

Transformation of Co₃O₄ during Ethanol Steam-Re-forming. Activation Process for Hydrogen Production

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The transformation of Co₃O₄ during steam-re-forming of ethanol was investigated at atmospheric pressure in the 523–673 K temperature range using a bioethanol-like mixture. The initial and after reaction materials were characterized by the Brunauer–Emmett–Teller method, X-ray diffraction, Raman spectroscopy, scanning electron microscopy, transmission electron microscopy, and in situ magnetic measurements. The performance in the ethanol steam-re-forming of the initial material and of those materials obtained under the reaction conditions was determined. During the activation process, in situ magnetic measurements and catalytic evaluation were carried out simultaneously. At 573 K, ethanol is dehydrogenated to acetaldehyde over Co₃O₄. At higher temperatures, Co₃O₄ is reduced to CoO and small metallic cobalt particles. Simultaneously, the material becomes active for the ethanol steam-re-forming reaction. Up to 5.2 mol of H₂/mol of ethanol is obtained at temperatures as low as 623 K, and only methane (<3%) is obtained besides hydrogen (>72%) and carbon dioxide (>25%).

Introduction

Co₃O₄ is considered an interesting material in catalysis. It has been reported to be an effective catalyst in oxidation reactions,^{1,2} and it has been used to support noble metals.^{3–5} Moreover, Co₃O₄ is a common precursor of metallic cobalt in the preparation of cobalt catalysts, and its transformation under different reduction conditions has been the subject of recent research.^{6,7}

We have recently studied supported cobalt catalysts in the steam-re-forming reaction of ethanol.^{8–11} The goal of this process is to obtain hydrogen from ethanol, a renewable source which can be easily obtained from biomass. Some overall proposals for the use of biomass resources in this direction have been put forth.¹²

Hydrogen is yielded through the catalyzed reaction



However, under operation conditions, other side reactions can take place, and undesirable products, such as methane and carbon monoxide, are usually obtained.

Specifically, there is considerable interest in producing CO-free hydrogen, necessary for low-temperature fuel cell systems whose electrodes would otherwise be poisoned by CO. The reported cobalt-based catalysts have been shown to be effective for this purpose.^{10,11} ZnO-supported cobalt catalysts in their calcined form contained the Co₃O₄ phase, which transformed to CoO and Co under steam-re-forming conditions.¹⁰ These changes depended on the reaction conditions and determined the catalytic behavior of the samples. Moreover, under the reaction conditions, the presence of both metallic and oxidized cobalt on the surface of catalysts was determined by in situ diffuse reflectance infrared spectroscopy (DRIFT).¹⁰ To gain a better understanding of the role of cobalt species as the active phase in this reaction, we analyzed the catalytic behavior of unsupported Co₃O₄ in the steam-re-forming of ethanol. A study of its transformation under different reaction conditions is reported, and the catalytic performance of evolved materials is evaluated.

We used X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) derived techniques, Raman spectroscopy, and in situ magnetic measurements for characterization. Etha-

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nol steam-re-forming was carried out using a water/ethanol bioethanol-like mixture to explore the possibility of using ethanol as obtained from biomass without an ulterior distillation process as well as to evaluate the capabilities of the materials to produce H_2 from a renewable and environmentally friendly fuel source.

Experimental Section

Co_3O_4 Preparation. The cobalt oxide sample (Co_3O_4) was prepared by the citrate method from cobalt(II) nitrate and citric acid aqueous solutions.^{2,13} An excess of citric acid (5 wt %) was used to ensure complete complexation. The mixture was dried at 383 K, and the resulting spongy, amorphous citrate was calcined in air at 973 K for 16 h.

