Hydrogen production from ethanol with low carbon monoxide generation in a one-pot reaction with iron oxides as catalysts

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ABSTRACT

Bulk γ-Fe_2O_3 (maghemite) and Fe_3O_4 (magnetite) were synthesized with Fe(III) hydroxyacetate as an intermediate during the preparation step. The fresh and used catalysts were characterized by X-ray diffraction, N_2 adsorption at 77 K, Mössbauer spectroscopy at 298 K, diffuse-reflectance spectroscopy, and thermogravimetric analysis. The solids were used as catalysts in the ethanol hydrotreatment within the range of 673–758 K. The catalysts showed a satisfactory selectivity for H_2 and an especially low CO production. These activities and selectivities were analyzed in conjunction with the structural properties of the oxides. Magnetite seemed to be a more appropriate catalyst than maghemite since the latter was converted into magnetite at reaction temperatures higher than 713 K because of the reducing atmosphere.

Introduction

Energy surrounds us in all aspects of life and the ability to harness and use that resource for constructive ends—and as economically as possible—is the current challenge of society. Fossil fuels have been the energy source up to the present, to produce heat and electricity upon oxidative combustion. In this reaction, one of the by-products obtained is CO_2, which contributes to the atmospheric greenhouse effect. Researchers worldwide are seeking alternative energy sources to supplant the use of nuclear and fossil-fuel-based energies.

Therefore any advance in sustainable development must gradually incorporate renewable energy sources to avoid the consumption of nonrenewable natural resources. The development of clean, green technologies for energy production is a major challenge today mainly with respect to their use in mobile sources. Fortunately, many means of producing energy with much less damaging impacts on our environment are available.

The use of hydrogen as a substitute for the fossil fuels constitutes a relevant way of reducing greenhouse-gas emissions and improving air quality, especially in highly congested urban areas. Hydrogen is an environmentally clean fuel that

appears to be a solution for use both in internal-combustion engines and in feeding fuel cells for stationary and mobile applications, with that gas already being the primary energy source for fuel cells [1].

An environmentally clean production of hydrogen is possible through the electrolysis of water by means of energy sources that are renewable (e. g., solar energy). This process, however, is not economically profitable because of the current energy costs. The new ecology-friendly technologies for hydrogen production point to biomass as the best energy feedstock. For this purpose, research on the production of hydrogen from the reforming of alcohols by catalysis has strongly increased in recent years. Alcohols are also convenient to store and transport [2]. For example, bio-ethanol—produced industrially from sugar cane, corn, or cereal fermentation—is an especially renewable fuel with low toxicity and high energy density.

Several authors have studied the steam reforming of ethanol. Freni el al [3,4]. found that Rh/Al_2O_3 produced hydrogen with a low ethylene content. Liguras et al. [5] reported a good activity and high stability for Ni/Al_2O_3 catalysts in the same process, whereas Fierro et al. [6] and Nishiguchi et al. [7] have focussed on the catalytic behavior of Ni/Cu and Cu/CeO_2.

In addition, different oxides have been used as catalysts in the ethanol-hydrotreatment process. Llorca et al [8] studied this synthesis using MgO, γ-Al_2O_3, SiO_2, TiO_2, V_2O_5, ZnO, La_2O_3, CeO_2, and Sm_2O_3 as catalysts and obtained the most promising results with ZnO. Barroso et al. [9] observed that if a bulk catalyst based on Ni–Zn–Al was used, the increase of Ni loading produced an enhancement in the selectivity for hydrogen, but an increasing amount of CO production was also obtained. Sánchez-Sánchez et al. [10], however, obtained a low selectivity for CO with an average selectivity for hydrogen at approximately 60% using Ni supported on Al_2O_3 modified with Ce, Mg, Zr, and La. Finally, Muroyama et al. [11] observed that ethanol reforming carried out on $NiFe_2O_4$ and $NiMn_2O_4$ catalysts produced a lower activity and hydrogen selectivity as a result of carbon deposition.

