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# Propane dehydrogenation to propylene over Pt-based catalysts

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Propane catalytic dehydrogenation to propylene was investigated over novel platinum-based catalysts, and the BET, $H_2$-chemisorption, $H_2$-TPR, $H_2$-TPD, $C_3H_6$-TPD and $O_2$-pulse techniques were used for catalyst characterization in this paper. The results showed that the addition of Zn and Ce promoters into Pt-based catalyst could remarkably improve the performances of dehydrogenation. Highly propylene selectivity, about 99%, was obtained in the dehydrogenation reaction. This improvement in catalytic performances could be attributed to the strong surface interactions, which modified the surface properties of the active platinum metal and the support, and further improved the catalytic performance of Pt-based catalyst.

**KEY WORDS:** platinum catalyst; promoter effect; catalytic dehydrogenation; propane; propylene.

## 1. Introduction

The selective propane dehydrogenation to propylene is a very important industrial process since it produces a valuable raw material for polypropylene manufacture. In this process, Pt–Sn catalysts exhibit more advantages than other catalysts due to their comparative lower deactivation rate and high selectivity for dehydrogenation reactions. Numerous studies have shown that Sn promoter is a crucial component of platinum-based catalysts for the high dehydrogenation performance of light paraffin [1–4]. Nowadays, a lot of research work is being carried out to further improve the stability, selectivity and activity of Pt–Sn catalysts by the addition of some alkali metals such as Li, Ba, K, Ca and others, or by the utilization of non-acidic and thermal stable supports, such as $MgAl_2O_4$ and $ZnAl_2O_4$ [5–8]. However, the dehydrogenation performance of Pt–Sn catalysts is still not very satisfactory, especially in the stability and selectivity. The reasons for the deactivation for platinum-based catalyst in light paraffin dehydrogenation are mainly related to the aggregation of platinum particles and carbon deposition. Therefore, the promoters which can suppress coke reaction or produce a strong interaction between active platinum metal and promoter or support may greatly improve the catalytic properties of platinum-based catalysts. So far, there is limited amount of research concerning the development of platinum-based catalyst without Sn promoter.

This study aimed to examine the effects of Ce and Zn promoters addition to platinum/alumina catalyst in propane dehydrogenation.

## 2. Experimental

### 2.1. Catalyst preparation

Trimetallic Pt–Ce–Zn/$\gamma$-$Al_2O_3$ catalyst was prepared by impregnating with excess aqueous solution of $Zn(NO_3)_2$ and $Ce(NO_3)_3$ on a commercial $\gamma$-$Al_2O_3$ ($S_{BET}$: ≥250 $m^2/g$, previously 40–60 mesh sieved and calcined in air at 550 °C for 4 h) firstly, the sample was dried in air at 120 °C for12 h and subsequently calcined at 500 °C for 4 h. Finally, the Pt component was added as described previously. In all cases, the loadings of Ce, Zn and Pt were 1.1, 0.5 and 0.3 wt% respectively. The bimetallic and monometallic catalysts were prepared in the same way.

### 2.2. Catalytic activity evaluation

Propane dehydrogenation was carried out in a quartz fixed-bed reactor flow equipment at atmospheric pressure. 0.3 g catalyst was previously reduced under flowing pure $H_2$ (12.6 ml/min) at 576 °C for 2.5 h. Then the reaction mixture composed of $H_2$, $C_3H_8$ and Ar ($H_2/C_3H_8/Ar$ molar ratio = 1:1:5) was fed to the reactor. The total GHSV was 3800 $h^{-1}$. Five minutes after the reaction beginning, the gas compositions of reactant and products were analyzed by an FID chromatographic system (Shimadzu GC14-C) with a Porapak-Q packed column.

### 2.3. Catalyst characterization

#### 2.3.1. Surface area measurements

The BET surface area of the catalyst was determined by $N_2$ physi-sorption using an automatic analyzer (NOVA 4000, Quantachrome, USA). The samples were

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outgassed for 1 h under vacuum at 300 °C, prior to adsorption.

### 2.3.2. Pulse chemisorption of hydrogen

Pulse chemisorption of hydrogen experiments were carried out on a conventional setup, consisting of a programmable temperature furnace and a chromatographic system (Shimadzu GC-8A). Before pulse chemisorption experiments, the samples (0.2 g) were reduced under flowing pure $H_2$ (99.99%) at 576 °C for 2.5 h, then purged in Ar (99.99%) at 550 °C for 2 h and cooled to 25 °C in flowing Ar. The pulse size was 0.32 ml 5% (V/V) $H_2$ in Ar mixture and the time between pulses was 3 min.

