Hierarchical MgAl_2O_4 supported Pt-Sn as a highly thermostable catalyst for propane dehydrogenation

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Abstract: Highly thermal stability is an essential property for propane dehydrogenation (PDH) catalysts that need to be regenerated frequently in oxidative atmosphere. A kind of hierarchical MgAl_2O_4 with flower-like morphology is prepared by alcohothermal method and used to support Pt and Pt-Sn. The materials are characterized by ICP-AES, SEM, TEM, XRD, Py-IR, and N_2 physi-sorption. Hierarchical MgAl_2O_4 supported Pt shows great thermal stability under oxidizing atmosphere at 800°C . Supported Pt-Sn catalyst for PDH shows high stability of performance during 10 cycles of dehydrogenation-regeneration runs. The high stability could originate from the existence of relatively abundant $\text{MgAl}_2\text{O}_4(111)$ facets on MgAl_2O_4 .

Keywords: propane dehydrogenation; MgAl_2O_4 ; Pt-Sn; thermostable catalyst

1 Introduction

Propylene is one of the most important petrochemical industry products, which can be used to produce polypropylene, acrylonitrile, propylene oxide, propenoic acid and so on. Since the demand of propylene in global market is growing rapidly in recently years, propane dehydrogenation (PDH), as an on-purpose technology for propene production, has become an attractive option to fill the widening gap between the demand and the production[1].

All the commercial PDH processes suffer from coking problem and the PDH catalyst need to be regenerated frequently [2, 3]. During this process, the catalysts are undergone oxidation treatment at high temperature to remove coke and the agglomeration of Pt particles, widely used in several PDH processes[1-3], is *inevitable*. This would further increase the complexity of catalyst regeneration process. For example, a oxychlorination reaction is used to re-disperses Pt in the Oleflex process[4, 5]. Therefore, the thermal stability of PDH catalyst is of great practical importance[6].

Magnesium aluminate (MgAl_2O_4) has high thermal stability, mechanical strength and lower surface acidity, and is useful in heterogeneous catalysis[7, 8]. Numerous research work has been reported to testify the high performance of this kind of material using as the dehydrogenation catalyst support[9-11]. But the *thermal* stability of these catalysts is seldom concerned. Recently, Li et al[12] discovered that the specific MgAl_2O_4 facets could stabilize Pt nanoparticles in oxidizing atmospheres. They rationalize that the exceptional stabilization originates from the epitaxially

matched structure and the strong electronic attractions[13]. Based on these findings, stable supported precious metal catalysts could be developed.

In this work, hierarchical MgAl_2O_4 was prepared by using alcohothermal method and used as carriers for Pt and Pt-Sn. The thermal stability and the catalytic performances of Pt and Pt-Sn supported on MgAl_2O_4 synthesized with different methods were compared. The influence of the morphology on the catalysts' thermal stability is revealed and providing a way to develop highly stable catalysts for PDH processes.

2 Experimental

2.1 Catalysts preparation

The hierarchical MgAl_2O_4 spinel was synthesized according to ref.[12], in which stoichiometric quantities of $\text{C}_9\text{H}_{21}\text{AlO}_3$ (99.9%, Sinopharm) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%, Sinopharm) were mixed in ethanol (99.99%, Shanghai Titan Scientific). After stirring for 1h, the compound was heated to 150 °C and held for 12 h. After evaporating the ethanol at room temperature, the solid was dried at 90 °C overnight. Finally, the powders were calcined at 800 °C for 12 h in air. This spinel was denoted as MgAl_2O_4 -ALT. For comparison, a MgAl_2O_4 sample was prepared by co-precipitation method[12]. Stoichiometric quantities of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%, Sinopharm) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.99%, Sinopharm) were mixed in deionized water. The ammonia was added into the solution dropwise under stirring until the pH reached ~9.5. After stirring for 12 h, water was evaporated and solids were obtained by following procedures described above. This sample was denoted as MgAl_2O_4 -CPT.

Supported Pt catalysts were prepared by incipient wetness impregnation using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (99.9%, Sinopharm) as Pt precursor. Supported Pt-Sn catalysts were prepared by co-impregnation method using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (99.9%, Sinopharm) as metal precursors[14]. The Sn/Pt molar ratio of 0.5 was used in this study. After impregnation, all the samples were dried at 120 °C for 12 h and calcined at 550 °C for 5 h. In all catalysts, the load of Pt is 1.0%.

