Research paper

Semihydrogenation of 2-methyl-3-butyn-2-ol on Pd-Zn nanoalloys: Effect of composition and heterogenization

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ABSTRACT

Influence of composition and heterogenization to titania matrix of Pd-Zn nanoparticles has been studied in selective hydrogenation of the triple bond of 2-methyl-3-butyn-2-ol (MBY). Pd-Zn bimetallic nanoparticles with the various molar ratios Pd/Zn have been obtained by chemical reduction method. Composition-controlled sol-gel technique was employed to synthesize Pd-Zn/TiO$_2$ catalysts. The structure properties of the bimetallic catalysts were characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Computer modeling for XRD patterns was first used to identify the composition of Pd-Zn alloy and to determine the particle size. For the colloidal and embedded nanoparticles dependences of physicochemical and catalytic properties on composition are different being determined respectively by geometric and electronic effects. The addition of zinc with Pd/Zn ratio of 1 increased selectivity to alkene at 99% conversion from 92.9% for the Pd catalyst to 96.9% for bimetallic catalysts, which is mainly caused by alloy formation.

1. Introduction

The area of alloy nanocatalysis now attracts a lot of attention. The catalytic properties of metals can be improved by alloying [1]. The catalyst containing two or more metals can show significantly different catalytic properties compared with the monometallic one. It is crucial that the metals in nanoalloy mutually reinforce and complement each other, i.e., "synergistic effects" are observed. Multi-metallic systems are widely used in various reactions [2]. For the selective hydrogenation of alkyne alcohols efficient heterogeneous catalysts are generally composed of several metals. Pd-Zn alloyed catalysts find application in selective hydrogenation of phenylacetylene [3,4], 1-butene and 1, 3-butadiene mixture [5], acetylene [6–9], 1-pentyne [10], 2-methyl-3-butyn-2-ol (MBY) [11–13]. Compared to monometallic Pd catalyst, the developed Pd-Zn catalysts showed a higher selectivity to semi-hydrogenated product. Several mechanisms are believed to be responsible for the enhanced catalytic performance of bimetallic systems in alkyne hydrogenation, including the peculiarities of the interaction of the catalytic center with a triple and double bonds of the reactants [8,14], as well as electronic and ligand effects [15–17]. High selectivity to alkenes caused by the charge-transfer phenomena between the Pd and second metal may favorably decrease alkene adsorption, and is achieved by adding an electron-donor compound to the nanoparticles of Pd [18–21]. The catalytic properties of the metal can be precisely controlled by nanoparticles size and shape [22–24] as well as composition of the multi-metallic systems [25–27] which gives the possibility of rational design of catalytic properties. By varying the metal ratio in a bimetallic nanoparticle, various ensembles of surface atoms can be obtained. The type and relative amount of these surface atoms will determine the catalytic behavior of the nanoparticle. Optimizing the ratio of two metals can substantially enhance catalytic activity and selectivity of bimetallic catalysts.

The creation of continuous microreactors is a significant achievement for producing fine chemicals and pharmaceuticals. Several advantages distinguish them from other types of reactors. This technology allows increasing the yield of products, carrying out reactions in the kinetic regime and under mild conditions, improving the ecological safety of the processes. To synthesize catalytic coating on inner surface of a microreactor titania films with embedded nanoparticles were recently prepared via sol-gel method combined with evaporation induced self-assembly [28,29]. This method provides fine tuning of the texture, thickness, pore size of the support, as well as the size of the metal

particles, the metal content and the composition of active component. The immobilization of the nanoparticles in a support matrix applied for the synthesis of catalytic coating results in the drastic changes of their properties. The considerable attention should be paid to morphological and structural changes of the nanoparticles during different stages of the synthesis, when a thorough understanding of the origin of the catalytic reactivity of supported nanoparticles is desired. The above literature survey witnesses that Pd-Zn bimetallic supported catalysts have high selectivity to alkenes in hydrogenation of triple bond. The optimal composition of the nanoalloy remains to be open question. It is worth noting that, to the best of our knowledge, there have been no reports demonstrating the effect of the composition of Pd-Zn nanoparticles on activity and selectivity to semi-hydrogenated alcohol in 2-methyl-3-butyne-2-ol hydrogenation, an important industrial intermediate used in the synthesis of fine chemicals and vitamins [30].