### 2.3.3. Temperature-programmed hydrogen reduction

TPR experiments were carried out in the same setup as pulse chemisorption of hydrogen experiments. Before TPR experiment, the catalysts (0.08 g) were treated *in situ* by flowing dry Ar at 500 °C for 1 h, after cooled down to room temperature, the furnace was heated to 800 °C at a rate of 10 °C/min in 5% $H_2$/Ar stream (30 ml/min). The apparatus was calibrated by the reduction of CuO.

### 2.3.4. Temperature-programmed desorption

$H_2$-TPD experiments were carried out in the same setup as TPR. Before TPD experiments, the catalysts (0.2 g) were reduced under flowing pure $H_2$ at 576 °C for 2.5 h. After the reduction the catalyst cooled to 25 °C in flowing $H_2$. The gas stream was switched to Ar and subsequently a TPD experiment was performed (10 °C/min up to 540 °C).

$C_3H_6$-TPD measurements were carried out on an ASAP 2010C chemisorption analyzer. Samples (0.35 g) were reduced under flowing pure $H_2$ at 500 °C for 2.5 h then purged in flowing dry Ar at 580 °C for 2 h and cooled to 20 °C in flowing Ar. Then the catalysts were kept in the pure propylene gas flow for 30 min at 20 °C, and then the catalysts were washed with flowing dry Ar for 1 h. The temperature was ramped up at 6 °C /min while the generated products were monitored by an online mass spectrometer (Omnisorp. Corp.).

### 2.3.5. Coke quantitative analysis

The amount of coke formed on catalysts during the reaction was determined by a special $O_2$-pulse technology on a gas chromatograph flow system. The pulse experiments were carried out at 800 °C by injecting pulses of pure $O_2$ (99.99%) to the coke deposited catalysts (0.03 g), which was maintained under flowing Ar between two successive pulses. The $CO_2$ generated was continuously monitored with a TCD cell and recorded. Pulses of pure $O_2$ stopped until deposited carbon entirely converted to $CO_2$. Then the amount of generated $CO_2$ was converted to the amount of deposited coke on catalyst.

## 3. Results and discussion

### 3.1. Catalytic activity evaluation

The effects of Ce and Zn promoters on the performance of Pt/$\gamma$-$Al_2O_3$ catalyst in propane dehydrogenation are shown in figure 1. It can be seen that the Pt/$\gamma$-$Al_2O_3$ catalyst shows the poorest activity and stability, which suggests that the rates of hydrogenolysis and coke reactions are significant for the product distribution. Addition of Ce to Pt/$\gamma$-$Al_2O_3$ catalyst results in an increase of initial conversion from 34% to 44%. However, the propylene selectivity (initial: 64%, final: 88%) markedly decreases. Although the addition of Zn to Pt/$\gamma$-$Al_2O_3$ results in only a small increase in conversion of propane, the initial selectivity to propylene is greatly promoted (from 78% to 99%). The highest dehydrogenation activity, selectivity and stability are obtained over Pt–Ce–Zn/$\gamma$-$Al_2O_3$ catalyst. The initial conversion increases from 35% to 45%. When reaction finishes, the conversion of propane is maintained to 35%. At the same time, highly selectivity to propylene (99%) is obtained in the whole course of reaction.

### 3.2. Catalyst characterization analysis

### 3.2.1. Textural property

Table 1 summarizes the results of specific surface area and $H_2$-chemisorption measurements. The specific surface area of promoted bi or trimetallic catalysts is less than that measured for the mono-Pt/$\gamma$-$Al_2O_3$ catalyst. When Ce promoter exists, a slight increase in specific surface area is observed. Platinum dispersion estimates, which were calculated from pulse chemisorption at