Catalytic Test. The ethanol steam-re-forming reaction was carried out at atmospheric pressure in the temperature range 523–723 K over 100 mg of sample diluted with inactive SiC (catalyst bed volume of 0.6 mL). The reagent feed was a gaseous mixture of ethanol, water, and argon (GHSV = ca. 5000 h^{-1}). A constant mixture of C_2H_5OH/H_2O , volume ratio 1:4, molar ratio ~1:13 (HPLC purity grade), was supplied by a Gilson 307 piston pump and vaporized at 453 K. The Ar supply (99.9995% purity) was maintained using a Brooks (model 5850TR) mass flow controller. The sample was first heated to 573 K under Ar, then the $C_2H_5OH + H_2O$ mixture was introduced, and the sample was subjected to the following temperature cycle: 573 → 623 → 673 → 623 → 573 → 523 K. All stages lasted 2 h, except the peak temperature stage (673 K), which lasted 26 h.

Products were analyzed on-line by gas chromatography as described previously.⁸ The detection threshold of CO was ca. 20 ppm. Response factors for all products were obtained with appropriate standards before and after the catalytic test.

Characterization Methods. Conventional and high-resolution TEM and selected-area electron diffraction (ED) were performed with a Philips CM-30 instrument equipped with a LaB_6 source and operating at 300 kV (point-to-point resolution of 0.19 nm). Samples were deposited on copper grids with a holey-carbon-film support. Magnification and camera constants were calibrated using appropriate standards in the same electron-optical conditions. Fourier transform images were obtained on the digitalized parts of the negatives.

SEM was carried out on a Hitachi S-2300 microscope. The samples were covered with a gold layer.

XRD data were collected at a step width of 0.02° by counting 10 s at each step using a Siemens D-500 X-ray diffractometer equipped with a Cu target and a graphite monochromator.

Raman spectroscopy was performed with a Jobin Yvon T64000 instrument using an Ar ion laser as an illumination source (514.5 nm) and a CCD detector cooled at 140 K. The Raman instrument was coupled to a standard Olympus microscope (50 \times magnification), and the collection optics system was used in the backscattering configuration. The laser power at the sample was limited to 3 mW to prevent overheating.

Specific surface area measurements were carried out by using the Brunauer–Emmett–Teller (BET) method on a Micromeritics ASAP 2000 apparatus.

For in situ magnetic measurements, 215 mg of the sample was introduced into a quartz reactor, which allowed thermal treatment and magnetic characterization to be undertaken. Ethanol steam-re-forming was carried out under continuous flow at atmospheric pressure. A feed of argon saturated with a vapor mixture of C_2H_5OH/H_2O with a molar ratio of 1:13 was generated by bubbling argon (40 mL min^{-1}) through a saturator (GHSV = ca. 10000 h^{-1}). The outlet of the reactor was connected on-line to a gas chromatograph equipped with two thermal conductivity detectors, which permitted the accurate quantification of hydrogen and carbon monoxide through molecular sieves of 5 Å, as well as that of carbon

dioxide and methane, passing the products through a Porapak Q column. Magnetic measurements were performed by the Weiss extraction method in an electromagnet with fields of up to 21 kOe (2.1 T) at 300 K, as described elsewhere.¹⁴ The sample was first exposed to Ar at 573 K, and the first magnetic measurement was recorded. After that, the sample was again heated at 573 K under Ar and the inert gas replaced by the reaction mixture of Ar + $C_2H_5OH + H_2O$. After 1 h of monitoring the reaction by gas chromatography, the reaction mixture was again replaced by Ar, the temperature was lowered to room temperature, and the next magnetic measurement was recorded. The same procedure was conducted at 623 and 673 K.

