

## Propane dehydrogenation over PtSnMg/Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub> catalysts: effect of the amount of Mg loading

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**Abstract.** A series of PtSnMg/Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub> catalysts with different Mg loading amounts were synthesized by chemical co-deposition method and their propane dehydrogenation catalytic performances were tested. The catalysts were characterized by XRD, BET, TG, XPS. It was found that alkali metal Mg can reduce the surface acidity of carrier, improve the catalytic performance. Propane conversion peaks at Mg loading of 0.6wt.%, increasing Mg loading further than this saw a decline in conversion.

### 1. Introduction

Propene is one of the most important bulk chemicals in petrochemical industry and mainly used in the synthesis of polypropylene, acrylonitrile, propylene oxide and so on[1], in particular, its derivative polypropylene, which is widely used in the daily life. In the recent years, with the rapid development of China's real estate, packaging, textile industry, automobile industry, the traditional propene production process has been unable to meet the growing demand, in addition, due to the discover in abundance of shale gas in the USA and the uncertain price of oil in future, the catalytic propane dehydrogenation (PDH) has received much attention as an alternative way for producing propene. Now there are three companies owning the technology of industrial production of propane dehydrogenation[2,3]: UOP's Oleflex, Lummus's Catofin and Krupp Uhde's Star. A large number of companies chose UOP's Oleflex and the core part of its PDH device is the catalyst. They used catalyst PtSn/Al<sub>2</sub>O<sub>3</sub> (produced by UOP), the propane conversion was about 35% and the propene selectivity was 84% in the reaction (600-700°C). Lummus's Catofin used Cr-based catalysts (produced by Süd-Chemie AG). Cr-based catalysts[4,5] have the advantage of price, so does the carrier Al<sub>2</sub>O<sub>3</sub>, in addition Al<sub>2</sub>O<sub>3</sub> has a good mechanical stability[6,7,8]. Krupp Uhde's Star technology was applied in only one device in Egypt, the catalyst was PtSn/ZnAl<sub>2</sub>O<sub>4</sub> (produced by Uhde). For the purpose of getting a cheap and stable carrier, we used chemical co-deposition method to synthesized a composite oxide carrier Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub>. After loading the traditional PtSn[9], we got the standard catalyst - PtSn/Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub>. Mg is an alkali metal, so it may reduce the surface acidity of carrier[10]. We do the experiments to test whether Mg could improve the catalytic performance and what is the appropriate content of Mg.



## 2. Experimental

### 2.1. Catalyst preparation

$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 150ml deionized water were added into a 250ml beaker, after stirring for 5min, drops of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  was added until the pH of solution is between 4.8 to 5.1, then using the centrifuge (3800r/min) 10min to separate the precipitate. Washed the precipitate several times, dried at  $80^\circ\text{C}$  for 8h, calcined at  $550^\circ\text{C}$  for 4 h, then composite oxide  $\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$  was obtained. Loading 0.4wt.% Pt: Added  $\text{H}_2\text{PtCl}_6$  and  $\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$  into a round flask, stirring 12h, also dried at  $80^\circ\text{C}$  for 8h, calcined at  $550^\circ\text{C}$  for 4 h. The steps of loading 0.6 wt.% Sn and (0.2wt.%, 0.4wt.%, 0.6wt.%, 0.8wt.% and 1.0wt.%) Mg was the same as above steps.

### 2.2. Catalytic evaluation

Propane dehydrogenation of the catalyst (mass 0.3g) was carried out in quartz tube fixed-bed reactor. The reaction conditions: the fed gas mixture was  $\text{N}_2:\text{H}_2:\text{C}_3\text{H}_8=35:8:7$ (molar ratio); the propane weight hourly space velocity (WHSV) is  $3.0\text{ h}^{-1}$ ; the reaction temperature is  $590^\circ\text{C}$ ; the data was directly analysed by N2000 chromatography data workstation of Zhejiang University through GC-7800(FID,  $\text{Al}_2\text{O}_3$  packed column). The following formulas were used to measure the propane conversion and propene selectivity.

Content of propane in feedstock = (C2 in product  $\times 2/3$  + C1 in product  $\times 1/3$  + propane in product + propene in product)

Propane Conversion = (content of propane in feedstock - content of propane in product)  $\times$  (content of propane in feedstock) $^{-1} \times 100\%$

Propene Selectivity = content of propene in feedstock  $\times$  (content of propane in feedstock - content of propane in product) $^{-1} \times 100\%$

