

Catalytic Dehydrogenation of Methylcyclohexane by Pt Nanoparticles Supported on Nitrogen doped Carbon

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Abstract. Pt nanoparticles supported on nitrogen doped carbon (Pt/CN) catalysts with different surface areas were obtained and characterized by transmission electron microscope (TEM) and brunner-emmetteller (BET). The characterized results showed that Pt nanoparticles dispersed uniformly on the support surface, and the surface area of the Pt/CN catalyst increased with the increase of annealing temperature. Subsequently, the catalytic performance of Pt/CN catalysts for methylcyclohexane dehydrogenation was studied. The activity of Pt/CN catalysts in methylcyclohexane dehydrogenation increased with the increase of the surface area, Pt/CN-1000 catalyst has the largest surface area and the highest catalytic activity, with the methylcyclohexane conversion of 99% and the TOF value of 424.78 h⁻¹ at 180 °C for 150 minutes.

1 Introduction

As a renewable clean energy, hydrogen energy is gradually applied to replace the traditional fossil energy. However, hydrogen is easy to leak, flammable and explosive under normal temperature and pressure, which makes it difficult for large-scale storage and long-distance transportation. A series of hydrogen storage materials, such as MOFs, metal hydride, organic liquid hydrogen storage materials, are utilized to store hydrogen and solve the problem [1,2]. Organic liquid hydrogen storage materials can store and release hydrogen through hydrogenation and dehydrogenation process. They have attracted the attention because of the large amount of hydrogen storage, safe and cheap. The commonly used organic hydrides are cyclohexane, methylcyclohexane, decalin, etc. However, the dehydrogenation temperature of the organic liquid hydrogen storage materials is high (around 300 °C), which makes the dehydrogenation products further dehydrogenation and carbonization on the catalyst surface, resulting in catalyst deactivation and hydrogen impurity [3-5]. Therefore, it is very important to develop a low temperature and high efficiency catalyst for organic liquid dehydrogenation.

Noble metals (such as Pt, Pd, Rh, Ir) have been employed as organic liquid dehydrogenation catalysts [6-12]. Pt is favoured by researchers for its excellent stability and oxidation resistance. In order to improve the activity of catalysts, Pt based bimetallic catalysts have been reported. Another strategy to improve catalytic activity is using carbon-based materials as the supports. The surface can be modified with functional groups which can change the dispersion of active components and surface electronic structure. Nitrogen doped carbon

support is one of the most widely used carbon-based supports. Nitrogen doped carbon support not only has the advantages of traditional carbon materials, N species on the surface of nitrogen doped carbon support can anchor the active component, improve the surface electronic structure of the active component and enhance the catalytic activity.

In this paper, a series of nitrogen doped carbon supported Pt catalysts were synthesized for the dehydrogenation of methylcyclohexane. The physical and chemical properties of the catalyst were characterized by BET and TEM. The study on the dehydrogenation of methylcyclohexane showed that the larger specific surface area of the catalyst, the better dehydrogenation performance of methylcyclohexane. Pt/CN-1000 exhibited the best catalytic activity which was four times of commercial Pt/C (TOF value).

2 Experimental

2.1 Materials

Methylcyclohexane (CH₃C₆H₆), glucose (C₆H₁₂O₆), dicyandiamide (C₂H₄N₄), chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O), sodium borohydride (NaBH₄), sodium hydroxide (NaOH), ethanol (CH₃CH₂OH) and Pt/C were purchased from Shanghai Chemical Reagent Company. SiO₂ colloidal was purchased from Aldrich. All reagents were used as received and without any other purification.

2.2 Catalysts Preparation

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Synthesis of Nitrogen doped Carbon Support (CN). In a typical experiment, a mixture of dicyandiamide (2 g), glucose (2 g) and SiO₂ colloidal (8 g) in H₂O (40 mL) was added to 150 mL round-bottom flask and evaporated at 120 °C. The products were annealed in a tubular furnace at 700-1000 °C for 3 hours under Ar atmosphere. After centrifugation, washing to neutral and drying, nitrogen doped carbon support (CN) was obtained.

