Pt Nanoparticles Supported on Nitrogen doped Carbon as an Efficient Catalyst for Decalin Dehydrogenation

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Abstract. A novel Pt/CN catalyst was synthesized by sodium borohydride treatment. The physical and chemical properties of Pt/CN catalyst were characterized by X-ray diffraction (XRD), brunner-emmet-teller (BET), transmission electron microscope (TEM) and High-resolution transmission electron microscopy (HRTEM). The characterized results showed that the catalyst has a high specific surface area, mesoporous structure and the mean size of Pt nanoparticles is 2.59 nm. Subsequently, the catalytic performance of Pt/CN catalyst for decline dehydrogenation was studied. Pt/CN catalyst exhibited excellent performance in decalin dehydrogenation with the conversion of decalin was 30.70%, and the selectivity of naphthalene was 90.86% at 200 ℃ for 150 minutes. When the reaction temperature increased to 210 ℃, the conversion of catalyst increased to 52.02%, and the selectivity of naphthalene reduced to 90.21%. The possible reason may be attributed to the difficulty in converting decalin to tetralin. This paper would provide a novel method for the synthesis of efficient dehydrogenation catalyst of decalin..

1 Introduction

Hydrogen energy has attracted wide attention because of its environmental friendliness, recyclability and high combustion calorific value. It is considered to be one of the best alternatives to traditional fuels. However, hydrogen is easy to leak and explode at ambient temperature, which making it difficult to store and transport. In order to solve this problem, many hydrogen storage technologies have been studied, such as high-pressure gaseous hydrogen storage, liquefied hydrogen storage, metal alloy hydrogen storage and organic liquid hydrogen storage [1-3]. Decalin has been widely favored as an organic liquid hydrogen storage material due to its high hydrogen storage capacity (7.3 wt%) and inexpensive price. As a strong endothermic reaction, the reaction of decalin dehydrogenation requires to be carried out at high temperature, which makes the catalyst easy to coking and deactivation [4, 5]. Therefore, it is urgent to develop an efficient catalyst for decalin dehydrogenation.

Noble metals (such as Pt, Pd, Rh, Ir) were used as active component for decalin dehydrogenation [6,7]. Among them, Pt was widely used because of its high catalytic activity and oxidation resistance. To further improve the catalytic activity of catalyst for decalin dehydrogenation, a series of attempts have been made. One method to improve the dehydrogenation activity of decalin was added the second component (such as W, Re, Ir) to prepare bimetallic catalyst [6,7]. Another method to improve the dehydrogenation performance of decalin was regulated the catalyst supports, such as Al_2O_3 and carbon-based support [8-11]. Carbon-based support was one of the commonly used catalyst support for decalin dehydrogenation, which surface could be controlled and modified by the functional groups. The dehydrogenation performance of decalin was affected by the type of carbon materials, pore structure and specific surface area. Li and coworkers [9] studied the effect of carbon nanofiber (tubular (t-CNFs), fishbone (f-CNFs) and plate (p-CNFs)) supports with different morphologies on the dehydrogenation performance of decalin, and found that the best dehydrogenation performance of decalin was obtained by using the p-CNFs as the support. Sebastián and coworkers [10] pointed out that the catalyst with large specific surface area can obtain better initial activity, the small pore size would hinder the mass transfer of the products, thus reducing the dehydrogenation activity of decalin. Lee and coworkers [11] found that Pt nanoparticles could be dispersed effectively by oxidation treatment of carbon support, which can improve the dehydrogenation activity of decalin. Therefore, a fine carbon support was important to improve the dehydrogenation performance of decalin.

In this paper, a novel nitrogen-doped carbon supported Pt catalyst with large specific surface area and pore size was synthesized. The experimental results showed that the Pt/CN catalyst exhibited excellent activity of decalin dehydrogenation. The conversion of decalin was 30.70% and 50.02% at 200-210℃ for 150 minutes, respectivly.The catalyst physical and chemical property was obtained by XRD, BET, TEM and HRTEM.

