Deactivation characteristics in *n*-heptane reforming reaction catalyzed over small Pt, Ir and Pt–Ir bimetallic clusters in NaY

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The deactivation characteristics of highly dispersed (about 1 nm) Pt, Ir and Pt–Ir bimetallic clusters in NaY were studied by hydrogen chemisorption, coke analysis and temperature programmed oxidation of used catalyst in *n*-heptane reforming reaction. As the Ir content was increased, the amount of coke decreased. Most of coke was located around the metal cluster and this coke decreased the selectivity of dehydrocyclization in *n*-heptane reaction. The higher activity and more improved activity maintenance of Pt–Ir/NaY bimetallic catalysts than those of Pt/NaY are related to the less amount of coke formation.

Keywords: Pt; Ir; Pt–Ir bimetallic cluster; NaY zeolite; deactivation; *n*-heptane reforming reaction; TPO; coke

1. Introduction

Deactivation of catalyst in reforming reactions is caused by numerous processes, but it is known to be primarily due to carbonaceous deposit (coke) on the catalyst surface [1]. Such bimetallic catalysts as Pt–Re/Al_2O_3 [2], Pt–Ir/Al_2O_3 [3] and Pt–Sn/Al_2O_3 [4] have been found to have more improved activity maintenance than Pt/Al_2O_3. However, this stability of bimetallic catalysts has not been completely understood.

Yang et al. [5] recently reported that very small (about 1 nm) Pt–Ir bimetallic clusters were formed inside the NaY zeolite supercage and had specific characteristics different from those of Pt and Ir monometallic cluster and of the physical mixtures of the corresponding monometallic clusters. The deactivation process depends on the characteristics of active sites: size of metal cluster, kinds of support

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material and metal component, and the operating conditions. The objective of this work is to study the deactivation characteristics of small (about 1 nm) Pt, Ir and Pt–Ir bimetallic clusters in NaY. We also report the effect of coke on the activity and selectivity of the catalysts in *n*-heptane (*n*-C_7) reforming reaction.

2. Experimental

Monometallic Pt and Ir cluster in NaY (abbreviated as Pt(x)/NaY and Ir(x)/NaY, x indicates weight percent) were prepared by calcining and reducing $Pt(NH_3)_4^{2+}$-exchanged NaY and $Ir(NH_3)_5Cl^{2+}$-exchanged NaY with O_2 and H_2 at 300°C, respectively. Pt–Ir bimetallic clusters in NaY (Pt(x)Ir(x)/NaY) were prepared by calcining and reducing co-ion-exchanged NaY with O_2 and H_2 at 300°C, respectively. The detailed characteristics of the catalysts were reported elsewhere [5].

The *n*-C_7 reforming reaction was carried out with 100 mg of catalyst in a micro-flow, fixed-bed reactor for 240 min at 400°C and atmospheric pressure. The reaction feed was composed of a mixture of H_2 and *n*-C_7 in ratio of 8.5 to 1 and the total flow rate was 67 ml/min. The reaction products were analyzed by an on-line HP 5890A GC equipped with a 50 m cross-linked methyl silicon fused silica capillary column and a FID detector. After the reaction, the catalyst was cooled to room temperature in a flow of He for temperature programmed oxidation (TPO) of coke. TPO spectra were obtained using a high through-put pressure reducing system combined with a computer interfaced mass spectrometer (VG Quadrupoles SX 300). TPO was performed by raising the temperature from 25 to 600°C at a rate of 8°C/min in a 5% O_2/N_2 flow of 60 ml/min. The CO_2 evolution was monitored and recorded every 10 s during TPO. The amount of coke and the atomic H/C ratio of coke on catalysts were determined by a CHN-analyzer (Heraeus, CHN-O-Rapid). Coked catalyst samples obtained after C_7 reforming reaction for 240 min were cooled to room temperature in a flow of He and transferred to a glove box in order to avoid contamination by water and other gases. This coked catalyst wrapped with Sn foil was introduced to the CHN-analyzer.

