



Biphasic oxidation reactions promoted by amphiphilic catalysts based on red mud residue



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ABSTRACT

Biphasic oxidation reactions of organic contaminants with H₂O₂ were promoted by amphiphilic catalysts prepared from red mud residue and carbon nanostructures. Contaminants oxidation is especially important for petroleum treatment, since S and N compounds are extremely unwanted mainly due to environmental issues. Also, government regulations around the levels of these pollutants in fuels are becoming increasingly strict. The amphiphilic catalysts were tested in oxidation of different model molecules: Sudan IV lipophilic dye, thiophene, dibenzothiophene and quinoline and showed very good removal, reaching 100% of contaminants oxidation. The amphiphilic catalysts act in two steps of biphasic oxidation: (i) favor the formation of a reversible emulsion between the organic contaminated phase and the aqueous oxidized phase and (ii) catalyze Fenton reaction. After reaction, the emulsion can be easily separated by a magnetic process into two phases: decontaminated organic phase and aqueous phase with oxidized contaminants.

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1. Introduction

Red mud (RM) is a by-product of aluminum extraction from bauxite ores via the Bayer process [1]. It is estimated that for each ton of alumina (Al₂O₃) produced, 0.5–2 tons (on a dry weight basis) of red mud is generated with a global production of about 120 million tons of red mud per year [1–3]. RM exhibits several environmental hazards due to its high alkalinity (pH > 11), sodium and heavy metal contents [3] and in some cases, large volumes stored in inappropriate areas. In 2010, a red mud reservoir in Hungary collapsed and ca. 700.000 m³ of the mud with a pH around 12 was released from the reservoir to the nearby cities [4] causing 12 deaths and lots of injury.

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, such as metallurgy (recovery of metals [5]), wastewater and waste gas treatment [6], sorption of contaminants [7–9], agriculture, building construction and ceramics [10]. RM has also been used in catalytic applications [11]. Some of these uses as catalysts are in hydrogenations (e.g. of toluene [12], tetrachloroethylene [13,14] and polyaromatic compounds such as

anthracene oil [15,16], naphthalene [17], phenanthrene and pyrene [18]), in oxidations (e.g. of methane [19], chlorohydrocarbons [20], plastic wastes [21] and other volatile organic compounds (VOCs) [22,23]), in catalytic pyrolysis of plastic wastes [24], in upgrading of pyrolysis bio-oil [25], and also as support for catalytic ammonia decomposition [26].

Nowadays there is also an increasing environmental concern about the pollution caused by fossil fuels. During fuel combustion, molecules containing S or N form SO_x and NO_x pollutants, the main responsible for acid rain. Moreover, S-contaminants poison car catalysts preventing them to remove most of the gas pollutants produced during combustion. Ever stricter legislation has been implemented all over the world to limit the content of sulfur and nitrogen in petroleum fuels. And for this reason, the development of new technologies for S and N removal are necessary.

In this work, biphasic oxidations promoted by modified red mud were studied. Red mud was modified by controlled CVD [27] to produce amphiphilic catalysts that act on the interface of biphasic systems [28], especially for oxidation reactions.

Chemical vapor deposition (CVD) is currently the most common technique to grow carbon nanostructures, such as CNTs [29]. Several reasons explain this preference. First, it is technically easy to carry out as in its simplest version it only requires an oven, a tubular reactor, and a set of mass flow controllers to feed the gas mixture. Secondly, a large number of parameters can still be varied

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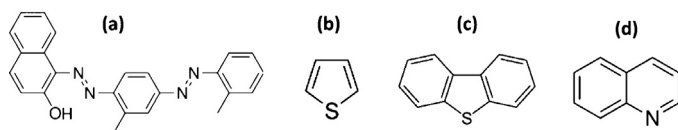


Fig. 1. Chemical structure of substances used in oxidation tests: (a) Sudan IV dye, (b) thiophene, (c) dibenzothiophene and (d) quinoline.

and investigated, both during the catalyst treatment and the CNT growth, which influence both the yield and quality of the CNTs [30].

The mechanism more accepted nowadays for the growth of carbon nanofilaments is known as the vapor–liquid–solid (VLS) mechanism. The VLS mechanism comprises three successive steps. Firstly, a carbon containing gas precursor adsorbs and dissociates on the surface of the catalyst particle to form elementary carbon atoms. Secondly, the carbon atoms dissolve in the bulk of the nanoparticles to form a liquid metastable carbide and diffuse within the particle. Finally, solid carbon precipitates at the rear side of the nanoparticles to form a carbon nanoflament [30].

The reproducibility of CVD synthesis is shown by several works [31,32]. In the last five years, CNTs have been produced in large scale by CVD technique. Nowadays, the parameters to control the characteristics and reproducibility of CNT synthesis are well known.

Recent studies have shown that amphiphilic materials are very efficient in biphasic reactions [33–35], because of their ability to form emulsions between immiscible liquids [28].