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2 Experimental

2.1 Materials

Decalin ($CH_{10}H_{18}$), chitosan (($C_6H_{11}NO_4$)N), melamine ($C_3H_3(NH_2)_5$), chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), sodium borohydride ($NaBH_4$), sodium hydroxide (NaOH) and methanol (CH_3OH) were purchased from Shanghai Chemical Reagent Company. SiO_2 colloidal was purchased from Aldrich. All reagents were used as received and without any other purification.

2.2 Catalysts Preparation

The first step was to synthesize nitrogen-doped carbon support. Under specific experimental conditions, Chitosan (1 g), melamine(1 g) and silica colloid (4 mL) were mixed evenly in 20ml H_2O, then added into a 50ml round-bottom flask, and evaporated at 100 ℃. After drying, the product was annealed at 900℃ in nitrogen atmosphere for 3 hours. The nitrogen-doped carbon support was obtained by Etching of sodium hydroxide and washing to neutrality. The second step is to prepare Pt/CN catalyst. H_2O (20 mL), CN supports (200 mg), and $H_2PtCl_6.6H_2O$ (320 μL, 0.1g/mL) were added into a 50ml round bottom flask, respectively, then stired it at room temperature for 24 hours. The dispersion was reduced by Sodium borohydride. Finally, the product was centrifuged, washed and dried.

2.3 Catalysts Characterizations

The crystal structure of nitrogen-doped carbon supported platinum catalyst was analyzed by X-ray diffraction (XRD). The specific surface area of the catalyst was studied by brunner-emmet-teller (BET). The microstructure of the catalyst was studied by transmission electron microscope (TEM) and High-resolution transmission electron microscopy (HRTEM).

2.4 Catalytic Dehydrogenation of Decalin

Catalyst (150 mg) and Decahydronaphthalene (330 mg) were added into the reaction tube. The air of the reaction tube was changed to argon. Then, the reaction is carried out at in an oil bath. The gas and liquid products were analyzed by Gas chromatograph (GC).

3 Results and Discussion

3.1. Physicochemical properties of Pt/CN catalyst

The XRD pattern of CN and Pt/CN were shown in Fig. 1. The strong C(002) diffraction peak on CN pattern appeared at 24.39°. Compared with CN pattern, four distinct diffraction peaks appeared at 39.7°, 46.24°, 67.45°and 81.29°, which belong to the Pt(111), Pt(200), Pt(220) and Pt(311). It indicated that Pt/CN catalyst has been successfully synthesized.

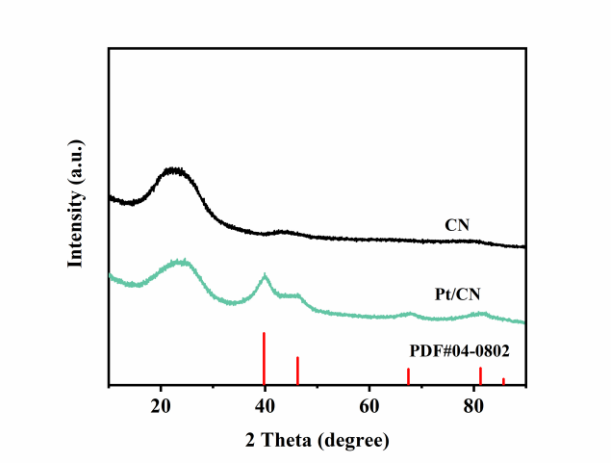

Fig. 1. XRD patterns of CN and Pt/CN catalyst

The structural properties were characterized by BET, and the results were shown in Fig. 2. Pt/CN catalyst had large specific surface area and mesoporous structure. The specific surface area of Pt/CN catalyst was 850.86 $m^2 \cdot g^{-1}$ and the pore size was 10.1 nm.

