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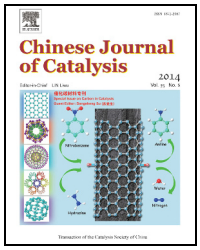

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Conversion of isopropyl alcohol over Ru and Pd loaded N-doped carbon nanotubes

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ABSTRACT

Ru and Pd (2 wt%) loaded on pure and on N-doped carbon nanotubes (N-CNTs) were prepared and tested using the isopropyl alcohol decomposition reaction as probe reaction. The presence of nitrogen functionalities (pyridinic, pyrrolic, and quaternary nitrogen) on the nitrogen doped support induced a higher metal dispersion: Pd/N-CNT (1.8 nm) < Pd/CNT (4.9 nm), and Ru/N-CNT (2.4 nm) < Ru/CNT (3.0 nm). The catalytic activity of the supports was determined first. Isopropyl alcohol conversion produces acetone on CNTs while on N-CNTs it led to both dehydration and dehydrogenation products. At 210 °C and in the presence of air, the isopropyl alcohol conversion was higher on the N-CNTs (25%) than on the CNTs (11%). The Pd loaded catalysts were more active and more selective than the Ru ones. At 115 °C, the Pd catalysts were 100% selective towards acetone for a conversion of 100%, whereas the Ru catalysts led to dehydration and dehydrogenation products. The nitrogen doping induced the appearance of redox properties when oxygen is present in the reaction mixture.

1. Introduction

Conversion of alcohols by dehydrogenation or dehydration is an interesting process, commonly used to investigate acid/base features of catalysts surface that are either oxide-based [1–3], or carbon-based [4–8]. Several studies have been dedicated to the research of correlations between the used techniques to characterize the acid-base properties of catalysts (adsorption of bases or acids, TPD...) and the conversion of alcohols, including isopropyl alcohol (IPA) [9–11]. In general, alcohols undergo dehydration to olefins and ethers mainly over acidic sites and dehydrogenation to aldehydes or ketones over basic or redox sites. These transformations occur through different mechanisms depending on the nature of the used materials [12]. The dehydration reaction of primary and secondary alcohols follows mostly a bimolecular elimination E2 concerted mechanism, which involves acid and sometimes basic sites of the catalyst leading to olefin and ether production. However, alcohol dehydration can also proceed through the unimolecular elimination mechanism E1cB, which implicates carbanion intermediates on solids that possess acid/base sites with high strength. On the other hand, the dehydrogenation reaction can occur over strong basic solid catalysts through a mechanism that involves the same intermediate carbanion to give olefins, albeit in this case, the ketone is produced by α-hydrogen abstraction. Another alternative mechanism for dehydrogenation

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is an oxidative process, in which redox centers and molecular or lattice oxygen are required. When converting IPA on acidic or basic solids, three parallel reactions can occur and the possible products can be propene, di-isopropyl ether, and acetone. The intramolecular dehydration of IPA to propene characterizes the surface acidity or the catalyst. The dehydrogenation reaction producing acetone characterizes the basic properties of the catalyst. The presence of redox sites can also promote dehydrogenation of IPA in the presence of oxidants [13]. The third reaction, which rarely occurs and depends on the strength of the sites, is the intermolecular dehydration of two molecules of alcohol, yields di-isopropyl ether. Dehydrogenation of IPA is also considered as an excellent test for metal supported catalysts. Indeed, decomposition of alcohols on various types of catalysts *via* dehydration or *via* dehydrogenation is an interesting process, because of its application to produce alkenes and carbonyl compounds such as formaldehyde or acetone. Several studies on the interaction of metallic or bimetallic catalysts with IPA were published [4,14–19]. In most of these investigations, IPA-metal interaction proceeds *via* the formation of isopropoxide (alkoxide) intermediate. This result was confirmed by a variety of surface characterization techniques. Therefore, isopropoxide species lead to the formation of acetone [20].

The acidity and basicity of carbon materials are two factors that impact their activity and selectivity, not only in typical acid-base reactions but also in many other, including redox transformations. In recent studies it was shown that N-doped nanostructured carbon materials exhibited enhanced anion exchange properties and a catalytic activity in redox reactions. So far, it has been demonstrated that the presence of nitrogen can be a key parameter that improves the catalytic performance of carbon materials [21–23].

