Journal of Hazardous Materials 263P (2013) 11–19

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

On the role of Fe^{3+} ions in Fe_xO_y/C catalysts for hydrogen production from the photodehydrogenation of ethanol

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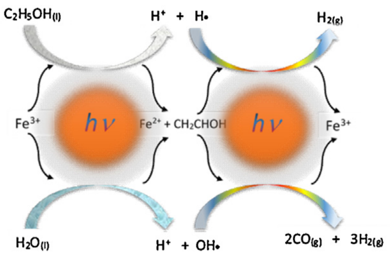
HIGHLIGHTS

- Iron oxides supported on carbon are photoactive catalysts.
- Photoactivity in dehydrogenation of ethanol depends of the amount of Fe^{3+} ions present in the catalysts.
- The capacity of UV–vis absorbance by the Fe_xO_y/C catalysts is significantly dependent of the amount of Fe^{3+} ions.
- A maximum of rate constant, $K = 2125\ \mu mol\ h^{-1}$, was obtained from the sample with 30 wt% Fe.

GRAPHICAL ABSTRACT

In Fe_xO_y/C photocatalyts important effect of Fe^{3+} ions in the photodehydrogenation of the ethano was noticed.



ARTICLE INFO

Article history:
Received 4 January 2013
Received in revised form 25 July 2013
Accepted 2 August 2013
Available online 12 August 2013

Keywords:
Fe_xO_y/C catalysts
Hydrogen production
Rietveld analysis
Non-local density functional theory
Ethanol photodehydrogenation

ABSTRACT

Fe_xO_y/C photocatalysts at different iron content were prepared by the incipient wet impregnation method and calcined at 773 K. The photocatalysts were characterized by means of nitrogen adsorption–desorption isotherms, surface fractal dimension, non-local density functional theory, X-ray diffraction, Rietveld refinement and UV–vis spectroscopy. The photocatalytic activity was evaluated using the photodehydrogenation of ethanol as a model reaction for the production of hydrogen. The specific surface areas of Fe_xO_y/C substrates, with 15, 20 and 30 wt% iron content, diminished from 638 to 490 m^2/g, as the iron content increased. X-ray diffraction analysis showed that iron oxides coexist as wustite and magnetite in samples with Fe contents of 15 and 20 wt%; for sample with 30 wt% Fe, wustite, magnetite and hematite phases were observed. The photophysical, textural and structural properties were modified by the hematite phase formed by thermal treatment. The Rietveld refinements denoted changes in occupancy of Fe^{3+} and Fe^{2+} in Fe_xO_y crystallites. A relationship between the Fe^{3+} ions content and the reactivity for the hydrogen production from the photodehydrogenation of ethanol (from 1360 to 2125 $\mu mol\ h^{-1}$), was evidenced.

1. Introduction

The notably increase in environmental pollution has been one of the main motivating many researchers to propose hydrogen as a promising clean fuel [1–3]. For this purpose, hydrogen production was intensively studied when produced by different sources such as water, methane, methanol and ethanol, among others, using

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http://dx.doi.org/10.1016/j.jhazmat.2013.08.015

semiconductor materials as photocatalysts [4–8]. The photocatalytic processes in liquid phase for hydrogen production have been well accepted since they can be performed at room temperature and at a low cost in comparison with other processes. Today, some research is being focused on the use of transition metals, or metal oxides, such as Ni–Cu–Fe/Al_2O_3 [9], n-Fe_2O_3 [10] and Fe-TiO_2 [11] as photocatalysts in the production of hydrogen.

Surface formation of excited states is a consequence of optical properties characteristic of iron oxides when they are illuminated by a light source with appropriate wavelength. Those states subsequently react with the reagents. In this process, the pairs of electron–hole (e^-/h^+) are generated within the conduction and valence bands of the solid material [12]. It is reported that in photoreactions carried out in aqueous solutions, the photoelectrons generated in the bulk of Fe_2O_3 colloids may migrate toward the interface of the crystallites, so reducing generation of relatively large quantum yield of water within the solids [13]. In addition, iron-based catalysts are particularly attractive due to their low cost and abundance in the earth's crust, in comparison with other transition metals.

In the photodehydrogenation of ethanol for hydrogen production, under catalytic conditions, two hydrogen atoms are eliminated from each molecule of ethanol to form molecular hydrogen according to the following reactions [14]:

$$C_2H_5OH_{(l)} \rightarrow CH_2CHOH_{(l)} + H_{2(g)} \qquad (1)$$

$$CH_2CHOH_{(l)} + H_2O_{(l)} \rightarrow 2CO_{(g)} + 3H_{2(g)} \qquad (2)$$

Finally

$$C_2H_5OH_{(l)} + H_2O_{(l)} \rightarrow 2CO_{(g)} + 4H_{2(g)}, \Delta G^\circ = 191.08\,\mathrm{kJ\,mol^{-1}};\ \Delta E = 1.98\,\mathrm{eV}$$

Although the overall reaction steps of the above reaction have been determined, details of the reaction mechanism vary according to reaction conditions and the specific catalysts employed. When iron oxides are used as photocatalysts, crystallite size effects and, particularly, Fe^{3+} concentration and lattice defects in crystalline structure of the catalysts into photodehydrogenation reaction of ethanol, are not clear.

