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X-ray diffraction study of Co_3O_4 activation under ethanol steam-reforming

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Abstract

The evolution of Co_3O_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 Co_3O_4 crystalline phase was determined, and under these conditions ethanol was dehydrogenated to acetaldehyde. At higher temperatures, Co_3O_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.

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:

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

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 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 Co_3O_4 under ethanol-steam-reforming conditions has been shown to produce its transformation, and magnetic measurements have allowed us to establish the appearance of 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 Co_3O_4. The Co_3O_4 phase is usually the cobalt-based phase precursor of metallic cobalt in cobalt-based catalysts. In these experiments, Co_3O_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 Co_3O_4 material under study was prepared by adding a NaOH solution until pH 12 over a $Co(NO_3)_2 \cdot 6H_2O$ 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 Cu $K\alpha_1$ radiation ($\lambda = 0.15406$ nm). The XRD profiles were collected in the 2θ angle between 34° and 54°, at a step width of 0.08° and by counting 5 s at each step. 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 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 $C_2H_5OH + H_2O$ 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 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 Co_3O_4 diluted with inactive SiC and a vaporized ethanol–water mixture ($C_2H_5OH:H_2O = 1:6$ molar ratio) diluted in He ($He/(C_2H_5OH + H_2O) = 3$ 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 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% H_2/Ar flow at a rate of 50 mL (STP) min^{-1} through the sample (weight around 20 mg). 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.

3. Results and discussion

Synthesized Co_3O_4 showed an XRD pattern which only contained peaks corresponding to Co_3O_4 spinel phase. The most intense reflection (3 1 1) appearing at $2\theta = 36.7°$ 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 $2\theta = 44.7°$ (20 nm). The BET surface area of the Co_3O_4 starting material was 44 m^2/g. The preparation of Co_3O_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 Co_3O_4. This experiment allowed to evaluate the catalytic behaviour of Co_3O_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 H_2 were formed (see Table 1) which indicated that the dehydrogenation of ethanol took place:

$$C_2H_5OH \rightarrow CH_3CHO + H_2$$

An increase of temperature to 648 K produced an increase of the ethanol conversion and besides acetaldehyde and hydrogen minor amounts of 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, Co_3O_4 activated after the

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

T (K)	t (h)[a]	Ethanol conversion (%)[b]	Selectivity (%)[c]				
			H_2	CO	CH_4	CO_2	CH_3CHO
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

[a] Cumulative time.

[b] Reaction conditions: $EtOH:H_2O = 1:6$; $He/(EtOH + H_2O) = 3$; total GHSV = 5000 h^{-1}.

[c] Water not included.

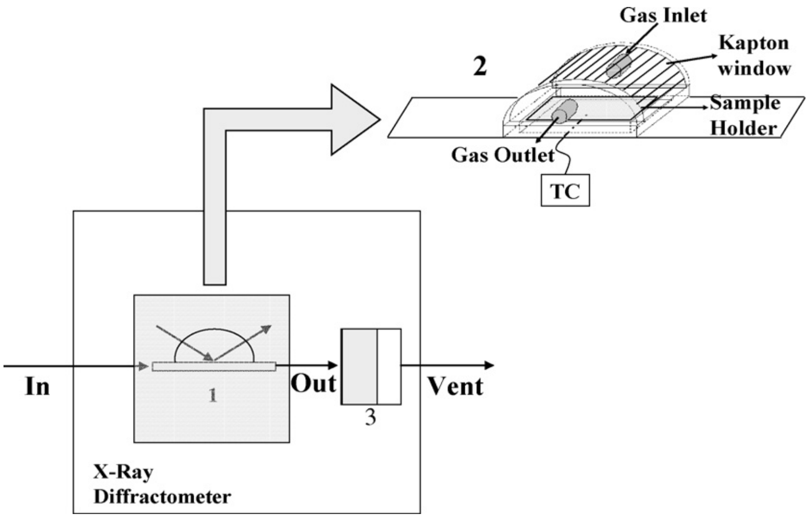

Fig. 1. Experimental system used to accomplish the XRD study under *operando* ethanol-steam-reforming conditions. (1) Anton Paar chamber; (2) designed reactor-cell; (3) micro gas chromatograph.

