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On the Catalytic Activity of Cobalt Oxide for the Steam Reforming of Ethanol

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Abstract The paper presents an investigation on the catalytic activity for the ethanol steam reforming of Co_3O_4 oxidized, reduced and supported on MgO, and of CoO in MgO solid solution. Only samples containing metallic cobalt are found to be active for reforming reaction. H_2-TPR characterization of aged samples shows that reaction mixture oxidizes a small fraction of metallic cobalt to Co^{+2}. A distinct role of Co^{+2} and Co^0 in the reaction is enlightened.

Keywords Ethanol steam reforming · Hydrogen · Cobalt oxide · Supported cobalt catalyst

1 Introduction

The progressive depletion of fossil resources and the need of green gas emissions control, have strongly focused the attention on the development of alternative energy sources. The bio-ethanol derived from biomasses is a good source because it is easy to transport, biodegradable, and low in toxicity and it could be directly used in steam reforming reaction, SRR.

The SRR of ethanol $CH_3CH_2OH + 3\ H_2O \rightarrow 6\ H_2 + 2\ CO_2$ is able to produce 6 mole of H_2 per mole of ethanol (H_2/EtOH = 6). Recent reviews [1, 2] reported extensive comparisons between catalytic properties of the most studied catalysts for SRR of ethanol, such as oxides, noble metal-based catalysts (Pt, Rh, Ru), nickel-based catalysts, and cobalt-based catalysts. Required performances include the production of CO-free hydrogen, and low cost and durability of the catalyst. Oxide-supported cobalt catalysts exhibit a good performance in ethanol SRR, with ethanol conversion of 90–100%, high selectivity to H_2 (60–75%), and low production of CO [3–13]. The non desired reactions may produce methane, ethane, ethene, acetone, and other C_2 and C_3-hydrocarbons.

The largest hydrogen yields in the temperature range 400–500 °C were found on Co/Al_2O_3 (H_2 67–75%) [3, 12], Co/ZnO (H_2 73–75%) [4, 7] and Co_3O_4 (H_2 73%) [8, 14]. However, pure Co_3O_4 has been scarcely investigated with respect to catalytic properties. The high selectivity of Co/Al_2O_3 was ascribed to the suppression of the methanation of CO and of the EtOH decomposition [3]. The CO selectivity is 0–20%, and depends on reaction temperature, material composition [3, 7, 9, 11], and ethanol/water molar ratio [12]. A significant decrease in CO formation is obtained by increasing the cobalt content up to 18 w/w% [9]. Co/ZnO catalyst prepared from $Co_2(CO)_8$ [7] and pure Co_3O_4 [8] show high selectivity for CO-free hydrogen production at temperature as low as 350–400 °C. Over these samples, the only products obtained are H_2, CH_4 and CO_2.

The polymerization processes of acetaldehyde [15] or CH_x species formed during reaction, originate large coke deposition on the surface which is the main cause of deactivation for all cobalt catalyst [4, 6, 7, 11, 13]. The amount and the nature of the deposited carbon (17–24 w/w% after 9 h of SSR at 400 °C [6]) depends mainly on the support, and on the reaction temperature. Co/Al_2O_3 catalysts deposit a large amount of coke that causes a progressive decay during few hours on stream [6, 13]. Co/MgO has been found more stable than Co/Al_2O_3 for the lesser coke formation due to a lower acidity of the support [13]. Even on Co/CeO_2

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heavy coke deposition was found, in spite of the oxygen storage capacity of the support [11].

Recent studies [4, 5, 7, 8, 14] reported the characterization in situ of various cobalt catalysts under ethanol SSR condition. It was found that, metallic cobalt particles and oxidized cobalt species were in equilibrium and contributed to the performance of the catalyst. But the possible role of individual oxidation state was not identified.

In the present work, with the aim to understand the role of different oxidation states of cobalt in reaction conditions, we have investigated the catalytic behaviours for the ethanol SRR of: (1) Co_3O_4 as such, (2) Co_3O_4 completely reduced, (3) Co_3O_4 supported on MgO, and (4) CoO in MgO solid solution. In addition, some attention is provided to the catalytic properties of Co_3O_4, due to its good performance, and the little attention received in the literature. Finally, it seems of interest to clarify whether the coke deposition, generally found on cobalt based catalysts, is due to kinetic conditions or to an intrinsic and unfavourable selectivity to reaction products leading to coke formation even at very low reagent concentrations.

2 Experimental

2.1 Samples Preparation

Co_3O_4 was prepared by thermal decomposition of cobalt nitrate $Co(NO_3)_2$ $6H_2O$ (750 °C, 2 h).

Co/MgO samples were prepared by wet impregnation of MgO, obtained by thermal decomposition of magnesium carbonate (1,200 °C, 5 h) with cobalt nitrate aqueous solution, drying at 100 °C, and heating in air at 600 °C for 1 h, in the following denoted as Co/MgO(600). A portion of Co/MgO(600) was reground and finally heated in air at 1200 °C for 5 h, in the following denoted as Co/MgO(1200). The cobalt concentration was 10 Co atoms per 100 magnesium atoms, corresponding to 14 wt.%.

