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Red mud based gold catalysts in the oxidation of benzyl alcohol with molecular oxygen

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ABSTRACT

Red Mud (RM) based gold catalysts were prepared by supporting gold nanoparticles (AuNPs) on the RM residue reduced either with H_2 or with ethanol – which promoted partial coating of the RM with carbon. The materials were characterized by X-ray diffraction, Mössbauer spectroscopy, elemental analysis CHN, transmission electron microscopy and EDS microanalysis. Their catalytic performance was evaluated in the liquid-phase oxidation of benzyl alcohol by molecular oxygen, for the first time, as far as we know. The results showed that AuNPs with diameters of around 10 nm were successfully supported and distributed on the surface of red mud based materials. Furthermore, carbon coating allowed better incorporation of AuNPs on the material surface and better dispersion of the material into the reaction solutions. AuNPs supported on RM reduced in ethanol and, therefore, coated with carbon showed better catalytic performance than AuNPs supported on MR reduced in hydrogen.

1. Introduction

Red mud is the main residue generated during the Bayer process of alumina extraction from bauxite [25]. Nearly 100% of the total red mud (RM) produced worldwide since 1890 (when the Bayer process started industrially) has been stored, accumulating more than 3 Bt of this hazardous waste. Low value applications have been found for the RM, i.e. road making, land reclamation, cement and ceramic production [36]. However, the composition of RM confers this material a potential of being useful in a variety of chemical applications. RM is mainly composed of Fe, Al, Si, Ti, Na, Ca and Mg oxides [2], which enables its use in metal recovery [28], adsorption of organic contaminants in water [17,21,61], adsorption of heavy metals in contaminated soils [16,20], CO_2 capture [48,53], Cr(VI) reduction [10], ammonia decomposition [32] and polymers addition [18].

RM has also been tested in catalytic applications [23], such as in the hydrogenation of toluene [42], tetrachlorethylene [39] and polycyclic aromatic compounds, i.e. anthracene oil [63], naphthalene [44], phenanthrene and pyrene [14]. Moreover, RM has been studied in oxidation reactions of organic compounds, such as methane, chlorinated hydrocarbons [19], waste plastics [29,65] and other volatile organic compounds (VOCs) [26].

Red mud is not often applied in its pure form, especially due to the high alkalinity, partial solubility in water and possible presence of heavy metals [49]. In most applications, RM is used after neutralization and/or acid treatment [4,17,48,53,61].

Few works show the application of red mud as support for metal catalysts, i.e. Ni/RM [7] or Ru/RM [32] for ammonia decomposition, Co/RM for phenol oxidation [31,51] and $MgCl_2$/RM for color removal of dye wastewater [62].

Coating of red mud with carbon has shown to be an important alternative to reduce leaching and alkalinity of this waste [12,35]. Some papers report the coating of red mud by different carbon structures, such as carbon nanotubes [13], and using different carbon sources, e.g. carbon from coal gangue [3], carbon of associated natural gas [60], carbon obtained by catalytic cracking of hydrocarbons [45] and carbon from methane decomposition [58].

The main advantage of using red mud as catalyst support is the application of an industrial useless residue produced in large scale with rich chemical composition. During the synthesis of the supports, large particles of iron oxy-hydroxides present in red mud

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are reduced to form large Fe^0 particles, which are responsible for the magnetic properties of the catalysts. More dispersed iron is found on the Si, Ti and Al oxides likely formed by solubilization and reprecipitation during the Bayer process. These small iron oxyhydroxides are reduced to Fe^0 nuclei that are able to catalyze the CVD reaction for the formation of high surface area carbon structures on the surface of the catalyst [37,59].

The oxidation of alcohols is considered an important process in organic synthesis due to the high industrial relevance of the carbonyl compounds produced. Many commercial processes use stoichiometric oxidants, such as chromates, permanganates or peroxides, thus generating large amounts of environmentally dangerous co-products. In this context, the development of catalytic processes that involve molecular oxygen as a final oxidant is an extremely important issue in catalysis science. Although a number of catalytic systems based on transition metals have been successfully applied in the oxidation of alcohols by molecular oxygen [5,6,30,46,52,55,64,66], gold nanoparticles (AuNPs) remain among the most promising catalysts for these reactions [1,3,15,27,43,54]. Supported AuNPs usually show a remarkable catalytic activity in the aerobic oxidation of alcohols and excellent selectivity for carbonyl compounds. Moreover, some of these catalysts have demonstrated a unique ability to promote the direct oxidative esterification of alcohols in methanol solutions [11,24,33,38,41,47,56]. In these systems, the alcohol oxidation and the subsequent oxidation of primarily formed aldehydes are connected in an effective tandem catalytic process to give corresponding methyl esters, compounds with many practical applications such as solvents, extractants or diluents.

The activity of gold as catalyst is known to be strongly depended on the interaction of AuNPs with the support and therefore on the support nature. Various solid materials have been applied to stabilize AuNPs; however, in spite of important progress, a search for efficient and collaborating supports for the use of AuNPs in oxidation reactions remains to be of a crucial importance.

