The effect of lanthanum in dehydrogenation of propane on Pt–Sn bimetallic catalysts

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Four catalysts, H_2PtCl_6–$5SnCl_2/\gamma$-Al_2O_3 (cat-1), $\{H_2PtCl_6$–$5SnCl_2 + xLaCl_3\}/\gamma$-$Al_2O_3$ (cat-2), $(Me_4N)[Pt(SnCl_3)_5]/\gamma$-$Al_2O_3$ (cat-3), and $\{(Me_4N)[Pt(SnCl_3)_5] + xLaCl_3\}/\gamma$-$Al_2O_3$ (cat-4) were prepared and their catalytic activities and stabilities in dehydrogenation of propane were investigated. It has been shown that the stabilities of the Pt–Sn bimetallic catalysts were improved by introducing lanthanum into the catalysts either by the conventional impregnation method with Pt- and Sn-containing salts or by using precursors derived from Pt–Sn bimetallic clusters. Results from XPS analysis indicated that addition of lanthanum could inhibit the reduction of tin in the catalysts, especially in cat-2. The distribution of pore capacity in a used cat-2 was mainly in the large and medium size range, but in a used cat-1 the distribution was mainly in the small to medium size range. Thermal gravimetric analysis (TGA) showed that weight loss in the used cat-1 was much more than that in the used cat-2. The results suggested that introducing lanthanum into the Pt–Sn bimetallic catalysts could effectively prevent them from coking.

Keywords: lanthanum, Pt–Sn catalyst, dehydrogenation of propane

1. Introduction

Alumina supported Pt–Sn bimetallic catalysts have been applied extensively in hydrocarbon reforming and dehydrogenation of alkanes [1–12]. There are two ways to support the Pt and Sn on the Al_2O_3: one way is to immerse the Al_2O_3 in $SnCl_2$ and H_2PtCl_6 solutions by consecutive impregnations or co-impregnation. Owing to the different adsorption capabilities of Al_2O_3 to Pt and Sn, it is impossible to evenly disperse these two metallic elements on the support surface. The other way is to synthesize a metal cluster of designed Pt-to-Sn ratio, and the cluster compound is then loaded onto the Al_2O_3 support. With the latter method, the homogeneous distribution of Pt and Sn, at a designed Pt/Sn ratio on the support is guaranteed, and the modification effect of Sn to a Pt/γ-Al_2O_3 catalyst can be fully optimized [3]. Previously [4] we have studied the dehydrogenation of propane with catalysts prepared by the above methods. It was found that the catalytic activity of dehydrogenation by metal cluster catalysts was much enhanced, and the stability was much higher than that of the conventional ones. However, their catalytic activity during the reaction over a prolonged time decreased because of the formation of coke and an excessive amount of reduced Sn in the Pt–Sn alloy. It was reported [13–18] that introducing a third metal was an effective way to solve the problem. In this work lanthanum was added to the conventional Pt–Sn catalysts and the Pt–Sn cluster catalysts. Its effect on the activity and stability of dehydrogenation of propane was then investigated. This has provided us with important information to improve the Pt–Sn catalysts.

2. Experimental

2.1. Preparation of catalysts

The conventional Pt–Sn catalyst with 1.0 wt% of Pt and Pt : Sn = 1 : 5 molar ratio was prepared by immersing the γ-Al_2O_3 (40–60 mesh, surface area 160 m^2/g) in $SnCl_2$/acetone solution for 12 h. Then the dried Sn/γ-Al_2O_3 was immersed in the H_2PtCl_6/ethanol solution for 12 h. The catalyst, Pt–Sn/γ-Al_2O_3, was dried at 100 and 200°C each for 1 h, and calcined at 550°C for 4 h. The Pt–Sn cluster compound was prepared as reported elsewhere [19]. The catalyst derived from the Pt–Sn cluster containing 1.0 wt% of Pt and with Pt : Sn = 1 : 5 molar ratio was prepared by impregnating γ-Al_2O_3 in an acetylacetone solution of the Pt–Sn cluster for 12 h. Its drying and calcining conditions were the same as for the conventional Pt–Sn catalyst.