treatment at 673 K under reaction conditions and ethanol was quantitatively reformed:

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

Only CH_4 being detected as by-product. After reaction at 673 K, the temperature was lowered to 648 K and then, the catalyst mainly produced the reforming of ethanol under near total ethanol conversion. This behaviour contrasts with that of the catalyst before the treatment at 673 K. A subsequent decrease of temperature at 623 K showed besides the production of H_2 and CO_2 the presence of CO and CH_4 (see Table 1). That may be related with the acetaldehyde decomposition which has been shown to occur over a cobalt-based deactivated catalyst under reforming conditions [13].

The change in the behaviour of the catalyst at 648 and 623 K before and after reaction at 673 K (see Table 1) may be related with its activation under reaction conditions. These facts accord with previous work carried out over Co_3O_4 prepared by the citrate method and tested under richer water content ethanol:-water mixtures. That work indicated that, after reaction, reduced cobalt phases appeared that could be related to the progressive activation of the solid [7].

The use of characterization methods under catalyst operation conditions is a powerful tool for in-depth study of materials transformation under reaction conditions [14,15]. The *operando*–XRD study on Co_3O_4 proposed in this work should allow a better knowledge of cobalt-based catalysts, which have been shown to be appropriate for the ethanol steam-reforming.

Fig. 1 shows the system used to accomplish the study. In brief, the designed experimental equipment allowed the recording of XRD patterns of a solid at variable temperature and under an appropriate gas flow. Simultaneously, evolved products could be analysed.

As stated in Section 2, in this work the evolution of bulk Co_3O_4 was followed as a function of temperature both under H_2 treatment and under ethanol steam-reforming conditions. Fig. 2 compiles the XRD patterns obtained *in situ* during the H_2 treatment. Initially, only peaks due to the reflections of Co_3O_4 are visible. Peaks at 2θ 36.7°, 38.4° and 44.7°, correspond to (3 1 1), (2 2 2) and (4 0 0) reflections of Co_3O_4 spinel. When the temperature was increased, these peaks progressively disappeared, and others due to CoO appeared (2θ 36.3° (1 1 1), 42.3° (2 0 0)). At 598 K, the main presence of CoO can be deduced from the XRD pattern in Fig. 2. At 623 K, CoO started to transform into fcc Co (reflections at 44.1° and 51.3° correspond to (1 1 1) and (2 0 0) planes, respectively). This progressive transformation corresponded well with the TPR experiment illustrated in Fig. 3. The two maxima of H_2 consumption at *ca*. 590 and 640 K are due to the two-step reduction of Co_3O_4:

$$Co_3O_4 \rightarrow CoO \rightarrow Co$$

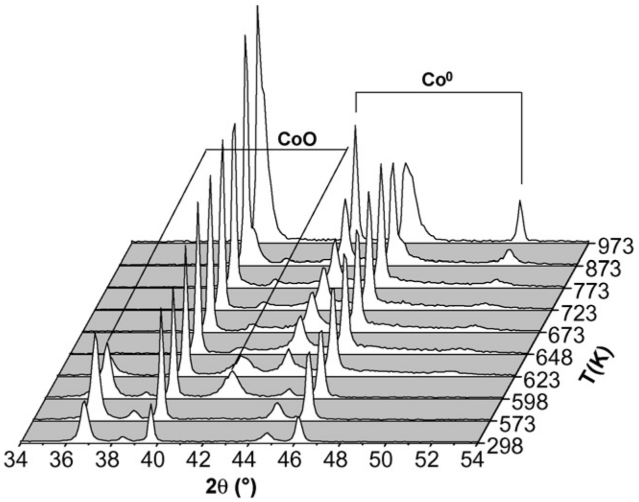

Fig. 2. XRD patterns corresponding to *in situ* reduction of Co_3O_4 under hydrogen as a function of temperature. Peaks (2θ) at 39.6° and 46.1° are due to Pt holder.