In recent years, fuel-cell development has led up to the point of investigating CO-free hydrogen production. The hydrogen for fuel cells is obtained through three catalytic steps: 1) ethanol steam reforming, 2) the water–gas-shift reaction, and 3) the selective oxidation of CO (i. e., via the so-called CO-PROX process) [12]. The development of a catalyst with a high hydrogen production and the simultaneous capability of consuming in a single step the CO produced as the by-product is therefore of extreme interest. To avoid multi-step processes, Remiro et al. [13] used a Ni/α-Al_2O_3 catalyst at 923 K and achieved total ethanol conversion and no carbon deposition. Horminella and coworkers [14] propose a two stages iron based catalyst methodology that implied higher temperature too to reach low CO in the final mixture products.

To that end the aim of the present work was to study the catalytic behavior of maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) with respect to ethanol hydrotreatment at 673–758 K, atmospheric pressure, and a constant molar ratio H_2O/ethanol of 9/1 in order to produce H_2 with a low content of CO. A high H_2O/ethanol ratio was used to simulate the mixture arising from biomass treatment. However, in order to use this hydrogen for a fuel cell it would be necessary to decrease the water content previously.

Hematite (α-Fe_2O_3) was discarded as a catalyst because of its very low activity [15].

Material and methods

Catalyst preparation

Maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) were obtained through a sol–gel method [16]. An aqueous solution of NH_4OH (30%, w/w) was added to a solution of $Fe(NO_3)_3.9H_2O$ in water (40%, w/v) up to pH = 9.8. The solid thus obtained was washed and centrifuged (at 2000 rpm for 5 min) in NH_4CH_3COO solution (5%, w/v) a total of five times then dried to constant weight in an oven at 333 K. The resulting solid was denoted IHA (i. e., iron-hydroxy-acetate).

The IHA was calcined at 690 K for 2 h in a stream of N_2 (100 cm^3/min) at a heating rate of 10 K/min. The iron oxide thus obtained was denoted m(f). The samples of this solid used in the reactions were indicated as m(673), m(713), or m(758); where the numbers refer to the catalytic test temperatures.

A fraction of m(f) was calcined for 2 h, at 573 K in a stream of air (150 cm^3/min) at a heating rate of 2.3 K/min. The iron oxide obtained was termed g(f). The samples of this solid used in the reactions were accordingly denoted g(673), g(713), or g(758); where the numbers indicate the catalytic test temperatures.

Catalyst characterization

The solids were characterized by N_2 adsorption at 77 K, X-ray diffraction (XRD), Mössbauer spectroscopy at 298 K (MS), diffuse-reflectance spectroscopy (DRS), and thermogravimetric-analysis (TGA).

The textural properties of specific surface area (S_g) and pore diameter (Dp), were measured in the Micromeritics equipment ASAP 2020 V1.02 E.

All XRD patterns were measured using a Phillips PW170 diffractometer with Cu $K\alpha$ radiation, between a $2\theta = 20–70°$ at steps of 0.02° and a counting time of 2 s/step.

The Mössbauer spectra at room temperature (RT) were obtained in transmission geometry with a 512-channel constant-acceleration spectrometer. A source of ^{57}Co in Rh matrix of a nominal 50 mCi was used. The velocity calibration was performed against a 12 μm-thick α-Fe foil. All isomer shifts (δ) cited here refer to this standard. The Mössbauer spectra were evaluated through the use of a fitting program named Recoil Spectral Analysis [17] under the assumption of Lorentzian lines. The spectra were folded to minimize geometric effects.

DRS uv–visible spectra within the 200–800 nm range were recorded in a CINTRA 20 spectrophotometer with an integrated sphere. The spectra were referenced against $BaSO_4$ powder.

TGA on a Shimadzu TGA-50 instrument was carried out in order to determine the surface-carbon deposition onto the