Samples treated in O_2 at 550 °C were denoted as "sample(ox)", samples reduced in H_2 at 350–950 °C were denoted as "sample(red)".

2.2 Sample Characterization

XRD patterns were recorded in air with a Shintag X1 diffractometer with Cu Kα radiation in θ–θ configuration (2–70° range) at 0.05° step size, and 3 s acquisition time.

UV-Vis-DRS spectra were obtained with a Shimatzu UV-2401PC spectrophotometer, equipped with a $BaSO_4$ coated integrating sphere. Spectra were recorded in air, at room temperature, in the range 200–900 nm, with resolution of 2 nm. $BaSO_4$ was used as a standard.

H_2-TPR experiments were performed in a flow apparatus TPDRO 1100 Thermo, equipped with a TCD detector. A fresh sample was pre-treated in a flow of 10% O_2/He mixture (20 cm^3_{STP} min^{-1}) at 550 °C for 30 min, and then cooled in He to RT. Then, a 5% H_2/Ar mixture (10 cm^3_{STP} min^{-1}) was flown through the sample starting from RT and heating up to a final temperature of 950 °C, with a ramp of 10 °C min^{-1}. In some cases, the reduction ramp was stopped at 350 °C or at 600 °C. Samples were maintained at the final temperature for 2 h. Samples tested after catalysis, were studied as such avoiding exposure to air. The reduction degree of cobalt was evaluated from H_2 consumed, and reported as electron exchanged per Co atom, e/Co = 2(H_2 mol)/(Co mol).

2.3 Catalytic Tests

The catalytic activity was measured at atmospheric pressure in a flow apparatus equipped with mass flow controllers and GC analysis of reactants and products. Catalyst (0.050 g of pure Co_3O_4 or 0.300 g of Co/MgO samples) was placed in a fixed-bed linear quartz reactor. The feed of reagent mixture was obtained by bubbling an inert gas (helium or nitrogen) through a solution ethanol/water (12% v/v) in a saturator maintained at 1 °C by an electric cryostat. The EtOH concentration in the saturated flow was 5.8×10^{-5} M. The flow through the saturator was in the range 10–100 cm^3_{STP} min^{-1} with a GHSV of 23,600–2,36,000 h^{-1}, on the basis of a measured Co_3O_4 density of 1.96 g cm^{-3}, and the corresponding moles of supplied ethanol were $0.6–6.0 \times 10^{-6}$ mol min^{-1}. In some cases, a saturated flow of 25 cm^3_{STP} min^{-1} was diluted with inert gas up to 75 cm^3_{STP} min^{-1}, thereby lowering the reagent concentrations to one third. In all cases, the molar ratio water/ethanol was in the range 3.5–12, in excess with respect to the stoichiometric value.

Reaction stream was analyzed on line by a Varian 3400CX gas-chromatograph equipped with a column Hayesep Q (Alltech), maintained at 150 °C, and with a TCD and a FID detectors. Helium was used as carrier gas in order to analyze CH_3CH_2OH, CH_3CHO, CH_4, CO and CO_2. Nitrogen was used as carrier gas to analyze H_2O, H_2, CH_3CH_2OH, CH_3CHO, CH_4. The analysis of ethanol, acetaldehyde and methane were found equal with both carrier gases.

The ethanol conversion was evaluated from the inlet and outlet molar concentrations of the reagent, and reported as percent conversion: $([EtOH]_{in} - [EtOH]_{out}*100)/[EOH]_{in}$. The water consumed or formed in the reaction was evaluated from the inlet and outlet molar concentrations and reported as the ratio $[\Delta H_2O]/[EtOH]_{in} = ([H_2O]_{in} - [H_2O]_{out})/[EtOH]_{in}$. The evaluation of the extent of the

ethanol SRR, was reported as $[H_2]/[EtOH]_{in}$, the molar ratio between produced H_2 and incoming EtOH. The percent selectivity of products H_2, CO, CO_2, CH_3CHO, CH_4 was evaluated as the ratio of molar concentration of each product and the total concentration of products, and reported as $S_{product}$ = [product]*100/Σ[product]. The carbon balance, was evaluated from the total concentration of carbon-containing products and the concentration of converted EtOH.

3 Results and Discussion

3.1 Co_3O_4

X-ray diffraction pattern of Co_3O_4 as prepared shows diffraction lines only of Co_3O_4 cubic phase (JCPDS card. No. 43–1003), thus excluding the presence of other phases. The mean dimension of particles, calculated by the Debye-Sherrer equation, is 119 nm. The UV-Vis spectrum (Fig. 1, spectrum a) shows two broad bands at about 350 and 670 nm, which are characteristics of Co_3O_4 [16, 17].