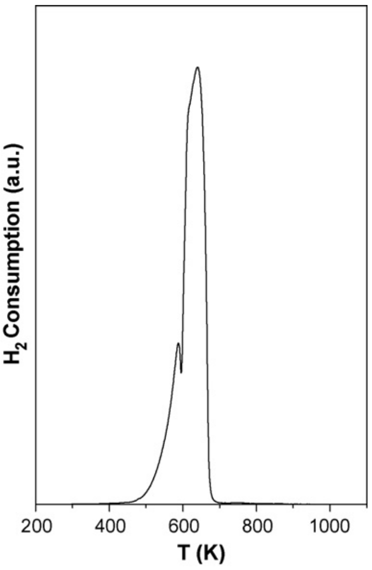

Fig. 3. TPR experiment of Co_3O_4.

At 648 K, CoO is no longer detected by XRD in the experimental conditions used in this work (see Fig. 2).

The two-step reduction of bulk Co_3O_4 had been previously demonstrated to take place at temperatures which depend on the calcination temperature used in its preparation. The calcination temperature in turn conditions the particle-size of the Co_3O_4 synthesized [16].

Diffraction patterns corresponding to the evolution of Co_3O_4 under ethanol steam-reforming conditions as a function of temperature appear in Fig. 4. At 573 K, the transformation of bulk Co_3O_4 into crystalline CoO starts to be observed. The developed cobalt(II) oxide partially evolved into metallic cobalt at temperatures above 623 K. Although the presence of a peak centred at *ca*. $2\theta = 44.4^\circ$ does not allow to distinguish between hcp and fcc cobalt ((0 0 2) reflection of hcp Co appears at 44.7° and (1 1 1) of fcc Co at 44.2°), the presence of peaks at *ca*. 47.6° and 51.5° points to the coexistence of both hcp and fcc Co phases ((1 0 1) reflection of hcp Co appears at $2\theta = 47.6^\circ$ and the (2 0 0) reflection of fcc Co at $2\theta = 51.5^\circ$). It should be stressed that under the reaction conditions used, CoO did not transform completely into metallic cobalt even at 673 K, and the coexistence of bulk CoO and Co phases was maintained when the reaction temperature was lowered to 623 K. However, as discussed above, under pure hydrogen, Co_3O_4 reduced to CoO at a lower temperature (598 K) and, in the 623–973 K range, single phase fcc Co was detected.

In contrast with XRD patterns obtained under hydrogen (Fig. 2), the quality of those obtained under ESR conditions diminished when the reaction temperature increased. The formation of carbon nanostructures, that may increase the sample volume and consequently produce a change of its diffraction plane, could contribute to this fact.

Turning again to the study under *operando* of steam-reforming of ethanol, the presence of the crystalline phases appearing in Fig. 4 can be correlated with the catalytic performance of the material in the ethanol reforming reaction which was simultaneously determined.

The activation process in terms of catalytic performance is well illustrated in Fig. 5 on the basis of hydrogen produced and ethanol converted at each temperature and along time. In the graph, it can be observed that initially there is an increase in the ethanol conversion, which then remains almost constant. Meanwhile, the temperature increases up to 573 K for 1 h, while simultaneously the production of H_2 decreases. Throughout this period of time, a progressive transformation of the Co_3O_4 spinel phase into CoO occurs, as depicted in Fig. 4, with the coexistence of Co_3O_4 and CoO occurring at 573 K. Consequently, a consumption of H_2 is expected to take place to accomplish the reduction process. A subsequent increase of temperature up to 623 K produced an abrupt increase of both ethanol conversion and hydrogen production, and at this temperature the cobalt formation was detected by XRD. However, at the transient temperature 598 K the selectivity to hydrogen remained low, that could be related with the reduction of CoO.

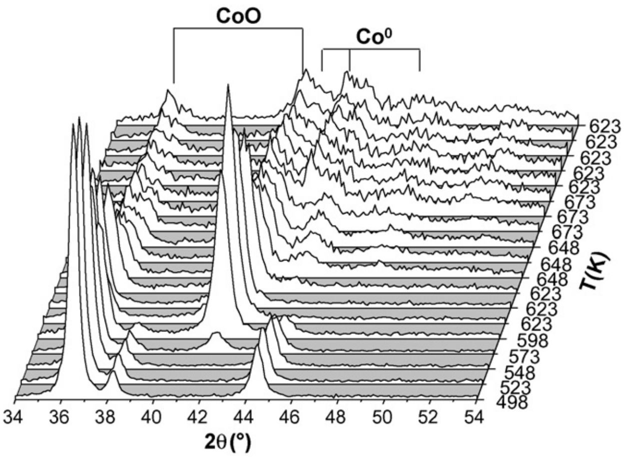

Fig. 4. XRD patterns corresponding to the transformation of Co_3O_4 under *operando* ethanol steam-reforming as a function of temperature.