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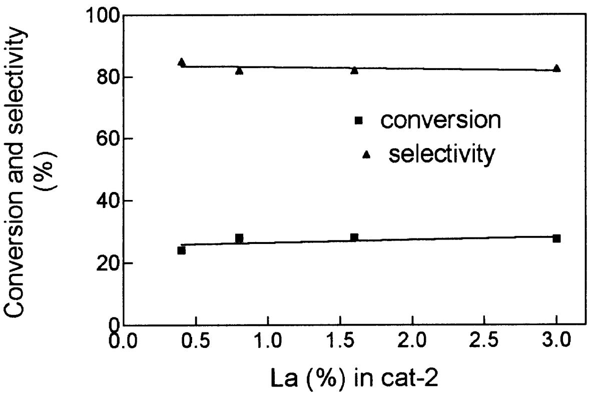

Figure 1. Effect of La on conversion and selectivity. Reaction conditions: GHSV = 2000 h^{-1}, $H_2 : C_3H_8 = 3 : 1$ (mole). Reaction temperature = 600°C.

The Pt–Sn–La catalysts were prepared by immersing the above mentioned catalysts in a $LaCl_3$/ethanol solution for 12 h and dried at 160°C for 4 h. In this work, four types of the catalysts were prepared and evaluated: (1) cat-1, conventional Pt–Sn catalyst; (2) cat-2, conventional Pt–Sn catalyst loaded with 0.4, 0.8, 1.6 and 3.0 wt% La; (3) cat-3, Pt–Sn bimetallic cluster catalyst; (4) cat-4, Pt–Sn bimetallic cluster catalyst loaded with 0.4, 0.8, 1.6 and 3.0 wt% La.

2.2. Dehydrogenation and product analysis

Dehydrogenation of propane was performed in a microreactor–GC combination system. The i.d. of the reactor was 6 mm and the charge volume of the catalyst was 1 ml (0.351 g). For each reaction the catalyst was pre-reduced in hydrogen, and then a mixture of desired ratio of H_2 to propane was passed through it. The products were analyzed by GC with a TC detector and a column of 2 m× ∅ 2 mm filled with Apiezon M/ Al_2O_3. The GC peaks were analyzed with a HP integrator.

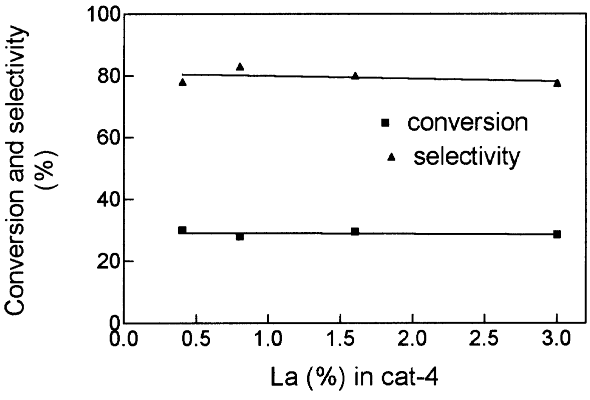

Figure 2. Effect of La on conversion and selectivity. Reaction conditions are the same as in figure 1.

Table 1
The effect of reduction time on the percent conversion of propane with cat-2. Reaction conditions: GHVS = 2000 h^{-1}, $H_2 : C_3H_8 = 3 : 1$ (mole)

Reduction time (h)		Reaction temperature (°C)					
		500	520	540	560	580	600
2	conv.	2.94	4.74	7.94	13.2	19.41	27.67
	selec.	100	97.8	96.0	87.9	86.2	84.4
4	conv.	2.92	5.10	8.25	13.26	19.91	27.90
	selec.	100	96.7	94.5	88.1	85.9	83.8

The surface area and pore distribution were measured with a Digisorb 2600 auto-adsorber. Catalysts for XPS measurement were pre-reduced in H_2 atmosphere at 100 and 200°C each for 1 h, then raised to 500°C at a programmed rate of 10°C/min, and reduced at 500°C for 4 h. Samples were finally transferred under N_2 atmosphere to an XSAM-800 spectrometer to obtain the XPS spectrum. Aluminum was used as an internal standard.

