

Physicochemical and catalytic properties of Pd/MoO₃ prepared by the sonophotodeposition method



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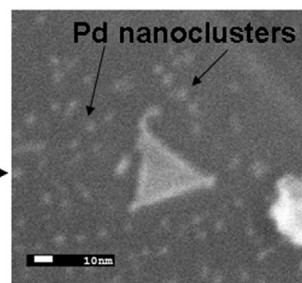
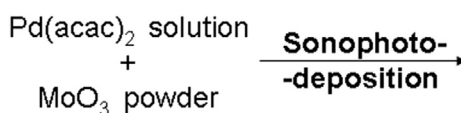
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HIGHLIGHTS

- Preparation of Pd/MoO₃ sample by sonophotodeposition method.
- The effect of sonophotodeposition on hydrogen bronze formation process.
- Palladium nanoclusters formation during sonophotodeposition treatment.

GRAPHICAL ABSTRACT

Preparation of Pd/MoO₃ catalyst



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ABSTRACT

Molybdenum trioxide-supported palladium catalyst Pd/MoO₃(SPD) is prepared by the sonophotodeposition procedure (SPD). This method combining sonication with ultraviolet irradiation is used at room temperature and atmospheric pressure and does not require the use of chemical reducing agent. For comparison, the Pd/MoO₃ catalysts are also prepared by the ultrasound irradiation and traditional impregnation - H₂ reduction methods. The Pd/MoO₃ catalysts are characterized by X-ray diffraction (XRD), electron microscopy (SEM, TEM, HRTEM), energy dispersive (EDS, STEM) analysis and X-ray photoelectron spectroscopy (XPS). The SPD treatment improves the platelets-like morphology of the MoO₃ oxide grains making more difficult formation of hydrogen bronzes H_xMoO₃ (x > 0.9) studied by microcalorimetric method. The “in situ” reduction of precursor ions during the SPD treatment generates much better dispersed Pd-nanoclusters than other preparation methods. It results in much higher activity of Pd/MoO₃(SPD) catalyst for the cinnamaldehyde hydrogenation than its MoO₃-supported counterparts and Pd/SiO₂, a reference catalyst.

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1. Introduction

Molybdenum trioxide and polymolybdates are highly important compounds in catalysis. They could be applied as catalysts,

catalysts precursors or supports for noble metals (Pt, Pd) - containing catalysts.

Upon high temperature treatment of MoO₃ with hydrogen, molybdenum bronzes H_xMoO₃ are generated which could be the precursors providing various types of catalytic active sites [1]. The Mo-OH groups created in these structures could display catalytic activity via metallic as well as acid functions observed in

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dehydrogenation and dehydration of propan-2-ol [2], isomerization of pentane, heptane [3], hydroisomerization reactions of linear C5–7 hydrocarbons [4,5]. Furthermore, hydrogen present in the bronze phases participated for the hydrogenation of unsaturated C=C bonds in alkenes [6,7]. Hydrogenation of ethylene on $H_{1.6}MoO_3$ formed in the Pt/ MoO_3 catalyst proceeded without gaseous H_2 [7]. The DFT calculations for the ethylene - $H_xMoO_3(010)$ bronze system showed that the Mo-OH species could also participate in the adsorption of ethylene [8]. The interaction between protonic H of the Mo-OH group and π electrons of ethylene resulted in weak physisorption of ethylene in the tilted configuration which facilitated the transfer of hydrogen to the C=C bond. In our previous work similar effect has been observed in the hydrogenation of cinnamaldehyde (CAL), a reactant with C=C and C=O conjugated bonds on the Pd/ MoO_3 catalysts [9]. The conditions of catalytic tests facilitating hydrogen bronzes formation promoted the hydrogenation of C=C bond of CAL reactant.

The MoO_3 has also been studied as the support for noble metal particles, such as Pt, Pd, etc. In catalytic reactivity of these systems, apart from the ability to hydrogen molybdenum bronzes formation also modification of electron properties of metal sites by the MoO_3 played a significant role. Zosimova et al. [10] reported that hydrogen species migration via spillover in the Pt/ MoO_3 structure generated additional active sites active for toluene hydrogenation. Only those MoO_x particles that are in close vicinity to the Pt-particles took part in the formation of these additional active sites. An electron interaction between Pt, Pd particles and MoO_3 support is a well known effect [10–12]. Jackson et al. [12] reported that platinum in the Pt/ MoO_3 sample was positively charged ($Pt^{\sigma+}$) due to metal –support interaction. The enhanced sulfur tolerance of Pt/ MoO_3 catalysts has been also attributed to the electron deficient $Pt^{\sigma+}$ metal species [10,13].

