



Effect of calcination atmosphere on the catalytic properties of PtSnNaMg/ZSM-5 for propane dehydrogenation

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ABSTRACT

The influence of calcination atmosphere (flowing air, static air and flowing N₂) on the catalytic properties of PtSnNaMg/ZSM-5 catalysts for propane dehydrogenation was investigated. The catalysts were characterized by XRD, BET, TEM, and TPR. Results showed that the calcination atmosphere affected greatly the catalysts in many ways including surface area, the structure of the metallic phase and the interaction between platinum and tin, which are related to their catalytic behaviors. Among the catalysts studied, the PtSnNaMg/ZSM-5 catalyst calcined in flowing air exhibited the best catalytic performance.

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1. Introduction

Platinum–tin catalysts have been intensively studied due to their applications in the hydrocarbon dehydrogenation and naphtha reforming processes [1–4] due to high catalytic properties. However, it has been reported that the catalytic performances of the catalysts would be dependent on the catalyst preparation methods [5–12]. Among these, calcination is an important factor to influence the catalytic properties [13,14]. In our previous work [15], we investigated the effect of calcination temperature on catalytic properties of PtSnNa/ZSM-5 for propane dehydrogenation. It was demonstrated that proper calcination temperature could enhance the catalytic activity of propane dehydrogenation. This phenomenon could be attributed to the strong interaction between Pt and Sn, whereas high temperature calcination could lead to the Pt sintering and suppress the dehydrogenation reaction. Huang et al. [16] investigated the effect of calcination atmosphere on Cu/Al₂O₃ catalyst for carbon monoxide oxidation and found that high temperature calcination in oxidizing atmosphere led to a redispersed copper surface and loss of activity, while in reducing atmosphere produced sintering of copper surface and increase of activity. However, to the best of our knowledge, the studies on calcination atmosphere have been scarcely made for the supported Pt–Sn catalysts.

The aim of the current work was to investigate the effect of calcination atmosphere on the structural characteristics and the catalytic properties of PtSnNaMg/ZSM-5 catalysts used in the

dehydrogenation of propane. The characterization of the catalysts was carried out by using XRD, BET, TEM, and TPR.

2. Experiment

2.1. Catalyst preparation

PtSnNaMg/ZSM-5 catalysts were prepared by sequential impregnation method. The powder H-ZSM-5 was impregnated in an aqueous solution of 0.587 M Mg(NO₃)₂ at 80 °C for 4 h, then dried at 80 °C for 3 h. Afterwards, the sample was impregnated at 80 °C for 4 h in solutions mixture of 0.033 M H₂PtCl₆, 0.153 M SnCl₄ and 0.427 M NaCl. Finally the prepared sample was dried at 80 °C for 3 h. The metal content in the sample was 0.5 wt.% Pt, 1.0 wt.% Sn, and 1.0 wt.% Na, 0.5% Mg, respectively.

Afterwards, the prepared sample was fully agglomerated with 5.0 wt.% alumina during the process of pelletization. After heating at 120 °C overnight, the sample was divided into three portions. They were calcined at 500 °C in flowing air (a flow rate of 100 ml/min), static air in a muffle furnace and flowing N₂ (a flow rate of 100 ml/min) for 4 h, respectively (part of each sample was taken out after cooling to room temperature for TPR experiment), followed by reduction for 8 h in flowing H₂ at 500 °C. The different catalysts are denoted as Cat-A, Cat-B, and Cat-C, respectively (see Table 1).

2.2. Catalyst characterization

The BET surface area and pore volume were obtained from nitrogen isotherms determined at liquid nitrogen temperature on

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Table 1
Textural properties of the various samples.

Catalysts	Atmosphere	Color	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_p (ml g^{-1})	Relative crystallinity ^a (%)
ZSM-5	Static air	White	332.1	0.2786	100
Cat-A	Flowing air	White	309.2	0.2732	36
Cat-B	Static air	White	298.4	0.2517	36
Cat-C	Flowing N_2	Gray	284.3	0.2467	37

^a Relative crystallinity considering the ZSM-5 sample as 100% crystallinity.

an automatic analyzer ASAP2020 from Micromeritics. Samples were degassed at 350 °C for 4 h prior to the analysis. The powder X-ray diffraction patterns of the samples were obtained on a XD-3A diffractometer using Cu $K\alpha$ radiation in the scan 2θ range of 5°–40°. The samples were checked for crystallinity by comparing the intensity of peak of the samples with that of parent ZSM-5 zeolites which was considered to be 100% crystalline. The Temperature-programmed reduction (TPR) was measured in TP-5000 apparatus. Prior to the TPR experiments, 0.15 g catalyst was dried in flowing N_2 at 100 °C for 1 h. Five percentage H_2/N_2 was used as the reducing gas at a flow rate of 40 ml/min. The rate of temperature rise was 10 °C/min up to 800 °C. Conventional transmission electron microscopy (TEM) studies were conducted using JEOL-2000 instrument. High-resolution TEM was performed using JEOL-JEM2010 apparatus. Samples were prepared by grinding, suspending and sonicating them in ethanol and placing a drop of the suspension on a copper grid with a perforated carbon film.