Synthesis of Pt/CN Catalysts. H₂O (40 mL) was added in 100 mL round-bottom flask, and then CN support (400 mg) and H₂PtCl₆·6H₂O (640 μL 0.1g/mL) were added. After stirring for 24 hours at room temperature, the dispersion was reduced by NaBH₄. After centrifugation, washing and drying, the catalysts were obtained and labelled as Pt/CN-x (where x represents the annealing temperature).

2.3 Catalysts Characterizations

The morphologies of catalysts were performed on transmission electron microscope (TEM, JEM-2100UHR). The surface area and pore size of catalysts were determined at Micromeritics ASAP 2020 instrument by N₂ adsorption/desorption isotherm.

2.4 Catalytic Dehydrogenation of Methylcyclohexane

Catalyst (120 mg) and methylcyclohexane (420 μL) were sealed into the reaction tube, and the air in the reaction tube was replaced by argon. Subsequently, the reaction tube was heated to 180 °C (the temperature of catalyst surface) for the dehydrogenation reaction.

3 Results and Discussion

3.1. Physicochemical properties of Pt/CN catalysts

The N₂ adsorption/desorption isotherms and pore size distribution curves of Pt/CN catalysts were shown in Fig. 1 and the processed data were listed in Table 1. The BET surface areas of Pt/CN-x (x=700-1000) catalysts increased gradually with the increase of temperature and were mainly distributed in the 595.65-884.86 m²·g⁻¹. However, there were no significant difference in the pore size of the catalysts. As shown in Fig. 1(b), the pore sizes were mainly distributed in the 10.1-10.7 nm.

In order to better understand the catalytic performance of the Pt /CN-x (x = 700-1000) catalysts, the catalysts were tested by ICP-AES, and the detailed data are shown in Table 1. The Pt loading of Pt/CN-x (x=700-1000) catalysts were 2.35 wt%, 2.63 wt%, 2.95 wt%, 3.34 wt%, respectively. The results show that with the increase of surface area, the amount of Pt adsorbed on the support surface increases gradually. The results revealed that all Pt/CN catalysts have homogeneous mesoporous structure and Pt/CN-1000 catalyst has the highest surface area and the highest Pt loading amount.

| Sample | Pt (wt%) | S _{BET} (m ² /g) | d _{BJH} (nm) |
|------------|----------|--------------------------------------|-----------------------|
| Pt/CN-700 | 2.35 | 595.65 | 10.1. |
| Pt/CN-800 | 2.63 | 699.53 | 10.7 |
| Pt/CN-900 | 2.95 | 762.31 | 10.3 |
| Pt/CN-1000 | 3.34 | 884.86 | 10.2 |

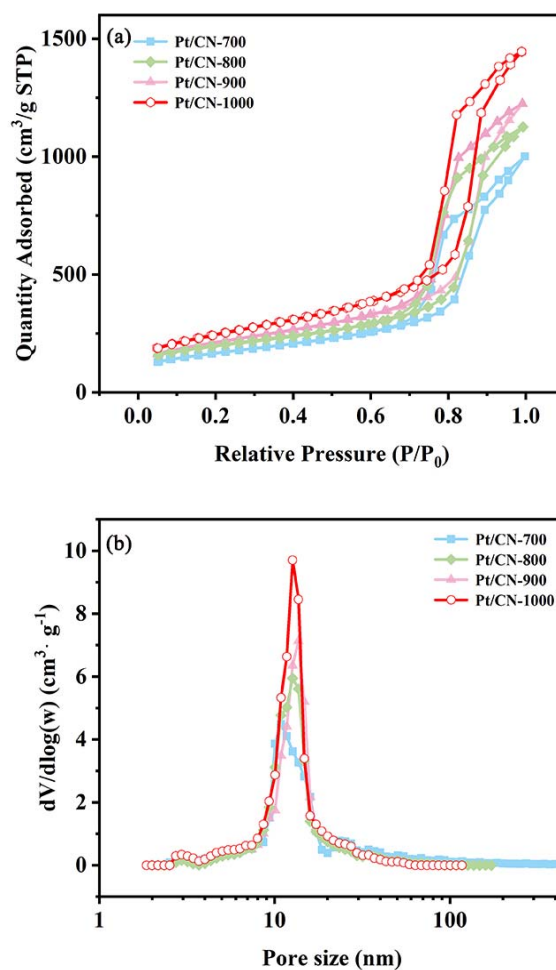


Fig. 1. The N₂ adsorption/desorption isotherms and pore size distribution curves of Pt/CN catalysts

