Channel effect of nC_6 aromatization on Pt / KL catalysts

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Designed Pt/KL catalysts were prepared and characterized by CO chemisorption and XRD. Pulse catalytic tests using *n*-hexane as the probe were performed. The results showed that Pt particles located in the L-zeolite channels were fundamental for aromatization, and the spatial effect of the channels was essential for dehydrocyclization. Obstruction of the channels, while having no influence on the high Pt dispersion, affects the product distribution of nC_6 in addition to a sharp reduction in reactivity.

Keywords: L-zeolite; Pt/KL catalyst; aromatization; channel effect; basicity; dispersion

1. Introduction

Since Bernard reported the high activity and selectivity of Pt/KL catalysts for the aromatization of straight-chain paraffins [1], much research has been done in recent years to identify the origin of these exceptional properties. One line of thought is that the basicity of L-zeolite may account for this high selectivity to benzene [2,3], because the activity and selectivity for aromatization are improved when the zeolite is exchanged with cations that increase the basicity of the zeolite support [4]. But more and more research tends to favor geometric interpretations. A molecular graphics study of *n*-hexane interaction with a Pt cluster inside the L-zeolite channel shows that the spatial requirement in the channel enhances the curving of nC_6 around itself with both ends attached to a single Pt atom [5]. It is suggested that the spatial limitations within the channel maximize the van der Waals interaction of the curved hydrocarbon with the channel walls. This leads to a stable cyclic intermediate. Tauster and Steger [6,7] proposed that the unidimensional channel of L-zeolite collimated the diffusing flux of nC_6 molecules so that their long axes were parallel to the channel. The high selectivity observed for L-zeolite catalysts may result from terminal adsorption of the nC_6 on the Pt surface. From the product distribution and catalytic activity observed for the hydrogenolysis of MCP on Pt/KL, Alvarez proposed that geometric effects play an important role since the product distribution of nC_6 aromatization showed higher than statistical selectivity towards 3MP [8]. Ostgard et al. also suggested that the MCP molecules were oriented inside the zeolite channel [9].

Our work seeks to explain the roles that the basicity of L-zeolite, Pt dispersion and the channel effect play, as well as interrelationships among them, by observing the changes of the Pt dispersion and the product distribution of nC_6 aromatization on Pt/KL catalyst after altering the channel space by depositing Ba^{2+} cations into the L-zeolite channels.

2. Experimental

2.1. CATALYST PREPARATION

The KL zeolite was synthesized and characterized by XRD (fig. 1). Before use, it was calcined at 450°C for 4 h to remove adsorbed water from the channels.

Catalysts 1–3 were prepared by separately impregnating 2 g KL zeolite with 2 ml $Ba(NO_3)_2$ solution containing 1%, 3% and 5% Ba. After addition of the Ba solution, the slurry was at room temperature for 30 min, then dried under infrared light (about 100°C) and calcined at 450°C for 4 h. The calcined Ba/KL zeolites were impregnated with 2 ml $Pt(NH_3)_4(NO_3)_2$ solution containing 1% Pt respectively, held at room temperature for 30 min, dried and calcined again at 450°C for 4 h. These are labeled as Ba–Pt/KL, 3Ba–Pt/KL, 5Ba–Pt/KL.

The preparation procedure for catalyst 4 was in reverse to that for catalysts 1–3. We first impregnated KL zeolite with $Pt(NH_3)_4(NO_3)_2$ solution, dried and calcined as above. This was then impregnated with 5% Ba solution, dried and calcined. This catalyst is labeled as Pt–5Ba/KL.

It was confirmed by examining with XRD that the deposited Ba did not destroy the L-zeolite structure.

For reference, the following catalysts were used. Catalysts 5 and 6 were prepared by impregnating 1% Pt on KL zeolites using $Pt(NH_3)_4$ $(NO_3)_2$ and H_2PtCl_6 solutions separately and labeled as Pt/KL(B) and Pt/KL(A) according to the basicity and acidity of their metal precursor. Catalyst 7 was prepared by the ion exchange of 1% Pt onto KL zeolite with $Pt(NH_3)_4(NO_3)_2$ solution and labeled as Ptex/KL.

2.2. CO CHEMISORPTION

Volumetric chemisorption measurements were carried out at 35°C in a Chemisorb 2800 unit. About 0.4 g powder catalyst was used for each sample. The samples were first reduced in flowing H_2 at a ramp rate of 10°C from room temperature to 400°C and held at 400°C for 3 h. Then they were evacuated at 400°C at 5.00×10^{-3} Torr and cooled to 35°C. The measurements of the chemisorption isotherms were performed under 100, 150, 200 and 250 Torr, and the chemisorbed CO was calculated by extrapolating the isotherm to zero pressure. The metallic Pt dispersion was obtained by assuming the chemisorption stoichiometry factor as 1.00.

