



Preparation of bimetallic gold catalysts by redox reaction on oxide-supported metals for green chemistry applications



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ABSTRACT

The major problem in successful preparation of bimetallic supported catalysts is the formation of an extended contact area between the monometallic phases. The selective deposition of Au on the surface of nanoparticles of a primary oxide-supported metal has been performed by a redox method that is based on the reduction of the second metal (M2) ions with hydrogen adsorbed on the surface of first metal (M1) or with M1 itself. The gold containing bimetallic catalysts with different atomic ratios and metal combinations Au–M1 (M1 = Pd, Pt, Rh, Ru, and Au–RuO_x) deposited on oxide supports (TiO₂, SiO₂ or θ-Al₂O₃) have been prepared by this method with special emphasis on the preparation of low-loaded gold containing bimetallic catalysts. The samples were characterized by X-ray diffraction analysis (XRD), scanning transmission electron microscopy (STEM), temperature programmed reduction (TPR) analysis, CO adsorption, X-ray photoelectron spectroscopy (XPS), Diffuse reflectance Fourier-transform IR spectroscopy of adsorbed CO (DRIFTS–CO). By varying the conditions of the preparation procedure, the direct contact area was obtained either between two metal phases (Au/M1) or between metal and a metal oxide phase (Au/M1O_x) that changed the catalytic properties of primary supported M1. The prepared bimetallic catalysts exhibited the high activity in various reactions: from the Cl–VOC oxidative degradation to the up-to-date “green” reactions aimed at the synthesis of fine chemicals from ethanol and glycerol.

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1. Introduction

Bimetallic catalysts are widely used for transformation of the natural and industrial feedstock to useful products [1–3]. Improving the catalytic performance (activity, selectivity and durability) and minimizing the noble metal content are the major advances of bimetallic catalysts. A variety of methods has been used successfully to prepare bimetallic catalysts with an enhanced catalytic activity and unique catalytic properties [3,4]. Commonly, the bimetallic nanoparticles are preliminarily synthesized in a stabilized sol and then are supported on a carrier, yet unstable solid solutions are often formed by this way [5,6]. Another drawback is stabilizing agent removal [7–9]. Non-selective deposition of metals (impregnation, co-precipitation methods) leads to formation of the bimetallic particles with the presence of monometallic ones as well. In addition, the structure of bimetallic particles is hard to control [10–12]. Therefore, the major problem in the preparation of supported bimetallic catalysts is the selective formation of an extended

contact area between the monometallic phases [13,14], i.e. a developed contact area between the monometallic particles (clusters, amorphous species, nanocrystallites).

The selective deposition of a metal on the surface of another metal can be performed by redox methods. The proposed redox methods [14] are based on the reduction of the second metal M2 ions either by the pre-supported first metal M1 (direct redox reaction, DRR) [15–18] or by a reducing agent adsorbed on the surface of the first metal, for instance, hydrogen (the redox reaction with adsorbed species, RRA) [19–22]. The outermost electronic configurations, the atomic radii of the metals, and the low preparation temperature seem to be important factors for the different states of these bimetallic catalysts, and M2 can be monolayer dispersed on the surface of M1 or the surface solid solutions, and even the particles of comparable sizes are formed [19,23]. The M2 deposition can be induced with preadsorbed hydrogen under an inert gas (M1 = Pd, Pt) or only under an H₂ gas flow (M1 = Rh, M2 = Ge [24]). The high electrochemical potential of M2⁰/M2ⁿ⁺ does not guarantee the complete deposition. The nature of the oxide support affects the character and completeness of the M2 deposition as well [24]. Prolong treatment in the redox system results in submonolayer adatom structures [25].

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The supported bimetallic catalysts prepared via redox deposition have been studied in the gas-phase reactions of toluene hydrogenation, cyclohexane dehydrogenation, hydrocarbon oxidation, exhaust gas purification and in the liquid-phase reactions (citral hydrogenation, glycerol hydrogenolysis) [14,20,24]. Nevertheless, the catalytic properties of redox prepared bimetallic catalysts on oxide supports are poorly studied, especially in environmental catalysis and catalytic transformations of the biomass derived products.

The high standard redox potential of gold makes the redox method the best choice to prepare gold-containing bimetallic catalysts with strong Au–M1 interaction. Despite the reported successful preparation of the supported gold bimetallic catalysts via redox deposition [19,20], the majority of the research groups working on the development of gold-based catalysts used the preparation procedures based on deposition of bimetallic particles from the preliminary synthesized sols. This way excluded strong interaction between the metallic nanoparticles and a support [26] that results in intensive leaching of nanoparticles from the support to the reaction volume during the liquid-phase catalytic processes [27,28], which are the most promising in conversion of natural derived substrates.

In our previous studies, we have shown that the redox prepared Au/Pd/TiO₂ catalyst is more active and stable in oxidation of sulfur containing volatile organic compounds (SVOC) than the Pd/TiO₂ and Au/TiO₂ samples [29], and the Au/Ru/Al₂O₃ catalyst performs preferential CO oxidation in a mixture with NH₃ that is impossible on monometallic samples [30]. Thus obtained Au–CuO_x catalytic systems are active in the aerobic gas-phase ethanol selective oxidation to acetaldehyde under very mild conditions [31].

The objective of this work is the elaboration of redox methods for the preparation of oxide-supported M2–M1 (Au–Pd, Au–Pt, Au–Rh, Au–Ru, Au–RuO_x) bimetallic catalysts with different atomic ratios, metal content, and evaluation of their catalytic behavior in the oxidative degradation of dichloromethane and in the oxidation of the platform molecules: ethanol, 1,2-propanediol, glycerol to high-value products. Hydrogenation of glycerol to 1,2-propanediol was also discussed. Especially we were interested in preparation and investigation of the catalysts with low-loadings of the noble metals.

