

# X-ray diffraction study of $\text{Co}_3\text{O}_4$ activation under ethanol steam-reforming

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Available online 15 November 2006

## Abstract

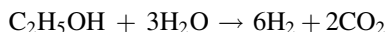
The evolution of  $\text{Co}_3\text{O}_4$  during ethanol steam-reforming was investigated under *operando* conditions by using XRD measurements. The study was carried out at atmospheric pressure as a function of reaction temperature, flowing a 1/6 ethanol/water mixture. XRD measurements and catalytic evaluation were simultaneously accomplished using a reactor-cell specially designed for these purposes. Up to 548 K, only the presence of  $\text{Co}_3\text{O}_4$  crystalline phase was determined, and under these conditions ethanol was dehydrogenated to acetaldehyde. At higher temperatures,  $\text{Co}_3\text{O}_4$  reduced to crystalline CoO and small metallic cobalt particles. Simultaneously, the material became active for the ethanol steam-reforming reaction. At 623 K, the material which showed by XRD the presence of both CoO and Co phases, was very selective in the steam-reforming of ethanol.

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**Keywords:** *Operando* X-ray diffraction; Ethanol steam-reforming; *In situ* techniques; Hydrogen production; Cobalt oxides

## 1. Introduction

Catalysed ethanol steam-reforming is considered a promising route for producing hydrogen which is yielded through:



Among others, one advantage over other sources of hydrogen is that ethanol is a renewable source which can be easily obtained from biomass [1,2]. However, undesirable side-reactions can take place and products other than hydrogen and  $\text{CO}_2$  are usually obtained, the selectivity of the process being a key aspect to be considered for a potential applicability [2,3]. Specifically, there is considerable interest in producing CO-free hydrogen to be used in fuel-cells which operate at low temperatures to avoid the poisoning of their electrodes by CO [4,5]. We have shown in previous works that cobalt-based catalysts are appropriate to produce hydrogen from the steam-reforming of ethanol, giving

high selectivity values. In some cases, a transformation of the cobalt phases initially present in the catalyst has been determined after reaction [6]. On the other hand, the treatment of  $\text{Co}_3\text{O}_4$  under ethanol-steam-reforming conditions has been shown to produce its transformation, and magnetic measurements have allowed us to establish the appearance of  $\text{Co}^0$  as a function of reaction temperature [7].

A key aspect in heterogeneous catalysis is the knowledge of the active species. However, catalysts are usually only characterized before and/or after reaction, thereby, making it impossible to determine the catalysts' characteristics during operation. On the other hand, X-ray diffraction (XRD) technique has been successfully employed to *in situ* characterize several catalytic systems [8–10].

Taking into account the interest in the use of cobalt-based catalysts for ethanol steam-reforming and the lack of previous characterization studies under operation conditions, an *operando* study by X-ray diffraction was carried out over  $\text{Co}_3\text{O}_4$ . The  $\text{Co}_3\text{O}_4$  phase is usually the cobalt-based phase precursor of metallic cobalt in cobalt-based catalysts. In these experiments,  $\text{Co}_3\text{O}_4$  evolution was followed both under hydrogen and under ethanol steam-reforming conditions, thereby determining simultaneously the XRD pattern and the products formed.

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The simultaneous determination of both parameters under several variable reaction conditions was made possible by using the experimental equipment developed for this work. The goal of this study is to bring a better knowledge of cobalt-based catalysts which have been shown to be appropriate for the ethanol steam-reforming.

## 2. Experimental

The  $\text{Co}_3\text{O}_4$  material under study was prepared by adding a NaOH solution until pH 12 over a  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution at 353 K. The solid was filtered, washed, dried at 373 K for 16 h and calcined in air at 723 K for 4 h.

The powder X-ray diffraction study was carried out under *operando* conditions in a Siemens D-500 X-ray diffractometer equipped with an ANTON PAAR chamber in which we placed a special reactor-cell containing the sample (0.02 g). Temperature was measured by a thermocouple in contact with the sample holder.

The system allowed recording of the XRD patterns of the sample under a flow of reactant gases at different temperatures. The reactor-cell was directly connected to a gas microchromatograph (4900 Varian Inc.) to analyse the products formed. The XRD patterns were recorded using nickel-filtered  $\text{Cu K}\alpha_1$  radiation ( $\lambda = 0.15406$  nm). The XRD profiles were collected in the  $2\theta$  angle between  $34^\circ$  and  $54^\circ$ , at a step width of  $0.08^\circ$  and by counting 5 s at each step. An ethanol–water mixture ( $\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O} = 1:6$  molar ratio) was introduced by bubbling a constant flow of 20 ml/min of Ar through an appropriate thermostated saturator. The Ar supply was maintained using a Brooks (Model 5850TR) mass flow controller. The sample was first heated up to 473 K under Ar, then the  $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$  mixture was introduced and measurements were performed at various temperatures starting from 523 K. Structural changes and reaction products were monitored simultaneously at increasing temperature stepwise from 523 to 673 K, and then down to 623 K. When the activation process under hydrogen was carried out, after the thermal treatment under argon, a flow of pure  $\text{H}_2$  (20 ml/min) was introduced into the XRD chamber with increasing temperature up to 973 K.

