

Preparation of CNF-supported Pt catalysts for hydrogen evolution from decalin

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ABSTRACT

A HCHO reduction method was used to prepare Pt/CNF catalysts for decalin dehydrogenation to produce pure hydrogen. The effects of pH adjustment, Pt loading and especially reduction temperature were discussed based on zeta potential and metal particle size measurement and XPS and TPR characterization. It was shown that the efficiency of Pt loading was significantly enhanced by adjusting the pH and the activity of the Pt/CNF catalyst was consequently improved. Higher Pt loading did not lead to better catalyst activity because of the growth of Pt particles. Increasing the reduction temperature promoted the reduction of Pt species but not changed the particle size. Complete reduction of the Pt catalyst was preferred to increase the catalyst activity. Excellent activity and selectivity were observed for the catalyst reduced at 80 °C with a real Pt loading of 5.40 wt.%, yielding 729.9 mol H₂/mol Pt in 2 h.

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1. Introduction

As a clean energetic fuel, hydrogen has come on stage because of the serious shortage of fossil fuels and the problems of global warming. For hydrogen to play the big roles, it is necessary to establish a viable hydrogen energy system that meets the requirement of cheap production and safe storage and transportation. Liquid organic hydrides such as decalin [1–4], tetralin [5–7] and cyclohexane [8,9] are typical hydrogen carriers with a high energy density, being easy to be transported for long distance by the use of existing infrastructure built for fossil fuels delivery. When needed, these hydrides can release high purity hydrogen under suitable conditions at a refueling station, stationary power site, or possibly even directly on-board a vehicle.

Among all the liquid organic hydrides, decalin is an environmental-friendly and low-cost candidate. Pure hydrogen evolution via decalin dehydrogenation can be realized at mild temperatures in a superheated “liquid-film state” or “wet-dry condition” over supported precious metal catalysts [1–3,8,9]. Carbon materials such as activated carbon [1–4], carbon nanotubes [10] and carbon nanofibers (CNFs) [11–13] are good supports for the metals.

CNFs have high aspect ratio, large external surface, less micropores, and stable chemical properties. In our previous study, we used CNFs with platelet microstructure to support Pt and observed the high activity in decalin dehydrogenation [13]. In addition, we found the performance of the Pt/CNF catalyst was strongly affected by the metal particle dispersion; the maximum hydrogen production rate was observed on the catalyst with Pt particle sizes of ca 2.0 nm. Therefore, the preparation of Pt catalysts with properly dispersed Pt particles is important for this process.

A good control of the nano-particle size can be achieved by the ethylene glycol reduction method as we have used in our previous study. However, glycolate anions are likely to form from the oxidation of ethylene glycol in alkaline solution, which are apt to be adsorbed on the metal colloids [14]. Though playing virtually the role of a colloid stabilizer, they might decrease the activity of the metal [15]. Removing these organics is possible by heat treatment, but is often accompanied with the unfavorable aggregation of the particles and coke formation on the metals. In addition, in comparison with some prevailing reductants used in industry, such as formaldehyde (HCHO) and methanol, ethylene glycol lacks apparently in cost-advantage.

In the present study, a HCHO reduction method has been used to prepare well-dispersed Pt/CNF catalysts for decalin dehydrogenation. In addition to the manipulation of metal particle sizes, an effort has also been made to increase the loading efficiency of Pt particles on the CNF support by pH adjustment. Moreover, the effects of reduction temperature on the dispersion and chemical state of Pt particles and consequently the catalytic properties of the catalyst have been discussed in detail.

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2. Experimental

2.1. Synthesis of CNFs

CNFs were synthesized by a chemical vapor deposition method using CO as the carbon source and ultra-fine Fe_3O_4 as the catalyst. The procedure was the same as that described in [16]. The CNFs as synthesized were then purified with 4 mol/L HCl aqueous solution at 60 °C for 4 h under vigorous agitation to remove the metal residue contained in CNFs.