2.3. PULSE CATALYTIC TEST

Catalysts were tested in a single pass stainless steel microreactor system. 130 mg samples were used. The flow rate of reactant H_2 was 120 ml/min and reaction pressure was 30 psig. Initially, the catalyst was purged with N_2 and the temperature ramped from room temperature to 300°C and stayed at 300°C for 30 min in order to drive out adsorbed water. This was then heated to 500°C and after 1 h reduction in H_2, we carried out the pulse experiments. Tail-gas was analyzed by an on-line gas chromatograph equipped with a flame ionization detector and a 69 m × 200 µm isotriacontant SCOT capillary column. The data were processed by a C-R1B chromatograph data microprocessor.

3. Results and discussion

The XRD results confirmed the KL zeolite structure and that all the Ba impregnated catalysts also possess the L-zeolite structure (fig. 1).

From the catalytic test results in table 2, it is seen that catalyst Pt/KL(B) is a much better catalyst than Pt/KL(A) in nC_6 aromatization activity and selectivity. CO chemisorption dat may to some extent account for this disparity. As shown in table 2, Pt dispersions of Pt/KL(A) and Pt/KL(B) are significantly different. The dispersion of catalyst Pt/KL(B) is 91% and we can say that metallic Pt is well dispersed inside the zeolite channels; however, for catalyst Pt/KL(A) the dispersion is

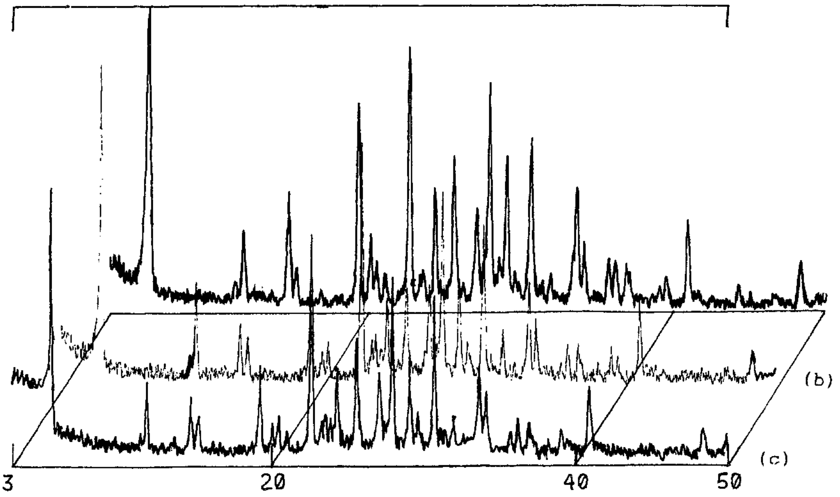

Fig. 1. XRD patterns of (a) KL zeolite, (b) 5Ba–Pt/KL catalyst, (c) Pt–5Ba/KL catalyst.

Table 1
Results of CO chemisorption

	Pt/KL(B)	Pt/KL(A)	Ptex/KL	Ptex/KL (washed)
CO/Pt	0.91	0.02	0.53	0.52
	Ba–Pt/KL	3Ba–Pt/KL	5Ba–Pt/KL	Pt–5Ba/KL
CO/Pt	0.90	0.94	1.0	0.26

only 1.8%, which means that Pt exists in a bulk state. Since the impregnation process was performed at room temperature, even if there exists some ion exchange of the complex cation $Pt(NH_3)_4^{2+}$ with some zeolite cations, most of which are located in the channels, energy limitation would argue that most $Pt(NH_3)_4^{2+}$ ions cannot replace cations of the zeolite and occupy their sites. Therefore we prefer to assume that there exist strong electronegative cation-attracting sites, from which the basicity of the zeolite originates, which we describe as "basic sites". These "basic sites" would strongly attract $Pt(NH_3)_4^{2+}$ and since the surface inside the channels is much larger than that outside, most Pt particles will be located in channels in the case of catalyst Pt/KL(B). In contrast, for catalyst Pt/KL(A), because of the strong repulsion of the "basic sites" for $PtCl_6^{2-}$ anion, Pt cannot enter the zeolite channels and will agglomerize on the outside surface. The following will show it is the basicity of zeolite that determines the high Pt dispersion.

Our results show that unlike traditional catalysts, the L-zeolite catalysts which have Pt loaded by ion exchange, have poor Pt dispersion and low activity and selectivity for benzene. Detailed work by Ostgard et al. confirmed our result [9]. Since the ion-exchange method cannot attain higher Pt dispersion on basic KL zeolites than an impregnation method does, we can infer that the basicity of KL zeolite plays an important role in Pt dispersion. It is shown in table 2 that catalyst Ptex/KL yields a large amount of acid catalysed cracking products. This is because the catalyst preparation by ion exchange will result in much "introduced acidity" during H_2 reduction. The fact that after washing Ptex/KL catalyst with 5% K_2CO_3

Table 2
Tail-gas distribution from pulse catalytic tests (mol%)[a]

