Reforming of hexane with Pt/zeolite catalysts

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Aromatization and isomerization of *n*-hexane catalyzed by Pt/zeolite were investigated. For Pt/K-β and Pt/K-mordenite as well as for Pt/K-L, the addition of KCl resulted in an increase in selectivity for benzene formation accompanied with a decrease in selectivity for hydroisomerization. A parallelism was found between changes in the benzene selectivity with the KCl addition and in the terminal cracking index. The treatment of Pt/K-FSM-16 with K_2CO_3 resulted in a decrease in cracking products and an increase in benzene selectivity. At 523 K, Pt/H-FSM-16 catalyst showed high selectivity for methylcyclopentane and cyclohexane. At 623 K, it showed high and durable isomerization activity.

Keywords: aromatization, isomerization, zeolites, platinum, modification

1. Introduction

Catalytic reforming of hydrocarbons is an important industrial process for producing aromatics and increasing the octane number of hydrocarbons in the gasoline boiling range. PtRe/Al_2O_3-Cl, one of the conventional reforming catalysts, is known to be very effective for the production of aromatics with more than eight carbon atoms from C_{8+} heavy naphtha. However, the C_6 and C_7 paraffins present in light naphtha are hardly converted into aromatics by use of this kind of catalysts [1–3]. Hence the catalysts for aromatization of light naphtha are being investigated in order to extend the sources of aromatics.

Platinum supported on non-acidic KL-zeolite was found to show exceptionally high selectivity for transformation of C_6 paraffin of light naphtha into benzene [4,5]. Unlike the conventional, bifunctional reforming catalyst (PtRe/Al_2O_3-Cl), the non-acidic Pt/KL catalyst is monofunctional, having only a metal function [1,4–6]. Bernard [4], Besoukhanova and co-workers [5], and later Larsen and Haller [6] proposed that the properties of the Pt metal were significantly modified by its interaction with the surrounding L zeolite structure and field. We have already reported that addition of KCl to the catalysts prepared by ion exchange produces sites with high electron-donating ability on the Pt particles, resulting in high activity and selectivity for benzene formation in the aromatization of *n*-hexane [7,8]. In view of this observation, we aimed to investigate the effect of KCl addition as well as that of zeolite structure in the aromatization of *n*-hexane catalyzed by zeolite-supported platinum.

Isoparaffins are also important components for increasing the octane number of gasoline. Especially in recent years, in view of the environmental protection, the isoparaffins components in gasoline are expected to gradually increase and replace aromatics. Obviously, the requirement of isomerization of straight-chain paraffins in light naphtha into branched paraffins with high octane number will be increasingly emphasized in the future. In the present study, the isomerization of *n*-hexane has been also investigated using various Pt/H-zeolite catalysts.

2. Experimental

The zeolites used in this study were as follows: L (Tosoh, $Si/Al_2 = 6.2$), β (Tosoh, $Si/Al_2 = 25.6$), M (mordenite) (Tosoh, $Si/Al_2 = 19.1$) and USY (ultrastable Y) (Tosoh, $Si/Al_2 = 6.3$). A mesoporous material having a uniform channel size of ca. 27.5 Å, FSM-16 (Toyota, $Si/Al_2 = 40.0$), was also used. Zeolite-supported platinum catalysts, with 0.50 wt% of Pt loading, were prepared by ion exchange (IE) or incipient wetness impregnation (IWI) of K- or Na-zeolite with an aqueous solution of $[Pt(NH_3)_4]Cl_2$. The dried Pt/K-zeolite (IE) samples were impregnated with KCl (KCl/Pt = 4.0, molar ratio) and dried. The catalysts thus prepared were named Pt/K-zeolite+KCl. The catalysts were calcined in air at 573 K for 2 h and then reduced in H_2 at 773 K for 0.5 h before the use for reaction. The H_2-reduced Pt/K-zeolite samples were ion exchanged with 1.0 M aqueous solution of K_2CO_3 at 353 K for 2 h, and designated as Pt/K-zeolite-K_2CO_3. Proton-form zeolite was obtained by ion exchange of M-zeolite (M = K or Na) with NH_4Cl aqueous solution followed by calcination at 773 K. Pt/H-zeolite catalyst was pre-

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pared by the same ion exchange method as described above.

The reaction of n-hexane was carried out using a conventional fixed-bed reactor. The experimental conditions were as follows: reaction temperature of 523–743 K, total pressure of 0.2–0.5 MPa, H_2/n-hexane molar ratio of 6.0 and weight hourly space velocity (WHSV) of 2.4–24 h^{-1}. All data were obtained after 1 h time on stream because the catalytic activity was virtually unchanged thereafter.