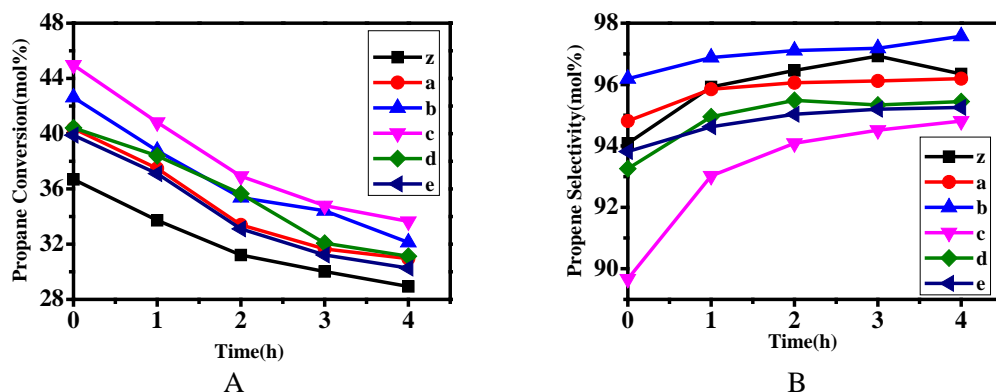
### 2.3. Catalyst characterization

Wide-angle XRD patterns were measured by a powder X-ray diffractometer (Rigaku D/max-2500) using Cu  $\text{K}\alpha$  radiation, the anode was operated at 40 kV and 100mA, the scanning rate is  $8^\circ/\text{min}$  from  $3^\circ$  to  $100^\circ$ . Micromeritics' ASAP 2020/Tristar 3000 was used to test the specific surface area, pore size and distribution. TG was in the charge of NETZSCH's TG209 to determine the amount of coke deposition the catalyst after the reaction, the sample was heated from room temperature to  $1000^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$  in air atmosphere. XPS was recorded by Kratos Analytical' Axis Ultra DLD, the test condition: X-ray source is Al  $\text{K}\alpha$  ( $h\nu=1486.6\text{ eV}$ ), using C1s line( $284.6\text{ eV}$ ) as the internal standard to calibrated the binding energies.

## 3. Results and discussion

### 3.1. Propane dehydrogenation catalytic performances

Figure 1. shows the catalytic performances of different Mg loading catalysts, z is the standard catalysts (initial propane conversion was 36.69%, final conversion was 28.94%; initial propene selectivity was 94.09%, final selectivity was 96.35%). After loading Mg, the propane conversion increased obviously, no matter the initial conversion or the final conversion. Especially catalyst C, it has the highest conversion, the initial conversion improved from 36.69% to 44.97%, the final conversion was 5 point higher than z. The amount of Mg loading is not the higher the better, the 0.6wt.% is the top point, loading more Mg will reduce the propane conversion. For propene selectivity of the catalysts, they were all nearly or higher than 90% in the whole reaction.

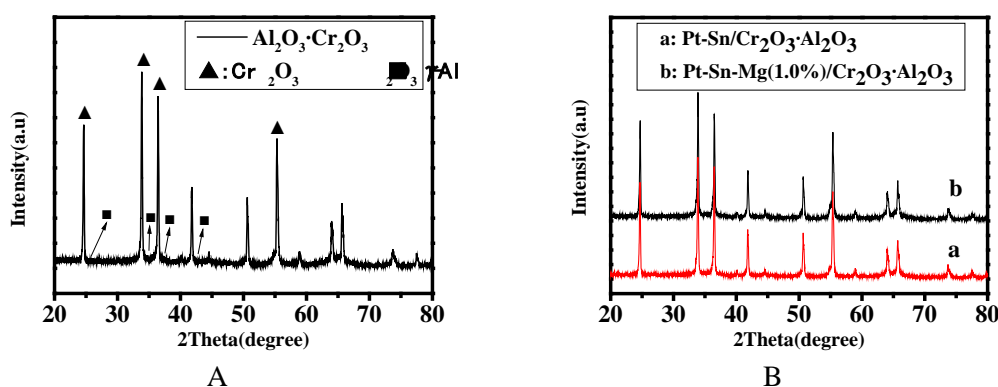


**Figure 1.** (A) Propane Conversion and (B) Propene Selectivity of the catalysts

z: Pt(0.4%)-Sn(0.6%)/Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub>      a: Pt-Sn-Mg(0.2%)/Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub>  
 b: Pt-Sn-Mg(0.4%)/Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub>      c: Pt-Sn-Mg(0.6%)/Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub>  
 d: Pt-Sn-Mg(0.8%)/Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub>      e: Pt-Sn-Mg(1.0%)/Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub>

### 3.2. Catalyst characterization

**3.2.1. XRD results** Several characteristic peak positions of Cr<sub>2</sub>O<sub>3</sub> (24.7°, 33.9°, 36.5°, 55.4°, PDF Number: 84-0315) and Al<sub>2</sub>O<sub>3</sub> (25.6°, 35.2°, 37.8°, 43.4°, PDF Number: 75-1863) are given in Figure 2. (A), which proved that the synthesized compound is composite oxides: Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub>. Due to the low loading amount of Pt, Sn and Mg and highly dispersed on the surface of the carrier, it was difficult to find their own characteristic peak as shown in Figure 2. (B).