	C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5	2MP	3MP	nC_6	MCP	Bz
Pt/KL(B)	7.5	8.9	9.0	1.8	2.8	0.9	1.1	–	–	–	–	65.8
Pt/KL(A)	6.5	7.5	5.2	1.3	2.7	0.7	2.5	6.3	4.4.	44.8	3.7	14.9
Ptex/KL	14.9	20.0	10.1	1.4	4.0	1.0	1.9	–	–	–	–	46.6
(washed)	6.3	6.9	6.7	1.1	2.7	0.8	1.4	–	–	–	–	73.9
Ba–Pt/KL	6.8	8.7	9.1	1.9	4.2	1.1	1.9	–	–	–	–	65.3
3Ba–Pt/KL	6.0	7.4	8.7	2.2	5.2	2.0	3.7	0.7	0.5	0.5	1.5	61.4
5Ba–Pt/KL	2.8	1.8	2.7	0.5	1.7	0.5	8.7	4.5	3.9	34.3	3.6	32.0
Pt–5Ba/KL	1.6	1.3	2.2	0.2	1.7	0.3	5.3	7.3	5.7	42.5	6.6	21.0

solution [10] the cracking products C_1–C_3 sharply decrease and the benzene yield rises from 46.6 to 73.9% verifies the existence of introduced acid. Data in table 1 indicate that K_2CO_3 washing does not affect the Pt dispersion on Ptex/KL catalyst (fig. 2). The Pt dispersion of catalyst Pt/KL(B) is nearly 1.8 times as high as that of Ptex/KL catalyst (after washing), but the aromatization activity is not correspondingly higher but instead even lower. Therefore, we can also infer that a high Pt dispersion is not a sufficient reason for the excellent properties of Pt/KL catalysts. We now address the question of whether the channel effect is the key factor. Would the aromatization activity decrease when the channels are blocked? With this in mind, we designed catalysts 1–3. As previously discussed, the impregnated cations tend to deposit in the channels, excessive cations will fill out the channels. Ba^{2+} ions are used to block the channels because there are well studied Pt/BaKL catalysts in which even if the Ba exchange capacity reaches 30% there is still a high dispersion and high activity [11,12]. Thus using Ba^{2+}, we can bypass additional unnecessary interactions.

From the catalytic results of Ba–Pt/KL, 3Ba–Pt/KL, 5Ba–Pt/KL catalysts, it can be seen that with the addition of Ba^{2+}, aromatization reactivity decreases. Adding 1% Ba hardly affects the reactivity, while after impregnation with 3% Ba reactivity begins to decrease and when 5% Ba was used, the reactivity sharply decreases. Data in table 2 indicate that Ba does not have evident interaction with Pt; at least in 1–5% impregnation limit, Ba does not result in Pt agglomerization. From the above results, we can conclude that (1) Pt dispersed outside channels, even if it is highly dispersed, does not give high aromatization (assuming all channels are blocked by 5% Ba); (2) hindered channels, even if the Pt is well dispersed inside the

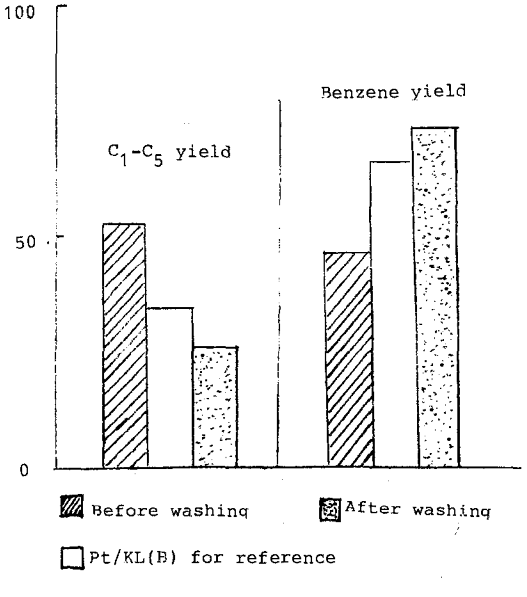

Fig. 2. The K_2CO_3 washing is effective for Ptex/KL catalyst.

channels, will decrease the activity (assuming the deposited Ba only reduce the channel space). The actual situation is between the two limits.

It is intuitionally obvious that when the Pt have been well dispersed in channels, impregnating Ba^{2+} will not only decrease the activity but also the CO/Pt ratio, since most Pt will be locked in the channels. The specially prepared Pt–5Ba/KL catalyst verified this supposition. When the Ba cations are deposited, the benzene yield drops from 65.8 to 21.0% and correspondingly the CO/Pt ratio drops from 0.91 to 0.25. XRD measurement shows no signal of Pt agglomerization (fig. 1).

Another fact which can support our view of the channel effect is the abnormally large quantity of nC_5 in the product distribution of 5Ba–Pt/KL and Pt–5Ba/KL catalysts. The increase in nC_5 can be easily interpreted by spatial limitation according to the graphic study [5]: nC_6 molecules enter unblocked channels and terminally adsorb at the Pt surface, but when there is spatial hindering which is caused by Ba deposit they cannot curve around to form rings, consequently there is terminal cracking.

In summary, the basicity of the L-zeolite is responsible for high Pt dispersions. Pt located inside the channels lead to aromatization. The high Pt dispersion alone cannot account for the high activity and selectivity of nC_6 aromatization on Pt/KL catalysts. The channel effect is an essential factor and obstruction in channels, even if it has no influence on high Pt dispersion, can decrease the reactivity and selectivity.

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