2.2 Catalysts characterization

The metal loading of the catalyst was determined by ICP-AES (Agilent ICP-725ES, Agilent Technologies, USA). The metal particle size and distribution were characterized by CO-Chem (AutoChem II, Micromeritics, USA). The sample was first heated up to 500°C and reduced in 5 vol% H_2/Ar for 1 h before the test. The morphology and particles size were detected by HRTEM (JEM-2100, JEOL, Japan) and SEM (HITACHI-S3400N, HITACHI, Japan) techniques. For the HRTEM, the accelerating voltage was 200 kV, the point resolution was 0.23 nm, and the linear resolution 0.14 nm. X-ray diffraction (XRD) was performed on a Rigaku D/Max 2550 VB/PC diffractometer using $\text{Cu K}\alpha$ radiation. The surface physical properties were detected by N_2 adsorption (ASAP 2020, Micromeritics, USA). The surface acidity was detected by Py-IR (Nicolet 6700, Thermo, USA). The pyridine was adsorbed at 50 °C for 1h, then evacuated at 200 °C for 1h. After cooled to 50 °C, the infrared spectrum was recorded at 1700-1400 cm^{-1} wave region.

2.3 catalysts tests

The PDH reaction was carried out in a $\mu\text{BenchCAT}$ reactor (Altamira

Instruments, USA) equipped with a quartz reactor with an inner diameter of 6 mm. The catalyst loading was 0.1g for all catalyst testing experiments. All the experiments were carried out at 575 °C, $\text{WHSV}_{\text{propane}} = 14.7 \text{ h}^{-1}$ and a hydrogen-to-propane molar ratio of 0.8. Argon was used as a balance gas to achieve a total flow of 76.15 mL/min. The gas composition ($\text{C}_1\text{-C}_3$ hydrocarbons, H_2 ,) was analyzed online with a 4-channel micro-GC (INFICON 3000, USA).

To verify the thermal stability, the monometallic Pt samples were firstly reduced at 500 °C in pure H_2 for 100 min, then subjected to further calcination at 800 °C for 3, 12 and 24 h respectively, then reduced again for characterization. The suffixes -fresh, -800-3, -800-12, and -800-24 were used to denote the calcination temperature and time, respectively. The stability of Pt-Sn catalysts were tested in 10 cycles of dehydrogenation-regeneration runs, during which cokes deposited on catalysts were removed at 500 °C in air (20 ml/min) for 100 min, reduced in pure H_2 (20 ml/min) at 500 °C for another 100 min before each dehydrogenation process.

3 Results and discussion

3.1 Characterization results of spinel

(Fig. 1 should be inserted here)

Scanning electron microscope (SEM) of the two samples synthesized with alcohothermal method (denoted as $\text{MgAl}_2\text{O}_4\text{-ALT}$) and co-precipitation method (denoted as $\text{MgAl}_2\text{O}_4\text{-CPT}$) were shown in Fig. S1(a, b). The morphologies of the two samples are different. $\text{MgAl}_2\text{O}_4\text{-ALT}$ has flower-like laminated structure formed by aggregation of nano-sheets (Fig. S1a), and $\text{MgAl}_2\text{O}_4\text{-CPT}$ is composed of some

clumps with irregular shapes and sizes (Fig. S1b).

X-ray diffractograms (XRD) (Fig. S2) of both samples detected crystalline magnesium aluminate spinel structures (PDF NO. 21-1152). The coherent crystal sizes determined by Scherrer equation for MgAl_2O_4 -ALT are around 11 nm, which is about two times larger than that of MgAl_2O_4 -CPT. The differences in crystallite sizes were confirmed by HRTEM images. Fig. 1a shows that crystallites in spinel MgAl_2O_4 -ALT are around 15 nm and have abundant $\text{MgAl}_2\text{O}_4(111)$ facets with lattice fringe space of 0.466 nm, and the shape of this kind of crystallite has been deduced to be cuboctahedron[12]. In comparison, the crystallites of spinel MgAl_2O_4 -CPT are smaller and have randomly exposed crystal facets (Fig. 1b).