This study is aimed to investigate the effects of intermetallic formation of Pd-Zn nanoalloys on the semi-hydrogenation of MBY. The effects of Pd/Zn molar ratios and embedding to titania matrix on the activity and selectivity of the catalysts are investigated. The possible reasons for the difference in the activity and selectivity between the nanoparticles and final catalysts will be presented.

2. Experimental

2.1. Catalyst synthesis

The colloids of Pd-Zn nanoparticles with the various molar ratios Pd/Zn were prepared by reduction by solvent method in the presence of a polyvinylpyrrolidone (PVP) as a stabilizer [31]. The nanoparticle precursors were $Pd(CH_3COO)_2$ (46.5% Pd, Aurat) and $ZnCl_2$ (98%). The procedure is described elsewhere [32]. The prepared colloids were purified by adding acetone and redispersed in ethanol. All operations were carried out in the atmosphere of argon. The molar fraction of metals was varied in order to synthesize nanoparticles with different composition.

Pd-Zn/TiO_2 catalysts were synthesized by sol-gel method in the presence of Pluronic F127 according to the procedure described elsewhere [12,33], followed by evacuation at 573 K for 2 h under a residual pressure of 13 mbar and reduction at 523 K or 773 K for 2 h. The samples are noted according to their activation procedure, the number denotes temperature of reduction. The molar composition of the final solution was 1Ti(O-iPr)$_4$: 0.009Pluronic F127: 32C_2H_5OH: 8C_4H_9OH: 1.3H_2O: 0.18HNO_3.

Pd/TiO_2 and PdZn/TiO_2 coatings were synthesized using a sol with the same molar composition. Before the supporting, the silica capillary was preliminarily washed with a 1 M solution of NaOH at 313 K for 30 min in order to improve the adhesion of the coating. A portion of sol was used to dip-coat the inner wall of fused silica capillaries with diameter 530 μm, a length of 10 m at a rate of 1 cm/s. The capillaries were kept in a glove box for 24 h at a relative humidity of 80%, followed by calcination at 573 K under a residual pressure of 13 mbar with a heating rate of 1 K/min to remove the surfactant. After evacuation PdZn/TiO_2 and Pd/TiO_2 coatings were obtained with a nominal Pd loading of 0.84 wt.% and 1.09 wt.%, a total catalyst loading of 1.10 mg and 1.15 mg, respectively.

2.2. Characterization

The sample morphology, the average Pd-Zn nanoparticle size and particle size distribution were observed under a high resolution JEOL JEM-2010 transmission electron microscope operating at 200 kV with a structural resolution of 0.14 nm. Samples for transmission electron microscopy (TEM) measurements were prepared by deposition onto a perforated carbon fixed on copper grid. The average particle size was estimated from micrographs using the equation $d_n = \Sigma n_i d_i / \Sigma n_i$ for > 200 particles (usually up to 400 individual particles were counted). The

local elemental analysis of the samples was carried out by an Energy Dispersive X-ray Analysis (EDS) method using an EDAX spectrometer equipped with a Si (Li) detector with a resolution of 130 eV.

The bulk composition of the "as prepared" nanoparticles, precipitate of colloids and solution after capillary washing was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Perkin–Elmer Optima 4300-DV). An aliquot of the colloids or precipitate was dissolved in HNO_3 and diluted with deionised water. After the reaction, the total catalyst loading in the capillary was determined by withdrawing 4 ml of concentrated nitric and 4 ml of sulfuric acid at 0.5 ml/min through the capillaries. The chemical composition of the powder catalysts was determined by X-ray fluorescence spectroscopy (XRF) using a VRA-30 analyzer with a Cr anode of an X-ray tube.