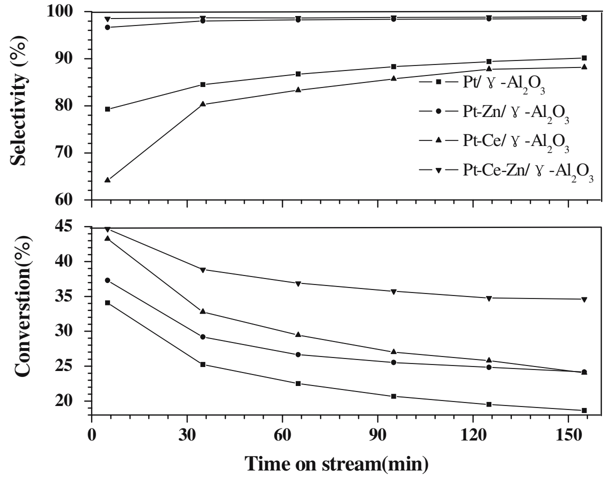

Figure 1. Dependence of dehydrogenation activity and propylene selectivity of mono, bi- and tri-metallic catalysts for propane on reaction time at 576 °C.

Table 1
Specific areas and Pt dispersion of the catalysts

| Catalyst | Loadings (wt%) | | | Spec. area ($m^2/g$) | Pt dispersion |
|---|---|---|---|---|---|
| | Pt | Zn | Ce | | |
| Pt/$\gamma$-$Al_2O_3$ | 0.3 | – | – | 250 | 0.16 |
| Pt–Ce/$\gamma$-$Al_2O_3$ | 0.3 | – | 1.1 | 245 | 0.37 |
| Pt–Zn/$\gamma$-$Al_2O_3$ | 0.3 | 0.5 | – | 229 | 0.36 |
| Pt–Ce–Zn/$\gamma$-$Al_2O_3$ | 0.3 | 0.5 | 1.1 | 335 | 0.35 |

25 °C using the assumption H: Pt = 1 [9,10], are listed in Table 1. It is seen that the addition of Zn or Ce to Pt/$\gamma$-$Al_2O_3$ increases platinum dispersion, which benefits the conversion of propane to propylene.

### *3.2.2. Temperature-programmed hydrogen reduction*

The effects of addition of Ce and Zn promoters on the reducibility of Pt/$\gamma$-$Al_2O_3$ catalyst were studied by TPR shown in figure 2. The amounts of total hydrogen consumption were quantified and the results are given in Table 2. It can be seen that all catalysts exhibit a sharp reduction peak at about 700 °C. The origin of the 700 °C peak is unknown, but it may be related to the reduction of contaminant ions in alumina support, as described in literature [11]. When Pt is present, this peak becomes broad. Over Pt/$\gamma$-$Al_2O_3$ catalyst, curve a displays two reduction peaks, one near 241 °C and the other near 467 °C. The first reduction peak is the reduction of Pt oxides which interact weakly with $Al_2O_3$ support and the second reduction peak is the reduction of Pt oxides which interact strongly with the support. For Pt–Ce/$\gamma$-$Al_2O_3$ catalyst, curve b indicates that the presence of cerium results in the second reduction peak of Pt oxides shifts to lower temperature, from 467 °C to 432 °C. It shows that interactions between Ce promoter and Pt oxides could take place. It has been reported that the strong interaction between $CeO_2$ and Pt oxides could promote the reduction of Pt oxides [12]. From the hydrogen consumption data, Table 2, party of cerium species is reduced. For Pt–Zn/$\gamma$-$Al_2O_3$ catalyst, curve c dose not show obvious difference from that of Pt/$\gamma$-$Al_2O_3$ catalyst, but the amounts of hydrogen consumption is slightly higher than those in Pt/$\gamma$-$Al_2O_3$ catalyst. The profile of Pt–Ce–Zn/$\gamma$-$Al_2O_3$ catalyst is distinctly different from those of any other catalysts. In the low temperature area, only one big reduction peak appears and shifts to higher temperature. It shows that the predominant Pt oxides may strongly interact with promoters or support. The strong interactions between active platinum metal and promoters or support strongly influence the reducibility of catalyst. Previous studies have shown that one of the important reasons for platinum-based catalyst during the dehydrogenation of light paraffin is the sintering of supported platinum particles. Over the trimetallic catalyst, the migration and aggregation of platinum particles may be suppressed in a degree by the strong interaction.