Afterward, the sample was subjected to a reduction treatment under pure hydrogen (40 mL min^{-1}) at 673 K, and a new magnetic measurement made. Following the reduction treatment, the steam-re-forming of ethanol was again performed at this temperature, and a new magnetic measurement was recorded after 1 h of reaction. Saturation magnetization values were obtained by plotting the magnetization against the field strength for each experiment. The extent of reduction and the amount of reduced cobalt present were determined by comparing the saturation magnetization with the total cobalt content of the sample and the specific saturation magnetization of bulk cobalt. In addition, the comparison between remnant magnetization, M_r , and saturation magnetization, M_s , was used to calculate the weight fraction of cobalt particles larger than the critical superparamagnetic diameter, using the ratio $2M_r/M_s$.¹⁵

Results and Discussion

Synthesized Co_3O_4 was characterized by different techniques: BET surface area measurement, SEM, XRD, Raman spectroscopy, and TEM. The BET surface area was 3.8 $m^2 g^{-1}$, following previous research involving Co_3O_4 prepared by the citrate method.² Parts a and b of Figure 1 show SEM images of the sample, where polyhedral-shaped particles of different sizes can be observed. Characterization by XRD, Raman spectroscopy, and TEM indicated that no phases other than Co_3O_4 were present in the initial sample.

Figure 2 (pattern a) shows the X-ray diffractogram which exclusively contained diffraction peaks corresponding to the Co_3O_4 spinel phase, with a mean crystal size of about 70 nm (calculated using the Scherrer equation). Figure 3 (spectrum a) depicts the Raman spectrum showing bands at 469, 512, 607, and 674 cm^{-1} with relative intensities corresponding to that of pure Co_3O_4 .¹⁶ In Figure 4A a representative TEM image of the sample is depicted. Well-faceted crystals with particle sizes in the range 50–120 nm are present. From high-resolution TEM images and electron diffraction of individual particles, it appears that the particles are single crystals. As an example, the electron diffraction of the encircled area in Figure 4A shows a cubic Co_3O_4 particle oriented along the [001] crystallographic direction. No other phases different from Co_3O_4 were detected in this sample.

The catalytic performance of Co_3O_4 in ethanol steam-re-forming was studied at increasing temperatures as described in the Experimental Section. Results are compiled in Table 1 in terms of ethanol conversion and product selectivity (water excluded) at each temperature over time.

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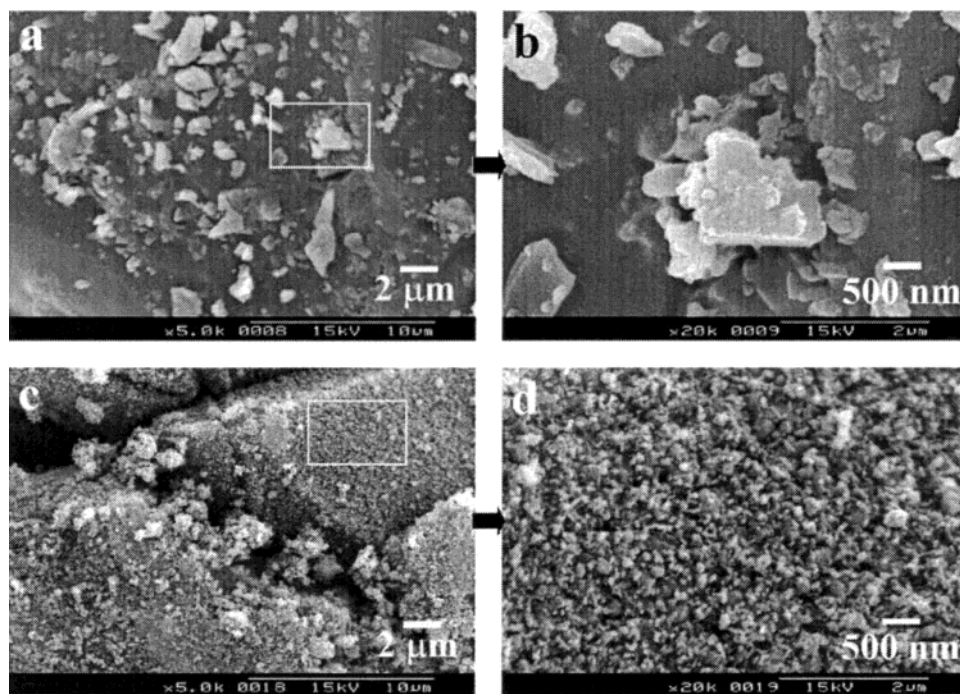


Figure 1. Scanning electron microscopy images at 5000× and 20000× magnification corresponding to Co₃O₄ as prepared (a, b) and after reaction at 673 K (c, d).