The TEM photographs and particle size chart of Pt/CN-x (x=700-1000) catalysts are shown in Fig. 2. It can be seen from Fig. 2 that the surface of the nitrogen doped carbon support are honeycombed structure and Pt nanoparticles are uniformly distributed on the surface. The size distribution of Pt nanoparticles was obtained by counting 200 particles in TEM images. The size of Pt nanoparticles on the supports with different annealing temperatures was slightly different, and the average Pt particle size of all Pt/CN catalysts was mainly distributed in 2.35-2.76 nm. It is revealed that the size of Pt particles is also affected by the surface area of the catalyst support.

Table 1. Physical parameters sections of Pt/CN catalysts

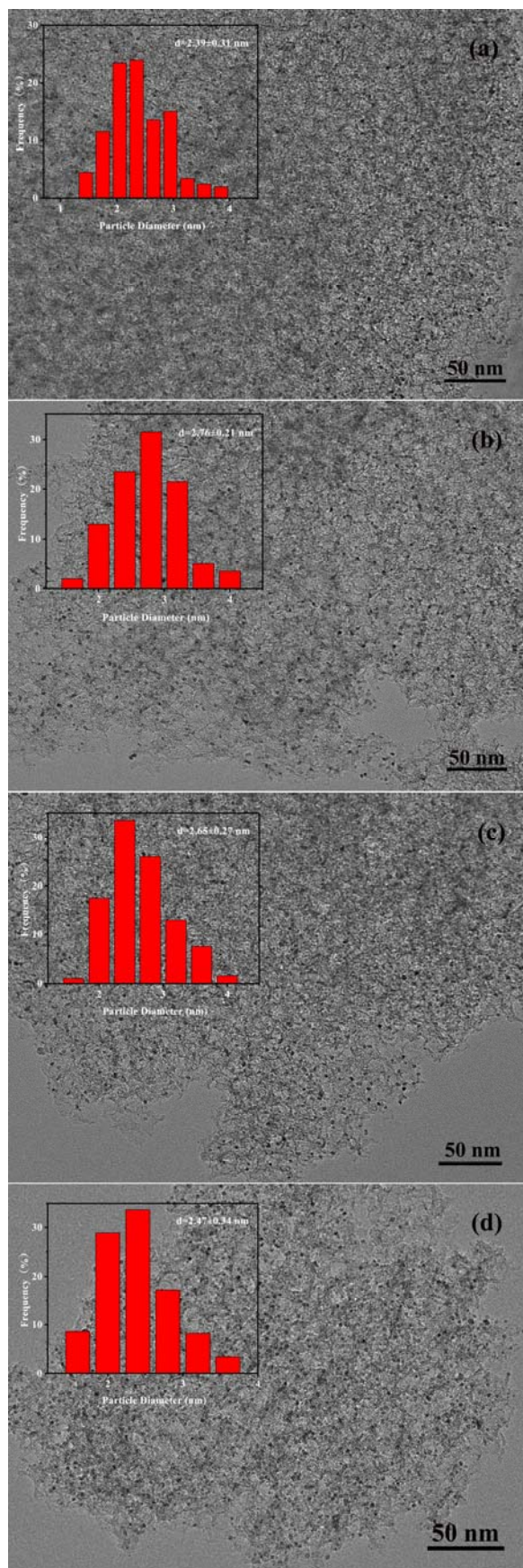


Fig. 2. TEM images of Pt/CN catalysts

3.2 Catalytic activity

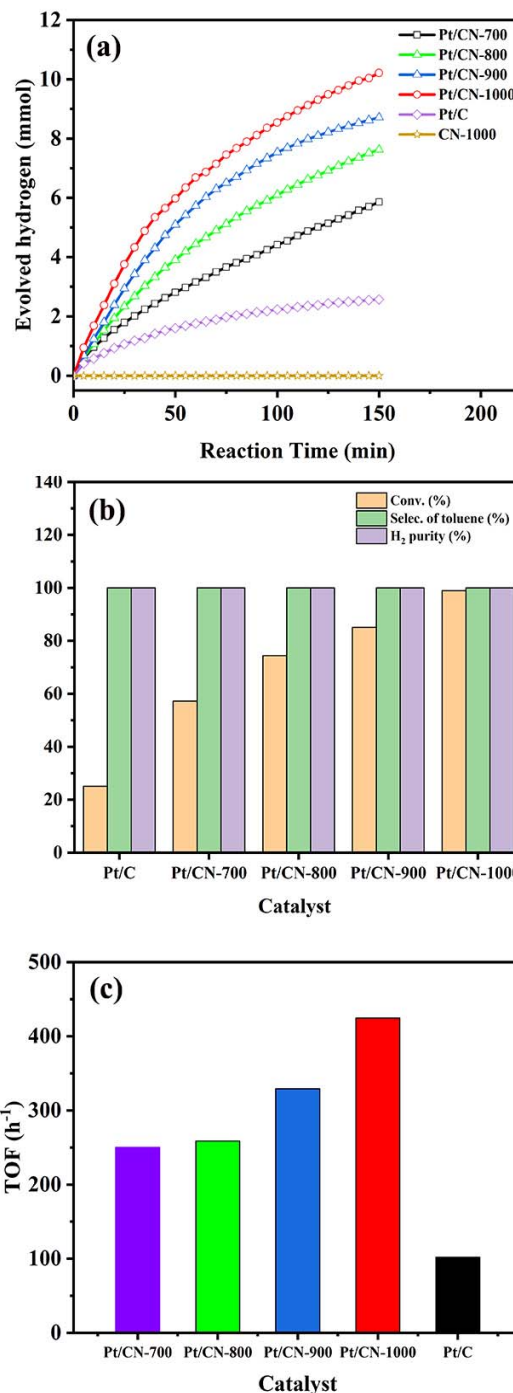


Fig. 3. Catalytic performances of Pt/CN catalysts

The catalytic performances of Pt/CN- x ($x=700-1000$) catalysts over dehydrogenation of methylcyclohexane were shown in Fig. 3. Compared with commercial Pt/C catalyst, Pt/CN- x ($x=700-1000$) catalysts have better performance in dehydrogenation of methylcyclohexane. Among them, Pt/CN-1000 has the highest hydrogen production and conversion, and the conversion reaches 99%. To compare the catalytic activity of the catalysts more clearly, the turnover frequencies (TOF) of the catalysts are shown in Fig. 3(c). With the increase of annealing temperature, the TOF value of Pt/CN- x ($x=700-1000$) catalysts increase gradually. The TOF value of Pt/CN-1000 catalyst was 424.78 h^{-1} , which was

4 times of commercial Pt/C. It indicated that higher catalytic activity can be obtained with larger specific surface area and Pt/CN-1000 catalyst exhibited the best catalytic activity in methylcyclohexane dehydrogenation .

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4 Conclusions

In this work, Pt nanoparticles supported on nitrogen-doped carbon catalysts were synthesized. By adjusting the annealing temperature of the support, mesoporous Pt/CN catalysts with different surface areas were obtained. It was found that with the increase of annealing temperature, the specific surface area of the catalyst increased gradually, and the catalytic activity for methylcyclohexane dehydrogenation increased gradually. The Pt/CN-1000 catalyst has the highest catalytic activity and the conversion of methylcyclohexane reaches 99% and the TOF value is 424.78 h^{-1} at $180 \text{ }^\circ\text{C}$.

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