Significance of surface oxygen-containing groups and heteroatom P species in switching the selectivity of Pt/C catalyst in hydrogenation of 3-nitrostyrene

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ABSTRACT

The selectivity of 3-nitrostyrene (NS) hydrogenation over 0.5 wt-% Pt catalysts supported on carbon materials can be switched simply by changing reduction temperature. When the reduction temperature was 150 °C, 1-ethyl-3-nitrobenzene (ENB) was mainly produced in a selectivity of 93% at a conversion of 95% (at 100 °C). When the reduction was conducted at a higher temperature of 450 °C, in contrast, the main product was switched to 3-aminostyrene (AS) in a selectivity of 96% at a conversion of 91%. That is, the Pt/C catalysts reduced at low and high temperatures could preferentially catalyze the hydrogenation of vinyl and nitro groups of NS, respectively. This switching of the product selectivity may be ascribed to actions of surface oxygen-containing functional groups and surface hetero P species. The quantity and nature of these surface species were examined in detail by a few different methods. For the low-temperature reduced catalyst, surface acidic groups present close to Pt nanoparticles ($\sim$2 nm) would interact with the nitro group of a NS molecule and make its vinyl group more likely to interact with the surface active metal species of Pt nanoparticles; this facilitates the hydrogenation of the latter and produces ENB selectively. For the high-temperature reduced catalyst, however, P species would interact with Pt and form Pt-PO$_x$ complex, on which a NS molecule is likely to be adsorbed with its nitro group, facilitating the selective production of AS via its hydrogenation. It is demonstrated that surface functional groups and surface hetero atoms (like P), in addition to main active metal species (like Pt), should have direct actions in the catalysis for such a catalyst that exposes a larger quantity of surface functional groups and/or hetero atoms compared to the number of supported metal nanoparticles.

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1. Introduction

Carbon materials, as versatile catalyst supports, have attracted extensive attention [1,2], owing to their low cost, excellent chemical stability, tunable electronic structure, optimum porosity, and abundant surface oxygen functional groups (SOFGs). The SOFGs (such as carboxyl, carbonyl, lactone, and phenolic hydroxyl) have significant impacts on the properties such as polarity, hydrophobicity, acidity, and electronic state. The properties of carbon materials can be modified by heteroatom doping (N, P, S, etc.) [3–5]. The doping of electron-rich nitrogen to carbon materials may change the surface structure, increase the hydrophilicity, enhance π-binding ability, and improve electron transport [6,7]. Phosphorous-doped carbon materials have different geometrical structure compared to parent materials and the electronic state of neighboring C atoms can be altered by creating a negative charge [8,9]. For carbon-supported metal catalysts, the SOFGs and surface heteroatom dopants of carbon materials could influence the dispersion of metal nanoparticles thereon [10–14] and the adsorption of organic substrates [15–19] and metal precursors [20,21]. To design and fabricate carbon-supported metal catalysts and understand reaction mechanisms on their surface, it is desirable to clarify the effects of SOFGs and heteroatom dopants on their catalytic actions in detail. However, such a systematic study still remains unexplored issues although the interactions between

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metal nanoparticles and carbon surface have been investigated in the past two decades [22,23].

Although selective hydrogenation has widely been used in the fine chemical industry, such as in the production of flavors, fragrances, pharmaceuticals, pigments, dyes, and agrochemicals [24–27], the preparation of more active catalysts and the understanding of reaction mechanisms are still important topics in the field of catalytic chemistry and chemical engineering [28]. Selective hydrogenation of 3-nitrostyrene (NS), having two functional groups of nitro and vinyl in a molecule, is a useful model reaction for the investigation of the catalysis of supported metal catalysts. It is reported that metal-support cooperation [29,30], alloy [31–33], intermetallic compounds [32,34], metal-ligand (modified with organics) [2,35,36], and single-atom catalysis [37] are often used as effective strategies for designing the catalysts that are selective to the hydrogenation of nitro group of NS. It is indicated that the chemoselectivity of NS hydrogenation (3-aminostyrene, 3-ethylnitrobenzene) can be switched over a Pt-quinoline@IL (ionic liquid)/CNT (carbon nanotube) catalyst by adding acid or basic organics into the reaction system [38]. In Rh/HAP (hydroxyapatite) catalytic system, the chemoselectivity can be varied by changing the source of hydrogen from H_2NNH_2 (product was 3-aminostyrene) to H_2 (product was1-ethyl-3-nitrobenzene) [39]. Those results indicate that the product selectivity can be controlled by reaction conditions for the same supported metal catalysts but those catalytic systems need complicated catalyst synthesis procedures and unfavorable additives. The present authors expected that the product selectivity of conventional carbon-supported metal catalysts could be modified by changing the amount and nature of surface functional groups of the supports, which would contribute directly or indirectly to the catalysis on their surface.