Very low specific surface area of MoO_3 oxide (lower than $2\text{ m}^2\text{ g}^{-1}$) is a great disadvantage making difficult synthesis of catalysts with well dispersed metal (Pt, Pd) particles. Commonly used preparation method included impregnation of MoO_3 oxide with $PdCl_2/H_2PtCl_3$ aqueous solution followed by calcination (at $400\text{ }^\circ\text{C}$) or hydrogen reduction. However, the Pd-, Pt- MoO_3 -supported catalysts with very low metal loading, 0.01–0.5 wt % were commonly obtained by this procedure [14–18]. For instance, the Pt/ MoO_3 catalyst of as low metal loading as 0.1 mol % was studied for acrolein hydrogenation [14]. The metal loading in the MoO_3 -supported catalysts studied for conversion of heptane and propanol-2-ol was also very low, 0.01 mol. % of Pt, Pd, Rh, Ir and Ru [15,16]. Preparation of Pt/ MoO_3 catalysts by oxidation of Pt–Mo alloy precursors was more effective, as it produced catalysts of higher Pt loading but relatively large Pt particles 19–35 nm were formed [10]. Our previous studies showed that a colloid-based reverse “water-in-oil” microemulsion method produced the catalysts of high 2%Pd and 2%PdPt metal loading and uniform metal particles ca. 8–10 nm in size, but they aggregated to form large agglomerates [9,19]. The Pd/ MoO_3 catalysts of 1–2 wt % Pd and much better dispersed Pd nanoparticles (ca. 8 nm) were formed when impregnation of MoO_3 was carried out using non aqueous medium, namely acetone solution of $Pd(ac)_2$ [9].

In the present paper a novel method of Pd/ MoO_3 catalyst preparation is used, so called sonophotodeposition method (SPD). In this method sonication is combined with photocatalytic reduction of metal precursor ions carried out “in situ” [20–24]. This method is carried out at room temperature and atmospheric pressure and does not require the use of chemical reducing agent. The reducing agents are electrons produced as a result of the ultraviolet absorption by semiconducting material, MoO_3 oxide in our studies, while ultrasounds assure enhanced penetration of reagents in the support grains and help in the metal ions reduction. SPD

method has already been effectively applied for the synthesis of various nanomaterials, among them several titania-based photocatalytic systems, Pd/ TiO_2 [22,23] and bimetallic PdAu/ TiO_2 ones [24]. Thus, present study focuses on preparation of MoO_3 -supported palladium catalyst [Pd/ MoO_3 (SPD)] by the sonophotodeposition method. Physicochemical properties and catalytic reactivity of Pd/ MoO_3 (SPD) sample for the cinnamaldehyde hydrogenation are compared with those observed for the Pd/ MoO_3 catalyst prepared by conventional impregnation - reduction method.

2. Experimental

2.1. Preparation of Pd-containing catalysts

Commercial molybdenum oxide (Johnson Matthey, surface area $1.7\text{ m}^2/\text{g}$) was used as the supports. The 1.2%Pd/ MoO_3 (SPD) catalyst was prepared by sonophotodeposition procedure according to previously described procedure [22]. Shortly, 1 g of MoO_3 powder was dispersed in 120 cm^3 of H_2O : CH_3CN (30:70, v/v) solution consisting of 0.034 g of palladium(II) acetylacetonate and 0.1 g of oxalic acid. The preparation was carried out under argon flow (70 mL/min) at temperature of $20\text{ }^\circ\text{C}$. The suspension was first kept in dark for 30 min and then sonophotodeposition was performed by illuminating the suspension for 60 min with a low pressure mercury lamp (6 W, $\lambda_{\text{max}} = 254\text{ nm}$) and with ultrasonic bath (35 kHz, 560 W, Sonorex Digitec-RC, Bandelin) switched on. Then, the product was recovered by slowly evaporation in rotary evaporator, dried at $110\text{ }^\circ\text{C}$ for 10 h, and calcined at $300\text{ }^\circ\text{C}$ for 4 h under air flow (30 mL/min). For comparative purposes, a bare MoO_3 was also treated by the sonophotodeposition at palladium-free reaction medium (denoted as MoO_3 (SPD)).

The 1%Pd/ MoO_3 (N) catalyst was prepared by impregnation of MoO_3 support with acetone solution of $Pd(ac)_2$ followed by reduction with hydrogen (5% H_2 in N_2) at temperature of $250\text{ }^\circ\text{C}$ (3 h) [9].

2%Pd/ SiO_2 (Silica Davisil 634, surface area $559\text{ m}^2/\text{g}$) used as the reference catalyst was prepared as described before [9]. The synthesized catalysts were stored in contact with air.

2.2. Methods of characterization

The content of palladium (wt %) in the catalysts was determined by XRF method using Skaray Instrument EDX 3600H Alloy Analyzer.

The X-ray diffraction (XRD) patterns were obtained with a Philips X'PERT diffractometer using Cu $K\alpha$ radiation (40 kV, 30 mA).

The X-ray Photoelectron Spectroscopy (XPS) measurements were carried out with a hemispherical analyzer (SES R4000, Gamdata Scienta). The unmonochromatized Al $K\alpha$ and Mg $K\alpha$ X-ray source with the anode operating at 12 kV and 20 mA current emission was applied to generate core excitation. All binding energy values were corrected to the carbon C 1s excitation at 285.0 eV. The samples were pressed into indium foil and mounted on a holder. All spectra were collected at pass energy of 100 eV except survey scans which were collected at pass energy of 200 eV. Intensities were estimated by calculating the integral of each peak, after subtraction of the Shirley-type background, and fitting the experimental curve with a combination of Gaussian and Lorentzian lines of variable proportions (70:30).

Electron Microscopy (SEM, TEM) studies were performed by means of Field Emission Scanning Electron Microscope JEOL JSM-7500 F equipped with the X-ray energy dispersive (EDS) system. Two detectors were used and the images were recorded in two modes. The secondary electron detector provided SEI images,

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