Turnover rates for heptane reforming over Pt/L zeolites with different alkali cations

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A series of 0.6 wt% Pt/BaL catalysts with different alkali cations have been tested for heptane reforming at 440°C, 0.16 atm heptane, 0.95 atm H_2, 6.7 atm He, 3 to 5 h of reaction, and conversions between 2 and 10%. As the cations in the zeolite are progressively changed from lithium to cesium, the turnover rates for hydrogenolysis and dehydrocyclization increase by about 5–10 times, while the turnover rate for isomerization remains unchanged. Since the turnover rates for hydrogenolysis and dehydrocyclization are similarly affected, exchanging lighter alkali cations for heavier ones increases the aromatics selectivity by a small amount, from 72 to 82%. These results indicate that metal–support interactions have a moderate effect on the heptane reforming activity, but only a weak effect on the selectivity.

Keywords: Turnover rates; heptane reforming; Pt/BaL zeolite catalysts

1. Introduction

In an early study of hexane dehydrocyclization over Pt/L zeolite, Barthomeuf and coworkers [1] found that the activity and selectivity for this reaction greatly increased as heavier alkali cations were exchanged for lighter ones in the zeolite pores. These authors concluded that metal–zeolite interactions were responsible for the unusual catalytic properties of the platinum. Later, Larsen and Haller [2–4] confirmed that the zeolite environment modifies the electronic properties of the metal particles. However, work by other groups has indicated that the platinum in L zeolite behaves just like platinum on other nonacidic supports, such as MgO or SiO_2, provided there is no difference in particle size [5–8]. Very small particles exhibit high activity and selectivity for converting alkanes into aromatics [7]. It is proposed that L zeolite is unique in its ability to prevent agglomeration and carbon fouling of the platinum particles at the high temperatures and hydrogen pressures needed for dehydrocyclization [8].

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These recent results call into question Barthomeuf's assertion that metal–support interactions strongly influence the reforming activity of Pt/L zeolite. Moreover, the interpretation of her results is not straightforward, because the catalyst performance was evaluated in terms of the benzene yield at high conversion, not in terms of the intrinsic turnover rates. This prompted us to reexamine the effect of metal–support interactions on the reforming activity of Pt/L catalysts. Platinum was deposited on a series of BaL zeolites with different alkali cations. The cation distribution and the platinum particle size in the zeolites were characterized by a variety of techniques. These results were presented in our first paper [9]. In this article, we report on the relationship between the cation distribution and the turnover rates for heptane hydrogenolysis, isomerization, and dehydrocyclization.

2. Experimental

The Pt/BaL catalysts were prepared according to the method described in ref. [9]. Barium was exchanged into the zeolite at 25°C, and the sample calcined at 590°C to move the barium inside the double six-membered rings and the ε-cages [10]. Then different alkali elements were exchanged into the BaL, followed by drying at 120°C. Platinum of about 0.6 wt% was added to each zeolite sample by incipient wetness impregnation of $Pt(NH_3)_4Cl_2$. These catalysts were heated in air from 25 to 350°C over 11 h, then calcined for 3 h at 350°C. The catalyst compositions were analyzed by inductively coupled plasma emission spectroscopy.

The heptane reforming activity of the catalyst was determined by the procedure described in our second paper [11]. Each sample, weighing 0.19 g, was charged to a fixed-bed microreactor, heated in 100 cm^3/min H_2 to 500°C over 1 h, and reduced at 500°C for 2 h. The samples were cooled to 25°C and the platinum dispersions measured in situ by hydrogen titration of adsorbed oxygen. After this measurement, the samples were heated in 100 cm^3/min H_2 to 440°C, and the reaction begun by feeding 0.16 atm heptane, 0.95 atm H_2 and 6.7 atm He at 240 cm^3/min. This flow rate yielded a residence time of 5.5×10^{-5} h at 25°C and 1 atm pressure, based on the total bed volume. The activity of the catalysts declined over the first 3 h of the run, but remained fairly constant thereafter. Between 3 and 5 h on stream, the reaction products were recorded at five different flow rates, corresponding to heptane conversions between 2 and 10%. A plot of the product concentrations versus inverse flow rate generated straight lines. The reaction rates were calculated from the slopes of these lines. The hydrocarbon products were analyzed by gas chromatography, using a J&W Scientific Megabore capillary column (DB-1 active phase, 30 m in length) and a flame ionization detector. After the run, the samples were cooled to 25°C, and the platinum dispersions measured again by hydrogen titration of adsorbed oxygen.