3. Results and discussion

3.1. Effect of lanthanum on the catalytic activity and selectivity

For a catalyst pre-reduced with H_2 at 100 and 200°C each for 1 h, and at 400°C for 2 h, the effect of La in a Pt–Sn catalyst on the activity of dehydrogenation of propane was as shown in figures 1 and 2. The increasing amount of La added had no obvious effect on the activity and selectivity of cat-2 and cat-4. This effect was still insignificant even up to 3.0 wt% of La addition. In contrast, a tiny amount of alkali metal was sufficient to result in a noticeable drop in the catalytic activity [14]. Based on the above result, a 0.8 wt% loading of La was chosen for all catalysts used in this work.

Table 2
The effect of reduction temperature on the percent conversion of propane with cat-2. Reaction conditions: GHVS = 2000 h^{-1}, $H_2 : C_3H_8 = 3 : 1$ (mole)

Reduction temperature (°C)		Reaction temperature (°C)					
		500	520	540	560	580	600
400	conv.	2.94	4.74	7.94	13.20	19.41	27.67
	selec.	100	97.8	96.0	87.9	86.2	84.4
550	conv.	2.91	4.90	8.19	12.96	19.12	27.10
	selec.	100	97.1	91.8	87.1	85.4	82.5

Table 3
The effect of reduction time on the percent conversion of propane with cat-4. Reaction conditions: GHVS = 2000 h^{-1}, $H_2 : C_3H_8 = 3 : 1$ (mole)

Reduction time (h)		Reaction temperature (°C) 500	520	540	560	580	600
2	conv.	3.22	5.21	7.96	13.4	20.28	28.23
	selec.	100	97.2	96.7	93.0	90.7	83.0
3	conv.	3.38	5.44	8.69	13.20	19.17	27.00
	selec.	100	100	97.1	94.4	91.4	85.3
4	conv.	3.06	4.91	7.36	10.49	14.58	20.30
	selec.	100	98.7	97.5	96.0	90.7	84.2

Table 4
The effect of reduction temperature on the percent conversion of propane with cat-4. Reaction conditions: GHVS = 2000 h^{-1}, $H_2 : C_3H_8 = 3 : 1$ (mole)

Reduction temperature (°C)		Reaction temperature (°C) 500	520	540	560	580	600
400	conv.	3.22	5.21	7.96	13.40	20.28	28.23
	selec.	100	97.2	96.7	93.0	90.7	83.0
500	conv.	3.25	5.10	8.21	12.97	18.73	26.05
	selec.	100	98.6	96.0	92.8	88.7	80.0
550	conv.	2.37	4.44	7.11	11.83	18.24	25.54
	selec.	100	98.0	96.5	90.5	87.0	83.6

3.2. The effect of temperature and time on reduction of the catalysts

For the two catalysts (cat-1 and cat-3) free of La used in this study, a noticeable drop in their catalytic activities has been observed [4] when the reduction time at high temperatures was lengthened from 2 to 4 h, and the reduction temperature was raised from 400 to 550°C. For the other two 0.8 wt% La-containing catalysts (cat-2 and cat-4), the catalytic activity and selectivity on cat-2 was found unaffected by the variation of reduction temperature and time under the same conditions. The results are shown in tables 1 and 2. However, for the Pt–Sn metal cluster catalyst loaded with La (cat-4), the catalytic activity was affected by time and temperature in reduction, and the results are shown in tables 3 and 4.