Platinum metal dispersion measurements by volumetric hydrogen chemisorption were carried out in a conventional glass vacuum system at room temperature. Detailed procedures were described elsewhere [7].

3. Results and discussion

3.1. Aromatization of n-hexane

3.1.1. Effect of catalyst preparation method

Figure 1 compares the results of the aromatization of n-hexane over the different zeolite-supported platinum catalysts prepared by ion exchange (IE) and incipient wetness impregnation (IWI) method, respectively. Irrespective of the zeolite structure, the catalysts prepared by the IE method gave higher n-hexane conversion than those prepared by IWI. For the K-β zeolite, there was no clear difference in the products distribution between the IE and IWI catalysts. Monobranched hexanes (i-C_6), 2- and 3-methylpentane, were the predominant products over both catalysts. On the Pt/K-FSM-16 (IE) catalyst, the selectivity for benzene formation as well as n-hexane conversion were higher than those on the IWI sample; the dehydrogenation and hydroisomerization were predominant on both IE and IWI catalysts. For the L and FSM-16 zeolites, the IE catalysts gave higher hydrocracking (C_1–C_5) selectivity than the IWI catalysts, in agreement with the expected formation of Brønsted acid upon reduction of the IE catalysts. For the catalysts prepared by the IWI method, the Pt/K-FSM-16 zeolite gave a slightly higher activity and benzene selectivity than the purely siliceous Pt/(Si)FSM-16 sample. According to these findings all catalysts were prepared hereafter by the ion exchange (IE) method.

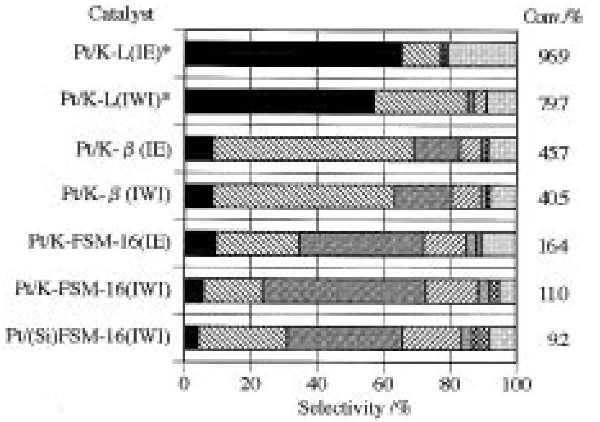

Figure 1. Effect of preparation method on the catalytic performance of Pt/K-zeolite catalysts. (■) Benzene; (▧) 2- and 3-methylpentane (i-C_6); (▩) isohexenes (C_{6e}); (▨) methyl-cyclopentane (MCP); (▩) methylcyclopentenes (MCPe); (▩) others; (▤) cracking products (C_1–C_5). $T = 743$ K; $P = 0.2$ MPa; H_2/hexane = 6.0; WHSV = 24 h^{-1}; $^*P = 0.5$ MPa; WHSV = 2.4 h^{-1}.

3.1.2. Effect of zeolite structure

The influence of the zeolite structure on the catalytic performance of Pt/K-zeolite catalysts for the aromatization of n-hexane has been investigated. Although the Pt/K-L catalyst showed lower activity in the conversion of n-hexane than Pt/K-β, it exhibited the highest selectivity for benzene formation (figure 2). The Pt/K-β catalyst gave the highest n-hexane conversion among the catalysts; in this case the hydroisomerization was predominant and the selectivity for branched hexanes was close to 60%. For the K-M, K-USY and K-FSM-16 zeolites, there were no significant differences in the activity; the hydroisomerization and dehydrogenation products (i-C_6 and C_{6e}) were principally obtained.

The H/Pt ratio of the various Pt/K-zeolite samples is also shown in figure 2. There is no obvious correlation between the H/Pt ratio and the catalytic performance. For instance, Pt/K-β with the low H/Pt showed a high activity for the conversion of n-hexane, and Pt/K-FSM-16 exhibited a low activity although its Pt dispersion was the highest. The very high dispersion of Pt on MCM-41 materials has been recently reported by Schuth et al. [9]. Several groups have reported that extremely small platinum particles incorporated within the pores of KL zeolite are ideal for n-hexane aromatization [10–13]. The results shown in figure 2 indicate that the activity for n-hexane aromatization is not entirely dependent upon the size of platinum particles but affected by the zeolite types.