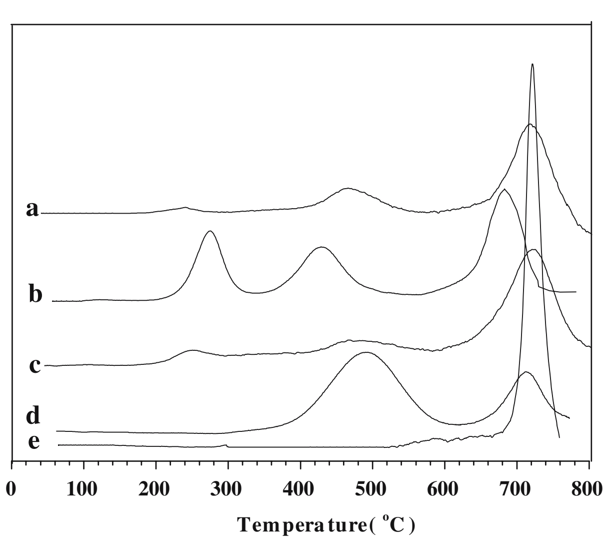

Figure 2. $H_2$-TPR profiles of the catalysts (a) Pt/$\gamma$-$Al_2O_3$, (b) Pt–Ce/$\gamma$-$Al_2O_3$, (c) Pt–Zn/$\gamma$-$Al_2O_3$, (d) Pt–Ce–Zn/$\gamma$-$Al_2O_3$, (e) $\gamma$-$Al_2O_3$.

Table 2
Total hydrogen consumption (THC) in $H_2$-TPR experiments (from 25 to 800 °C

| Catalyst | THC (m mol $H_2$/g·cat) | Catalyst | THC (m mol $H_2$/g·cat) |
|---|---|---|---|
| $\gamma$-$Al_2O_3$ | 0.03 | Pt–Zn/$\gamma$-$Al_2O_3$ | 0.09 |
| Pt/$\gamma$-$Al_2O_3$ | 0.06 | Pt–Ce–Zn/$\gamma$-$Al_2O_3$ | 0.12 |
| Pt–Ce/$\gamma$-$Al_2O_3$ | 0.11 | | |

### *3.2.3. $H_2$-TPD and $C_3H_6$ -TPD*

Hydrogen is one of the products of dehydrogenation reaction. The amount of chemisorption hydrogen can strongly affect the performance of the catalyst. The $H_2$-TPD technique was used to measure the effect of promoters on the property of catalyst to absorb hydrogen. TPD of hydrogen adsorbed during reduction and cooling in flowing $H_2$ is shown in figure 3. The amounts of desorbed hydrogen were quantified and the results are given in Table 3. Our experiment results show that over $\gamma$-$Al_2O_3$ sample, the phenomena of desorption hydrogen can not take place. For Pt/$\gamma$-$Al_2O_3$ and Pt–Ce/$\gamma$-$Al_2O_3$ catalysts, only one obvious desorption peak, about 300 °C, is observed. The amounts of desorption hydrogen over Pt–Ce/$\gamma$-$Al_2O_3$ catalyst are about two times of that over Pt/$\gamma$-$Al_2O_3$ catalyst. The presence of Zn brings about not only the obvious low temperature desorption peak, about 150 °C, but also a higher temperature desorption peak (about 400 °C). The amounts of desorption hydrogen increase greatly due to the addition of Zn. Usually, low temperature desorption peaks are assigned to hydrogen on metallic Pt [13]. High temperature desorption peaks are assigned to spillover

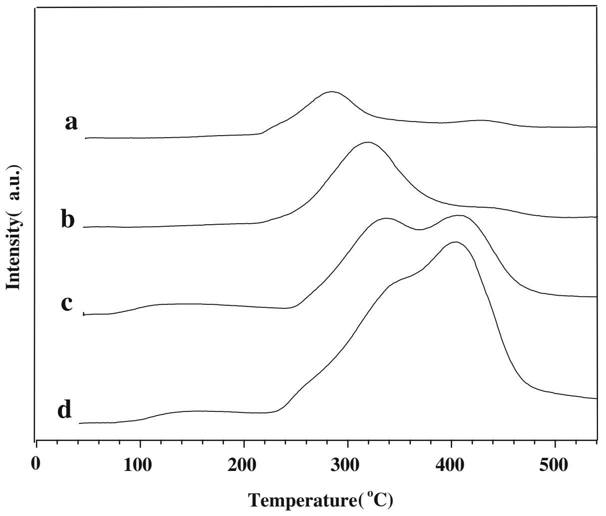

Figure 3. $H_2$-TPD profiles of the catalysts (a) Pt/$\gamma$-$Al_2O_3$, (b) Pt–Ce/$\gamma$-$Al_2O_3$, (c) Pt–Zn/$\gamma$-$Al_2O_3$, (d) Pt–Ce–Zn/$\gamma$-$Al_2O_3$.

