et al. [4]. Therefore, the active sites for *n*-hexane aromatization is decreased and the reaction activity of CVD modified zeolite is reduced. In order to further certify this point, we co-impregnated with excess KCl solution when Pt was loaded. After this treatment, the pore size and pore volume of KL zeolite is greatly reduced (the internal and external surface area are 20 and 55 m²/g, respectively). Also, the activity for *n*-hexane aromatization on Pt/KL–KCl is greatly decreased compared to Pt/KL as seen in Table 1. These results confirm the importance of the effective pore structure of the L zeolite.

Fig. 5 shows the aromatization reactivity as a function of reaction times using *n*-hexane containing 0.2 ppm thiophene as reactant. As sulfur poisoning proceeds, the benzene yields on all samples are decreased. After modification, the Pt/SiKL zeolites show a higher sensitivity to sulfur poisoning. It has been suggested that the resistance to sulfur poisoning comes from the low bonding energy of electronegative sulfur

atoms with electron-deficient platinum clusters [22,23]. Hence, the higher the electron excess is, the worse the sulfur-resistance is. Since CVD modification of non-acidic KL zeolite causes the appearance of new basic sites, which makes the Pt loaded more electron-rich, Pt/SiKL zeolite is therefore easier to be poisoned by sulfur.

4. Conclusion

Chemical vapor deposition occurred on the framework oxygen ions of the non-acidic zeolite. Silica thus deposited effectively narrowed the pores of KL zeolite and destroyed some of active sites for 1,6-cyclization of *n*-hexane in Pt supported KL zeolite, which confirmed the importance of the effective pore structure on the excellent Pt/KL catalyst for *n*-hexane aromatization. Due to the appearance of new basic sites such as K₂O in the CVD modified KL zeolite, the interaction between the Pt metal and the zeolite support was strengthened. Both CO adsorbed IR spectra and sulfur-poisoning results showed that Pt particles became more electron-excess after silica-coating. More efforts, however, are needed to improve both the catalytic reactivity and sulfur resistance of Pt/KL zeolite.

Acknowledgements

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