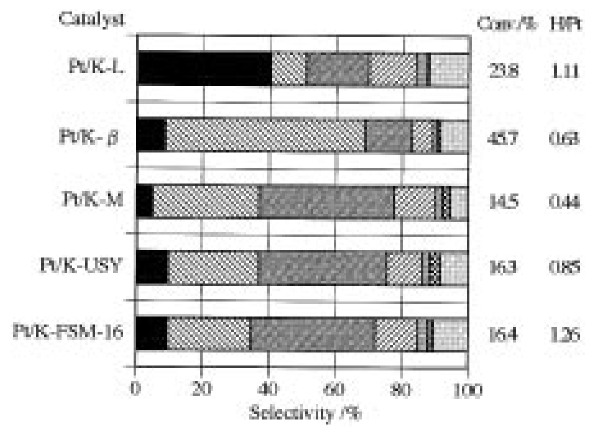

Figure 2. Effect of zeolite structure on the catalytic performance of Pt/K-zeolite catalysts. For symbols see figure 1. $T = 743$ K; $P = 0.2$ MPa; H_2/hexane = 6.0; WHSV = 24 h^{-1}.

3.1.3. Effect of exchanged cation

It has been known that for the non-acidic Pt/L-zeolite catalyst, the stronger the support basicity, the higher the benzene selectivity in the aromatization of *n*-hexane [1,5,6]. The influence of alkali cations (Na, K) on the catalytic activity and selectivity of different Pt/zeolite catalysts was investigated and the results are shown in figure 3. The Pt/K-β catalyst exhibited higher activity for benzene formation than the Pt/Na-β sample. For the M and FSM-16, K-exchanged zeolites showed lower *n*-hexane conversion than the Na-exchanged ones. However, it is worth noting that the Pt/K-β and Pt/K-FSM-16 catalysts gave rise to higher benzene selectivity than the Pt/Na-β and Pt/Na-FSM-16, respectively. This result is consistent with the observation that the zeolite with stronger basicity led to a higher selectivity for benzene formation [1,5,6].

3.1.4. Effect of KCl addition

We have already reported that potassium chloride acts as an effective additive to the Pt/K-L catalyst prepared by ion exchange, producing highly active, selective and stable catalysts for *n*-hexane aromatization [7]. Figure 4 shows the effect of KCl addition on the catalytic performance of K-zeolite-supported platinum catalysts. Except for the Pt/K-L sample, addition of KCl onto the Pt/K-zeolite catalysts resulted in a decrease in *n*-hexane conversion. However, for Pt/K-β and Pt/K-M as well as for Pt/K-L, the addition of KCl led to an increase in the selectivity for benzene production accompanied with a decrease in the selectivity for hydroisomerization. In contrast, the addition of KCl to the Pt/K-USY and Pt/K-FSM-16 catalysts resulted in a decrease in benzene selectivity.

In general, the benzene selectivity increases linearly with *n*-hexane conversion over the zeolite-supported Pt catalyst in the monofunctional aromatization of *n*-hexane [14,15]. Obviously, both the Pt/K-β+KCl and Pt/K-M+KCl catalysts would show much higher benzene selectivity than the respective samples without KCl addition, if they were compared at the same conversion levels.

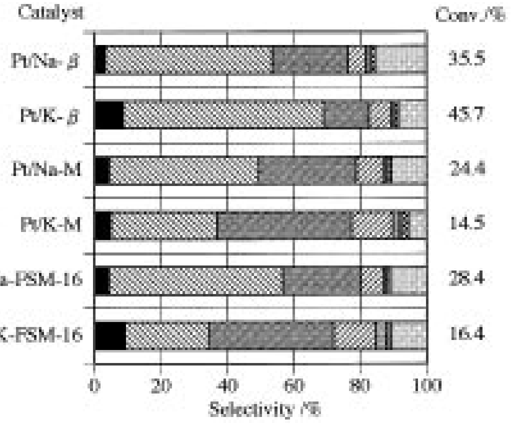

Figure 3. Effect of alkali cation on the catalytic performance of Pt/zeolite catalysts. For symbols see figure 1. $T = 743$ K; $P = 0.2$ MPa; H_2/hexane = 6.0; WHSV = 24 h^{-1}.