Standard catalytic tests were carried out in a Microactivity Reference equipment (PID Eng&Tech. S.L.) at atmospheric pressure using, 0.1 g of  $\text{Co}_3\text{O}_4$  diluted with inactive SiC and a vaporized ethanol–water mixture ( $\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O} = 1:6$  molar ratio) diluted in He ( $\text{He}/(\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}) = 3$  molar ratio). Products were analysed on-line with a microchromatograph (4900 Varian Inc.). The catalytic performance as a function of temperature was analysed. Following a reaction temperature change, the first data point was taken after 1 h, each temperature was kept at least 4 h in order to achieve a new steady state.

BET surface areas were determined by  $\text{N}_2$  adsorption at 77 K using a Micromeritics ASAP9000 apparatus.

Temperature-programmed reduction (TPR) experiments were carried out with a Micromeritics Autochem II apparatus equipped with a thermal conductivity detector. The reduction profiles were obtained by passing a 12%  $\text{H}_2/\text{Ar}$  flow at a rate of

50 mL (STP)  $\text{min}^{-1}$  through the sample (weight around 20 mg). The temperature was increased from 300 to 1000 K at a rate of  $10 \text{ K min}^{-1}$ , and the amount of hydrogen consumed was determined as a function of temperature.

## 3. Results and discussion

Synthesized  $\text{Co}_3\text{O}_4$  showed an XRD pattern which only contained peaks corresponding to  $\text{Co}_3\text{O}_4$  spinel phase. The most intense reflection (3 1 1) appearing at  $2\theta = 36.7^\circ$  was used to determine the crystallite size using the Scherrer equation [11]. A particle size of 21 nm was obtained, which was similar to that calculated from the (4 0 0) reflection at  $2\theta = 44.7^\circ$  (20 nm). The BET surface area of the  $\text{Co}_3\text{O}_4$  starting material was  $44 \text{ m}^2/\text{g}$ . The preparation of  $\text{Co}_3\text{O}_4$  was accomplished by precipitation with NaOH because the presence of sodium has been shown to be effective in avoiding deactivation phenomena of cobalt-based catalysts for ethanol steam-reforming [12]. The analysis of the sodium content of sample showed a value of 0.2% (wt/wt) Na.

As stated in Section 2, a separate standard catalytic test (Table 1) was carried out over  $\text{Co}_3\text{O}_4$ . This experiment allowed to evaluate the catalytic behaviour of  $\text{Co}_3\text{O}_4$  in the steam-reforming of ethanol and to determine if the sample was activated under the reaction conditions used in this work. The sample was exposed at 623 K to a flow of ethanol/water (1:6 molar ratio). At this temperature, low values of ethanol conversion were achieved and acetaldehyde and  $\text{H}_2$  were formed (see Table 1) which indicated that the dehydrogenation of ethanol took place:



An increase of temperature to 648 K produced an increase of the ethanol conversion and besides acetaldehyde and hydrogen minor amounts of  $\text{CO}_2$  were detected. Table 1 shows that a subsequent increase of temperature at 673 K produced a significant increase in the ethanol conversion which in turn increased with time. Apparently,  $\text{Co}_3\text{O}_4$  activated after the

Table 1  
Catalytic results from the standard test of ethanol-steam-reforming

T (K)	t (h) <sup>a</sup>	Ethanol conversion (%) <sup>b</sup>	Selectivity (%) <sup>c</sup>				
			$\text{H}_2$	CO	$\text{CH}_4$	$\text{CO}_2$	$\text{CH}_3\text{CHO}$
623	1	18	59.4	–	–	–	40.6
623	4	20	54.8	–	–	–	45.2
648	5	29	61.4	–	–	2.2	36.4
648	9	30	59.8	–	–	1.7	38.5
673	10	48	63.9	–	0.5	5.5	30.1
673	14	50	63.4	–	0.9	6.5	29.2
673	19	100	72.8	–	5.8	21.4	–
673	24	100	71.6	–	6.2	22.2	–
648	25	99	68.4	1.3	8.3	21.7	0.3
648	29	98	68.9	1.1	6.4	23.6	–
623	30	90	61.6	11.4	9.1	11.7	6.2

<sup>a</sup> Cumulative time.

<sup>b</sup> Reaction conditions:  $\text{EtOH}:\text{H}_2\text{O} = 1:6$ ;  $\text{He}/(\text{EtOH} + \text{H}_2\text{O}) = 3$ ; total GHSV =  $5000 \text{ h}^{-1}$ .

<sup>c</sup> Water not included.

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