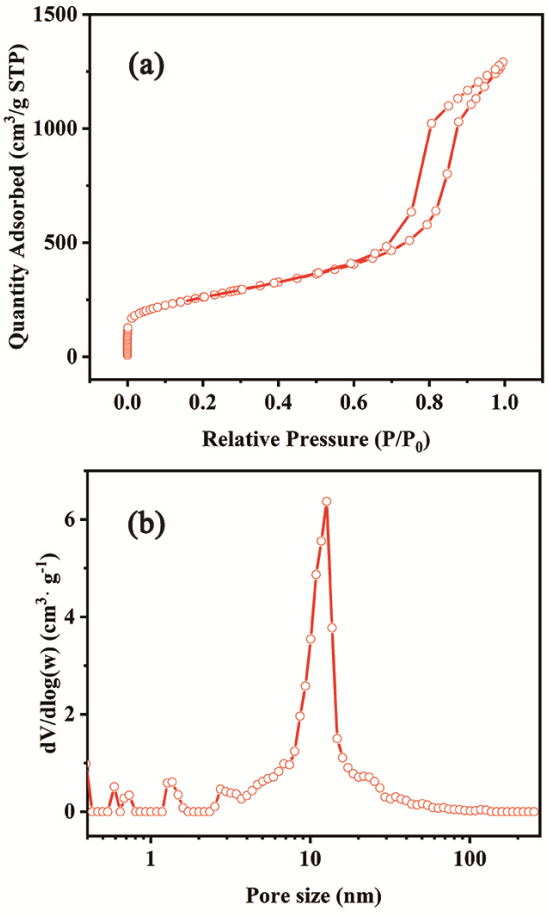

Fig. 2. The N_2 adsorption/desorption isotherms and pore size distribution curves of Pt/CN catalyst

The morphology and Pt size distribution of the catalyst was shown in Fig. 3. Fig. 3(a) and (b) showed the surface of catalyst had a lot of pore structures and Pt

particles were evenly distributed on the support. To investigate the size of Pt particles, 200 Pt particles in Fig 3(b) were counted. Fig. 3(d) showed the size of Pt particles were in the range of 1.75~3.6 nm, and the average size of Pt nanoparticles was 2.59 nm. As shonwn in Fig. 3(c), the lattice stripe gap of Pt particles were uniform and the spacing of lattice stripe was 0.226 nm corresponding to the crystal plane of Pt (111).