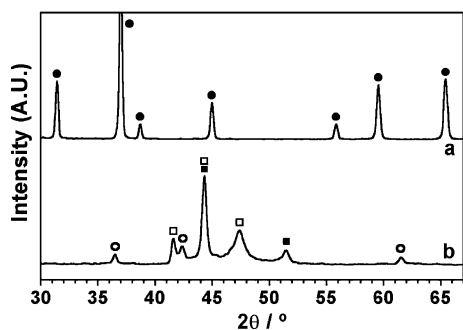


Figure 2. X-ray diffraction profiles recorded for Co₃O₄ as prepared (a) and after reaction at 673 K (b): ●, Co₃O₄; ○, CoO; ■, β-Co; □, α-Co.

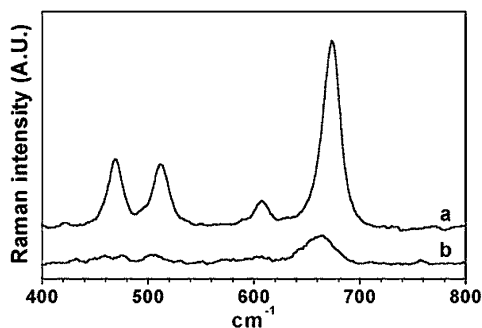
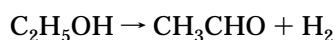


Figure 3. Raman spectra recorded for Co₃O₄ as prepared (a) and after reaction at 673 K (b).

Initially, at 573–623 K, the sample exhibited low activity and the only products were hydrogen and acetaldehyde with a CH₃CHO:H₂ molar ratio of ca. 1:1. This is consistent with the dehydrogenation reaction of ethanol to acetaldehyde:



It has been shown that this is also the first step in the

ethanol steam-re-forming reaction over ZnO-supported cobalt catalysts.¹¹ Increasing the reaction temperature to 673 K produced a progressive increase of activity with time. After 1 h at 673 K, 48.8% of the ethanol had been converted, mainly to hydrogen and acetaldehyde, and minor amounts of carbon dioxide, methane, and ethylene were also produced. After 1 h further at 673 K, 100% of the ethanol had been converted to hydrogen and carbon dioxide, with minor amounts of methane. In other words, the catalyst experienced an activation process under the reactant stream at 673 K. The distribution of products was then very close to that expected for ethanol steam-re-forming (75% H₂, 25% CO₂). The activation process in terms of catalytic performance is well illustrated in Figure 5 on the basis of the number of moles of hydrogen and carbon dioxide produced with respect to that of ethanol introduced. In both graphics, there is an abrupt increase in the production of H₂ and CO₂ at 673 K. The final values of the number of moles of H₂ and moles of CO₂ per mole of ethanol introduced at this temperature were close to the maximum stoichiometric values for the steam-re-forming reaction (6 and 2, respectively). Catalytic behavior at 673 K was maintained after 1 day of reaction (Table 1). However, longer reaction periods produced a progressive carbon deposition and catalyst deactivation.

Having been activated under reaction conditions at 673 K, better catalytic performance of the material was observed at lower temperatures (see Table 1 and Figure 5).