Although the BET surface area of the two samples are similar ($95 \text{ m}^2/\text{g}$ for MgAl_2O_4 -ALT and $93 \text{ m}^2/\text{g}$ for MgAl_2O_4 -CPT), their pore structures are quite different. The pore volume and pore diameter of MgAl_2O_4 -ALT are $0.66 \text{ cm}^3/\text{g}$ and 27 nm respectively, while they are $0.37 \text{ cm}^3/\text{g}$ and 14 nm for MgAl_2O_4 -CPT. Since primary spinel crystal itself is a non-porous material, the sample pore originates from the stacking of primary particles, whose difference could be observed from Fig. S1. MgAl_2O_4 -ALT has a more openly pore orifice.

The surface acidity of these two supports was determined by Pyridine-IR spectra (Fig. S3). IR adsorption peaks around 1540 cm^{-1} and 1450 cm^{-1} are attributed to Brønsted acid site and Lewis acid site, respectively[14]. It is apparently that there are more Lewis acid sites on MgAl_2O_4 -ALT[15].

3.2 Thermal stability of $\text{Pt}/\text{MgAl}_2\text{O}_4$

(Table. 1 should be inserted here)

The Pt loadings of Pt/MgAl₂O₄-ALT and Pt/MgAl₂O₄-CPT determined by ICP-AES are 0.80 wt% and 0.81 wt%, respectively. The mean particle sizes were calculated to be 2.1 nm and 2.0 nm for freshly reduced Pt/MgAl₂O₄-ALT and Pt/MgAl₂O₄-CPT, respectively, based on the sizes of at least 200 random particles (Fig. S4), which match well with CO chemisorption results (Table 1) .

After calcined in air at 800 °C for 3 h, 12 h and 24 h, the two samples exhibit different structure stabilities. As shown in Table 1, Pt particle size of Pt/MgAl₂O₄-ALT remains almost unchanged while that of Pt/MgAl₂O₄-CPT increases from 2.0 to 4.3 nm, these results were verified by TEM images as well (Fig. S5). It also should be noted that Pt particle size distributions of Pt/MgAl₂O₄-ALT-800-24 centered at around 2.5 nm (Fig. S5a), while that of Pt/MgAl₂O₄-CPT-800-24 centered at two points around 2.4 nm and 5.5 nm (Fig. S5b). Furthermore, HRTEM images (Fig. S6) reveal that small Pt particles after thermal treatment tend to be located on the MgAl₂O₄(111) facets, while some large platinum particles can be found existing on other surfaces like MgAl₂O₄(311) (Fig. S7).

Peden et al[12] pointed out that MgAl₂O₄(111) facets can stabilize Pt nanoparticles. This stabilization originates from the epitaxially matched structure. The average distance between an oxygen sub-layer of MgAl₂O₄(111) and Pt upper layer is 2.16 Å, which is very close to the distance between two oxygen layers in bulk spinel (2.22 Å) or two Pt layers in bulk spinel (2.26 Å), indicating a strong interaction between interfacial oxygen and Pt[12]. Therefore, in our cases, more MgAl₂O₄(111)

on MgAl_2O_4 -ALT would be the reason for its ability to stabilize Pt particles resistant of sintering.

3.3 Performance and stability of Pt-Sn/ MgAl_2O_4

Pt particles on MgAl_2O_4 -CPT support have superior thermal stability. However, when used as propane dehydrogenation catalyst, its selectivity to propene is low (it is below 90.0% as shown in Fig. S8), in consistence with previous reports[16]. Therefore, some promoters should be added, among which Sn is the most frequently used one[17-19]. Usually, tin exists as SnO_x species and forms suitable structures to promote catalysts' performances. During H_2 reduction pretreatment or the reaction processes, SnO_x could be reduced to Sn^0 and alloy with Pt if they bound with oxide support weakly[20]. That would cause the loss of catalytic activity. Therefore, the stability of Pt-Sn catalysts was further tested here.

(Fig. 2 should be inserted here)

It can be seen from Fig. 2 that propane conversions for Pt-Sn/ MgAl_2O_4 -ALT and Pt-Sn/ MgAl_2O_4 -CPT are similar (~33%) at the start of reaction, but decreased with time on stream (TOS) and reached ~29% after 3.3 h of operation. The propene selectivities increase with TOS and reached around 99% for both catalysts at stabilized stage (Fig. S9). The gradual deactivation of Pt surfaces that are highly active but less selective to propene by coke deposition would be the reason for observed selectivity increase with TOS [21-24].