In the present work, AuNPs supported on the modified red mud materials, i.e. reduced by H_2 or coated with carbon through the reduction with ethanol, were prepared and their catalytic performance in the liquid-phase aerobic oxidation of benzyl alcohol was studied, for the first time as far as we know.

2. Material and methods

2.1. Synthesis of supports and catalysts

Two different supports based on red mud residue were produced, denominated as RMH and RMC. The raw RM suspension (ALCAN) was first washed with milli-Q water and dried in the oven at 80 °C. RMH support was produced via reduction with hydrogen, and RMC by CVD (chemical vapor deposition) reaction of RM with ethanol as carbon source. Both processes took place in similar conditions, i.e. 100 mg of RM placed in horizontal oven and heated to 700 °C (heating rate of 10 °C min^{-1}) under flow of the reactant mixture (50 mL min^{-1}). The final temperature was kept over 3 h before cooling down. The reactant mixtures used were 15% H_2 in N_2 and 15% ethanol in N_2, respectively for reduction and CVD reactions.

The red mud based supports were impregnated with $Au(en)_2Cl_3$. $Au(en)_2Cl_3$ was synthesized as follows: $HAuCl_4{\cdot}3H_2O$ (100 mg) was dissolved in Milli-Q water (1 mL) under magnetic stirring. Then, ethylenediamine (45 μL) and ethanol (7 mL) were added to the solution. After 20 min stirring at room temperature, $Au(en)_2Cl_3$ was separated from the supernatant by centrifugation, washed with ethanol and dried under vacuum at room temperature. The cationic gold ethylenediamine complex $Au(en)_2^{3+}$ was adopted here as the gold source in despite of the anionic chloroauric complex of $AuCl_4^-$ in order to increase the attachment and distribution of gold nanoparticles by adsortive process, mainly onto the electron rich surface of the carbon filaments. The use of gold complexes in similar procedures is well described in the literature, as reported by Corma et al. [9].

The catalysts were produced from $Au(en)_2Cl_3$ (10.8 mg) and the corresponding support (RMH or RMC, 500 mg), with their amounts being calculated to obtain the materials with approximately 1 wt% of Au. Prepared gold catalysts were named as RMH-Au or RMC-Au, respectively. The mixture of $Au(en)_2Cl_3$ and the support with Milli-Q water (ca. 150 mL) was heated at 70 °C to allow the complete and slow evaporation of water favoring the better dispersion of the gold catalyst on the support surface. The mixture was finally dried under vacuum at room temperature and at 65 °C in an oven for more than 12 h. The powder obtained was heated to 300 °C and kept at this temperature for 2 h under nitrogen atmosphere.

2.2. Characterization of the catalysts

The catalysts synthesized were characterized by X-ray diffraction (XRD – Rigaku Geigerflex equipment using Co Kα radiation from 10 to 80° (2θ) at 4° min^{-1}), Mössbauer spectroscopy (CMTE – MA250 spectrometer using $^{57}Co/Rh$ source at room temperature and α-Fe as reference), elemental analysis CHN (Perkin-Elmer analyzer), atomic absorption spectrometry (AA – Hitachi-Z8200 spectrometer), transmission electron microscopy – TEM (microscope Tecnai G2 200 kV – SEI) and EDS microanalysis (JEOL JXA-8900 RL at 15 kV).

2.3. Catalytic tests

The reactions were carried out in a stainless steel 10 mL autoclave with magnetic stirring. A mixture of benzyl alcohol (2.5 mmol), methanol (2 mL), K_2CO_3 (if any) and the catalyst (30.0 mg, 1.5 μmol of Au, 0.06 mol% with respect to the substrate) was inserted in the reactor. The autoclave was pressurized with oxygen to 10 atm and heated to 130 °C in an oil bath under stirring. The reactions were followed by gas chromatography (GC – Shimadzu QP2010-Plus equipment using a Carbowax 20 M capillary column). The reactions were monitored over time by the analysis of small aliquots diluted 25 times with methanol analyzed by chromatography. The reaction products were identified by GC–MS on a Shimadzu QP2010-Plus equipment using 70 eV.

3. Results and discussion

3.1. Synthesis of supports and catalysts

The red mud based gold catalysts RMH-Au and RMC-Au were prepared with the RM reduced with H_2 and with ethanol, respectively. The reduction with ethanol promotes a partially coating of the RM with carbon. Pure red mud was modified before application in order to overcome its limitations, such as: (i) leaching, (ii) low specific surface area and (iii) no magnetism. The supports produced with the modified red mud are magnetic and less subjected to leaching in a contact with a liquid phase. Moreover, RM partially coated with C (after CVD with ethanol) presents a higher surface area. The catalysts RMH-Au and RMC-Au were characterized by different techniques that provided information about their structure, morphology and composition, especially about gold, iron and carbon.

3.2. Characterization of the catalysts

X-ray diffraction (XRD) was applied in the study of the crystalline phases formed during the synthesis. No peaks related to

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