The behavior of unsupported Co₃O₄ differed from that of ZnO-supported Co₃O₄ (10% Co, w/w). A poor performance in the ethanol steam-re-forming has been found for the ZnO-supported sample, with no significant activation under similar reaction conditions at 673 K.¹⁰ Taking into account the behavior of the Co₃O₄ sample in the catalytic test and, specifically, the activation

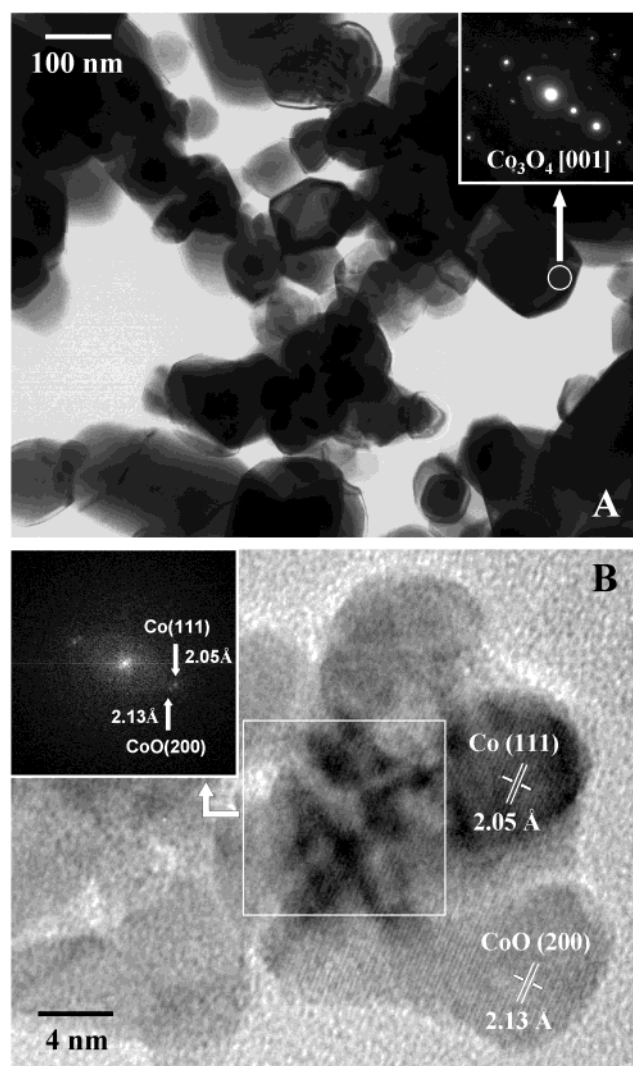


Figure 4. (A) Bright-field TEM image corresponding to Co_3O_4 as prepared and selected-area electron diffraction pattern (inset) of the marked area. (B) High-resolution TEM corresponding to the catalyst after reaction at 673 K and Fourier transform image of the marked area.

Table 1. Catalytic Performance of Co_3O_4 in the Ethanol Steam-Re-Forming Reaction at Atmospheric Pressure ($\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}:\text{Ar} = 1:13:70$, GHSV = 5000 h^{-1})

T/K	t^a/h	conv/%	selectivity ^b /%					CH_3CHO
			H_2	CO	CO_2	CH_4	C_2H_4	
573	2	0.5	49.3					50.7
623	4	8.7	49.5					50.5
673	5	48.8	51		2.8	1.2	0.2	44.8
673	6	100	73.1		25.3	1.6		
673	30	100	73.3		25.1	1.6		
623	32	100	72.2		25.1	2.7		
573	34	100	56.5	3	13	3.9	0.1	23.5
523	36	40.4	54.4		5.3	1.5		38.8

^a Cumulative reaction time. ^b Water not included.

process observed at 673 K during ethanol steam-reforming, we have characterized in detail the resulting material after reaction at 673 K to gain insight into the cobalt active phase for this reaction.

SEM images showed particles of spherical shape which were much smaller than those in the original Co_3O_4 sample (Figure 1c,d). This transformation was also accompanied by an increase of the specific surface

area (BET). The specific surface area of the sample after reaction was $19.6 \text{ m}^2 \text{ g}^{-1}$, more than 5 times higher than the value obtained for the initial Co_3O_4 .

The X-ray diffraction pattern of the material after reaction at 673 K did not contain any peak due to the parent Co_3O_4 phase (Figure 2, pattern b). This sample exhibited diffraction lines corresponding to metallic cobalt and CoO (mean crystal size ca. 10 nm).