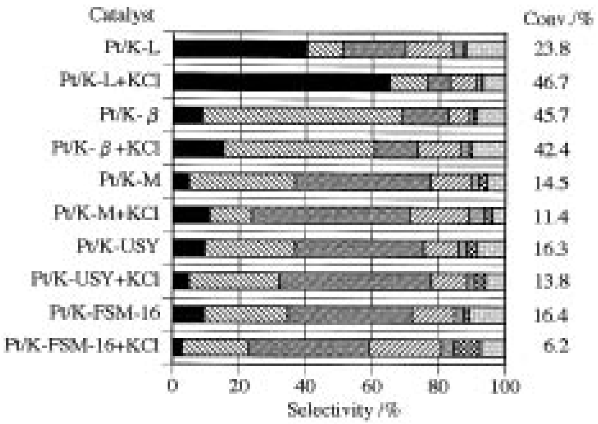

Figure 4. Effect of KCl addition on the catalytic performance of Pt/K-zeolite catalysts. For symbols see figure 1. $T = 743$ K; $P = 0.2$ MPa; H_2/hexane = 6.0; WHSV = 24 h^{-1}.

So far, the excellent catalytic performance of Pt/K-L catalyst in the aromatization of *n*-hexane has been ascribed to both the electronic effect of the platinum particles [5,6] and the geometric effect of the zeolite support [16–18]. The "terminal cracking index" (TCI), defined as the C_5/C_4 molar ratio in the cracking products, was proposed by Tauster and Steger [18]; it has been suggested that the higher the TCI value the easier the terminal adsorption of *n*-hexane molecule onto the Pt surface. The terminal adsorption of *n*-hexane on the Pt particles surface would result in the formation of benzene via 1,6 ring closure and dehydrogenation. The relationship between the TCI value and benzene formation rate per unit Pt surface (turnover numbers, TON) or benzene selectivity over the various catalysts is shown in table 1. The TCI value increased with increasing TON and benzene selectivity, when KCl was added to the Pt/K-L, Pt/K-β and Pt/K-M catalysts, respectively. On the other hand, when KCl showed a detrimental effect on

Table 1
Correlation between terminal cracking index (TCI) and benzene formation activity and selectivity [a]

Catalyst	TON (mol-benzene (mol-Pt)$^{-1}$ h^{-1})	Benzene selectivity (%)	TCI
Pt/K-L	1036	40.3	1.51
Pt/K-L+KCl	3284	65.0	3.87
Pt/K-β	746	8.6	1.64
Pt/K-β+KCl	1230	15.2	1.71
Pt/K-M	193	4.9	1.54
Pt/K-M+KCl	341	11.0	1.81
Pt/K-USY	224	9.6	1.44
Pt/K-USY+KCl	94	4.8	1.14
Pt/K-FSM-16	147	9.3	0.75
Pt/K-FSM-16+KCl	16	2.8	0.57

[a] $T = 743$ K; $P = 0.2$ MPa; H_2/hexane = 6.0; WHSV = 24 h^{-1}.

the TON value and benzene selectivity, the TCI was decreased by KCl addition. These results indicate that the increase in benzene production activity and selectivity over the Pt/zeolite catalysts to which KCl was added might be attributed to the promotion of selective terminal adsorption of *n*-hexane on the Pt surface. In fact, we have already found that on the Pt/K-L+KCl catalyst the presence of the electron-rich site of the Pt particles, as revealed by low C–O stretching frequency, should be advantageous to terminal adsorption of *n*-hexane, leading to high selectivity for benzene formation; in addition, the increased selectivity for benzene production found with the Pt/K-L+KCl catalyst may be partly ascribed to the decreased acidity resulting from the KCl addition, as revealed by the decrease in cracking yield [8].

However, the effect of KCl addition on the Pt/K-β and Pt/K-M catalysts was not as remarkable as on the Pt/K-L catalyst. The β ($7.6\ \text{Å} \times 6.4\ \text{Å}^{**}$, $5.5\ \text{Å} \times 5.5\ \text{Å}^{*}$) [1] and Y ($7.4\ \text{Å}^{***}$) zeolites have three-dimensional channels, and the pores of L ($7.1\ \text{Å}^{*}$), M ($6.5\ \text{Å} \times 7.0\ \text{Å}^{*}$) and FSM-16 ($27.5\ \text{Å}^{*}$) zeolites are unidimensional. Obviously, the differences in the effect of KCl addition on the zeolite catalysts may not be ascribed to the differences in the channel dimension and pore size of zeolites. Furthermore, no clear relation between the TCI and benzene selectivity was observed when the zeolites with different structure are compared.

