Short communication

Supported nanometric platinum–nickel catalysts for solvent-free hydrogenation of tetralin

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ABSTRACT

This paper aims to report a method of synthesizing alloyed platinum-nickel nanoclusters on activated carbon to enhance its hydrogenation performance of tetralin without adding solvents. The activated carbon provides a high surface area, while the highly-dispersed platinum acts as the hydrogen adsorption and dissociation site, in addition the Ni can alloy with Pt to induce more electron deficiency. Due to such favorable conditions, the bimetallic Pt–Ni/AC catalysts show good conversion and selectivity for hydrogenation of tetralin within a very short time. Furthermore, after six consecutive cycles, no prominent fluctuations in activity and selectivity are observed. Thus, the supported platinum–nickel nanocatalysts with excellent efficiency and prolonged lifetime for tetralin hydrogenation harbors great significance for future nanocatalyst design.

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1. Introduction

Optimal design and operation of aromatic hydrogenation process are important tasks because it is widely applied in the synthesis of fundamental raw materials, such as cyclohexane, cis- and trans-decalin and the production of high-quality diesel fuels [1,2]. A large concentration of aromatics in diesel oil decreases its quality such as cetane value, and increases the particle emissions from diesel engines [3,4]. Furthermore, the existing environmental legislations have brought more stringent requirements in terms of the aromatic content in diesel fuels [5–7]. This triggers extensive researches on highly active catalytic systems for hydrotreating processes in refinery industry.

As compared with the traditional transition metals, noble metal catalysts are efficient and productive for aromatic compounds in hydrotreating reactions [8–11], which allows them to function under relatively mild conditions. Moreover, the adsorption and activation of aromatic molecules will be indeed enhanced with positive charge (e.g., semiconductor with positive holes or electron deficiency with a partially occupied d-band) through stronger sorbate–adsorbent interactions [12]. Herein, a new idea for the synthesis of synergetic catalysts based on the combination of the above two features has been applied in hydrogenation reactions.

In this experiment, the as-prepared nickel particles supported on carbon are modified by platinum via a galvanic replacement reaction to form platinum–nickel bimetallic nanocrystals. The prepared catalysts are thoroughly characterized by a variety of different techniques, and their catalytic activity has been evaluated by the solvent-free hydrogenation reaction of tetralin to decalin. The results indicate a remarkable enhancement of the catalytic performance in comparison with the monometallic catalysts owing to the synergetic effect of multifunction catalytic sites.

2. Experimental section

2.1. Catalyst synthesis

The nano-Ni catalysts were synthesized at room temperature through the reduction of 0.45 g nickel(II) precursor ($NiCl_2 \cdot 6H_2O$) by the 85 wt.% hydrazine hydrate, with the polyvinyl pyrrolidone (PVP) as a protective agent. Typically 1.25 g activated charcoal (Sigma Aldrich, LOT-242276) was dispersed in the suspension as the support Ni loading of 8.2 wt.%. The slurry was maintained at 30 °C for 12 h. Then the solution was filtered, washed thoroughly with deionized water and ethanol, and dried in a vacuum oven at 60 °C.

The Pt–Ni/AC sample was prepared by a galvanic replacement reaction with 0.5 g the as-prepared nano-Ni catalysts and an aqueous $H_2PtCl_6 \cdot 6H_2O$ solution (50 mL, 1.55 mM) at 30 °C for another 12 h [13–17]. The loading of Pt on the nano-Ni catalysts was 2.8 wt.%. The as-prepared bimetallic Pt–Ni/AC catalysts were reduced at 480 °C in a H_2 flow for 3 h before use.

For comparison purpose, the carbon support was also impregnated directly with the noble metals in order to prepare the monometallic

Table 1
Textural properties of the supports and the reduced catalysts.

Catalyst	Surface area ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Average pore size (nm)	d_{XRD}[a] (nm)	d_{TEM}[b] (nm)
Activated carbon (AC)	863	0.60	5.4	–	–
Ni/AC	552	0.43	5.7	24.9	–
Pt/AC	833	0.58	5.4	16.0	11.3 ± 3.2
Pt–Ni/AC	757	0.47	5.0	21.0	17.8 ± 4.8

  [a] Metal particle diameter from the XRD diffraction peak using the Scherrer formula.
  [b] Average diameter from the TEM photograph.

Pt/AC catalyst, while the Ni/AC catalyst was obtained through a further reduction of the as-prepared nano-Ni catalyst as references.

2.2. Catalyst characterization

Textural parameters have been calculated from the nitrogen adsorption–desorption isotherms at −196 °C with a Micromeritics ASAP 2020 analyzer. Specific surface areas were calculated by BET method and pore size distributions were calculated from desorption branch of the isotherm by the BJH model. Transmission electron micrographs (TEM) were observed on a FEI Tecnai G2 F20 operated at an accelerating voltage of 200 keV. And the X-ray diffraction (XRD) patterns were collected on a Shimadzu powder X-ray diffractometer (Cu Kα, λ = 1.540 Å). Diffraction patterns were collected from 20° to 90° at a rate of 2°/min. The VG MARK II equipment was used in this experiment to carry out the X-ray photoelectron spectroscopy (XPS) analysis. A monochromatic MgKα (1253.6 eV) X-ray source was used as radiation. Position of the energy scale was adjusted to place the C 1s feature peak at a position of 284.6 eV.

