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Effect of rare earth additives on the properties of the platinum/ alumina catalyst

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Abstract

The conversion of methylcyclopentane or *n*-hexane was studied on Pt/Al_2O_3 and Pt–RE/Al_2O_3 catalysts (RE = La, Nd, Tb, Ho, Tm and Y). The addition of rare earth (RE) increases the aromatization yield of methylcyclopentane, *n*-hexane and cyclohexane. We found that all of the RE elements make the temperature peaks of TPR shift to lower temperatures. The magnetic susceptibility of the Pt–RE catalyst is found to be higher than that of the Pt catalyst. A relationship between the aromatization yield of cyclohexane and the magnetic susceptibility of the Pt–RE/Al_2O_3 catalysts has been observed. The pulse CS_2 poisoning technique has been used to study the active sites of the catalysts for dehydrogenation of cyclohexane.

1. Introduction

Rare earth elements have been extensively studied as catalytically active promoters [1,2], but the conversion of hydrocarbon on Pt–RE catalysts has seldom been reported. Previous studies showed that rare earth elements such as holmium, dysprosium and samarium can modify the catalytic properties of Pt/Al_2O_3 or Pt–Sn/Al_2O_3 for the conversion of *n*-heptane or cyclohexane [2,3]. The active sites of the Pt/Al_2O_3 catalyst have been investigated [4]. It has been found that Pt/Al_2O_3 and Pt–Ce/Al_2O_3 catalysts have two different kinds of active sites [5].

In this paper, we have investigated the effect of some rare earth elements on the catalytic and surface properties of Pt/Al_2O_3 catalyst and the role of rare earth elements (La, Nd, Tb, Ho, Tm and Y) acted as additives in Pt/Al_2O_3 catalyst.

2. Experimental details

2.1. Preparation of Pt–RE/Al_2O_3 catalysts

A series of catalysts containing platinum (0.3 wt.%) and rare earth element (0.3 wt.%) were prepared by co-impregnation of γ-Al_2O_3 with a surface area of about 180 m^2 g^{-1} in the solution of H_2PtCl_6 and rare earth chloride. The content of chlorine in the catalysts was about 0.9 wt.%. The new prepared catalysts were dried at 378 K for 4 h and calcined in air at 773 K for 2 h before evaluation.

2.2. Catalytic reduction and activity

All catalytic reactions were carried out in a device that has been described previously [3]. In a typical experiment, the loaded catalyst was 100 mg and reduced under flowing H_2 at 30 ml min^{-1} at 773 K for 2 h before being used. The catalytic activities for the aromatization of methylcyclopentane and cyclohexane on Pt/Al_2O_3 and Pt–RE/γ-Al_2O_3 catalysts were measured at 773 K and under atmosphere. The samples (1 ml) were injected into a microcatalytic reactor. The reaction products were analyzed by a combination of gas chromatography and data integration.

2.3. The measurement of active sites

In order to study the effect of active sites on Pt/Al_2O_3 and Pt–RE/Al_2O_3 catalysts, CS_2 was used as a catalyst poison and the dehydrogenation of cyclohexane was used as a test reaction. After the catalysts were reduced, the catalytic activities were determined, and followed by poisoning the catalysts at 553 K with a ratio of carbon disulfide to cyclohexane at 1:300. The mixture of CS_2 and cyclohexane was injected into the reactor with a rate of 1.0 ml per 6 min until the activity disappeared. The details of the measurement of active sites have been described previously [4].

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2.4. Temperature programmed reduction (TPR)

The TPR experiments were carried out in a flowing gas stream. The catalysts were dried at 378 K for 1.5 h prior to the TPR experiments. The experimental conditions were controlled as follows: catalyst loading, 150 mg; flow velocity of the mixed gas (H_2, 10 vol.%, and N_2, 90 vol.%), 40 ml min^{-1}. All TPR experiments were started at room temperature with a heating rate of 5 K min^{-1} to 803 K.

2.5. Magnetic properties of the catalysts

The magnetic susceptibilities of Pt/Al_2O_3 and $Pt–RE/Al_2O_3$ catalysts were measured by a Faraday magnetic balance. The magnetic susceptibility of a sample in the reduced or adsorbed form was measure in a specially made sample tube [6], which was set in a Dewar flask. The apparent magnetic susceptibility and metallic component susceptibility of the $Pt–RE/Al_2O_3$ were obtained using Weidemann's law [6]. The Weiss constant of the sample was calculated by the Curie–Weiss law

$$\chi_M = C/(T-Q)$$

where χ_M is the molar susceptibility, C is the Curie constant, T is the absolute temperature (K) and Q is the Weiss constant.