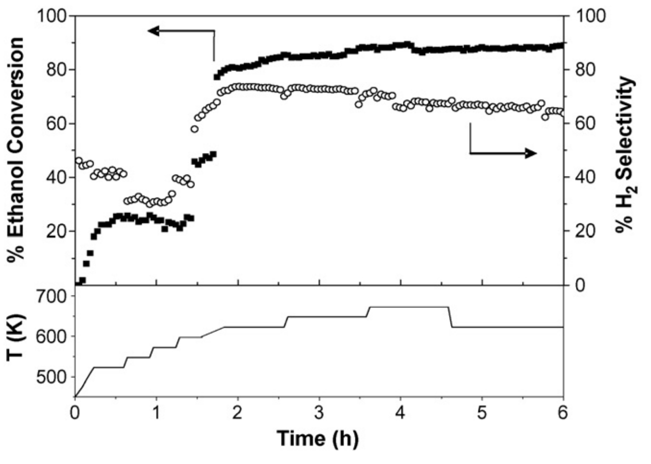

Fig. 5. Ethanol conversion and hydrogen selectivity profiles of catalyst as a function of the temperature and time of the *operando* XRD/steam-reforming experiment.

Table 2
Catalytic behaviour on the ethanol steam-reforming, and main crystalline phases determined by XRD under *operando* conditions

T (K)	Ethanol conversion (%)[a]	Selectivity (%)[b]					Detected by XRD
		H_2	CH_4	CO_2	CH_3CHO	C_3H_6O	
523	25	41.6	–	0.8	57.5	0.1	Co_3O_4
548	24	31.1	–	1.1	67.7	0.1	Co_3O_4
573	22	31.8	–	1.6	66.5	0.1	Co_3O_4-CoO
598	46	40.8	0.7	5.5	53.0	–	Co_3O_4-CoO
623	81	73.0	2.0	25	–	–	CoO-Co^0
648	85	71.5	2.2	26.3	–	–	CoO-Co^0
673	89	67.2	2.1	30.7	–	–	CoO-Co^0
623	88	64.0	2.2	33.8	–	–	CoO-Co^0

[a] Reaction conditions: EtOH:H_2O = 1:6; Ar/(EtOH + H_2O)= 40; total flow = 20 ml/min.
[b] Water not included.

Table 2 compiles the product selectivity at each reaction temperature under *operando* conditions. Up to 573 K, the main products obtained were hydrogen and acetaldehyde. This indicates that the initial reaction step could be the dehydrogenation reaction of ethanol to acetaldehyde. This has been recently reported for supported cobalt catalysts [13].

Initially, the selectivity to hydrogen was lower than that to acetaldehyde, probably because there is a consumption of hydrogen for Co_3O_4 reduction. At 623 K and up to 673 K the product distribution indicated that the main reaction was the ethanol steam-reforming reaction, which could be related to the presence of metallic cobalt. Methane was the only by-product under these experimental conditions and acetaldehyde was no longer detected. However, longer reaction periods produced a progressive deactivation of the catalyst, probably through carbon deposition.

4. Conclusions

It is concluded that the Co_3O_4 spinel phase itself is not active in the ethanol steam-reforming reaction. The Co_3O_4 transformation into CoO and metallic Co under reaction conditions, as detected under *operando* conditions, yields a material highly active and selective for the steam-reforming of ethanol. Evolved hydrogen from ethanol dehydrogenation, acts successively as a reducing agent of the Co_3O_4 and CoO phases. However, the presence of other products in the reactant atmosphere modifies both the temperature at which the reduction steps take place and the characteristics of the final encountered cobalt phase with respect to the evolution of Co_3O_4 under hydrogen. Further improvements to avoid catalyst deactivation are needed.

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