



Gold nanoparticles supported on modified red mud for biphasic oxidation of sulfur compounds: A synergistic effect



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ABSTRACT

Gold nanoparticles were supported on the surface of three different matrixes based on red mud waste: (i) pure red mud, (ii) reduced red mud and (iii) partially carbon coated red mud, in order to produce different catalysts for desulfurization reactions. The catalysts were extensively characterized by X-ray diffraction, Mössbauer spectroscopy, thermogravimetric analyses, electron microscopies (SEM and TEM), energy dispersive spectroscopy (EDS) and BET surface area. Results showed that gold was successfully supported and distributed on the surface of red mud based materials as nanoparticles with diameters around 30 nm. The catalyst prepared with carbon coated red mud has shown to be twice more efficient than others for biphasic desulfurization reactions. This result can be associated with its amphiphilicity, which allows the catalyst to be located on the interface of biphasic systems. In this position a synergistic effect occurs between gold nanoparticles that adsorb S containing molecules and red mud Fe sites that promote the formation of OH radicals. The same effect is not observed for catalyst with hydrophilic supports.

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1. Introduction

Red mud (Rm) is the waste by-product of the Bayer process used to extract alumina (Al_2O_3) from bauxite ores for the production of aluminum metal [1]. It is estimated that for each ton of alumina (Al_2O_3) produced, 0.5–2 ton (on a dry weight basis) of red mud are generated with a global production of about 120 million tons of red mud per year [1,2]. Rm poses several environmental hazards due to its high alkalinity ($\text{pH} > 11$), sodium and heavy metal contents [2] and, in some cases, some large volumes are stored in inappropriate areas. In 2010, a red mud reservoir in Hungary collapsed and an amount around $700,000 \text{ m}^3$ of mud with a pH around 12 was released from the reservoir to the nearby cities [3].

In this context, the development of technologies to give red mud a proper destination is of great interest. Rm has been applied in different areas [4], especially in catalysis. Its properties such as iron content mainly as ferric oxide (Fe_2O_3), relatively high surface area, sintering resistance, resistance to poisoning and low cost make it an attractive potential catalyst for many reactions [5]. Rm has been applied recently to several kinds of catalytic reactions: hydrodechlorinations [6], hydrogenations

[7–9], coal liquefaction [10], biomass liquefaction [11], bio-oil upgrade [12,13], catalytic pyrolysis [14], conversion of waste oil and plastic [15], methane combustion [16], ammonia decomposition [17], methane conversion into syngas [18], hydrocracking reductions [19], biodiesel production [20], biphasic reactions [21,22] and oxidations [21,23,24]. One of the oxidation reactions widely studied recently is the oxidation of sulfur compounds in petroleum [25–28], also known as oxidesulfurization (ODS). It is well known that the sulfur impurities present in fuels are an important source of air pollution, acid rain and they also affect pollution control devices. In order to decrease pollution, ever-stricter legislation has been implemented all over the world to limit the content of sulfur in petroleum fuels. And for this reason, the development of new technologies for sulfur removal is necessary [29].

The deep oxidesulfurization depends on high selectivity of the catalyst due to low sulfur concentrations (less than 50 ppm). In order to improve the Rm capability to remove sulfur contaminants, this work investigated the activity of gold catalysts prepared with different Rm supports. Gold nanoparticles have a differentiated affinity for sulfur [30–32] and were used to enhance the activity of Rm supports in the oxidation of sulfur compounds. The catalysts prepared by gold nanoparticles and active supports may have different and exclusive properties due to a synergistic effect between them.

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Hereon are described recent results involving the preparation and characterization of different red mud materials with supported gold nanoparticles and their application in the oxidation of sulfur contaminants of petroleum fuels.

2. Experimental

2.1. Synthesis of supports and catalysts

Three different supports based on Red Mud residue were produced, i.e. Rm, RmH₂ and RmEt. Raw red mud suspension was obtained from ALCAN. The first support, Rm, corresponds to the raw residue suspension washed with distilled water and dried at 80 °C. In order to produce the second support, RmH₂, the dried Rm was submitted to a reduction reaction with H₂ up to 700 °C for 3 h with heating rate of 10 °C min⁻¹. For the synthesis of RmEt support, a CVD (Chemical Vapor Deposition) reaction was carried out with dried Rm and ethanol as carbon source. The system was also heated up to 700 °C for 3 h with rate of 10 °C min⁻¹ but under flow of ethanol.

The gold complex Au(en)₂Cl₃ was first synthesized. 100 mg of HAuCl₄·3H₂O was stirred with 1 mL of Milli-Q water until complete solubilization. Then 45 μL of ethylenediamine was inserted together with 7.0 mL of ethanol. After 20 min the complex could be purified by centrifugation followed by separation of the supernatant, washing the precipitate with ethanol and drying under vacuum.

The catalysts were produced with 54 mg of the complex Au(en)₂Cl₃ and 500 mg of the support (Rm, RmH₂ or RmEt) in order to obtain materials with 5% of Au. Around 150 mL of Milli-Q water was added to this mixture, leaving it stirring for about 15 min. The mixture was then heated up to 70 °C and kept under magnetic stirring until complete evaporation of water and it was finally dried under vacuum and in an oven at 65 °C for about 14 h. A red powder was obtained, which was heated (10 °C min⁻¹) up to 300 °C for 2 h under N₂ atmosphere (to prevent any oxidation or damage to the structure of Rm).