Hereon, it is described the application of magnetic amphiphilic composites produced from red mud to promote biphasic oxidation with H_2O_2 of four hydrophobic molecules: Sudan IV dye, thiophene and dibenzothiophene (models for sulfur containing contaminants of petroleum industry) and quinoline (model for nitrogen containing contaminant of petroleum industry). These materials also have the ability of breaking emulsions under action of an external magnetic field, enabling the easy separation of the phases and recovering of the catalyst.

2. Experimental

For the production of amphiphilic catalysts CVD (chemical vapor deposition) reactions were carried out with ethanol at ca. 6% in N_2 and 50 mg of red mud. The reaction was quenched at 700, 800 and 900 °C and the catalysts were named as RmEt700, RmEt800 and RmEt900, respectively. These catalysts produced were extensively characterized [27].

In order to evaluate the interaction of the catalysts on the interface of biphasic systems they were tested as emulsifiers and demulsifiers. Mixtures of water/cyclohexane were used to simulate petroleum mixtures with water. These mixtures were emulsified via addition of the amphiphilic catalysts (500 mg L^{-1}) and sonication. Stable emulsions were formed and characterized by optic

microscopy (Cole Parmer Instrument, 41500-50). These emulsions are naturally broken (phases separated) within 24 h. However, if an external magnetic field is approximated to the emulsion, it can be separated in 2 min.

Due to their amphiphilic properties the catalysts were employed in heterogeneous Fenton reactions in biphasic systems. Oxidation reactions were carried out with 5 mL of organic phase (500 mg L^{-1} in cyclohexane), 1 mL of aqueous phase of hydrogen peroxide (H_2O_2 30%) and 20 mg of the catalyst. The catalysts were left previously in contact only with the organic phase until adsorption equilibrium was reached. Sudan IV (Fig. 1(a)) removal was monitored by UV/vis spectroscopy (Shimadzu UV-2550 – characteristic wavelength 510 nm) and thiophene (Fig. 1(b)) removal by gas chromatography with FID detector (GC/FID, Shimadzu GC17A). Dibenzothiophene (Fig. 1(c)) and quinoline (Fig. 1(d)) oxidations were monitored by gas chromatography coupled to mass spectroscopy (GC/MS, Shimadzu QP2010 – PLUS). Oxidized products extracted by aqueous solution were analyzed by electrospray ionization mass spectrometry (ESI/MS, Agilent ion trap mass spectrometer). Reduction of contaminants concentration was studied over time.

Reuse tests of the amphiphilic catalysts were carried out. The catalysts were used up to five times with fresh solutions of oxidant and contaminants. Metal leaching was also measured after experiments by atomic absorption spectrometry.

3. Results and discussion

Pure red mud was characterized by atomic absorption spectrometry, energy dispersive spectroscopy (EDS), Mössbauer spectroscopy, X-ray diffraction and Raman Spectroscopy. The results showed the presence of 20 wt% of Fe (as Fe_2O_3) and Al_2O_3 (22%), CaO (5%), Na_2O (6%), MnO (0.4%), SiO_2 (11%), TiO_2 (3%) as the main components.

CVD reaction of ethanol and red mud (RM) was studied by TPRE (Temperature Programmed Reaction) experiments. It was observed that during CVD process ethanol reacts with RM promoting the reduction of the iron phase with carbon formation. The resulting composites based on reduced iron phases and carbon deposited on the surface were characterized by Mössbauer spectroscopy, XRD, CHN, BET surface area, SEM, TEM and Raman spectroscopy. The results showed a complex structure with magnetic and amphiphilic properties [27] as depicted in Fig. 2.

The magnetic property of the catalysts is a consequence of reduction of the iron phases present in RM to metallic iron Fe^0 and iron carbide Fe_3C . The distribution of these reduced iron phases vary with CVD temperature but all the catalysts produced are magnetic. Iron phases distribution was determined by Mössbauer spectroscopy. Table 1 shows the Mössbauer hyperfine parameters used for phase determination and also the relative subspectral area of each iron phase.

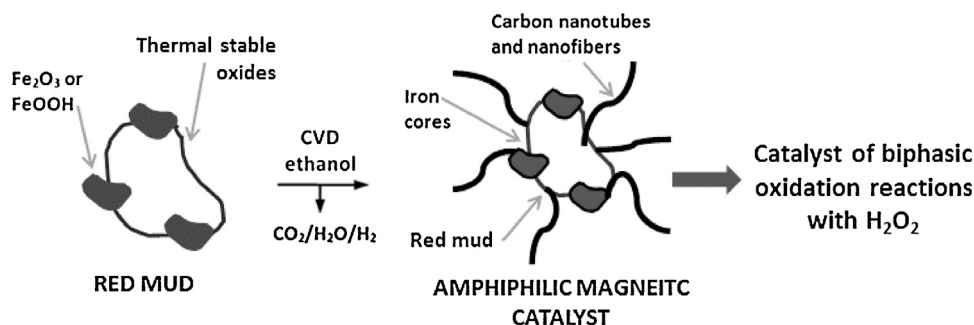


Fig. 2. Schematic structure of the composites obtained after CVD reaction of red mud with ethanol.

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