2.2. Preparation of Pt/CNF catalysts

The catalyst preparation via HCHO reduction method was performed in a three-necked glass flask. Typically, 500 mg purified CNF powder was firstly suspended in 50 ml deionized water at room temperature with ultrasonic vibration for 30 min. 10 ml H_2PtCl_6 aqueous solution (5.72 mg/ml) was then added dropwise into the CNF suspension within 2 h under vigorous agitation by a mechanical stirrer. NaOH solution (1 mol/L) was used to regulate the pH of the suspension to 13 in 2 h. After that, 5 ml HCHO solution (37 wt.%) was dropwise added into the flask in 1 h. The suspension was then heated with refluxing at certain temperatures for 3 h. The pH of the cooled suspension was adjusted to 3 using HCl solution (1 mol/L). The above preparation procedure was all conducted in flowing Ar to prevent the suspension from contacting with air. The resultant suspension was then filtered. The solid, i.e. the Pt/CNF catalyst was thoroughly washed with copious deionized water and then dried at 80 °C in Ar.

2.3. Catalytic dehydrogenation of decalin

Decalin dehydrogenation was carried out in a same way as reported in [13]. Simply, 0.2 g of Pt/CNF catalyst powder and 2 ml of decalin were fed into a glass reactor placed on a plate heater at 240 °C. The temperature inside the reactor was spontaneously maintained at 193 °C during the reaction due to the equilibrium of liquid evaporation and condensation. The products after 2 h reaction were analyzed by a gas chromatograph (HP 6890). The conversion of the decalin was defined as the ratio of mass change of decalin before and after the reaction to the mass of decalin added to the reactor before the reaction, and the selectivity to naphthalene was the molar ratio of the naphthalene among the products. The term of TON (turnover number) in the paper was referred to the cumulative moles of hydrogen produced from selective conversion of decalin on per mol metal during 2 h reaction.

2.4. Characterization of Pt/CNF catalyst

The Pt loading and the Pt concentration in solution and colloid were detected using inductively coupled plasma spectrometry (ICP) in an Optima 2100 DV apparatus (PerkinElmer Instruments).

The zeta potential of Pt colloid and CNFs was measured on a Malvern Nano-ZS Zetasizer. 50 mg CNFs was suspended in 50 ml 0.01 mol/L NaCl solution, and then supersonically treated for 15 min. The pH values of the Pt colloid and the CNF suspension were altered with 0.05 mol/L NaOH and 0.05 mol/L HCl solution, respectively.

The Pt particles on the CNF surface were observed on a high resolution transmission electron microscope (HRTEM, JEOL JEM-2100) in combination with selected area electronic diffractometer (SAED). X-ray diffraction (XRD) was performed on a Rigaku D/Max2550VB/PC with $\text{Cu K}\alpha$ radiation. X-ray photoelectron spectrometry (XPS) was conducted on a PHI 5000 Versaprobe spectrometer with an Al mono radiator (1486.6 eV, 250 W). Calibration of the spectra was readily accomplished using the silicon (IV) 2p level (103.4 eV) of quartz added deliberately in the samples. The Pt dispersion was determined using CO as adsorbate on a Micromeretics Autochem II equipped with a thermal conductivity detector. Temperature-programmed reduction (TPR) was also carried out on the Micromeretics Autochem II purged with a flow of 10 vol.% H_2/Ar in a temperature range from 40 °C to 450 °C.

3. Results and discussion

3.1. Effect of pH adjustment

It has been reported that the reduction of Pt^{4+} and the nucleation of Pt particles are facilitated in a basic solution through the rapid neutralization of the proton released during the reduction [17]. Smaller colloidal metal particles can be generated by increasing the pH value. Accordingly, the solution of Pt precursors is usually regulated to high pH value so as to synthesize nano-scaled Pt particles while implementing chemical reduction process in liquid media.

