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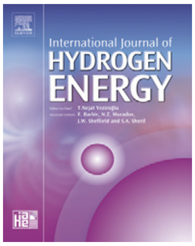

Development of robust Co-based catalysts for the selective H_2-production by ethanol steam-reforming. The Fe-promoter effect

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ABSTRACT

The effect of iron promoter on cobalt-based catalysts, active in the ethanol steam-reforming, was studied. $Fe_xCo_{3-x}O_4 (0 \leqslant x \leqslant 0.60)$ oxides prepared by co-precipitation and an Fe-doped Co_3O_4 prepared by wetness impregnation are analysed. The activation process of the oxides under reaction conditions was studied by *in situ* X-ray diffraction (XRD); the activation depended on the iron content of the oxides. The systems were characterized by means of temperature programmed reduction (TPR), XRD and tested in the ethanol steam-reforming reaction at 623–673 K. An optimal iron loading that gives rise to a high H_2selectivity and catalyst stability was determined.

1. Introduction

Nowadays, there is an increased need to reduce energy dependence on fossil fuels. Hydrogen is considered a renewable and environmentally friendly energy-carrier able to help in this process *via* its use in fuel cells systems. Moreover, the use of biomass-derived sources to produce H_2 is a very attractive route. In this context, ethanol is an alternative as hydrogen carrier [1,2]. Ethanol is an easy-to-handle liquid combustible and has a low toxicity. Catalysed ethanol steam-reforming is considered a promising process for hydrogen production which is yielded through:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2.$$

Despite its apparent simplicity this process is complex and proceeds *via* different intermediates which could produce undesirable by-products such as CO in the reactor-effluent. Different catalysts have been studied both in order to maximize hydrogen selectivity and to inhibit coke formation as well as CO production. These systems include: noble metals, such as Pt, Pd, Ru, Rh [3–6], nickel [7–9] and cobalt-based catalysts [10–12]. Moreover, not only the metal phase, but also the support used, has been shown to influence catalytic performance [13,14]. In Co-based catalysts Na^+ addition has been proposed to avoid the deactivation *via* carbon deposits [10,15]. Other studies have analysed the effect of the presence of Ni and Cu in cobalt-based catalyst [16]. Despite the fact that monometallic ZnO-supported Cu or Ni catalysts do not perform well in the reforming conditions used, the addition of Ni to ZnO-supported Co was found to have a positive effect in the catalytic performance for the production of hydrogen at low temperature (<573 K). Evidence for metal solid–solution formation as well as mixed oxides at the micro-structural level was determined. There is

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still interest in improving catalytic performance at low temperature using low water/ethanol ratio during long-time operation minimising the CO production. This is mainly due to the energy-cost derived for fuel transportation. Thus, as a natural continuation of research work in our group, the present paper presents recent advances in the bimetallic Co catalysts used in the ethanol steam reforming to produce hydrogen. For this purposes, we analyse the promoter effect of incorporating iron in cobalt catalysts based on a structurally well-defined form. The catalysts were characterized by means of *in situ* and *ex situ* X-ray diffraction (XRD), temperature programmed reduction (TPR), and tested in the ethanol steam-reforming reaction operating at a water to ethanol molar ratio of 6.

2. Experimental

2.1. *Preparation of catalysts*

The $Fe_xCo_{3-x}O_4$ samples were prepared by co-precipitation using $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ solutions and NaOH as precipitating agent. After aging at 333 K for 10 h, the suspension was filtered, washed with distilled water and calcined in air at 723 K for 4 h. An Fe-doped Co_3O_4 catalyst (ca. 1% w/w Fe) was prepared by wetness impregnation of a $Fe(NO_3)_3 \cdot 9H_2O$ solution over previously prepared Co_3O_4. The impregnate was dried at 373 K overnight and calcined in air at 723 K for 4 h.