In this research work, several Fe_xO_y/C catalysts containing FeO (wustite), FeO·Fe_2O_3 (magnetite) and Fe_2O_3 (hematite) catalysts with 15, 20 and 30 wt% Fe content were prepared by the incipient wet impregnation method. Although catalytic properties of activated carbon have already been evidenced in oxidative dehydrogenation reactions, they have been performed at 623 K [15]. Under those reaction conditions, the catalytic properties of activated carbon support can be observed. However, in this research work the photodehydrogenation of ethanol is performed under mild conditions, pH ≈ 7 and 298 K, hence, the carbon support will not be able to act as catalyst in Fe_xO_y/C materials. So that iron oxides immobilized on activated carbon, are responsible of the photodehydrogenation of ethanol. But, the textural properties of carbon such as surface area, volume pore and pore size, allow us to improve reaction kinetics.

Phase compositions, crystalline structures and lattice defects of Fe_xO_y/C catalysts were studied by X-ray diffraction, Rietveld refinement, non-local density functional theory (NLDFT) and UV–vis spectroscopic techniques. The correlation between crystalline structures and their photocatalytic properties in hydrogen production was investigated. A novel reaction mechanism in the photodehydrogenation of ethanol is proposed.

Table 1
Atomic fractional coordinates and occupancies utilized in the Rietveld method for the Fe_xO_y crystalline structures.

FeO (wustite)						
Face-centered cubic						Occupancy
FeO Fm3m (2 2 5)			Atomic fractional coordinates			
Atom	Type	Site	x	y	z	
Fe (1)	Fe^{2+}	4a	0.0000	0.0000	0.0000	0.02083
O (1)	O^{2-}	4b	0.5000	0.5000	0.5000	0.02083
FeO·Fe_2O_3 (magnetite)						
Cubic						Occupancy
FeO·Fe_2O_3 Fd3m (2 2 7)			Atomic fractional coordinates			
Atom	Type	Site	x	y	z	
O (1)	O^{2-}	32e	0.2577	0.2577	0.2577	0.16667
Fe (2)	Fe^{2+}	8a	0.1250	0.1250	0.1250	0.04167
Fe (1)	Fe^{3+}	16d	0.5000	0.5000	0.5000	0.08333
Fe_2O_3 (hematite)						
Rhombohedral						Occupancy
Fe_2O_3 R-3C (1 6 7)			Atomic fractional coordinates			
Atom	Type	Site	x	y	z	
Fe (1)	Fe^{3+}	6b	0.0000	0.0000	0.0000	0.1666
Fe (2)	Fe^{3+}	6a	0.0000	0.0000	0.2500	0.1666
O (1)	O^{2-}	18d	0.5000	0.0000	0.0000	0.5000

2. Experimental

2.1. Catalysts preparation

Fe_xO_y/C catalysts were prepared by the incipient wet impregnation method as follows: proper amounts of iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$ (Sigma–Aldrich) were added to three different beakers each containing 10 ml of deionized water to obtain 15, 20 and 30 wt% of iron content on carbon. Afterwards, carbon (CARBOCHEM, with a surface area of 900 m^2/g) was added to the iron nitrate solutions under constant stirring for 5 min. Next, solids were filtered and dried at 373 K for 24 h, and then calcined in air at 773 K to obtain the final Fe_xO_y/C catalysts.

2.2. Characterization

2.2.1. X-ray diffraction and Rietveld refinement

X-ray diffraction data were obtained in a Bruker Advance D-8 diffractometer with a Cu Kα radiation source and a graphite secondary monochromator beam. Intensities were obtained in 2-theta ranges between 32° and 110° with a step of 0.01° and a measuring time of 10 s per point. The crystalline structures of iron oxides were refined by the Rietveld method using Rietica software [16] and the parameters shown in Tables 1 and 2 [17–19]. In order to find quantitative changes in the densities obtained by the Rietveld refinement, theoretical density (Table 2) for each phase was calculated by the following equation:

$$\rho = \frac{(Z)(MM)(\text{Avogadro's\_number})^{-1}}{\text{Cell\_volume}}$$

where MM is the atomic weight for each case and Z is the number of molecules/cell.