In the present study, the pH of the $\text{H}_2\text{PtCl}_6/\text{CNF}$ suspension was initially adjusted to value 13 using NaOH solution. The formation of Pt colloid from the reduction of Pt^{4+} after adding HCHO as the reductant at a certain temperature (e.g. 80 °C) was thus accelerated.

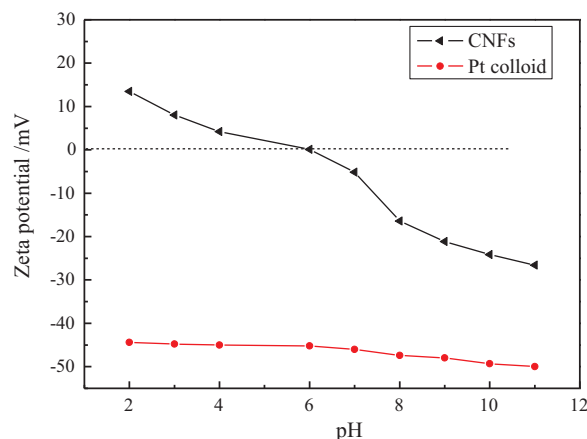


Fig. 1. Change in zeta potentials of Pt colloid and CNFs with pH.

Along with the oxidation of HCHO, the pH value of the suspension containing Pt colloid descended from 13 to 9. Despite the decline in alkalinity, the Pt colloid remained stable because its zeta potential was always negative in the wide pH range as displayed in Fig. 1, which reflects the existence of electrostatic repulsion between Pt particles [18].

For depositing the Pt colloidal particles onto the surface of CNF filaments, however, it depends on the electrostatic attraction between two different substances. As shown in Fig. 1, the zeta potential of CNFs is also negative under high pH while it can reach to zero at pH near 6 and move to positive when further reducing pH value. Since there is a huge zeta potential difference between the Pt colloid and the CNFs at low pH, a strong adsorption tendency of Pt particles onto the surface of CNFs could be expected. In view of this respect, an adjustment of pH value of the CNF suspension containing Pt colloid was made from basic (pH=9) to acidic (pH=3). Its effect on the Pt loading efficiency and consequently the catalytic properties of Pt/CNF catalyst is present in Table 1. It can be found that the Pt loading efficiency increases from 29.8% to 99.8% after altering pH value from 9 to 3, resulting in an increment of real Pt loading on the CNF support. Obviously, the pH adjustment is beneficial to the deposition of Pt colloidal particles on the support owing to the enhancement of the electrostatic attraction between them. Moreover, the conversion and selectivity of decalin dehydrogenation over the Pt/CNF catalyst are greatly improved after undergoing the pH adjustment step. The cumulative moles of hydrogen produced on per mol metal (TON) are promoted as well. This implies that in addition to possessing a higher real Pt loading the cata-

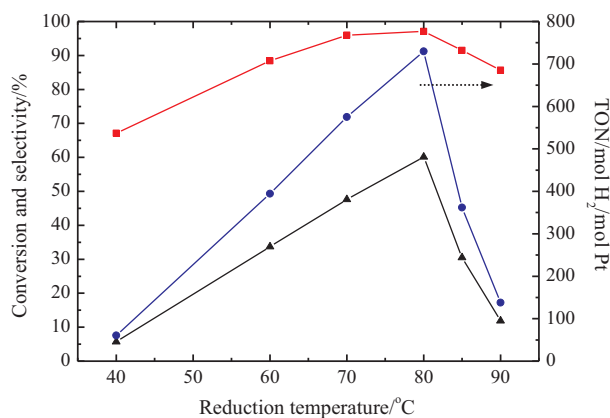


Fig. 2. Conversion and selectivity of dehydrogenation over 5.40 wt.% Pt/CNF catalysts reduced at different temperatures (\blacktriangle) conversion; (\blacksquare) selectivity; (\bullet) TON.

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