

Supported Bimetallic Au-Pd Catalysts for Selective Oxidation of Arabinose to Arabinaric acid

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Introduction

Supported gold nanoparticles have provoked more and more interest due to their specific activity in catalytic reactions [1]. It was shown by Corma that gold nanoparticles supported on cerium oxide are extremely effective in the selective oxidation of aldehydes to acids and also in oxidation of allylic alcohols [2]. In many cases, bimetallic systems like Au-Pd and Au-Pt show extra high activity and high resistance to deactivation due to synergistic effects [3].

The aim of the present work was to evaluate the influence of the supports nature (alumina and ceria) on the activity and selectivity of supported bimetallic Au-Pd catalysts in the aqueous-phase selective oxidation of arabinose to arabinaric acid.

Materials and Methods

The samples were prepared by DP at 80°C using HAuCl₄ and urea with subsequent chemisorption of Pd species from PdCl₂ acid solution at room temperature. Before tests several portions of obtained samples were heated in oxygen and hydrogen flows at 300°C or reduced with formaldehyde solution at room temperature during 24 hours, respectively. Alumina prepared by sol-gel from organic precursors (with S_{BET} =207 m²/g and average crystal size ~5 nm) and commercial CeO₂ (with S_{BET} = 22 m²/g and average crystal size ~19.6 nm) were used as the supports for the noble metals deposition. Prepared samples have been characterized by XPS, UV-Visible spectroscopy, XRD and TEM.

Catalytic experiments were performed in a semi-batch mode. After introduction of the catalyst (0.5 g, granule size < 50 µm) suspended in water, it was pre-reduced by hydrogen (AGA, 99.999 %) at 60 °C for a period of 10 min. Arabinose was introduced into the reactor as an aqueous solution. The oxygen flow rate through the reactor was 2.5 ml/min. The concentration profiles of the reactant and the products were monitored by means of high precision liquid chromatography (HPLC). The reactor set-up allowed *in situ* catalyst potential measurements. Potential measurements were performed versus Ag, AgCl/3M KCl electrode. Constant pH of reaction media was maintained by automatic titration device (Metrohm Titrino 751) at pH-stat mode by controlled addition of a NaOH solution.

Results and Discussion

The treatment of samples in different media influences the formation of various gold species such as: gold cations (Au⁺ and Au³⁺), finely dispersed partly charged gold nanoparticles

(Au^{δ-}) and gold metal particles (Au⁰) as well. Samples are characterized by a high content of gold cations even those significantly reduced which seems to be caused by reoxidation of samples exposed to air at room temperature. However, the relative contribution of gold cations is larger for Pd-Au-Al than for Pd-Au-Ce catalysts. On the contrary the content of Au nanoparticles with size less than 1 nm is higher for Pd-Au-Ce than for Pd-Au-Al catalysts. Two different mechanisms of gold species stabilization via interaction with Pd oxidic species and ceria were proposed. In the case of an inert support such as alumina gold species are in close interactions with Pd species which was revealed by the presence of charge transfer bond between Au and oxygen of palladium oxide at ~430 nm in UV-vis spectra. These interactions could be the base for the relatively high content of gold cationic species detected by XPS in Au-Pd-Al samples after different treatments. In case of Au-Pd-Ce samples gold species can interact with palladium oxide and ceria as well. Hence, in addition to the presence of Au-O species the interaction of gold species with ceria results also in the formation of nano sized gold species particular for the sample reduced with formaldehyde (Fig.1).

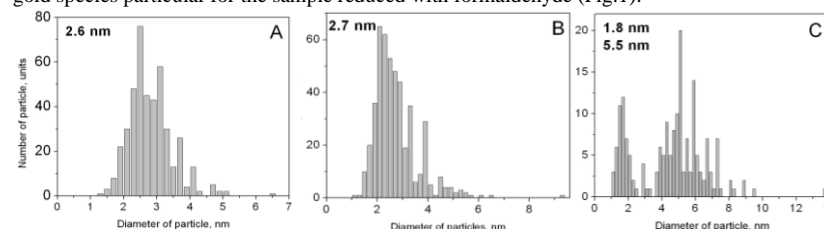


Figure 1. Gold particle size distribution according to TEM analysis for Au-Pd-Ce samples after different treatments: A – oxidation at 300°C, B - reduction with H₂ at 300°C, C – reduction by formaldehyde at RT.

The Au-Pd samples supported on ceria displayed high activity and selectivity in oxidation of arabinose to arabinaric acid in contrast with Au-Pd-Al ones.

Significance

Data obtained in this work could be applied for the development of new effective catalysts for industrial application.

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