2.3. Catalyst evaluation

The setup is consisted of a magnetic stirrer and a 100 mL high pressure stainless steel (SS-316) autoclave reactor. The catalytic performance of the bimetallic Pt–Ni/AC catalysts was investigated for hydrogenation of aromatic compounds, using tetralin as a model substrate under solvent-free condition. The activity tests were measured at 100 °C and under 6 MPa hydrogen pressure, containing 0.05 g catalyst and 3 mL tetralin without adding other solvents. After the reaction, liquid samples were centrifuged to separate the catalysts from the mixture and then analyzed with a gas chromatograph (Kexiao, GC-1690, OV-1) equipped with a flame ionization detector. The catalytic performance was evaluated by the tetralin conversion which was defined as the ratio of reacted tetralin to initial tetralin. Another factor in the evaluation was the turnover frequency (TOF) which was calculated by the
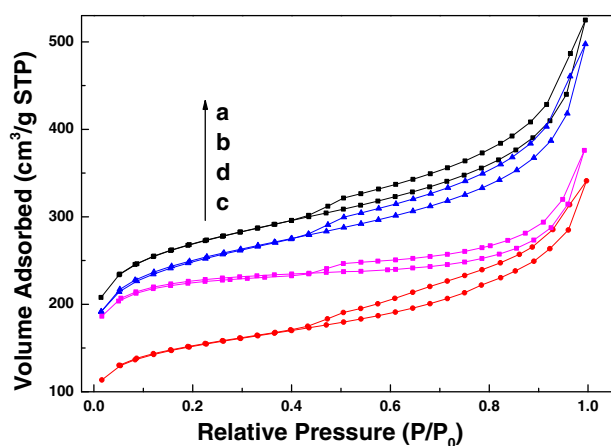
number of tetralin that got converted per time per total amount of platinum metal used in the catalyst.

3. Results and discussion

3.1. Physicochemical characterization of the catalysts

An overview of the structural properties of the catalyst was illustrated in Table 1. The adsorption/desorption isothermals and their pore size distribution were given in Figs. 1 and S1. All the samples showed a typical IV isotherm, which was the characteristic of mesoporous materials [18,19]. After the incorporation of the active components, the surface areas and pore volumes were a little lower than those of the pure carbon support (except for the uncalcined Ni/AC sample). This was caused by the introduction of Pt nanoparticles which could be grafted on the pore wall or occupied in the mesopores of the support [20]. However, the differences were not significant.

The TEM investigation provided direct evidence for the dimensional information about the metal nanoparticles. Fig. 2 showed well-defined spherical shapes with uniform size of metal nanoparticles in the bimetallic Pt–Ni/AC sample. The size distribution of the metal particles was determined from the diameters of 300 nanoparticles in an
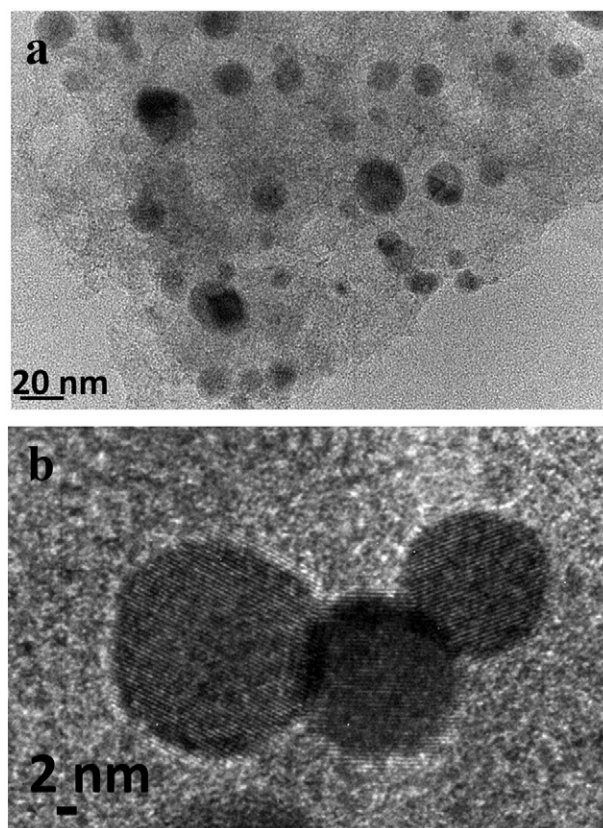

Fig. 1. Nitrogen adsorption–desorption isotherms of the supports and the reduced catalysts. (a) AC, (b) Pt/AC, (c) Ni/AC and (d) Pt–Ni/AC.

Fig. 2. TEM and HR-TEM image of the bimetallic Pt–Ni/AC catalysts.