XPS analysis showed that the majority of the tin for all catalysts after 4 h of reduction with H_2 at high temperature was still in the oxide form. The binding energies of $3d_{1/2}$ level in tin oxide and $3d_{5/2}$ level in metallic tin in the catalysts are listed in table 5. From the relative peak intensities of metallic tin and tin oxide, it can be seen that the amount of metallic tin in the conventional Pt–Sn catalysts is less than that in the catalysts formed from Pt–Sn metal cluster. In the conventional Pt–Sn catalysts, Pt and Sn are less tightly bound together than they are in the cluster compounds, and the added La atoms can easily squeeze in between the Pt and Sn atoms. This can minimize the reduction of Sn resulting from the spillover of H_2 on Pt, and also can prevent the excessive formation of metallic Sn in Pt–Sn alloy which is detrimental to the catalytic activity. In the Pt–Sn metal cluster catalysts, it is impossible for La to squeeze in between the Pt and Sn since they are bonded strongly with chemical bonds. In consequence, La can only inhibit the coagulation of the catalytic active centers during the process of reduction, and can hardly minimize the excessive reduction of Sn from the spill over of hydrogen on Pt [20]. Therefore, the effect of anti-reduction is more prominent in conventional La-containing catalysts and the effect of La on the conventional catalysts is much larger than on the metal cluster catalysts.

3.3. Catalytic stability

The four catalysts after reduction at 100 and 200°C each for 1 h, and at 400°C for 2 h were examined under GHSV = 2000 h^{-1}, $H : C_3H_8 = 3 : 1$ and $1 : 1$ molar ratios, and reaction temperature at 570°C. The activity versus time plots are shown in figures 3 and 4. It can be seen that catalysts were stabilized by addition of La, and their activities remained unchanged. However, for catalysts free of La, their activities decreased gradually. Surface areas and total pore volumes of the four used catalysts are listed in table 6. It can be seen that cat-2 and cat-4 have larger pore volumes than cat-1 and cat-3. The distributions of pore capacity for the two used conventional catalysts (cat-1 and cat-2) are shown in figures 5 and 6. It was found that the used cat-2 had a larger total pore volume, and narrower dis-

Table 5
The 3d binding energies of Sn in the four catalysts

	cat-1 $3d_{3/2}$	cat-1 $3d_{5/2}$	cat-2 $3d_{3/2}$	cat-2 $3d_{5/2}$	cat-3 $3d_{3/2}$	cat-3 $3d_{5/2}$	cat-4 $3d_{3/2}$	cat-4 $3d_{5/2}$
tin oxide (eV)	487.2	496.0	487.2	496.0	487.0	495.6	487.0	495.6
metallic tin (eV)	486.0	494.5	486.1	494.6	486.0	494.7	485.9	494.5
intensity ratio (Sn/SnO, SnO_2)	0.33		0.25		0.35		0.33	

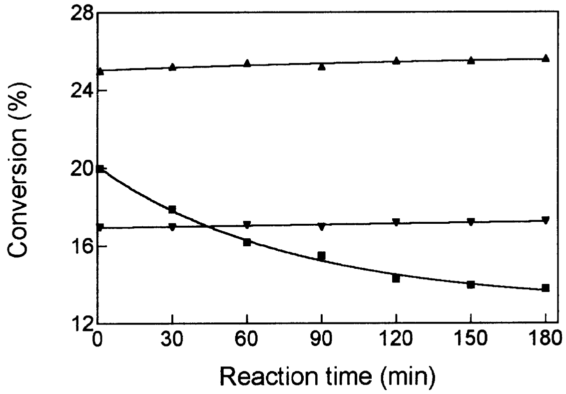

Figure 3. Relationship of reaction time and catalytic activity. Reaction conditions: GHSV = 2000 h^{-1}. Reaction temperature = 570°C. (▼) cat-2: $H_2 : C_3H_8 = 3 : 1$, (▲) cat-2: $H_2 : C_3H_8 = 1 : 1$, (■) cat-1: $H_2 : C_3H_8 = 1 : 1$.

tribution essentially in big and medium size pores. In contrast, a broad distribution mainly in pores of small and medium size was found in the used cat-1. This may be explained by serious coke formation in the used La-free conventional catalyst, and the reduction in pore size resulting from coke deposition in the support pore. However, after La was introduced into the catalysts, La could neutralize the acidic sites on the support and suppressed the coking of olefin products on the acidic support. Similar results in pore distributions were found in two used cluster catalysts. This demonstrates that La acts as an anti-coking agent in the catalyst, and stabilizes the catalytic activity by assuring the normal function of dehydrogenation in large and medium pores.