During the course of our investigation on the catalysis of ordinary carbon-supported noble metal catalysts, we have examined the activity of 0.5 wt-% Pt samples on a carbon material including several different SOFGs and hetero P atoms in the selective hydrogenation of NS in the present work. It is interesting to note that the product selectivity can be dramatically switched by reduction temperature; the low (150 °C) temperature reduced Pt catalyst selectively produces 1-ethyl-3-nitrobenzene (ENB) in a selectivity of 93% at a conversion of 95% while the high (450 °C) temperature reduced one 3-aminostyrene (AS) via hydrogenation of nitro group in a selectivity of 96% at a conversion 91%. Several different carbon-supported Pt samples were prepared using two parent carbon materials and those prepared via their surface modification in different ways and these were tested in NS hydrogenation. Various methods were used to characterize the surface of supported Pt nanoparticles and carbon supports and significant factors determining the product selectivity were examined and discussed. It should be noted that cooperation of Pt nanoparticles with SOFGs (in particular acidic groups) and interactions between Pt and hetero P species are significant for the product selectivity of the low-temperature and high-temperature reduced Pt/C catalysts, respectively. The results obtained will give new insights into the design, preparation, and catalysis of carbon-supported metal catalysts.

2. Experimental

2.1. Materials

Commercially available reagents, 3-nitrostyrene (Acros; ≥97%), $H_2PtCl_6 \cdot 6H_2O$ (Shanghai Jiu Ling; ≥99.9%), toluene, ethanol, and nitric acid (Beijing chemicals; ≥ 99.9%) were used as received. Two different raw carbon materials were used, activated charcoal (Sigma-Aldrich, untreated powder, 100–400 mesh, C3345) and

activated coconut carbon (Fujian Xin Sen, C ≥ 99.0%, ash ≤ 0.5%, bulk density 0.32–0.4 kg/L), which are abbreviated as ACH and AC, respectively, in the following. Phytic acid solution (Aladdin, 70%) was used as phosphine resource.

2.2. Catalyst preparation

Onto those ACH and AC carbon supports, 0.5 wt-% Pt was loaded by incipient wetness method. 13.3 mg $H_2PtCl_6 \cdot 6H_2O$ was dissolved in 10 mL ethanol and then 1.0 g carbon support was added to form a slurry mixture. The slurry was dried at 80 °C in a water bath while stirring and then kept at 80 °C in an oven overnight. Prior to usage, the Pt-loaded samples were reduced under pure H_2 flow at 150 °C for 2 h. The catalysts so reduced at the final temperature, T (150, 385, 450 and 500 °C), are referred to as Pt/ACH-T and Pt/AC-T in the following.

To modify the surface properties of carbon supports, the following treatments were made for ACH and AC samples. The samples were treated with a 5 mol/L HNO_3 solution at 30 °C for 20 h, then washed with H_2O and ethanol independently, and dried at 80 °C overnight, which were referred to as ACH-HNO_3 and AC-HNO_3. It was also treated with pure water at 30 °C for 20 h, washed with H_2O until the filter liquor became neutral, and dried at 50 °C overnight, which was referred to as ACH-H_2O. The AC also was treated with a phytic acid solution to dope heteroatom P in 1.7 wt-%, in which carbon support was impregnated with phytic acid with a weight ratio of 1000/517 in 10 mL ethanol solution at 30 °C for 24 h and then dried at 80 °C overnight, followed by calcination in nitrogen at increasing temperatures up to 550 °C at 2 °C/min and then at 550 °C for 2 h.

2.3. Catalyst characterization

The carbon supports and 0.5 wt-% Pt loaded catalysts were characterized by the following methods. Nitrogen adsorption-desorption experiments (BET) were performed with a Micromeritics ASAP 2020 surface area and porosity analyzer. X-ray photoelectron spectroscopy (XPS) measurements were carried on VG Microtech 3000 Multilab without sputtering. Transmission electron microscopy (TEM) images were collected on a JEOL JEM-2010 instrument operated at an accelerating voltage of 200 kV. Temperature programmed reduction (TPR) profiles were measured on Micromeritics AutoChem II 2920. For TPR, a sample (50 mg) was treated with argon at 100 °C for 1 h to remove H_2O and cooled to 50 °C. Then, the sample was heated at 5 °C/min to 700 °C in a stream of H_2/Ar mixture at a flow rate of 50 mL/min. The amount of H_2 consumed was measured by a gas chromatograph with thermal conductivity detector. The size and metal dispersion of Pt nanoparticles were examined by CO pulse adsorption at 50 °C with a pulse of CO/He (10%) on Micromeritics AutoChem II 2920. A sample weight was 50 mg and the volume of pulse was 50 mL/min. The nature and quantity of SOFGs were examined by temperature programmed decomposition (TPD) on QIC-20, Hiden, UK, with a mass spectrometer (TPD-MS). A sample (200 mg) was heated in Ar stream at 30 mL/min and at 5 °C/min from 100 to 1000 °C. The different SOFGs species were identified by analysis of TPD profiles obtained using the peak assignment and deconvolution procedures described by Figueiredo et al [40,41]. The amounts of CO and CO_2 released from 200 mg carbon supports were calibrated by those of CO and CO_2 released from a reference of 200 mg calcium oxalate. According to the chemical equation ($CaC_2O_4 \rightarrow CaO + C O_2 + CO$), CO_2 and CO were released and the corresponding MS signals were obtained. These calibration data were used to measure the amounts of CO and CO_2 released from carbon supports. The contents of P, S, and N contained in the carbon supports were measured by Inductively Coupled Plasma (ICP) on ThermoScientific