The X-ray pattern contained lines attributed to the fcc β -Co and hcp α -Co phases of metallic cobalt. It can be seen in Figure 2 that the width of the line centered at $2\theta = 44.3^\circ$ ($(111)_{\text{fcc}}$ and $(002)_{\text{hcp}}$) is significantly less than that of the other lines which correspond to only one cobalt phase ($(101)_{\text{hcp}}$ line at $2\theta = 47.3^\circ$ and $(200)_{\text{fcc}}$ line at $2\theta = 51.5^\circ$). Such distortions of the X-ray diffraction pattern of metallic Co have also been observed after reduction of silicate-supported cobalt samples, and were explained in terms of stretch defects of the structure, particularly the interchange of fcc and hcp coherent domains,¹⁷ as in zirconia- and alumina-supported cobalt catalysts.⁷

The Raman spectrum of the sample after the activation process (Figure 3, spectrum b) differed from that of the initial sample (Figure 3, spectrum a), which could be unambiguously attributed to Co_3O_4 . After reaction at 673 K, the Raman spectrum is dominated by a low-intensity, broad band centered at 663 cm^{-1} , although other spectral bands (e. g. at 503 cm^{-1}) may also be present. These bands are at lower wavenumbers than those seen with Co_3O_4 . However, the poor resolution of the spectrum and the ambiguity in the assignment of bands corresponding to CoO by different authors¹⁸ make the assignment of the spectrum difficult. The low intensity of bands when compared with those of spectrum a in Figure 3 is attributable to the reduction of most of the Co_3O_4 to metallic cobalt, which has no active modes in Raman spectra.

A detailed microstructural study has also been performed by transmission electron microscopy to complete the characterization of the material after reaction at 673 K on the nanometer scale. Figure 4B corresponds to an HRTEM image of the postreaction sample and the corresponding Fourier transform image. Particles (6–12 nm) with rounded contours are visible. The particle with the higher contrast exhibits a lattice spacing of 2.05 Å, which corresponds to the (111) planes of fcc metallic cobalt. The lattice fringes at 2.13 Å of the particle with a softer contrast correspond to the (200) planes of cubic CoO. As exemplified in Figure 4B (inset), there is close contact between Co and CoO phases in the postreaction sample, and no Co_3O_4 spinel phase remnant was detected.

All these characterization results point to a progressive reduction of Co_3O_4 to CoO and Co under the reaction conditions. The size of the cobalt particles is much smaller than that of the initial Co_3O_4 particles and could be determined by the reduction conditions.¹⁹

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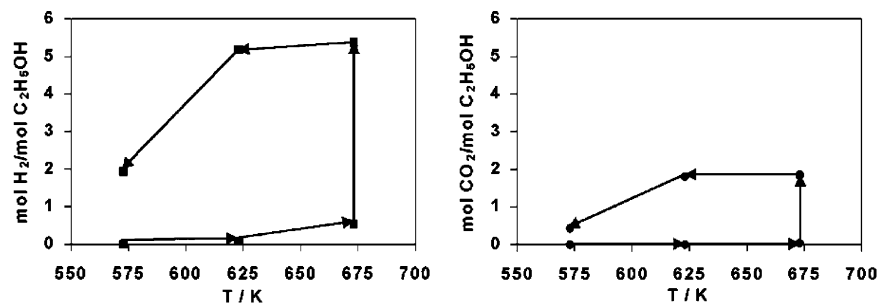


Figure 5. Molar ratios of hydrogen and carbon dioxide with respect to the amount of ethanol introduced as a function of ethanol steam-re-forming temperature.