Table 3
Total desorbed hydrogen (TDH) from $H_2$-TPD experiments (from 25 to 540 °C)

| Catalyst | TDH (m mol $H_2$/g·Pt) | Catalyst | TDH (m mol $H_2$/g·Pt) |
|---|---|---|---|
| $\gamma$-$Al_2O_3$ | – | Pt–Zn/$\gamma$-$Al_2O_3$ | 4.4 |
| Pt/$\gamma$-$Al_2O_3$ | 1.2 | Pt–Ce–Zn/$\gamma$-$Al_2O$ | 7.3 |
| Pt–Ce/$\gamma$-$Al_2O_3$ | 2.6 | | |

hydrogen [14,15], to strongly chemisorbed hydrogen [16], to hydrogen in subsurface layers of the platinum [17]. It shows that addition of Ce and Zn promoters to Pt/$\gamma$-$Al_2O_3$ catalyst can greatly promote its ability to adsorb hydrogen, especially in the high temperature range. The mechanism of the increase in spillover observed with Ce and Zn promoters is unclear. Similar results that addition of Sn can increase the amount of spillover of hydrogen were reported by others [18]. Pt sites are necessary for $H_2$ dissociation, and the amounts of hydrogen desorbed over Pt–Ce–Zn/$\gamma$-$Al_2O_3$ catalyst, corresponding to many monolayers on the available Pt, confirm that hydrogen must be on the support surface. Previous studies have shown that, over Pt–Sn/$\gamma$-$Al_2O_3$ catalyst, the high temperature adsorbed hydrogen aids in maintaining catalyst activity, most probably by reducing coking on the metal [11]. Therefore, the high amount of available reactive hydrogen over Pt–Zn/$\gamma$-$Al_2O_3$ and Pt–Ce–Zn/$\gamma$-$Al_2O_3$ catalysts could favor to reduce the coking on the surface and further increase the selectivity and stability of catalyst.

The interaction of propylene with the catalysts was examined by means of $C_3H_6$-TPD. The TPD spectra are presented in figure 4. TPD measurements clearly show that a small amount of propylene remains adsorbed on the catalysts and is released at different temperatures. The temperature of desorption peak reflects the extent of the interactions between propylene and catalysts. The desorption peak of propylene over Pt/$\gamma$-$Al_2O_3$ catalyst around 87 °C shifts to higher temperature (about 102 °C) as the presence of Ce promoter. However, an adverse trend appears due to the presence of Zn promoter. The desorption peak of propylene shifts to lower temperature (about 71 °C). A compromise temperature of desorption peak (about 82 °C) is observed over Pt–Ce–Zn/$\gamma$-$Al_2O_3$ catalyst. Obviously, the effects of Zn and Ce promoters on the interactions between propylene and catalysts are different. Zn promoter tends to decrease the interactions, however Ce promoter tends to increase the interactions. The desorption peak indicates that the addition of Zn weakens the adsorption of propylene thereby, decreasing the amount of adsorbed propylene and increasing the selectivity of propylene in propane dehydrogenation. It is concluded that the decrease in the amount of deposited coke upon addition of Zn is partly caused by the promotion of propylene desorption as a result of dehydrogenation. This enhanced propylene desorption prevents propylene from converting into higher-order dehydrogenation products, which are coke precursors. The role of Ce promoter in interactions between propylene and catalysts is opposite, which causes the appearance of a comparative higher amount of deposited coke upon addition of Ce. But, when Zn and Ce promoters coexist, a moderate adsorption of propylene may appear.