The stability of catalysts were tested in 10 cycles of dehydrogenation-regeneration runs (Fig. 2). At the 10th run of dehydrogenation, the

average propane conversion for the last one hour is 26.3% for Pt-Sn/MgAl₂O₄-ALT and 19.4% for Pt-Sn/MgAl₂O₄-CPT. It also should be noted that the initial propane conversion on Pt-Sn/MgAl₂O₄-CPT catalyst during 10 cycles also drops more quickly than that on Pt-Sn/MgAl₂O₄-ALT. But the deactivation rate in each cycle seems to be similar.

Coking is the dominant factor for deactivation during each dehydrogenation process. To illustrate the deactivation behavior, TG analysis of the catalysts after 10 cycles were carried out. Similar weight loss peaks centered at 425 °C and 580 °C can be found on the DTG curves (Fig. S10). The total weight loss of Pt-Sn/MgAl₂O₄-ALT is 2.20 wt%, which is a little bit lower than that of Pt-Sn/MgAl₂O₄-CPT, 2.37 wt%.

In regeneration process, catalysts were exposed to oxidative atmosphere to remove cokes deposited on Pt surfaces, but these hydrothermal conditions would facilitate agglomeration of Pt particles[12], resulting in the loss of catalysts' activities. Noting that steam generated in this process would further induce changes of Pt-Sn structure[25], that tin would segregate from PtSn particles to exposure more Pt active sites or sintering of Pt particle, depending on contacting time. The exposure of more Pt active sites would also partly account for the recovered activity and the low propene selectivity observed at the beginning of each dehydrogenation process.

Results from TEM images (Fig. S11) and CO chemisorption show that the freshly reduced Pt-Sn catalysts have the same mean Pt particle size, 1.4 nm, which are smaller than that of Pt/MgAl₂O₄ samples, indicating the enhancement of Pt dispersion by Sn. After 10 cycles of operation, mean Pt particle size of Pt-Sn/MgAl₂O₄-ALT

increases to 2.3 nm (2.4 nm estimated from CO chemisorption), while that of Pt-Sn/MgAl₂O₄-CPT increases to 4.0 nm (4.6 nm estimated from CO chemisorption). Besides, the BET surface area and pore volume of the two catalysts decrease slightly after the stability tests (Table. S1). Therefore, the sintering of Pt particles would account for the latter catalyst's higher extent of deactivation after 10 cycles of repeated usage.

(Fig. 3 should be inserted here)

It's interesting to note that TEM images (Fig. 3) show that the Pt particle size distribution of Pt-Sn/MgAl₂O₄-CPT after reaction-regeneration cycles has two peaks (one for Pt-Sn/MgAl₂O₄-ALT). Small Pt particles can be found closely adjacent to MgAl₂O₄(111) facets, while large Pt particles can be found on other crystal facets (Fig. S12). It's reasonable to deduce that the hierarchical spinel, MgAl₂O₄-ALT, could enhance the stability of supported Pt due to the existence of abundant MgAl₂O₄(111) facets. That's would be helpful for developing supported Pt catalyst with higher thermal stability and, for PDH process, reducing the cost of regeneration process.

Conclusion

A hierarchical spinel MgAl₂O₄ with flower-like morphology was synthesized by alcohothermal method, which has similar BET surface area to MgAl₂O₄ made from co-precipitation method. Supported Pt on the hierarchical MgAl₂O₄ has excellent thermal stability under oxidizing atmosphere possibly due to the existence of more MgAl₂O₄(111) facets. The hierarchical spinel supported Pt-Sn catalyst also shows higher stabilities for PDH due to the anti-sintering characteristics of this material.

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4 References

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Fig. 1 HRTEM images of MgAl₂O₄-ALT (a) and MgAl₂O₄-CPT (b).

Fig. 2 Conversion of propane in the stability tests of catalysts with 10 cycles of dehydrogenation-regeneration.

Fig. 3 TEM images of samples repeated 10 cycles of dehydrogenation-regeneration runs.

PtSn/MgAl₂O₄-ALT (a) and PtSn/MgAl₂O₄-CPT(b)

Table 1 The effect of calcination time on Pt particle size^a

Calcination time (h)	0	3	12	24
Pt-MgAl ₂ O ₄ -ALT	2.1 nm	2.5 nm	2.5 nm	2.4 nm
Pt-MgAl ₂ O ₄ -CPT	2.0 nm	3.6 nm	4.0 nm	4.3 nm

a, Particle size determined from CO chemi-sorption

Graphical abstract