3.1.5. *Effect of K_2CO_3 treatment*

We have already reported that neutralization of the protons, formed by the reduction of the catalyst prepared by ion exchange, with K_2CO_3 resulted in the increase in the benzene selectivity in *n*-hexane aromatization [19]. The same treatment was conducted for the Pt/K-β and Pt/K-FSM-16 catalysts, and the results are shown in figure 5.

The treatment of Pt/K-FSM-16 with K_2CO_3 resulted in the decrease in cracking products while hexane conversion was retained and benzene selectivity increased. This result is consistent with what has been reported in refs. [1,5,6,19], that the cracking/coking side reactions could be suppressed by decreasing the acidic sites of zeolite support, resulting in the increase in benzene selectivity.

The treatment of the Pt/K-β catalyst with K_2CO_3 resulted in a marked reduction in the conversion of *n*-hexane and a slight decrease in the selectivity for benzene. Similar to that of the Pt/K-FSM-16 system, because of the lower acidity of Pt/K-β-K_2CO_3 compared to Pt/K-β, however, the *i*-C_6 and cracking products were greatly decreased, while the selectivity for MCP was increased. It is not clear, at the moment, why the decrease in the activity resulted from the attempted ion exchange of Pt/K-β with K_2CO_3.

3.2. *Isomerization of n-hexane*

Recently, it has been shown that Pt-loaded H-β catalysts have very high activity and selectivity in *n*-hexane isomerization [20,21]. In the present work the proton-form zeolite-supported Pt catalysts, Pt/H-β, Pt/H-L and Pt/H-FSM-16, were used for the isomerization of *n*-hexane. The reaction was conducted at 523 K. As shown in figure 6, methylpentanes (*i*-C_6) predominated over Pt/H-β. The activity of Pt/H-L and Pt/H-FSM-16 was lower than that of the Pt/H-β catalyst, and selectivities for the cyclization products, methylcyclopentane (MCP) and cyclohexane, were considerably high on Pt/H-FSM-16, in particular.

The dependence of the activity and selectivity on the reaction temperature over the various catalysts, Pt/H-β, Pt/H-L and Pt/H-FSM-16, is given in figure 7. At the temperature of 523–623 K, the activities of the catalysts decreased in the order: Pt/H-β > Pt/H-L > Pt/H-FSM-16. The activity of the Pt/H-β catalyst increased

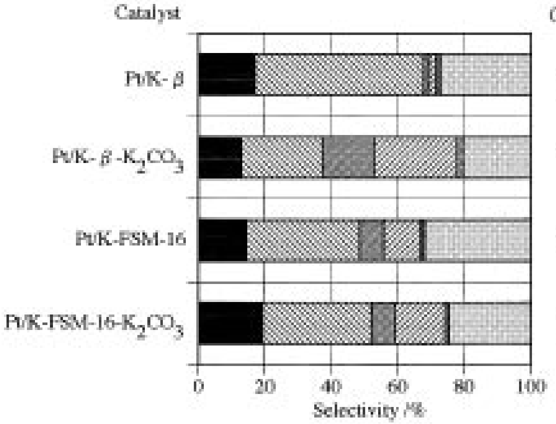

Figure 5. Effect of K_2CO_3 treatment on the catalytic performance of Pt/K-zeolite catalysts. For symbols see figure 1. $T = 743$ K; $P = 0.5$ MPa; H_2/hexane = 6.0; WHSV = $24\ h^{-1}$.

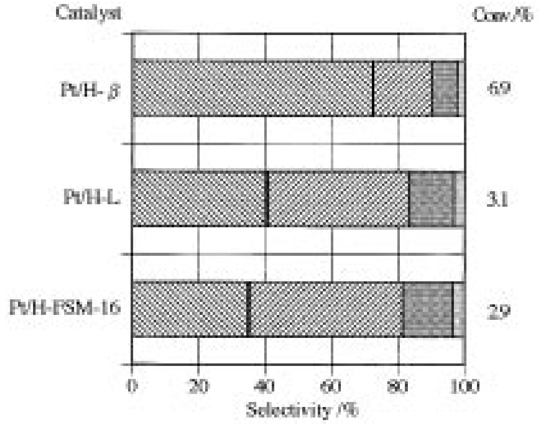

Figure 6. Isomerization of hexane over Pt/H-zeolite catalysts. (▧) *i*-C_6; (■) C_{6e}; (▨) MCP; (▩) c-hexane; (▦) C_1–C_5. $T = 523$ K; $P = 0.5$ MPa; H_2/hexane = 6.0; WHSV = $24\ h^{-1}$.