2. Experimental

M1 metals were supported as nanoparticles (NPs) on TiO₂ (Degussa P25, 45 m²/g; Acros P25, 61 m²/g), SiO₂ (KSKG, Russia, 300 m²/g), θ -Al₂O₃ (Russia, 95 m²/g) by the deposition–precipitation procedure similar to the one described in [29], or by incipient wetness impregnation of the support with an M1 precursor solution followed by thermal decomposition and reduction of the metal precursor [30,31]. The deposition–precipitation procedure included: (1) the preliminary hydrolysis of precious metal complexes in a solution until the formation of polyhydroxocomplexes [32], (2) the deposition of the complexes formed on the support surface in the slurry that is enhanced with alkali addition and heating the slurry, (3) the reduction of deposited hydroxo-compounds with hydrogen. To deposit the Au species, the prepared parent monometallic sample was saturated with H₂, and the required amount of an Au precursor solution (HAuCl₄) with a definite concentration was added to the monometallic sample. The reduction of M1 catalyst was provided just prior to the hydrogen adsorption and the Au deposition. In some cases, Au deposition followed the M1/support reduction (3) in the slurry (2) without separation of the later from the slurry as the sequential step of M1 preparation (Au/Rh/TiO₂ and Au/Pd/TiO₂ catalysts). After stirring the slurry for 0.5–2 h under an Ar or H₂

atmosphere, the sample was separated by filtering, washed, and dried. The well-known deposition–precipitation with urea (DPU) method [33] was also used to prepare the reference Au/Pt/TiO₂ and Au/RuO₂/Al₂O₃ samples. The gold containing samples were prepared avoiding their exposure to UV light and kept in darkness. The catalysts were marked as xAu, xM1, or xAu/yM1, where x and y were wt.%. The metal loading was calculated as: m (metal)·m (support)^{−1}·100%. Detailed description of the preparation procedures of the parent M1 catalysts and bimetallic samples can be found in supplementary information (S1–S6). Before testing, a sample was treated in addition as described in a test procedure.

The phase composition of the catalysts and the particle size of the supported metal were estimated by X-ray diffraction (XRD) analysis. X-ray diffraction patterns were recorded using a DRON-2 diffractometer with Ni-filtered Cu K_α radiation ($\lambda = 0.1542$ nm) in a step scanning mode with the counting time of 0.6 s per step. Identification of the phases was performed by comparison of the position and intensity of the peaks with the data from the files of International Center for Diffraction Data. The crystal size of nanoparticles was calculated from X-ray peak broadening (Scherer equation).

The morphology of the supported nanoparticles was studied using a Hitachi SU8000 field-emission scanning electron microscope (FE-SEM) or a high-resolution electron microscope JEM-2000FXII at 200 kV (TEM). Images were acquired in the bright-field STEM or TEM mode at the 30 kV accelerating voltage. Before measurements, the samples were mounted on 3 mm copper grids and fixed in a grid holder [34]. At least 10 images for each catalyst sample were used to calculate particle size distribution and average particle size according to the common equation: $d_{NPs} = \sum n_i d_i / n$, where n_i represents the number of particles with diameter d_i , n is a total number of calculated particles which is equal to 300.

The XPS study was used to evaluate the electronic state of the supported metal NPs in the catalysts and surface composition of the catalysts. X-ray photoelectron spectroscopy (XPS) measurements were performed on Gammadata-Scientia SES 2002 with Al K_α, $h\nu = 1486.6$ eV X-ray source at 10 kV and 20 mA. The binding energies were calibrated with the C 1s peak (285 eV) and additional spectra calibration with Au 4f_{7/2} (84.0 eV), Cu 2p_{3/2} (932.7 eV), and Ag 3d_{5/2} (368.3 eV). In order to preserve the gold cations from possible reduction, the XPS data were registered at −50 °C. The pressure in the experimental chamber was kept at 3.7×10^{-10} Torr. High-resolution (HR) spectra were recorded with analyzer energy passage 11.75 eV and density of the data collection 0.1 eV.

DRIFT spectra were recorded using a NICOLET “Protege” 460 spectrometer in the interval of 6000–400 cm^{−1} at a resolution of 4 cm^{−1} (500 scans). The adsorption of CO was performed at room temperature (20 °C) and CO equilibrium pressure of 15 Torr. Before the experiments, the sample was evacuated for 0.5–1 h at the temperature not exceeded that used to treat the catalyst during its preparation, i.e. 20–60 °C.

The metal dispersion and the specific metallic surface area were measured by CO adsorption at 25 °C (Pd) or 35 °C (Pt) in a pressure range of 120–900 Torr using an ASAP 2020 unit (Micromeritics) in the laboratory of “ASPECT-association”.

The TPR measurements were performed in the lab-constructed flow system. The sample pretreated in an Ar flow was heated from −50 to 850 °C at the rate 10 °C/min in a 4.6% H₂–Ar gas mixture supplied with a space velocity of 30 ml/min. Then the sample was kept at 850 °C until the hydrogen consumption ceased. To compare the intensities of obtained TPR curves these were specified to one basis (1 g of catalyst).

The prepared catalysts were tested in the following reactions: (1) oxidative degradation of dichloromethane (DCM); (2) oxidation of ethanol (EtOH); (3) oxidation of 1,2-propanediol (1,2-PD) and glycerol (Gly) to lactic acid (LA); (4) hydrogenation of glycerol (Gly) to 1,2-propanediol (1,2-PD). Oxidative degradation of DCM in

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