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A study of platinum–dysprosium–KL zeolite reforming catalyst

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Abstract

The activity and selectivity of Pt–KL and Pt–Dy–KL zeolite catalysts were studied with a pulsed micro-catalytic reactor. The activity for the aromatization of either *n*-hexane or methylcyclopentane (MCP) on Pt–Dy–KL zeolite catalysts containing dysprosium ranging from 0.1 to 0.5 wt.% is found to be higher than that with Pt–KL catalyst. The stability of the Pt–KL and Pt–Dy–KL catalysts has been studied using a poisoning method with carbon disulphide.

1. Introduction

It has been reported that the activity and selectivity of platinum-loaded zeolite KL catalyst for the dehydrocyclization of paraffin are quite high, but the stability of the catalyst is unsatisfactory [1,2]. There have been little published data regarding the effect of adding another elements into the Pt–KL zeolite reforming catalyst. The effect of rare earth elements on the surface and catalytic properties of Pt–KL catalyst is seldom reported [3,4]. Sivasanker's work showed that lanthanum can modify the acidic properties of Pt–KL catalyst [5]. Unfortunately, the activity of Pt–La–KL catalyst is decreased after adding 7 wt.% lanthanum into Pt–KL catalyst [5].

In this paper, we report the effect of dysprosium on the surface behavior and catalytic properties of Pt–KL catalysts. It is our hope that this initial study can provide some information and background for the development of a series of new platinum–RE–KL catalysts.

2. Experimental details

2.1. Preparation of catalysts

A series of catalysts containing platinum (0.8 wt.%) and dysprosium (in the range of 0.1–0.9 wt.%) was prepared by co-impregnating zeolite KL in aqueous solution of H_2PtCl_6 and $Dy(NO_3)_3$. The new prepared catalysts were dried in a micro-catalytic reactor for 1.5 h at 383 K and then calcined in air for 4 h at 773 K.

2.2. Reduction and activity of Pt–KL and Pt–Dy–KL catalysts

The reduction and activity of Pt–KL and Pt–Dy–KL catalysts were studied in a pulsed micro-catalytic reactor. The catalyst was reduced at 773 K for 2 h under a hydrogen atmosphere with a flow velocity of 60 ml min^{-1}. The reduction temperature was controlled at 773 K at rate of 5 K min^{-1}. Reactant (1 μl) was injected into the reactor each time. The reaction temperature was performed at 773 K for the aromatization of *n*-hexane or methylcyclopentane, and for cyclohexane at 593, 583, 573, 563, respectively. All of the reactions were carried out under hydrogen flow at a rate of 30 ml min^{-1}. Product analysis was carried out using gas chromatography and data integration.

2.3. Poisoning of the catalysts

In order to study the effect of poisoning on Pt–Dy–KL catalyst, CS_2 was used as a poison and the dehydrogenation of cyclohexane as a test reaction. The conversion of cyclohexane to benzene on the new prepared catalysts was determined after the catalysts were reduced under a hydrogen atmosphere. All of the catalysts were poisoned at 573 K by a mixture of carbon disulphide and cyclohexane in a ratio of 1:1000. One microliter of the mixture was injected into the reactor every 10 min until the activity of the catalysts disappeared.

2.4. Temperature programmed reduction (TPR)

The TPR experiments were performed in a flow apparatus and started from room temperature up to 773 K at a heating rate of 5 K min^{-1}. The loaded catalysts were dried at 383 K for 1.5 h prior to use.

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The experimental conditions were controlled as follows: catalyst loading, 150 mg; flow velocity of the mixed gases, 60 ml min^{-1} (H_2, 9 vol.%; N_2, 91 vol.%); gas pressure, 1 atm.