3. Results

The compositions of the 0.6 wt% Pt/BaL catalysts are shown in table 1. The cation to aluminum mole ratio is 1.0 in the BaL zeolites containing Li, Na, K and Rb, indicating that they are free of acid sites. On the other hand, CsBaL contains some acid sites since its cation to aluminum mole ratio is 0.96. Infrared spectra of the hydroxyl stretching region confirm these results. Only the CsBaL zeolite exhibited a band attributable to acidic hydroxyl groups at 3675 cm^{-1} [9,12]. Comparison of the distribution of cations in each sample reveals that the ability to exchange the alkali cation for barium and potassium improves with the cation size. Lithium achieved an exchange level of 7.8%, whereas rubidium achieved an exchange level of 45.9%.

As discussed in our previous paper [9], L zeolite contains four different cation positions labeled the A, B, C and D sites [13]. The locations of these sites are: A, center of double six-membered rings; B, center of ε-cages; C, between ε-cages; and D, along channel walls. Newell and Rees [10] found that the C and D sites are exchangeable at 25°C, whereas the A and B sites are not. However, by calcining the zeolite at 590°C or above, barium may be transferred from the C and D sites to the A and B sites [10,14]. Assuming that our preparation procedure transfers the same amount of Ba^{2+} to the A and B sites as observed by Newell and Rees, the distribution of cations in the C and D sites is as given in the last three columns of table 1. The values shown are the number of cations per unit cell, with the total charge on the C and D sites summing to 4.77 M^+. These data reveal that in LiBaL and NaBaL, a lot of barium and potassium is located in the positions along the main channel walls. By contrast, in RbBaL and CsBaL, most of these positions are occupied by the heavy alkali cations.

The performance of the 0.6 wt% Pt/BaL catalysts are compared in table 2. The platinum dispersions of the samples vary from 50 to 77% before reaction and from 40 to 70% after reaction. The Pt/BaL samples containing Rb and Cs exhibit a larger drop in dispersion during reaction than those containing Li, Na and K. The percentage decrease in dispersion is 9% for Pt/LiBaL, 12% for Pt/NaBaL, 0% for Pt/KBaL, 28% for Pt/RbBaL, and 44% for Pt/CsBaL.

Table 1
Composition of the Pt/BaL catalysts [9]

Alkali (M^+)	Platinum (wt%)	Cation/Al mole ratio	Cation distribution[a] (mol% of total)			Cations in C and D sites (No. per unit cell)		
			M^+	$2Ba^{2+}$	K^+	M^+	Ba^{2+}	K^+
Li	0.66	1.01	7.8	37.9	54.3	0.71	0.46	3.14
Na	0.76	1.00	15.5	35.7	48.8	1.41	0.36	2.64
K	0.64	1.01		30.1	69.9		0.10	4.56
Rb	0.57	1.00	45.9	29.9	24.2	4.19	0.09	0.40
Cs	0.54	0.96	37.2	28.4	34.5	3.26	0.00	1.15

[a] Barium counts double because of 2+ charge.

Table 2
Performance of the Pt/BaL catalysts for heptane reforming [a]

Alkali	Pt dispersion (%)		Turnover rate ($\times 10^{-2}$ s^{-1})					Aromatics selectivity[c] (%)
	before rxn	after rxn	C_1–C_6[b]	branched isomers	ethylcyclo-pentane	benzene	toluene	
Li	77	70	0.4	0.09	0.2	0.2	0.9	73
Na	50	44	1.0	0.03	0.1	0.9	1.8	73
K	62	62	1.2	0.16	0.6	0.9	1.8	69
Rb	72	52	2.2	0.04	0.3	5.7	4.4	82
Cs	72	40	1.9	0.13	0.7	3.2	5.2	82

[a] Reaction conditions: 440°C, 0.16 atm heptane, 0.95 atm H_2, 6.7 atm He, 3–5 h on stream, and conversions between 2 and 10%.

[b] Support activity subtracted out.

[c] Selectivity = 100 × (benzene + toluene rates)/(C_1–C_6 + benzene + toluene rates).

A correlation is also observed between the alkali cations and the heptane reforming activity. The turnover rates for heptane conversion to C_1–C_6 hydrocarbons, benzene and toluene increase with the cation size. For example, the turnover rates for formation of C_1–C_6 hydrocarbons, benzene and toluene are 5.5, 28.5 and 4.9 times higher over Pt/RbBaL compared to Pt/LiBaL. On the other hand, the turnover rates for formation of the branched isomers and ethylcyclopentane show no trend with cation size.

The empty reactor and the zeolite supports were also tested for heptane reforming at the standard conditions. The reactor and the zeolite supports only produce C_1 to C_6 hydrocarbons from heptane. Except for CsBaL, the L zeolites are no more active than the empty tube for this reaction. The reaction rate over CsBaL is about four times higher than the empty tube. In table 2, the rates of heptane conversion to C_1–C_6 hydrocarbons have been corrected to account for the reactivity of the supports.

