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Pd on boron-doped hollow carbon spheres – PdO particle size and support effects

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ABSTRACT

Boron-doped hollow carbon spheres (B-HCSs) were synthesized using a CVD injection method (BCl_3 in toluene; Ar; 900 °C; 4 h) using Stöber silica spheres as template. A Pd complex was loaded onto the B-HCSs using deposition and impregnation methods, and the materials were studied by XRD, SEM, TEM, Raman spectroscopy, TGA, ICP-OES, XPS, and ^{11}B solid-state NMR spectroscopy. The boron-doped carbon-supported Pd catalysts (Pd/B-HCS) were compared with a Pd-loaded boron-doped carbon nanotube (Pd/B-CNT) catalyst (both have a hollow interior) in the solvent-free oxidation of alcohols using oxygen as an oxidant at 125 °C under base-free conditions. The Pd particle size was varied (2.5–12 nm) by changing the Pd/B-HCS calcination temperature (200–550 °C), and this affected the activity but not the selectivity of the benzyl alcohol to benzaldehyde reaction. The data revealed the key role of the Pd particle size on the reaction that was influenced by the B–Pd–C interaction. The reaction rate depended on the mean size of Pd particles and showed a maximum when catalysts were calcined at 300 °C, revealing that the aerobic oxidation of benzyl alcohol catalyzed by the supported PdO (d_{Pd} > 2.5 nm) nanoparticles was not a structure sensitive reaction.

1. Introduction

The inertness of carbon in the form of nanotubes (CNTs) and other shaped carbons such as spheres (CSs) enables them to resist low-temperature oxidation for long periods of time. The chemical and physical properties of the new carbons can also be modified by both doping and functionalization processes, and these effects can be expected to influence the oxidative behavior of the carbons.

Studies have shown that the stability of carbon against oxidation can be enhanced by passivation with B_2O_3 (or P_2O_5) by a high-temperature treatment [1,2]. When the boron doping was increased, the oxidation temperature of the carbon nanotubes increased [3]. Also, the thermal stability of boron-doped hollow carbon spheres (B-HCSs) was found to be higher than that of undoped HCSs [4]. Recent studies have also shown that Pd loaded onto a boron-doped CNT (B-CNT) support gave palladium atoms which were adsorbed on the B-CNT surface above the axial boron-carbon bonds in the B-CNTs [5]. Thus, boron addition to modify the behavior of supported metals in the catalytic reactions is expected.

Boron inclusion enhances the resistance to oxidation of graphitic systems [6–12], but the sintering of metal particles can be typically minimized by increasing the interaction between the metal and the support by doping with boron [13,14]. Boron doping is also known to accelerate the homogeneous continuous graphitization process of carbon without formation of separate distinct carbon components. The boron is also known to enter substitutionally [15–17] into a carbon layer. It has also been found that boron can accommodate a wide variety of bonding configurations in the graphitic carbon structures.

Boron doping of carbons should lead to carbons that are well suited for use as supports in oxidation reactions. Indeed, we recently exploited this approach and found that boron doping of hollow carbon spheres (B-HCSs) gave supports that could be used in the Pd-catalyzed oxidation of benzyl alcohol [4]. From studies in the literature, the ease of carbon oxidation appears to follow the sequence: activated carbons > N-MWCNTs (N doped multiwalled CNTs) > MWCNTs > SWCNTs > B-MWCNTs (boron-doped multiwalled CNTs) [18–21].

To further exploit this approach of boron doping, we have investigated the impact of B doping by comparing B doping on two different carbons supports (HCSs and CNTs) both with hollow interiors. To vary the size of the Pd particles on the carbons, different catalyst preparation methods and activation methods have been used. We have used the benzyl alcohol oxidation reaction as the probe reaction to correlate the activity of the new Pd catalysts with their properties. In particular, the influence of the method of Pd complex deposition on different supports as well as the Pd loading and calcination temperature of the catalyst on the benzyl alcohol conversion and benzaldehyde selectivity has been investigated. The

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influence of the reaction conditions (viz. reaction time and temperature) on the catalytic performance has also been studied.