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[1] The number of asterisks indicates whether the zeolite channel systems are one-, two- or three-dimensional.

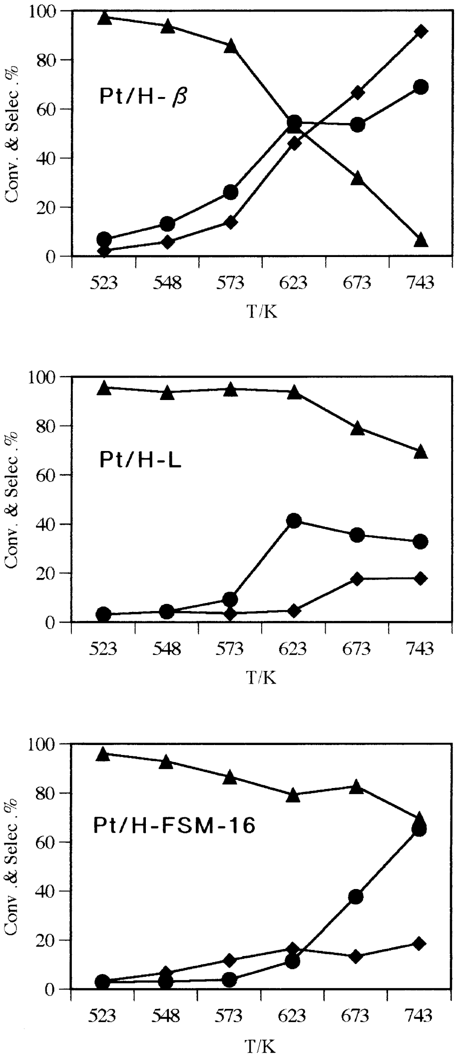

Figure 7. Effect of reaction temperature on the catalytic performance of Pt/H-zeolite catalysts. (●) Conversion (%); (▲) i-C_6 selectivity (%); (◆) C_1–C_5 selectivity (%). $P = 0.5$ MPa; H_2/hexane = 6.0; WHSV = 24 h^{-1}.

remarkably in the range 523–623 K but moderately at higher than 623 K. Because of the moderate acidity of H-β zeolite [21,22], however, the rate of hydrocracking increased sharply with increasing reaction temperature, resulting in the remarkable decrease in the isomerization selectivity.

As is distinct from the H-β catalyst, the Pt-supported H-L and H-FSM-16 catalysts showed considerably low activities and selectivities for cracking products but quite high isomerization selectivities at temperatures in the range of 523–573 K. In addition, both of the catalysts exhibited relatively high isomerization selectivity accompanied with low cracking selectivity at temperatures higher than 573 K. This could be a result of relatively weak acidity of H-L and H-FSM-16 zeolites [4,22,23,24]. For the Pt/H-L catalyst, there was a tendency towards the decrease in n-hexane conversion at temperatures higher than 623 K. Because of its unidimensional channel structure and relatively small pore size, L zeolite is susceptible to coking, resulting in the deactivation at high temperatures. In contrast, the conversion rate gradually increased with raising temperature over Pt/H-FSM-16. Thus Pt/H-FSM-16 was resistant to deactivation, probably because of the large pore size of FSM-16. It is noteworthy that the used Pt/H-FSM-16 sample was only slightly brown-colored in contrast to the blackened used Pt/H-L sample. In particular, at the temperatures higher than 673 K considerably high isomerization selectivity was obtained with the retardation of cracking.

4. Conclusions

Aromatization and isomerization of n-hexane catalyzed by Pt/K-zeolite and Pt/H-zeolite, respectively, and the effect of KCl addition and the K_2CO_3 treatment on the aromatization have been investigated. For Pt/K-β and Pt/K-M as well as for Pt/K-L, the addition of KCl resulted in the increase in the selectivity for benzene formation accompanied with the decrease in the selectivity for hydroisomerization. Although the Pt/K-FSM-16 catalyst showed lower activity and benzene selectivity in the aromatization of n-hexane than Pt/K-β, the treatment of Pt/K-FSM-16 with K_2CO_3 resulted in the decrease in cracking products and the increase in benzene selectivity. At temperature higher than 623 K, Pt/H-FSM-16 and Pt/H-L catalysts showed lower cracking selectivity and higher isomerization selectivity than Pt/H-β catalyst. The Pt-supported H-FSM-16 catalyst was found much more resistant to deactivation at high temperatures than the H-L sample.

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