In this study we reported on the synthesis and characterization of Ru and Pd catalysts supported on pristine and N-doped carbon nanotubes (CNTs). The catalytic features of the supports and their modification by the Pd and Ru incorporation were investigated using IPA conversion as probe reaction.

2. Experimental

2.1. CNT synthesis

The CNTs were synthesized by catalytic-CVD in a fluidized bed reactor using ethylene as carbon source and acetonitrile/N_2 as carbon/nitrogen source. The Fe catalyst supported on Al_2O_3 was pre-reduced under hydrogen during 30 min at 650 °C. A typical experiment was carried out initially with ethylene (600 mL min^{-1}) for 30 min to produce CNTs. N-CNTs were produced from acetonitrile/N_2 for 30 min. The produced carbon nanotubes were purified by aqueous solution of H_2SO_4 (50 vol%) under reflux for 3 h to facilitate the total dissolution of alumina and partial elimination of exposed iron particles contained in the nanotubes.

2.2. Ru/CNT and Pd/CNT catalyst preparation

In order to incorporate 2 wt% of Ru or Pd in the CNTs, the desired amounts of $Pd(NO_3)_2{\cdot}xH_2O$ and $Ru(NO)(NO_3)_x(OH)_y$ were added to an acetone solution (20 mL) containing 0.5 g of nanotubes. After stirring overnight at ambient temperature, the catalysts were filtered, washed with acetone and dried in an oven at 120 °C. The catalysts were then reduced at 300 °C for 2 hours in a horizontal oven under an Ar-H_2 flow (20 vol% H_2).

2.3. Characterization

The hybrid nanostructures were characterized using transmission electronic microscopy (TEM-FEI Tecnai-G2-20-FEI 2006, at 200 kV), CHN Perkin-Elmer elemental analyzer, Raman spectroscopy (SENTERRA at = 633 nm), and TG/DTA Shimadzu, under air (10 °C min^{-1} to 900 °C). Particle size distribution was determined using the ImageJ software on at least 300 nanoparticles. The textural characterization (BET surface areas, S_{BET}) of the materials was based on the N_2 adsorption isotherms determined at –196 °C with a Quantachrome Autosorb apparatus. EELS measurements for the K-edge absorption for C and N were used to estimate the stoichiometry of the nanotubes. EELS experiments have been performed with a Philips CM200 microscope. The samples were also analyzed by X-ray photoelectron spectroscopy (XPS) using a VG Escalab MKII spectrophotometer, which operated with a nonmonochromatized Mg K_α source (1253.6 eV).

2.4. Catalytic test

The activities of the catalysts were measured by the decomposition of IPA performed at atmospheric pressures, in a pyrex fixed bed microreactor placed inside a vertical furnace. Prior to the tests, the catalyst (0.1 g) was treated at 400 °C under 60 mL min^{-1} of N_2 then cooled to the reaction temperature. IPA at a partial pressure of 1.2 kPa was supplied to the reactor by a saturator fed with N_2 or air at a total flow rate of 60 mL min^{-1}. Reaction products were analyzed by on-line gas chromatography using an ATI Unicam 610 chromatograph equipped with a flame ionization detector and a 4 m column packed with Chromosorb PAW coated with 15% of carbowax 1500 for 2-propanol, acetone, propene and ether separation, and the other one Shimadzu GC-8A equipped with a silica gel column and TCD detector for CO_x analyses. The reaction features were defined as follows:

$$\text{Conversion} = \frac{n(\text{IPA}_{\text{in}}) - n(\text{IPA}_{\text{out}})}{n(\text{IPA}_{\text{in}})} \times 100$$

$$\text{Product yield} = \frac{\text{Fraction of IPA converted to product}}{\text{IPA}_{\text{in}}} \times 100$$

$$\text{Product selectity} = \frac{\text{Product yield}}{\text{Conversion}} \times 100$$

$$\text{Turnover frequency (TOF, min}^{-1}) = \frac{\text{Total feed (mol min}^{-1})}{\text{Metal loading (mol)}} \times \text{conversion}$$

3. Results and discussion

3.1. Material synthesis and characterization