3. Results and discussion

3.1. *Effect of dysprosium on the activity of Pt–KL catalyst*

The selectivities for the conversion of *n*-hexane and MCP on platinum reforming catalysts are listed in Table 1. These results showed that adding a suitable amount of dysprosium into Pt–KL catalyst is very important to improve the catalytic activity of Pt–Dy–KL catalysts. Our experimental results showed that the selectivities of the dehydrogenation and cyclization of *n*-hexane or MCP on Pt–Dy–KL catalysts are much better than on Pt–KL catalyst when dysprosium content is in the range of 0.1–0.5 wt.%. Surprisingly, when dysprosium content is more than 0.7 wt.%, the selectivity of Pt–Dy–KL catalysts is remarkably decreased. Dysprosium can change the selectivity and activity of Pt/Al_2O_3 since dysprosium can modify the acidity of the catalysts and improve the dispersion of platinum. This results in increasing the selectivity of aromatization and decreasing the selectivity of hydrocracking.

The results for the dehydrogenation of cyclohexane on Pt–KL and Pt–Dy–KL catalysts at different temperatures are listed in Table 2. The activation energy for the dehydrogenation of cyclohexane on Pt–KL and Pt–Dy–KL catalysts are also listed in Table 2. These results showed the activities of the Pt–KL and Pt–Dy–KL catalysts vary with temperature. The maximum yields of aromatization for both Pt–KL and Pt–Dy—KL catalysts are obtained at 593 K. The activation energy of the Pt–Dy–KL catalysts (dysprosium content from 0.1 to 0.5 wt.%) is found to be larger than that of Pt–KL catalyst. The optimum content of dysprosium in Pt–Dy–KL catalysts is found to be about 0.3 wt.%, but the corresponding relationship among dysprosium content, activation energy, and aromatization yield needs to be further investigated [6,7].

TABLE 1. Effect of dysprosium on Pt–KL catalysts for the conversion of MCP and *n*-hexane

Catalyst	Dy (wt.%)	*n*-hexane		Sb	MCP		
		Sh	Si		Sb	Si	Sb
Pt–KL	0	21.5	5.7	72.9	22.8	16.0	61.2
Pt–Dy–KL	0.1	22.4	2.9	74.7	22.0	14.3	63.8
Pt–Dy–KL	0.3	23.8	2.9	74.7	22.0	14.3	63.8
Pt–Dy–KL	0.5	25.2	1.1	74.0	24.3	5.3	70.4
Pt–Dy–KL	0.7	15.7	60.6	23.8	4.7	51.9	43.4
Pt–Dy–KL	0.9	17.4	62.0	20.5	7.6	48.3	44.2
Pt–Al_2O_3		48.1	21.8	31.0	55.3	20.3	24.4
Pt–Dy–Al_2O_3		44.8	9.0	46.2	46.1	18.1	35.9

S_h, S_i, S_b: selectivity for hydrocracking, isomerization and aromatization, respectively.

TABLE 2. Activity of the dehydrogenation for the reaction of cyclohexane on Pt–KL and Pt–Dy–KL catalysts

Catalyst	Dy (wt.%)	*E* (KL/mol)[a]	Aromatization			
			593 K	583 K	573 K	563 K
Pt–KL	0	119.9	55.6	41.5	28.1	18.9
Pt–Dy–KL	0.1	123.5	71.9	57.8	43.3	28.6
Pt–Dy–KL	0.3	141.1	74.9	58.1	39.6	24.1
Pt–Dy–KL	0.5	143.6	68.2	55.6	38.7	22.5

[a] E, activity energy.