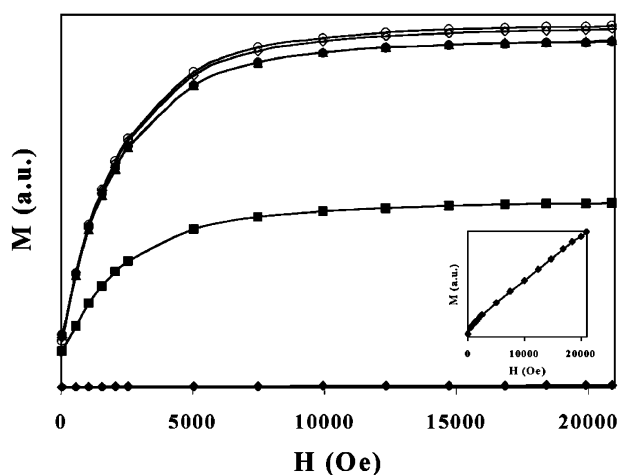


Figure 6. Magnetization curves recorded in situ for Co₃O₄ after (◆) ethanol steam-re-forming at 573 K (see also inset), (■) ethanol steam-re-forming at 623 K, (●) ethanol steam-re-forming at 673 K, (▲) ethanol steam-re-forming at 623 K, (○) hydrogen treatment at 673 K, and (◇) and ethanol steam-re-forming at 673 K.

To monitor the formation of metallic cobalt under the reaction conditions, we performed an in situ study combining magnetic methods and catalytic measurements. In this way it was possible to characterize the material that was present in the reaction chamber in terms of magnetic behavior and, simultaneously, determine its catalytic performance.

Figure 6 shows the magnetization curves recorded under different conditions in the 573–673 K temperature range. Initially, the Co₃O₄ sample was heated to 573 K under argon, and then the bioethanol-like mixture was incorporated into the inert gas. In both cases the sample behaved paramagnetically, as one would expect of Co₃O₄ or CoO.²⁰ When the reaction temperature was raised to 623 K and then 673 K, under the same reactant stream, metallic cobalt progressively emerged. In Figure 7 the amount of reduced cobalt is plotted as a function of reaction temperature. After reaction at 623 K, 51% of the total cobalt was in the reduced form, while at 673 K the amount of metallic cobalt increased to 96%.

In Figure 7 we plot catalytic effectiveness measured as the amount of hydrogen and carbon dioxide produced as a function of reaction temperature. At 573 K, only a minor amount of hydrogen is obtained and no CO₂ is detected. Taking into account the results of the catalytic

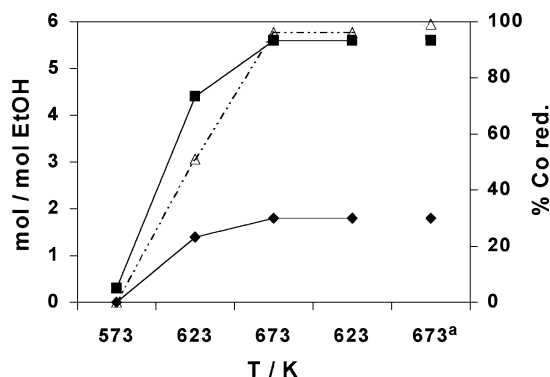


Figure 7. Extent of cobalt reduction (Δ) compared to hydrogen (■) and carbon dioxide (◆) produced as a function of ethanol steam-re-forming temperature. The superscript “a” refers to data obtained after hydrogen treatment at 673 K and ethanol steam-re-forming at the same temperature.

test mentioned earlier (Table 1), we assume these conditions lead to the dehydrogenation of ethanol to acetaldehyde. At 623 K and, even more so, at 673 K, there was a progressive formation of hydrogen and carbon dioxide in a 3:1 molar ratio (Figure 7), thus indicating that the re-forming of ethanol took place in a high extension. As stated above, the progressive formation of metallic cobalt was also seen. At 673 K, total conversion of ethanol (mainly to H₂ and CO₂) through steam-re-forming was attained, and under these conditions, 96% of the cobalt in the catalyst was in a metallic state. Both the degree of cobalt reduction and the performance of the catalyst were unchanged when the reaction temperature was then decreased to 623 K.