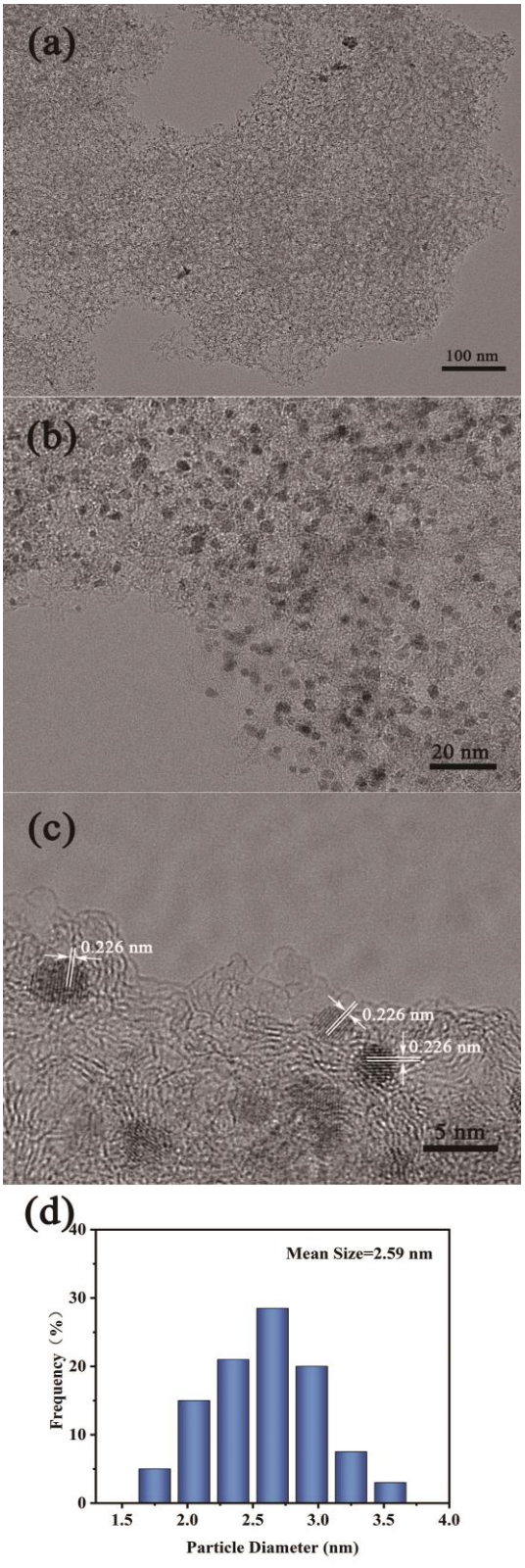

Fig. 3. (a) and (b) TEM images of Pt/CN catalyst; (c) HRTEM image of Pt/CN catalyst; (d) the size distribution of Pt particles

3.2 Catalytical activity

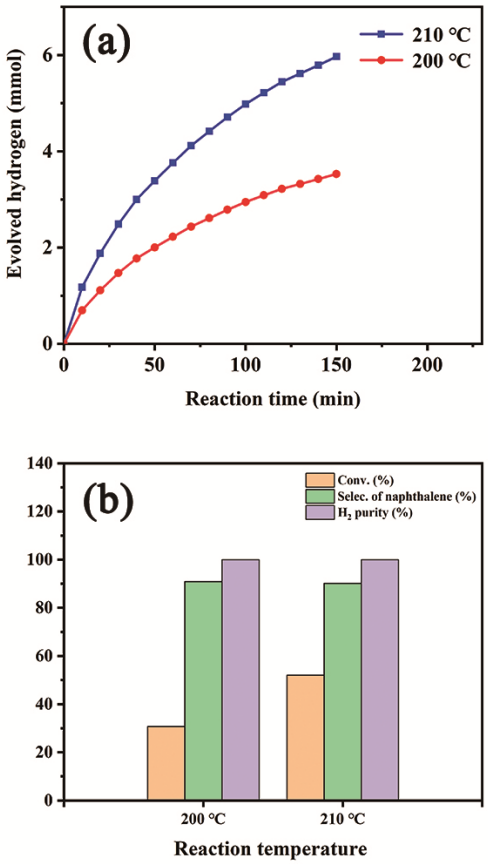

Fig. 4. Catalytic performances of Pt/CN catalyst

The catalytic performances of Pt/CN catalyst over dehydrogenation of decalin were shown in Fig. 4..The experimental results showed that the Pt/CN catalyst exhibits excellent decalin dehydrogenation activity with the conversion rate of 30.70% and the selectivity rate of 90.86% at 200 ℃. At 210℃ the conversion rate was 52.02% and the selectivity was 90.21%. With the decrease of temperature, the selectivity rate of naphthalene increases slightly. It indicated that it was easier for tetralin to be dehydrogenated than decalin.

4 Conclusions

In this work, a mesoporous Pt/CN catalyst with large specific surface area was successfully synthesized by sodium borohydride reduction. The specific surface area of the catalyst was 850.86 $m^2 g^{-1}$ and pore size of the catalyst was 10.1 nm. Pt nanoparticles were dispersed well on the surface of support with the mean size of 2.59 nm. The Pt/CN catalyst exhibited excellent catalytic performance for decalin dehydrogenation. Pt/CN catalyst catalyzed decalin dehydrogenation with the conversion rate was 30.70% (selectivity of naphthalene was 90.86%)

at 200 ℃and 52.02% (selectivity of naphthalene was 90.21%) at 210 ℃. This paper would provide a new strategy for the synthesis of efficient catalyst for decalin dehydrogenation.

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