3. Results and discussion

3.1. The effects of RE on the activity of the Pt/Al_2O_3 catalyst

3.1.1. The conversion of methylcyclopentane and n-hexane

Table 1 shows that the presence of rare earth elements in Pt/Al_2O_3 catalysts not only increases the selectivity of aromatization and isomerization but also decreases the selectivity of hydrogenolysis for the conversion of methylcyclopentane or *n*-hexane. The selectivity of aromatization or isomerization, however, is different with the addition of the different rare earth elements in the Pt/Al_2O_3 catalyst. Generally, aromatization is proceeds easily on small particles of metals, while hydrocracking is proceeds easily on large particles [7,8]. The addition of rare earth elements to the Pt/Al_2O_3 catalyst makes platinum particles smaller, and thus results in an increase in the selectivity of aromatization and a decrease in the selectivity of hydrocracking. The difference in selectivity in $Pt-RE/Al_2O_3$ catalysts compared to the Pt/Al_2O_3 catalyst is perhaps due to the change of metal and acid sites after adding rare earth elements.

3.1.2. The hydrogenation of cyclohexane on Pt/Al_2O_3 and $Pt-RE/Al_2O_3$ catalysts

Table 2 shows that the activity of dehydrogenation of cyclohexane in the $Pt–RE/Al_2O_3$ catalysts is higher than that in Pt/Al_2O_3 at various temperatures. This indicates that the rate of aromatization in $Pt–RE/Al_2O_3$ catalysts is faster and more sensitive to temperature than that in Pt/Al_2O_3, which implies that the change is related to activation energy. Therefore, we calculated the activation energy for the dehydrogenation of cyclohexane [8,9] (Table 2). The activation energy of the Pt/Al_2O_3 catalyst for the dehydrogenation of cyclohexane was found to be higher than that of $Pt–RE/Al_2O_3$ catalysts.

3.2. The effect of rare earth elements on reduction temperature

Table 3 shows that the $Pt–RE/Al_2O_3$ catalysts decrease the reduction temperature in the range from 4 to 10° after the addition of RE elements on Pt/Al_2O_3 during the TPR process. This result indicates that rare earth elements have the ability to supply electrons to Pt/Al_2O_3. The addition of rare earth elements decreases the ability of Pt/Al_2O_3 to supply electrons and lowers the interaction between Pt and Al_2O_3 at the same time. Thus, these rare earth elements are able to make the Pt reduction easier.

TABLE 1. The conversion of methylcyclopentane and *n*-hexane[a]

Catalyst	Methylcyclopentane				*n*-Hexane			
	S_H	S_I	S_A	S_A+S_I	S_H	S_I	S_A	S_A+S_I
Pt/Al_2O_3	33.8	7.2	55.2	64.4	51.1	2.4	46.6	49.0
$Pt-La/Al_2O_3$	33.8	10.8	55.4	66.2	48.3	5.0	49.6	54.6
$Pt-Nd/Al_2O_3$	30.9	13.4	55.7	69.1	42.1	8.9	49.1	58.0
$Pt-Tb/Al_2O_3$	25.3	17.5	57.2	74.7	38.6	11.9	49.5	61.4
$Pt-Ho/Al_2O_3$	25.0	14.8	60.2	75.0	37.7	11.0	51.4	62.3
$Pt-Tm/Al_2O_3$	30.8	10.4	58.8	69.3	41.2	8.2	50.6	58.8
$Pt-Y/Al_2O_3$	26.6	14.1	59.3	73.4	41.5	8.3	50.3	58.6

[a] S_H, hydrogenolysis selectivity; S_I, isomerization selectivity; S_A, aromatization selectivity.

TABLE 2. The dehydrogenation of cyclohexane on Pt/Al_2O_3 and $Pt–RE/Al_2O_3$ catalysts at different temperature and atmosphere pressure

Catalyst	Conversion yield (%)					
	593 K	583 K	573 K	563 K	553 K	E (kJ mol^{-1})
Pt/Al_2O_3	78.2	65.1	47.7	32.0	17.3	147.1
$Pt–La/Al_2O_3$	82.9	71.3	53.3	34.5	19.0	141.9
$Pt–Nd/Al_2O_3$	83.1	71.2	55.0	36.7	20.2	137.9
$Pt–Tb/Al_2O_3$	81.3	67.9	51.5	33.9	19.7	137.9
$Pt–Ho/Al_2O_3$	81.1	68.8	50.0	34.1	19.7	140.6
$Pt–Tm/Al_2O_3$	85.2	72.6	57.2	39.0	22.0	132.7
$Pt–Y/Al_2O_3$	80.3	69.0	52.7	34.0	18.8	144.1