On the basis of the characterization results obtained by TEM, XRD, and Raman spectroscopy on the post-reaction sample, the oxidized cobalt species detected by the in situ magnetic method in the activated material is most likely cobalt(II) oxide.

From magnetic measurements depicted in Figure 6, it can be deduced that, after ethanol steam-re-forming at 623 K, further H₂ treatment at 673 K produced the total reduction of cobalt species. However, when the reactant mixture was reintroduced after this treatment at 673 K, the percentage of reduced cobalt species decreased to 99% while the catalytic performance of the sample did not change (see Figure 7).

In conclusion, under ethanol steam-re-forming conditions, reduced and oxidized cobalt species were seen to coexist. Similar behavior has been observed with supported cobalt materials.^{9,10} The coexistence of oxidized and reduced surface species of cobalt under the reaction

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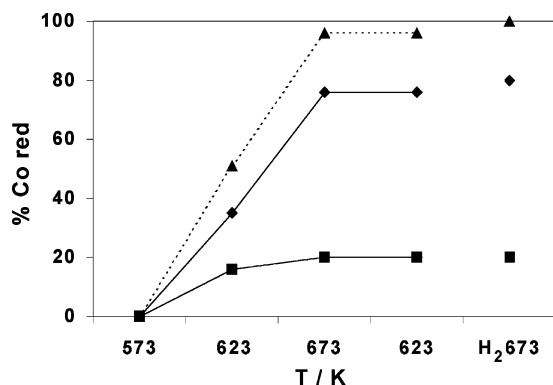


Figure 8. Extent of total metallic cobalt reduced (▲) with particle size smaller (◆) and larger (■) than the critical diameter as a function of ethanol steam-re-forming temperature. "H₂673" refers to data obtained after reduction treatment at 673 K.

conditions has been evidenced also by CO adsorption on ZnO-supported cobalt catalyst.¹⁰

As stated in the Experimental Section, magnetic measurements also provide information on the size of the metallic cobalt entities. The critical diameter is used to distinguish two domains in particle size distribution by comparing the remnant magnetization with the saturation magnetization.¹⁵ Figure 8 shows the amount of metallic cobalt with a particle size higher or lower than the critical diameter (around 10–12 nm) after ethanol steam-re-forming reaction at different temperatures. During the activation of Co₃O₄, metallic cobalt entities were formed progressively, mostly with sizes smaller than the critical diameter. At the end of the 673 K activation period, 76% of all the cobalt in the sample was in the form of particles under the critical diameter. The ratio between these entities and larger ones increases slightly during treatment under hydrogen. This distribution of cobalt particles is consistent with TEM characterization (see, for example, Figure 4).

Once again, the behavior of unsupported Co₃O₄ differs from that of ZnO-supported Co₃O₄, here in terms of reducibility under ethanol steam-re-forming conditions. Under similar experimental conditions, the degree of reduced cobalt was higher for unsupported Co₃O₄ than that reported for ZnO-supported Co₃O₄. Moreover, the fraction of cobalt particles with size under the critical diameter was lower in the ZnO-supported sample.¹⁰ It has been reported that the inclusion of Zn²⁺ in the structure of Co₃O₄ increases the threshold temperature for reduction of the mixed oxide to metallic cobalt.¹⁷ The easier reduction of unsupported Co₃O₄ under the reaction conditions, which produces a higher fraction of small cobalt particles, is probably responsible for its better catalytic behavior when compared to that of ZnO-supported Co₃O₄.

Conclusions

Over Co₃O₄, ethanol is dehydrogenated to acetaldehyde at 573 K under ethanol steam-re-forming conditions. At higher temperatures, unsupported Co₃O₄ is reduced to CoO and metallic cobalt. This process is accompanied by an activation of the material, which becomes an active and selective catalyst for ethanol steam-re-forming at temperatures as low as 623 K. Only a small amount of methane is obtained at this temperature, in addition to H₂ and CO₂. The absence of carbon monoxide makes this catalyst an interesting material for low-temperature fuel cell applications.

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