2. Experimental

2.1. Starting materials

TEOS (98%, Aldrich), NH_3 (25% Fluka), isopropanol (Merck 99%) and deionized water were used as reagents for the synthesis of silica spheres. HF (40% Associated Chemical) was used for silica removal, and a 1.0 M BCl_3 solution in toluene (Aldrich) was used as carbon and boron source, while HNO_3 (55%, Merck) was used for activation of the HCSs. B-CNT was prepared using acetylacetonates (Sigma–Aldrich, 99%) of the chosen metals dissolved in ethanol and mixed with magnesia powder to give a Fe/Al/MgO (1:1:12) catalyst [22]. Pyridine (99%, Saarchem), toluene (99% Merck), and $Pd(CH_3CO_2)_2$ (Next Chemical, SA) were used for the catalyst preparation and benzyl alcohol (99%, Fluka) was used as a model substrate.

2.2. Preparation of silica spheres with diameter (1000–1200 nm)

Monodisperse silica spheres (d = 1000–1200 nm) were synthesized following a modified Stöber procedure [23]. In this reaction, 22.4 ml of TEOS, 15.4 ml of NH_3, and 18 ml of deionized water were added into 130 ml of isopropanol after 1 h of aging under mild stirring at 40 °C. A further 22.4 ml of TEOS was then added to the above reaction mixture which was stirred at room temperature overnight, resulting in the formation of a white silica colloidal suspension. The silica particles were centrifuged, separated, and washed with ethanol and distilled water four times and dried at 80 °C for 12 h. They were finally sonicated for 15 min in a water and ethanol mixture to give well-separated monodisperse silica spheres.

2.3. Preparation of boron-doped hollow carbon spheres and nanotubes

Deposition of carbon onto the silica spheres was carried out using a CVD injection method. A 1 M BCl_3 in toluene solution was used as a carbon and boron precursor to make the B-HCSs. Briefly, the silica spheres were placed in a quartz tube and were heated to 900 °C for 4 h at a heating rate of 10 °C min^{-1} under an Ar flow (100 ml min^{-1}) at atmospheric pressure during which time the silica spheres shrank (750–800 nm). The BCl_3 containing solutions were placed in a 20 ml syringe and injected into the heated tube by means of a SAGE syringe pump (0.067 ml min^{-1} injection rate) over 4 h. The solutions were injected into the tube reactor (20 cm * 2 cm) via a specially designed quartz tube cooled by water [24]. When the solution injection was complete, the electrical furnace temperature was allowed to cool down to room temperature under an Ar flow. Black carbon/silica sphere composites were obtained. Removal of the silica using 20 wt% HF solution (15 ml HF was added to the 1.5 g carbon/silica composite and the mixture aged for 48 h) yielded hollow carbon spheres (B-HCSs). Before use as a support, the carbon supports were functionalized with concentrated HNO_3 solution at 90 °C for 8 h.

The B-CNTs were synthesized by the catalytic chemical vapor deposition (CCVD) method. The catalyst used in this study was Fe/Al/MgO [22] with a molar ratio of 1:1:12. A quartz boat containing 300 mg catalyst powder was inserted into the center of a quartz tube reactor. The reactor was heated at 900 °C in 5% H_2/Ar at a flow rate of 240 ml/min. At the required temperature, the 1 M BCl_3 in toluene solution was introduced into the reactor by means of a 20 ml syringe driven by a syringe pump at 1 ml/min^{-1} for 20 min.