2.2. Synthesis and characterization of the catalysts

Supports and catalysts were characterized by different techniques, i.e. temperature programmed reduction (TPR), X-ray diffraction – XRD, Mössbauer spectroscopy, thermal analyses – TG/DTA, electron microscopies – SEM and TEM, EDS microanalysis, particles size distribution and surface area and porosity by the BET method.

TPR analyses were carried out using a CHEM BET 3000 TPR Quantachrome equipment equipped with a thermal conductivity detector (TCD) with H₂ (5% in N₂) and heating rate of 10 °C min⁻¹. The powder XRD data WAS obtained in a Rigaku model Geigerflex equipment using Co Kα radiation scanning from 10 to 80° (2θ) at a scan rate of 4° min⁻¹. Silicon was used as an external standard. The transmission Mössbauer spectroscopy experiments were carried out in a spectrometer CMTE model MA250 with a ⁵⁷Co/Rh source at room temperature using α-Fe as a reference. TG analyses were carried out in a Shimadzu TGA-60, with a constant heating rate of 10 °C min⁻¹ under air flow (100 mL min⁻¹). The surface area was determined by nitrogen adsorption using the BET method with a 22 cycles N₂ adsorption/desorption in an Autosorb 1 Quantachrome instrument. Electron microscopies analyses were performed using a microscope SEG – Quanta 200 – SEI for SEM and a microscope Tecnai G2 200 kV – SEI for TEM. Analyses by energy dispersive spectroscopy (EDS) were performed in a JEOL JXA-8900 RL where samples were submitted to 15 kV voltage.

2.3. Catalytic reactions

The gold catalysts and also their pure supports were employed in heterogeneous Fenton reactions in biphasic systems for the oxidation of dibenzothiophene (DBT). Reactions were carried out with 5 mL of organic phase (50 mg L⁻¹ S of DBT in cyclohexane), 1 mL of oxidant aqueous phase (H₂O₂ 30%) and 20 mg of the catalyst. DBT removal was monitored by UV–vis spectroscopy (Shimadzu UV-2550 with photomultiplier detector R-928).

3. Results and discussion

Gold nanoparticles were impregnated on the surface of three different supports based on red mud (Rm) residue: (i) Pure Rm, (ii) Rm reduced with H₂, and finally (iii) Rm after CVD reaction with ethanol. Besides being hazardous and very available, red mud residue is rich in iron oxides (~30%), species of great chemical interest. It also contains thermally stable oxides, i.e. Al₂O₃ and SiO₂, which provide stability to the materials produced. The main disadvantages of pure Rm for the processes studied in this work are: (i) it is not magnetic, (ii) it may suffer leaching, (iii) it presents low surface area and (iv) it is very hydrophilic. In order to overcome these limitations, two supports based on Rm were prepared: (a) Rm reduced with H₂, a magnetic material that does not suffer leaching, and (b) Rm after CVD with ethanol, a magnetic material partially coated with carbon, which does not suffer leaching, has higher surface area and is amphiphilic. These supports led to the catalysts Au/Rm, Au/RmH₂ and Au/RmEt, respectively. These catalysts were extensively characterized in order to obtain information about their structure, morphology, iron phases, composition, surface area and porosity.

In order to characterize the crystalline phases formed in the catalysts Au/Rm, Au/RmH₂ and Au/RmEt, X-ray diffraction (XRD) was used. Fig. 1 shows X-ray diffraction patterns obtained for the three catalysts.

Some peaks related to metallic Au are observed in all XRD patterns of Fig. 1, showing that the impregnation method was efficient and Au was supported on the Rm materials in a crystalline form. The metallic Au phase was characterized according to PDF 1-1172.

In the sample Au/Rm, hematite is identified (PDF 1-1053) as the only crystalline iron phase. It is also possible to observe a characteristic peak of Al₂O₃ (2θ = 33°, PDF 10-414). As Rm has a complex composition, it is possible that peaks relating to other common

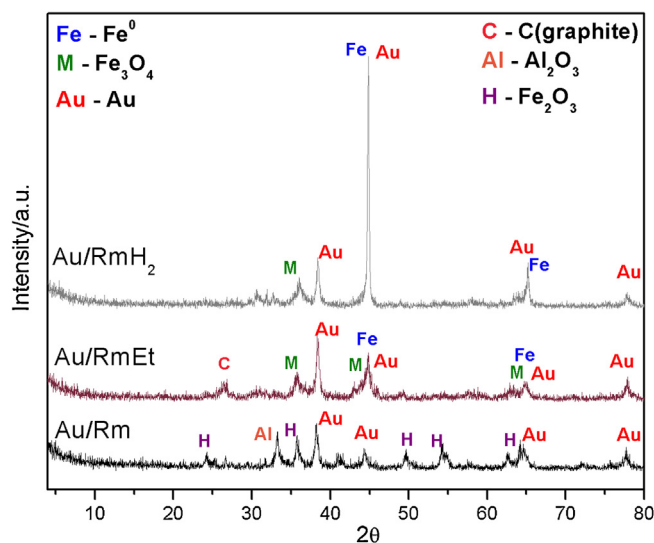


Fig. 1. XRD patterns obtained for samples Au/Rm, Au/RmH₂ and Au/RmEt.

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