The numbers of active metal sites before and after the reaction were determined by pulse chemisorption of hydrogen at room temperature in the reaction system. After the hydrogen preadsorbed during reduction or reaction was desorbed by Ar flushing at 400°C for 30 min, hydrogen pulses were injected by a 6-port valve with 51 μm loop volume at 5 min intervals in a stream of Ar (15 ml/min) until no more hydrogen was adsorbed by the thermal conductivity detector (TCD).

3. Results and discussion.

Fig. 1 shows the turnover frequencies (TOFs) of catalysts as a function of reac-

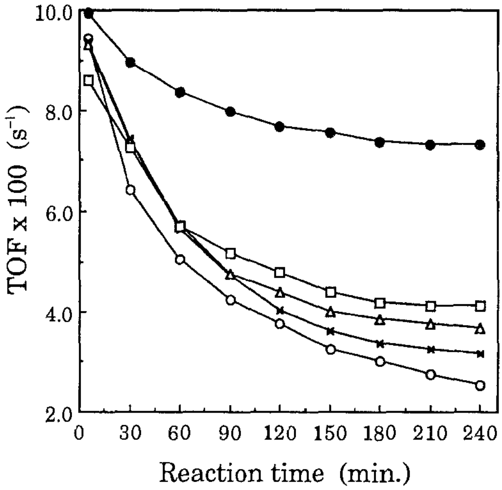

Fig. 1. *n*-heptane activity as a function of reaction time at 400°C. Pt(4)/NaY (○), Pt(3)Ir(1)/NaY (∗), Pt(2)Ir(2)/NaY (△), Pt(1)Ir(3)/NaY (□) and Ir(4)/NaY (●).

tion time. Ir(4)/NaY catalyst is more active than Pt(4)/NaY and the Pt–Ir/NaY bimetallic catalysts. Furthermore, the activity of Ir(4)/NaY catalyst was maintained at a higher level during reaction time. Pt(4)/NaY catalyst started at a higher activity, but steadily decreased with reaction time. After reaction of 240 min, the Pt(4)/NaY catalyst reached an activity lower than those of the Pt–Ir/NaY catalysts. This improved activity maintenance of Pt–Ir/NaY bimetallic catalysts is consistent with the result obtained with alumina supported catalyst [3].

The results of coke analysis and hydrogen chemisorption are given in table 1. H/M denotes the number of hydrogen atoms adsorbed irreversibly per metal atom. The amount of coke increased from 4.2 wt% on Ir(4)/NaY to 13.3 wt% on Pt(4)/NaY when increasing the content of Pt. Less coke formation on the Ir catalyst is also observed in the TPO spectrum of coke as shown in fig. 2. The coke formation

Table 1
The results of hydrogen chemisorption and coke analysis over the catalysts used in *n*-heptane reforming reaction

Catalysts	Hydrogen chemisorption (H/M)		Coke analysis	
	before reaction	after reaction	(wt%)	H/C
Pt(4)/NaY	0.95	0.26	13.3	1.34
Pt(3)Ir(1)/NaY	0.93	0.33	12.1	1.10
Pt(2)Ir(2)/NaY	0.93	0.39	11.3	1.00
Pt(1)Ir(3)/NaY	0.97	0.17	8.5	0.88
Ir(4)/NaY	0.99	0.09	4.2	0.75

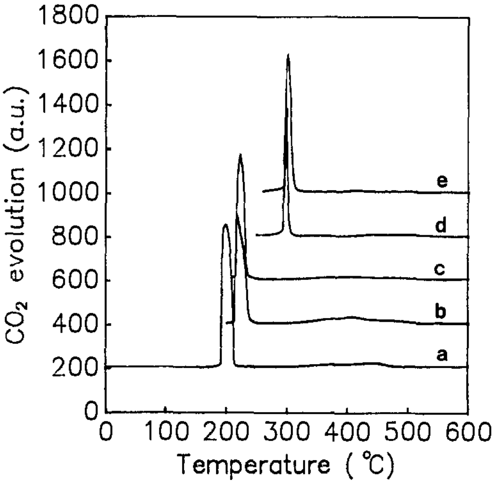

Fig. 2. CO_2 evolution during TPO of used catalysts in *n*-heptane reforming reaction for 4 h at 400°C and atmospheric pressure. Pt(4)/NaY (a), Pt(3)Ir(1)/NaY (b), Pt(2)Ir(2)/NaY (c), Pt(1)Ir(3)/NaY (d) and Ir(4)/NaY (e).