2.2. *Catalyst characterization*

The metal contents were determined by optical emission spectroscopy with inductively coupled plasma using Thermo Jasc el Ash equipment. Specific areas were calculated using the BET method on an ASAP-9000 Micromeritics. TPR experiments were carried in a Micromeritics Autochem II apparatus. The reduction profiles were obtained by passing a 12% H_2/Ar flow through the sample. The temperature was increased from 300 to 1000 K at a rate of 10 K min^{-1}, and the amount of hydrogen consumed was determined as a function of temperature. The powder XRD patterns were recorded in a Siemens D-500 X-ray diffractometer, using Ni-filtered Cu Kα1 radiation ($\lambda = 0.15406$ nm) and collected in the 2θ angle between 34° and 54°, at a step width of 0.08° and by counting 5 s at each step. XRD patterns were fitted using Rayflex software to calculate the lattice parameters. *In situ* XRD study was carried out under steam-reforming operation conditions using an ANTON PAAR chamber in which we placed a special home-made reactor-cell described elsewhere [17]. An ethanol–water mixture ($C_2H_5OH : H_2O = 1 : 6$ molar ratio) was introduced by bubbling a constant flow of 20 ml/min of Ar through an appropriate thermostated saturator. The sample was first heated up to 473 K under Ar, then the $C_2H_5OH + H_2O$ mixture was introduced and the temperature progressively raised up to 673 K. Structural changes and reaction products were monitored simultaneously. When the activation process under H_2 was carried out, after the thermal treatment under Ar, a flow of pure H_2 (20 ml/min) was introduced into the XRD chamber with increasing temperature up to 973 K.

2.3. *Catalytic test*

The ethanol steam-reforming was carried out at atmospheric pressure in the temperature range of 623–673 K using a U-shaped quartz reactor over 50 mg of sample diluted with inactive SiC under a GHSV = 5200 h^{-1}. The samples were heated to 573 K under Ar, then the C_2H_5OH/H_2O mixture was introduced, and the temperature raised up to 673 K. Complete product analysis was accomplished by on-line gas chromatography as described in detail elsewhere [10]. Response factors for all products were obtained with appropriate standards before and after each catalytic test. The selectivity of the products was calculated on the basis of molar percentage of each product evolved (water excluded) with respect to the total moles of products formed.

3. Results and discussion

3.1. *Composition and structure of oxidic samples*

The chemical composition and the BET areas obtained for the oxidic samples are compiled in Table 1. Fig. 1 shows a selected zone of the XRD patterns of $Fe_xCo_{3-x}O_4$ samples. For $x \leqslant 0.15$,

Table 1 – Chemical composition and BET surface-area of samples

Catalyst	Fe(% w/w)	Na(% w/w)	(m^2/g)
Co_3O_4	0	1.93	40.9
$Fe_{0.07}Co_{2.93}O_4$	1.53	2.83	33.8
$Fe_{0.15}Co_{2.85}O_4$	3.05	2.63	42.8
$Fe_{0.29}Co_{2.71}O_4$	5.55	0.14	33.7
$Fe_{0.44}Co_{2.56}O_4$	7.73	1.51	42.1
$Fe_{0.60}Co_{2.40}O_4$	10.63	1.93	31.4
Fe/Co_3O_4	0.73	3.27	22.2

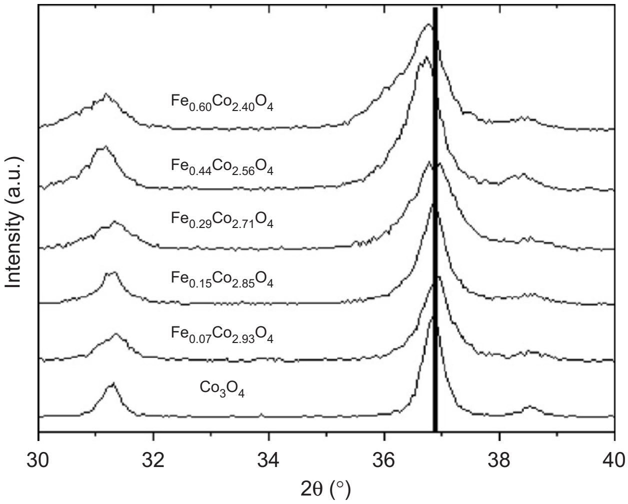

Fig. 1 – X-ray diffraction patterns of $Fe_xCo_{3-x}O_4$ fresh samples in a selected 2θ profile zone.