Photoelectron spectra were recorded using SPECS spectrometer with PHOIBOS-150-MCD-9 hemispherical energy analyzer (AlK$_a$ irradiation, hη = 1486.6 eV, 200 W). Binding energy (BE) scale was preliminarily calibrated by the position of the peaks of Au4f$_{7/2}$ (BE = 84.0 eV) and Cu2p$_{3/2}$ (BE = 932.67 eV) core levels. The binding energies (BE) of peaks was corrected taking into account the sample charging by referencing to the C1s peak (BE = 284.8 eV) corresponding to the surface hydrocarbon-like deposits (C−C and C−H bonds) accumulated on the surface during the storage in the atmosphere. The ratios of surface atomic concentrations of the elements were calculated from the integral intensities of photoelectron peaks corrected by corresponding relative sensitivity factors [34]. In addition to the survey photoelectron spectra, more narrow spectral regions Pd3d, Zn2p, Cl2p, N1s, C1s and Ti2p were recorded. For the survey spectra the pass energy of the analyzer was 50 eV, while that for the narrow spectral regions − 20 eV. Analysis of the individual spectral regions allowed determining the values of binding energies of the peaks, identification of the chemical state of the elements, as well as calculation of the ratios of the element atomic concentrations on the sample surface.

In order to characterize the nanoparticles by X-ray diffraction (XRD), the prepared colloids were purified by adding a large excess of acetone. The supernatant was decanted or centrifuged and the purified precipitate was dried at ambient conditions, then evacuated at 573 K (13 mbar) or reduced at 523 K or 773 K. XRD studies were carried out in a D8 Advance diffractometer (Bruker, Germany) using Ni-filtered CuKα radiation (40 kV and 40 mA) with a Bruker Lynx Eye strip silicon detector. Diffraction patterns were recorded utilizing Bragg-Brentano geometry over a range of 20–90° 2θ with a step size of 0.05 − 2θ, with each step measured for 3 s. To determine phases, the XRD patterns for nanocrystalline Pd-Zn compounds were simulated by Debye equation using DISCUSS program [35]. For modeling, the crystal structures of Pd (JCPDS 46–1043), and ZnO (JCPDS 36–1451) as well as the known bulk alloy phases of Pd-Zn (Pd$_{81}$Zn$_{19}$, Pd$_{1.35}$Zn$_{0.65}$ [36], PdZn [37], Pd$_{27.35}$Zn$_{99.27}$ [38], PdZn$_2$ [39] and Pd$_2$Zn [40]) were used.

2.3. Catalytic tests

Hydrogenation of MBY was carried out in an autoclave reactor with a total volume 130 ml at 323–333 K and 4–5 bar H_2 pressure under intensive stirring at 2000 rpm. The stirring rate was chosen such to exclude the influence of external mass transfer on the reaction rate. To minimize the effect of internal diffusion limitations, the samples were subjected to extensive grinding in an agate mortar prior to the catalytic tests. Prior to activity measurements, colloids were dried by vacuum evaporation of solvents at 323 K, 13 mbar for 2 h with the heating rate 1 K/min. The Pd-Zn/TiO_2 catalysts were reduced in situ at 523 K at a H_2 pressure of 10 bar for 2 h. A solution of 0.1 M MBY and 0.1 M of 1-butanol in methanol (50 ml) was purged in argon, transferred into the reactor and flushed with Ar under stirring. The temperature was set and allowed to stabilize (ca. 30 min). The system was pressurized with H_2 and intensive stirring was switched-on. Analysis of the reaction mixture was performed off-line with gas chromatograph Crystall 2000 M equipped with a SKTFT-50X capillary column (diameter: 0.22 mm,