decreased as the content of Ir increased in Pt–Ir/NaY. The smaller amount of coke formed on Ir could be explained by the higher cracking and lower dehydrocyclization activity of Ir than those of Pt as shown in fig. 3. A smaller amount of coke precursors may be formed on Ir because of the low dehydrocyclization activity. As the Ir content increased, the atomic H/C ratio of coke decreased and the oxidation temperature of the coke increased. The oxidation of coke on Pt(4)/NaY and Ir(4)/NaY exhibited a maximum at 200 and 307°C, respectively. The H/C ratio of coke is smaller on Ir(4)/NaY than on Pt(4)/NaY indicating that hard coke containing less hydrogen was formed on Ir(4)/NaY. The CO_2 peaks of the Pt–Ir/NaY bimetallic catalysts are present between those of Pt(4)/NaY and Ir(4)/NaY. The more the Ir content, the lower the H/C ratio and the higher the temperature of the CO_2 peak, indicating that the nature of coke formed on Pt–Ir bimetallic catalyst becomes harder than that on Pt. This result might be explained by the better ability of hydrogen transfer of the Ir metal [6]. Transferring hydrogen from the light coke to the chemisorbed reactant results in the formation of hard coke and provides sites for desorption of the product adsorbed on Ir and Pt–Ir bimetallic cluster. In our previous work [5], very small (about 1 nm in diameter) metal clusters of approximately the same size were formed inside the zeolite supercage of the catalysts. Therefore, there is no cluster size effect on the coke formation on Pt–Ir/NaY.

In general, the TPO spectrum of coked catalyst has two oxidation peaks, one at around 300°C and the other at around 450°C. It has been found that these two oxidation peaks are due to the presence of coke on the metal phase and acidic metal oxide supports (e.g. Al_2O_3) [7–10], respectively. Also, it is known that the oxidation

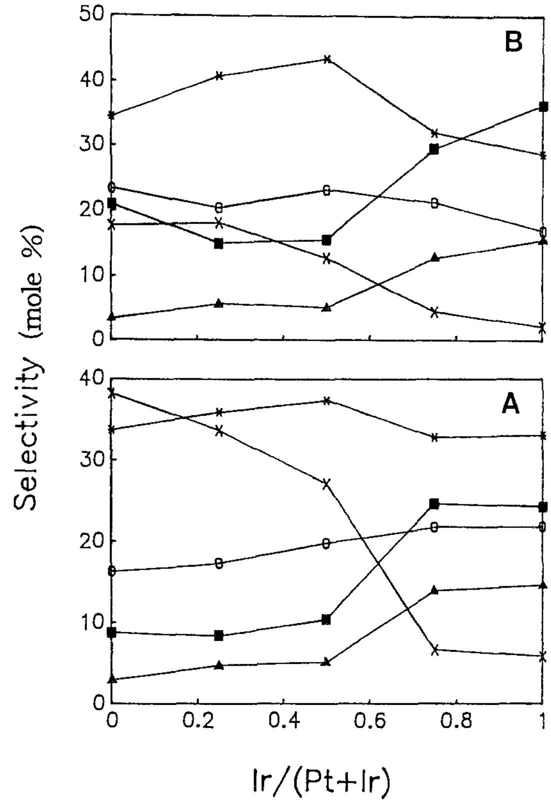

Fig. 3. Product distributions after 5 min of reaction (A) and 240 min of reaction (B) in *n*-heptane reforming as a function of Ir content. C_1 (▲), C_2–nC_6 (■), C_6 and C_7 isomers (∗), cyclic compound (○) and toluene (×).