2.4. Catalyst preparation

To a mixture of $Pd(CH_3CO_2)_2$ (53 mg) and toluene (100 ml) in a 200-ml two-necked flask at 80 °C was added pyridine (50 mg) during which time the brown suspension turned yellowish white to give a slurry containing $[Pd(py)_2(ac)_2]$ (py = pyridine; ac = acetate) [25,26]. Then, the B-HCS support (1 g) was added to the Pd slurry, and the mixture was stirred vigorously for 1 h at 80 °C to give a 2.5% Pd-loaded material. The obtained mixture was cooled to 0 °C, followed by filtration and washing with diethyl ether (20 ml) three times. The resulting solid was dried in vacuo at room temperature. This catalyst was called Pd/B-HCS. The catalyst was calcined for 3 h at various temperatures 80, 120, 180, 300, 400, 450, 500, 550, 600, and 650 °C and the calcined materials called Pd/B-HCS80, Pd/B-HCS120, Pd/B-HCS180, Pd/B-HCS300, Pd/B-HCS400, Pd/B-HCS450, Pd/B-HCS500, Pd/B-HCS550, Pd/B-HCS600, and Pd/B-HCS650, respectively. Two other catalysts were prepared by the same procedure as described above but using silica spheres and B-CNTs as supports. The material generated from silica spheres and B-CNTs calcined at 300 °C were called Pd/SiS and Pd/B-CNT. Also, 1, 2, and 3 wt% palladium-loaded catalysts were prepared by the same method and called Pd/B-HCS1, Pd/B-HCS2 and Pd/B-HCS3, respectively.

A catalyst was also made from an aqueous solution of the $Pd(CH_3CO_2)_2$ added to the B-HCS by incipient wetness impregnation. This sample was dried at 100 °C overnight and finally calcined at 300 °C for 3 h in air and named Pd/B-HCSImp.

2.5. Catalyst characterization

The chemical analysis of the catalysts was performed by using the ICP-OES technique to measure the Pd concentration (Spectro Genesis instrument). Approximately 50 mg of catalyst was used. The carbon was oxidized at 700 °C, and the samples dissolved in 5 ml HF, 4 ml HNO_3, and a few drops of $HClO_4$. This procedure was repeated twice after the acid evaporation. Finally, the residue was dissolved in aqua regia and heated until dryness, and an aqueous solution of HNO_3 (1%v/v) was then added and the solution transferred to a 50 ml volumetric flask for analysis. A JEM 100s, an FEI Tecnai G^2 Spirit and an FEI Tecnai F20 X-Twin at 200 kV FEG with an Oxford EDS system were used for transmission electron microscopy (TEM) studies. All samples were ultrasonically suspended in methanol and a drop of the suspension was transferred to a copper grid and allowed to dry before TEM analysis. The phase composition of the support and catalysts were determined by means of XRD analysis on a Bruker D2 phaser in Bragg Brentano geometry with a Lynxeye detector using Cu Kα radiation at 30 kV and 10 mA. The scan range was $10° < 2\theta < 90°$ in 0.040 steps, using a standard speed with an equivalent counting time of 1 s per step. The diffraction peaks were then compared with those of standard compounds reported in the Diffracplus evaluation package using the EVA (V11.0, rev.0, 2005) software package. A Perkin Elmer TG/DTA Thermo gravimetric analyzer was used to measure weight changes of samples heated in air or nitrogen at a constant heating rate of 10 °C/min. The sample mass used was varied between 0.005 and 0.01 g. Scanning electron microscopy (SEM) images were recorded using a Philips XL-30 instrument coupled to an energy dispersion unit using an EDX Link Analytical QX-20000 an accelerating voltage of 5 kV. The samples were mounted on a copper stub with conductive carbon sticky tape. A thin (*ca.* 5 nm) coating of gold was deposited onto the samples to reduce the effects of charging. Raman spectra of the spent catalysts were obtained on a T64000 Raman spectrometer (Jobin Yvon triple spectrometer) under ambient conditions. A 514.5 nm Ar laser was used as the exciting source with a power density of 1 mW cm^{-2} on the sample surface and a power of 2 mW. The measurements were referenced to Si at 521 cm^{-1} with 16 data acquisitions in 180 s. A low laser power was used because a higher laser power burned the samples. Boron nuclear magnetic resonance (^{11}B-NMR) spectroscopy was utilized to investigate the chemical