From the results of thermal gravimetric analysis (TGA), the weight loss in the La-free conventional Pt–Sn catalyst coked was 1.54% at 610–650°C, while that in the La-containing catalyst under the same condition was 0.81%. Moreover, judging from the pale gray color of the used La-containing catalyst and the dark color of the used La-free catalyst, the effective suppression in coke formation by La was further verified.

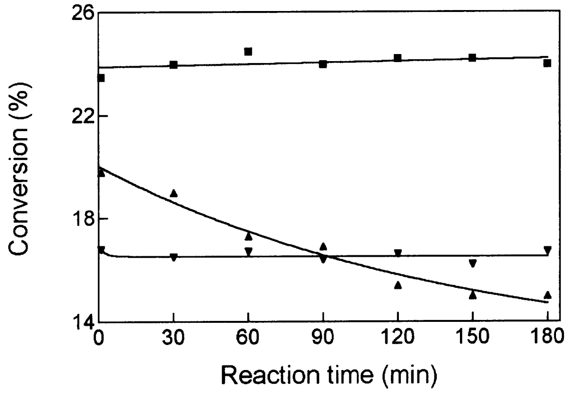

Figure 4. Relationship of reaction time and catalytic activity over cluster catalyst. Reaction conditions are the same as in figure 3. (■) cat-4: $H_2 : C_3H_8 = 1 : 1$, (▼) cat-4: $H_2 : C_3H_8 = 3 : 1$, (▲) cat-3: $H_2 : C_3H_8 = 1 : 1$.

Table 6
Surface area and pore distribution of the four used catalysts. Reaction conditions: GHVS = 2000 h^{-1}, $H_2 : C_3H_8 = 3 : 1$ (mole). Reaction time: 2 h

	cat-1	cat-2	cat-3	cat-4
surface area (m^2/g)	123	124	114	117
pore volume (ml/g)	0.2143	0.4431	0.2354	0.3285

4. Conclusion

In catalysts prepared from Pt–Sn bimetal cluster and by conventional impregnation methods, addition of La can result in a great improvement in the stability of the catalyst. Results of XPS, pore size distribution and TGA have revealed that La plays the roles of anti-coking and anti-reducing agent.

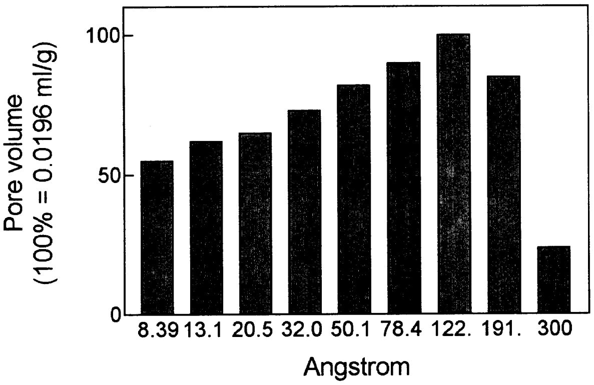

Figure 5. Distribution of pore cubic capacity against pore size in cat-1.

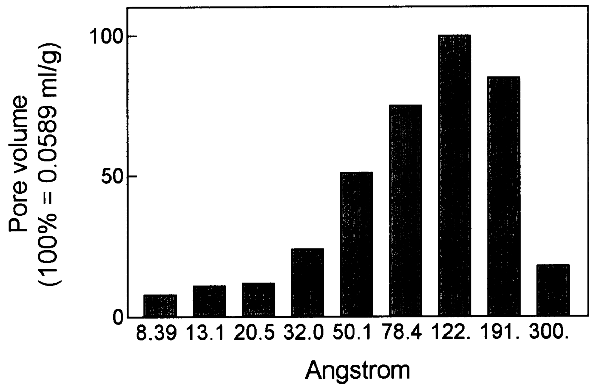

Figure 6. Distribution of pore cubic capacity against pore size in cat-2.

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