In the last column of table 2, the aromatics selectivity is listed for each catalyst. This calculation does not include the isomers. The aromatics selectivity is a weak function of the alkali cations in the zeolite, increasing from about 72% over the samples containing Li, Na and K to 82% over the samples containing Rb and Cs. The aromatics selectivity changes by a small amount over the different catalysts, because the hydrogenolysis and dehydrocyclization rates are similarly affected by varying the alkali elements in the zeolite.

4. Discussion

In our first paper, we characterized the distribution of platinum in the sample by transmission electron microscopy and chemisorption [9]. The L zeolites contain a bimodal distribution of platinum, consisting of a few large crystallites outside the pores and many small clusters, less than ≈ 7 Å across, inside the pores. We estimate that between 88 and 96% of the exposed platinum in the samples is associated with the clusters. Therefore, the turnover rates presented in table 2 are to a good approximation a measure of the intrinsic activity of the platinum clusters for heptane reforming.

The data in table 2 clearly show that the alkali element in the L zeolite changes the intrinsic activity of the platinum for hydrogenolysis and dehydrocyclization. The most plausible explanation for this trend is that the zeolite modifies the electronic state of the metal. In other words, the charge density on the platinum clusters increases with the size of the alkali element located along the channel walls. The increased charge density modifies the adsorbed hydrocarbon species in such a way as to increase the turnover rates for hydrogenolysis and dehydrocyclization. This interpretation is consistent with the infrared spectra for adsorbed carbon monoxide on these samples [9]. The main peak in the infrared spectra observed at 25°C shifts from 2065 to 2025 cm^{-1} as the alkali cation is changed from lithium to cesium. Shifts of this nature have been ascribed to electron transfer between the support and the metal particles [12,15]. Similar trends in both the position of the infrared band for adsorbed carbon monoxide and in the activity of the catalyst for alkane dehydrocyclization have been observed by Barthomeuf and coworkers [1]. These results are also consistent with the work of Larsen and Haller [2–4], who showed that the platinum particles become more electron rich as the zeolite basicity increases.

The alternative explanation of a geometric effect on the reaction rate seems less likely. For example, the trend in Pt/BaL reactivity cannot be ascribed to differences in the hydrocarbon diffusivity in the pores. If this were the case, then the reaction rates would be lower in zeolites containing the larger alkali elements, Rb and Cs. However, exactly the opposite trend is observed.

A potential complicating factor in this study, is the low hydrogen pressure used during heptane reforming. In our previous paper [11], we showed that the Pt/BaL samples deactivate in 1 atm of H_2 as a result of carbon deposition. Carbon deposition causes the heptane conversion rate to decrease by about 50% over the first 3 h of reaction, and is probably responsible for the lower platinum dispersion recorded after the run. Nevertheless, we do not believe that this invalidates the trend in turnover rates with alkali cation. The degree of deactivation was nearly the same on all five catalyst samples, such that the difference in turnover rates is evident at the beginning of the run as well as after 3 h of reaction. Furthermore, Iglesia and Baumgartner [8] have shown that the platinum particles outside the zeolite become fouled much faster than those inside the zeolite, so that after 3 h of reaction only the latter platinum should be contributing to the catalytic activity.

As shown in table 2, the drop in platinum dispersion during the run varies with the alkali cation size. The dispersion decreases by a greater amount on Pt/RbBaL and Pt/CsBaL, suggesting that coke accumulates at a faster rate on these catalysts.

This result is consistent with the higher turnover rates for hydrogenolysis observed over the catalysts containing the larger alkali elements.

Many different arguments have been put forward to explain why Pt/L zeolite is such an active and selective catalyst for alkane dehydrocyclization, including metal–support interactions [1–4], pore confinement effects [16–18], and, more recently, stabilization of the metal particles against agglomeration and coking [6–8]. The results obtained in our study demonstrate that metal–support interactions significantly influence the activity of platinum. However, since the turnover rates for hydrogenolysis and dehydrocyclization are equally affected, the metal–support interaction does not change the selectivity very much. An increase in aromatics selectivity from 72 to 82% is obtained on exchanging the heavier alkali elements for the lighter ones. By contrast, Davis [7] has observed a much larger effect of the platinum particle size on the aromatics selectivity. He found that for hexane dehydrocyclization over different Pt/zeolites at 460°C, the benzene selectivity (excluding isomers) increased from 52 to 92% as the H/Pt ratio increased from 0.78 to 1.56. Based on these comparisons, we conclude that the exceptional performance of Pt/L catalysts for alkane dehydrocyclization is more due to the zeolite's ability to stabilize extremely small platinum clusters than to its ability to alter the catalytic activity through a metal–support interaction.

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