TABLE 3. The reduction temperature in Pt/Al_2O_3 and Pt/Al_2O_3 catalysts

	Pt	Pt–La	Pt–Nd	Pt–Tb	Pt–Ho	Pt–Tm	Pt–Y
Temperature (K)	521 655	514 643	515 643	513 647	517 646	511 648	513 647

3.3. *Magnetic properties and activity of $Pt–RE/Al_2O_3$ catalysts*

Figure 1 shows the relationship between aromatization yield and susceptibility. We found that the aromatization yield for the conversion of cyclohexane to benzene and susceptibilities of the $Pt–RE/Al_2O_3$ catalysts varies with the changing of the rare earth elements, and the $Pt–Tm/Al_2O_3$ catalyst has the highest aromatization yield with the largest susceptibility. The effect of adding rare earth elements on both aromatization yield and susceptibility was found to follow the same order: $Tm > Nd > La > Ho \approx Tb > Y$.

This interesting relationship between aromatization yield and susceptibility could be ascribed to uncoupling electrons and d holes in Pt metal. This corresponding relationship shows that the catalytic activity is related to the electronic factor and d hole of the metals. It was proposed that the formation of a d hole favours the aromatic reaction of cyclohexane since these rare earth elements favour the formation of d holes [3,6].

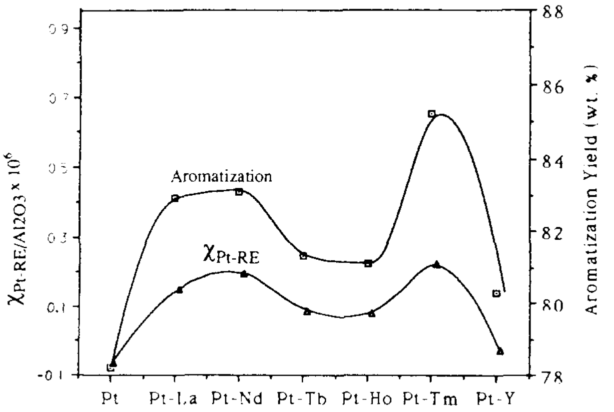

Fig. 1. Correlation between susceptibility $\chi_{Pt-RE}$and aromatization.

3.4. *The properties of active sites of the $Pt–RE/Al_2O_3$ catalysts*

Figure 2 shows the poisoning curve of the dehydrogenation of cyclohexane on Pt/Al_2O_3 and $Pt–RE/Al_2O_3$ catalysts. A straight line with an intersection suggests that there are two different kinds of active sites in the catalysts. The curves with small slopes are of α sites, while those with large slopes are of β-sites (Fig. 2). α sites are thought to be poisoned by CS_2, since the chemisorption of cyclohexane and the dehydrogenation of cyclohexane proceed on β-sites.

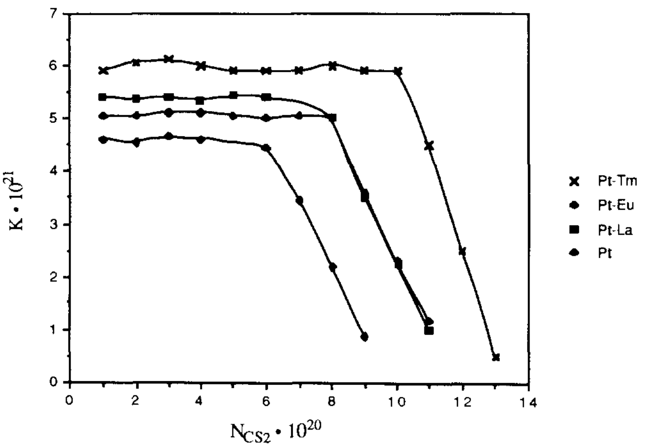

Fig. 2. Poisoning curving of dehydrogenation of cyclohexane on $Pt–RE/Al_2O_3$ catalysts. *K is the number of molecular conversions per second per gram of platinum; N_{CS2} is the number of CS_2 molecules per gram of platinum.

4. Conclusions

The addition of a rare earth increases the activity of the Pt/Al_2O_3 catalyst and lowers the reduction temperature. There is a corresponding relationship between the susceptibility and aromatization yield of cyclohexane on Pt–RE/Al_2O_3 catalysts. Two different kinds of active sites in Pt–RE/Al_2O_3 catalysts are found in the dehydrogenation of cyclohexane.

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