peak of coke on non-acidic SiO_2 or NaY support has not been found [10,11]. In this work, we used the non-acidic NaY as a support. However, a small amount of acid site may be generated during the reduction of platinum or iridium amine complex in the catalysts. 5.6 protons per unit cell were formed after H_2 reduction of Pt and Ir cations. The oxidation peak of coke on acidic HY catalyst showed a maximum at 458°C. Therefore, we believe that the high oxidation peak at around 400–460°C is due to the acid site on NaY (fig. 2). This area is less than 5% of that around 200–300°C. The H/M of Pt(4)/NaY was 0.95 before the reaction and decreased to 0.26 after the reaction of 240 min. This extent of decrease in the H/M ratio is similar to the decrease in activity (TOF) from 0.094 to 0.025 s^{-1} after the reaction from 5 to 240 min. Pt(3)Ir(1)/NaY and Pt(2)Ir(2)/NaY bimetallic catalysts showed a similar pattern between the extent of decrease in activity and of H/M. However, after the reaction of 240 min, the decrease in the activity of Ir(4)/NaY was not so much in spite of the large decrease in the ratio of H/M. Although Ir(4)/NaY catalyst maintained a high activity and contained a small amount of coke after the reaction of 240 min, Ir(4)/NaY did not chemisorb the corresponding amount of hydrogen. This unusual characteristic of Ir(4)/NaY should be studied in more detail. The deactivation of catalysts results mainly from the coke formed on the active sites. The irreversible chemisorption of hydrogen occurred on the metal clusters in NaY. The decrease in the amount of H_2 chemisorption indicates that part of the coke was formed on the surface of metal cluster and affected the physicochemical properties of metal clusters. As reported elsewhere [5], metal clusters of about 1 nm in diameter are mostly located inside the zeolite supercage in our samples. Therefore, it can be concluded that most of coke are located around the metal cluster inside the supercage and interact with the metal cluster, because coke cannot be burnt with O_2 below 300°C without the catalytic activity of Pt and Ir metal. It has been shown previously [7,8] that the modification of Pt/Al_2O_3 catalyst by addition of Re or Ir is able to inhibit the deactivation of the metal and alter the nature of the deposits on Pt/Al_2O_3 catalyst. It has also been reported [7,8] that the modification of Pt by Ir decreased the amount of light hydrocarbon deposits on the metal and increased the graphitic coke on the support. However, the modification of Pt by addition of Ir in NaY altered the nature of coke deposited around the metal cluster.

Fig. 3 shows the product distributions as a function of Ir content in the catalysts after the reaction of 5 min and 240 min, respectively. The composition of cyclic compound is 12.6% benzene, 1.8% xylene and 85.6% cyclohexane. C_6 and C_7 isomers are the main products in all catalysts. C_5 cyclic compounds were not produced, which is quite different from the production of C_5 cyclic compounds in C_7 reforming reaction catalyzed by Pt–Ir/Al_2O_3 [12]. As the Ir content increased, the selectivity of toluene significantly decreased and that of cracking products (C_1–C_6) increased. This is due to the high activity of Ir for cracking reaction. After 240 min time on stream, the selectivity of toluene significantly decreased and the selectivity of cracking products increased as compared with those of 5 min time on stream. This suggests that the ensemble size needed for dehydrocyclization reaction (*n*-heptane to toluene) decreased as coke was deposited on the metal cluster, resulting in the less activity to produce toluene.

4. Conclusions

As the Ir content in Pt–Ir/NaY increased, smaller amount of coke and hard type of coke were formed on and around the metal cluster. This coke decreased the selectivity for dehydrocyclization in *n*-heptane reforming reaction. The higher activity and more improved activity maintenance of Pt–Ir/NaY bimetallic catalysts are believed to be due to the decrease in the amount of coke. The nature of hard coke (H/C ratio) is dependent on the content of Ir in Pt–Ir bimetallic clusters.

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