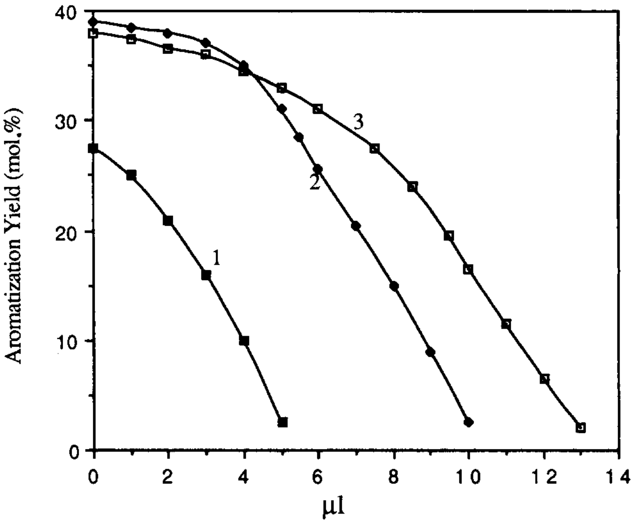

Fig. 1. Poisoning curves for Pt–KL and Pt–Dy–KL catalysts at 573 K. Curve 1, Pt–KL; curve 2, Pt–Dy(0.3wt.%)–KL; curve 3, Pt–Dy(0.5wt%)–KL.

3.2. *Effect of dysprosium on the resisting sulphur property of Pt–Dy–KL catalysts*

Sulphur poisoning is one of the most important factors in decreasing the catalytic activity of some catalysts [8,9]. We investigated the poisoning curves of the dehydrogenation of cyclohexane on Pt–KL and Pt–Dy–KL catalysts and found that the ability of the sulphur-resisting Pt–KL catalyst is worst compared to other Pt–Dy–KL catalysts. The results are shown in Fig. 1. For Pt–KL catalyst, the CS_2 poisoning amount is found to be about 5 for the Pt–Dy–KL catalysts while the CS_2 poisoning amount is at least twice as large. Xie and co-workers have shown that ionic oxide or salt has a tendency to single layer dispersing supported on a high specific surface [8]. Since platinum oxide and Dy_2O_3 in the Pt–Dy–KL catalysts are ionic compounds before reduction, platinum oxide and Dy_2O_3 are thus

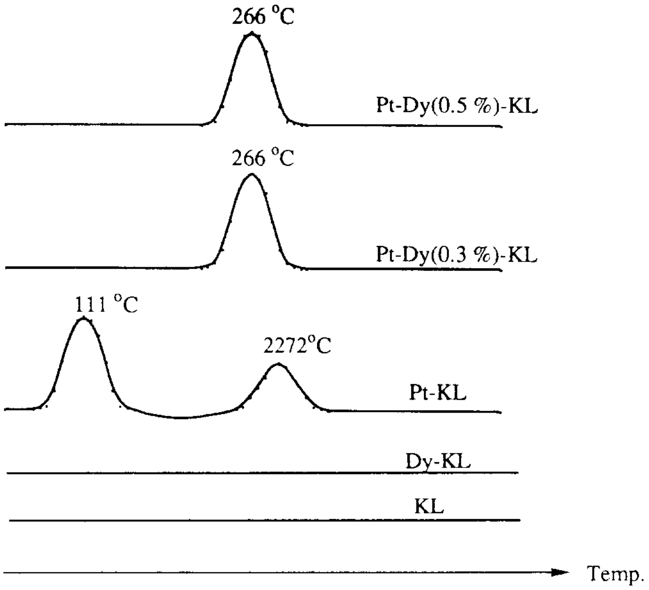

Fig. 2. TPR profiles of Pt–KL and Pt–Dy–KL catalysts.

dispersed as a single layer on zeolite KL. After sulphur reacted with platinum forming PtS, the single layer dispersing is changed and the catalytic activity of the Pt–Dy–KL catalysts is lost gradually.

3.3. Surface behavior of Pt–KL and Pt–Dy–KL catalysts

TPR experiments show that Dy^{3+} and Al^{3+} in Pt–KL and Pt–Dy–KL catalysts can not be reduced under our experimental conditions and that there are two different kinds of platinum valence Pt^{2+} and Pt^{4+} in the Pt–KL catalyst. It was found that the reduction temperature of Pt–Dy–KL catalysts is decreased after adding dysprosium into the Pt–KL catalysts. The TPR profiles of Pt–KL and Pt–Dy–KL catalysts are shown in Fig. 2. These results indicate that the rare earth element dysprosium plays a key role as an electron promoter which has been proved experimentally by magnetic susceptibility [10].

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