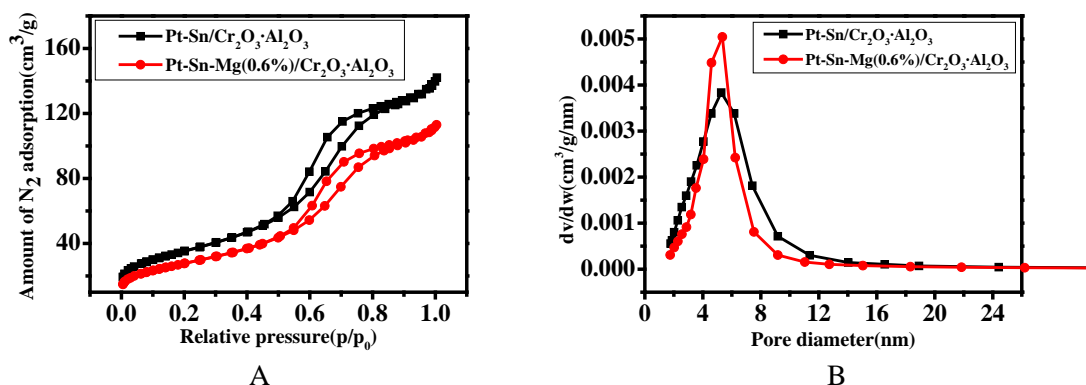


**Figure 2.** XRD spectrums of the catalysts

**3.2.2. BET results and N<sub>2</sub> adsorption-desorption results.** From Table 1. it can be seen that the BET Surface area of the carrier Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub> was up to 123.82 m<sup>2</sup>/g and the catalyst PtSnMg/Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub> was 100.52 m<sup>2</sup>/g still higher than 100 m<sup>2</sup>/g, which means more active Pt sites would be exposed in the reaction. Figure 3. (A) the N<sub>2</sub> adsorption-desorption isotherms exhibits the type IV isotherm hysteresis loops of type H1, indicated the catalyst was a kind of mesoporous material with a narrow pore size distribution. After loading Mg, a small part was into the holes and large part was on the surface so the pore diameter was rise slightly from 5.65nm to 5.77nm.

**Table 1.** BET of the catalysts

Catalyst	Surface area ( $\text{m}^2/\text{g}$ )
$\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$	123.82
$\text{Pt-Sn-Mg}(0.6\%)/\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$	100.52



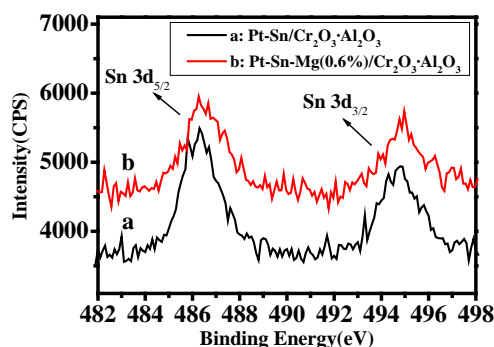
**Figure 3.**  $\text{N}_2$  adsorption-desorption isotherms (A) and Pore size distribution curve of catalysts (B)

**3.2.3. TG results** Coke is one of the reasons that make the catalysts deactivation. TG was used to analysis the coke. As shown in Table 2, compared to catalyst  $\text{PtSn}/\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ , after loading Mg, the coke of  $\text{PtSnMg}/\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$  reduced clearly, from 2.89wt.% to 1.40wt.%, indicated Mg can improve the ability of anti-coke deposition.

**Table 2.** Coke of the catalysts

Catalysts	Coke(wt.%)
$\text{Pt-Sn}/\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$	2.89
$\text{Pt-Sn-Mg}(0.6\%)/\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$	1.40

**3.2.4. XPS results** Figure 4. shows the XPS corresponding to the  $\text{Sn}3d_{5/2}$  binding energy of the catalysts[11]. A slight move to the high binding energy can be seen from  $\text{PtSn}/\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$  to  $\text{PtSnMg}/\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ , it indicated the alloying degree between Pt and Sn was changed, Sn could keep at a high valence:  $\text{Sn}^{2+}$ ,  $\text{Sn}^{4+}$ . That means there would be more active catalytic sites.



**Figure 4.** XPS spectra of the catalysts

#### 4. Conclusion

A series of PtSnMg/Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub> catalysts with different Mg loading amounts were prepared by chemical co-deposition method and the catalysts showed a prominent activity for propane dehydrogenation, proving Mg could improve the catalytic ability. With the increasing of Mg, the propane conversion was rising to the top at first and then fall down. The catalyst PtSnMg(0.6wt.%)/Cr<sub>2</sub>O<sub>3</sub>·Al<sub>2</sub>O<sub>3</sub> had the highest propane conversion: initial conversion was 44.97%, final conversion was 33.65% and propene selectivity was above 90% for the time-on-stream under study. These catalysts exhibited some promising results and could pave the way for commercial dehydrogenation catalysts with improved performance and durability.

#### Acknowledgements

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