2.3. Propane dehydrogenation

The catalytic experiments were performed in a stainless fixed bed tubular reactor, at 590 °C and atmospheric pressure using a catalyst charge of 1.0 g. The propane weight hourly space velocity (WHSV) was 3 h^{-1} and the mole ratio of $\text{H}_2/\text{C}_3\text{H}_8$ was 0.25. The reaction products were analyzed with an online GC-14C gas chromatography.

3. Result and discussion

3.1. Catalyst characterization

XRD patterns of the samples are depicted in Fig. 1. Regardless of the different calcination atmosphere treatments, the XRD patterns of the different catalysts are very similar to ZSM-5 structure, which suggests that the catalysts still maintain the well-ordered microstructure of ZSM-5. According to our previous results [17,18], the platinum particles were located mainly on the external surface of

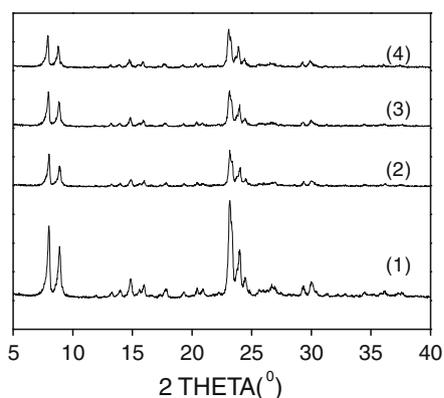


Fig. 1. XRD patterns of the different samples: (1) ZSM-5, (2) Cat-A, (3) Cat-B, and (4) Cat-C.

the zeolite, whereas part of tin, Na and Mg species could enter the channels of the zeolite. The absence of peaks for Pt should be due to the small loading amount. No phases containing different promoters could be detected on all catalysts, suggesting these species are incorporated in the network of the ZSM-5. Relative crystallinity data for all samples is shown in Table 1. It can be observed that the intensities of the (0 5 1) peak (at $\approx 23^\circ 2\theta$) decrease, implying these promoters can degrade the crystallinity of ZSM-5.

Fig. 2 shows the TEM images of the different catalysts. No agglomerated particles on Cat-A can be seen. As for cat-B, some agglomeration of metal particles on the surface of the support can be observed, which means some particles are heterogeneously distributed. It is interesting to note that the population of large particles for Cat-C increases drastically owing to their strong sintering of metal particles. Thus, it can be inferred that the metal particles distribution decreases in the order: Cat-A > Cat-B > Cat-C. In order to clarify the possibility of Pt sintering, selected area electron diffraction analysis is measured, as shown in Fig. 2(4), SADP taken from the agglomerated particles. By measuring three different groups of ring radius, the diffraction rings can be indexed as (1 1 1), (2 0 0), and (2 2 0) crystal faces of Pt. Therefore, these particles can be identified as Pt phase by such diffraction analysis. These findings suggest that the calcination atmosphere can affect the dispersion of Pt particles on the external surface of the catalysts effectively, which would have great impact on catalytic performance.

Despite high dispersion of Pt particles on Cat-A, we can't rule out the possibility of metal particles agglomeration, thus a close inspection of Cat-A is necessary. High-resolution TEM image of

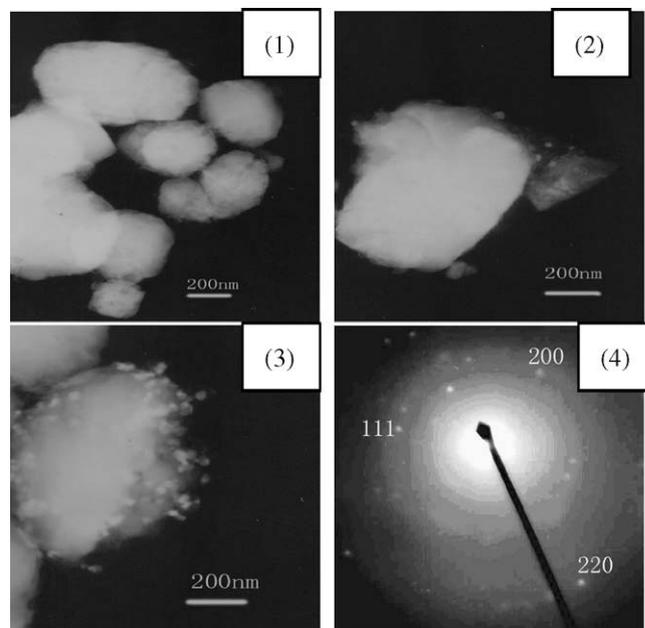


Fig. 2. TEM micrographs of the different catalysts: (1) Cat-A, (2) Cat-B, (3) Cat-C, and (4) SADP of the agglomerated particles.

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