### *3.2.4. Coke quantitative analysis*

The amount of coke on each used catalyst was quantified by $O_2$-pulse technique and the results are shown in figure 5. It shows that addition of Ce to Pt/$\gamma$-

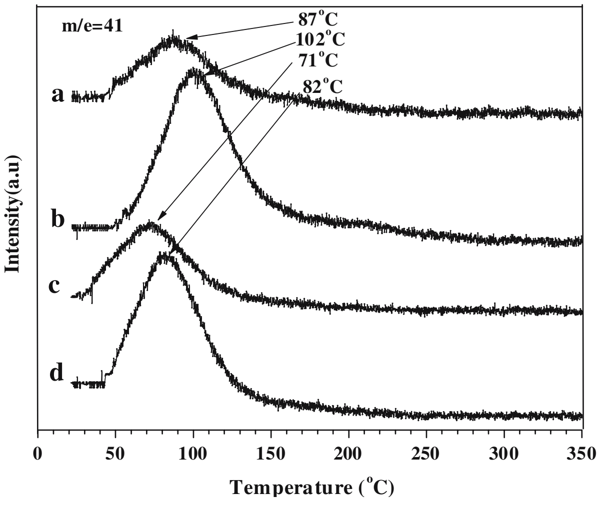

Figure 4. TPD measurements following propylene adsorption on the catalysts at 20 °C. (a) Pt/$\gamma$-$Al_2O_3$, (b) Pt–Ce/$\gamma$-$Al_2O_3$, (c) Pt–Zn/$\gamma$-$Al_2O_3$, (d) Pt–Ce–Zn/$\gamma$-$Al_2O_3$.

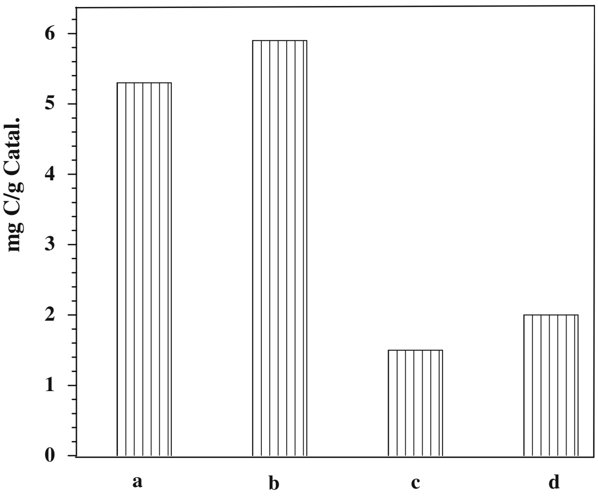

Figure 5. Amounts of deposited coke on the catalysts after $C_3H_8$ dehydrogenation reaction for 155 min at 576 °C (a) Pt/$\gamma$-$Al_2O_3$, (b) Pt–Ce/$\gamma$-$Al_2O_3$, (c) Pt–Zn/$\gamma$-$Al_2O_3$, (d) Pt–Ce–Zn/$\gamma$-$Al_2O_3$.

$Al_2O_3$ catalyst could not decrease the amount of coke, but the presence of Zn could greatly suppress the reaction of coke, which is consistent with the analysis of $C_3H_6$-TPD. The poor stability and selectivity of propylene over Pt/$\gamma$-$Al_2O_3$ and Pt–Ce/$\gamma$-$Al_2O_3$ catalysts are related to the high amount of coke over those catalysts. Coke can physically blocks active sites, resulting in the loss of activity. The amount of coke over Pt–Ce–Zn/$\gamma$-$Al_2O_3$ catalyst is much lower than those over Pt/$\gamma$-$Al_2O_3$ and Pt–Ce/$\gamma$-$Al_2O_3$ catalysts catalyst.

## 4. Conclusion

Platinum-based catalyst modified with Ce and Zn promoters are effective in propane catalytic dehydrogenation to propylene. It exhibits high stable and selective performance with respect to Pt/$\gamma$-$Al_2O_3$ catalyst. At 576 °C, 3800 $h^{-1}$, and $H_2/C_3H_8/Ar = 1/1/5$, 45% of initial propane conversion and 99% of propylene selectivity could be obtained over Pt–Zn–Ce/$\gamma$-$Al_2O_3$ catalyst while only 35% of initial propane conversion and 64% propylene selectivity were obtained over Pt/$Al_2O_3$. The introduction of Ce and Zn promoters could increase platinum particles dispersion and improve the thermal stability of Pt/$\gamma$-$Al_2O_3$, enhancing platinum particles’ ability to resist agglomeration. Ce and Zn promoters can also greatly increase the amounts of chemisorption hydrogen, which seems to be responsible for maintaining catalyst activity. Another an important role of Zn promoter is to promote propylene desorption, decreasing the amount of deposited coke and increasing the selectivity of propylene in propane dehydrogenation.

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