The H_2-TPR profile of Co_3O_4(ox) (Fig. 2, profile a) shows that the reduction starts at about 340 °C with a single and intense peak centred at 450 °C. The total H_2 consumption corresponds to e/Co = 2.7, confirming the total reduction of Co_3O_4 to Co^0. The Co_3O_4 reduction is known to be a two-steps process $Co_3O_4 \rightarrow CoO \rightarrow Co$ [18, 19] with an increase in the reduction temperatures, as the crystallite size increases [20, 21]. In fact, for a Co_3O_4 nano-sized (20–30 nm) investigated in our laboratory, two reduction steps have been clearly identified by two peaks, respectively at about 300 °C and 400 °C. In the present case, a single, intense and asymmetric peak at 450 °C is found as a result of the two peaks overlap, due to the larger particle size. However, Co_3O_4(ox) is already totally reduced by a treatment with H_2 at 350 °C for 2 h, with an e/Co = 2.7.

Results of characterization by XRD, UV-Vis-DRS and TPR are reported in Table 1.

Turning now to the catalytic activity, Co_3O_4(ox) is not active for SRR, in the temperature range 250–350 °C (Table 2). The main reaction envisaged is the ethanol dehydrogenation to acetaldehyde and hydrogen. At higher temperatures (350–550 °C) a steam reforming activity arises, as monitored by the values of the ratios H_2/EtOH (Table 2). The suggestion is that the reaction medium reduces the cobalt oxide to metallic cobalt, as generally accepted [5, 7, 8]. The ratio H_2/CH_3CHO less than one at low temperatures, and the negative values of the ratio $\Delta H_2O/EtOH_{in}$ up to 350 °C (i.e. water formation), provide a further proofs of the reducing action of the reaction medium.

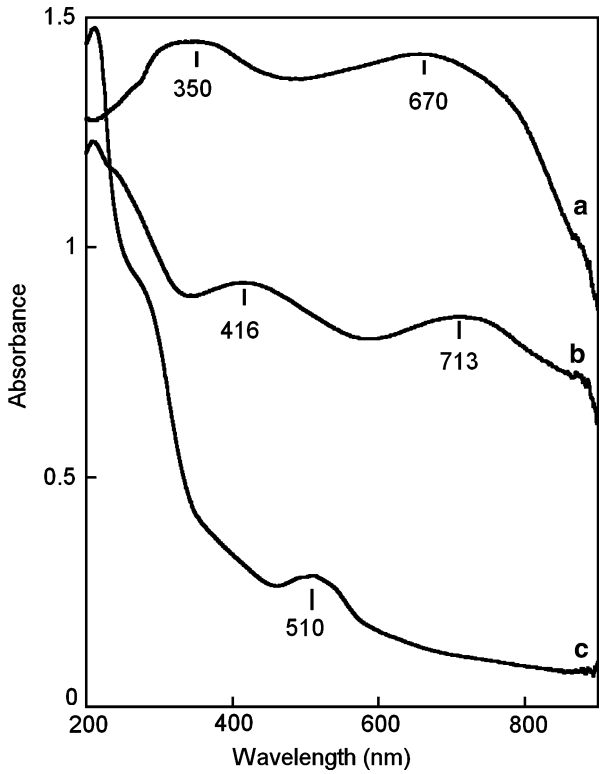

Fig. 1 UV-Vis diffuse reflectance spectra of samples as prepared: (a) Co_3O_4; (b) Co/MgO(600); (c) Co/MgO(1200)

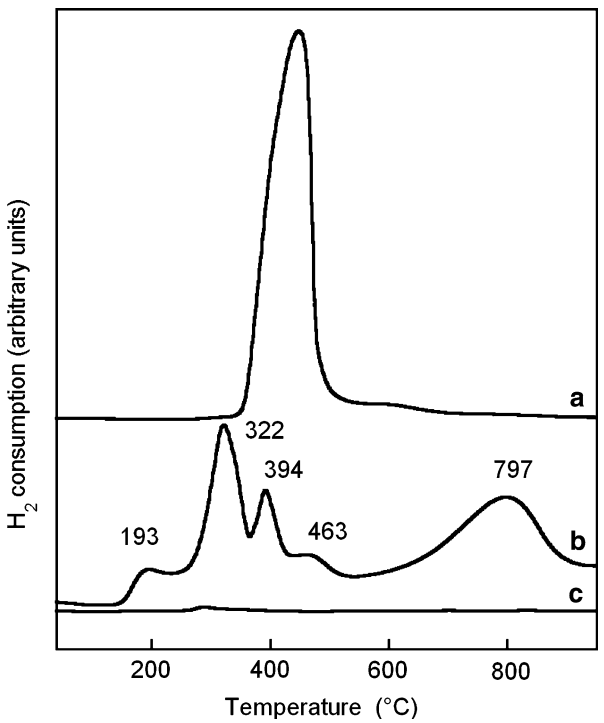

Fig. 2 TPR profiles of samples: (a) Co_3O_4, 0.010 g; (b) Co/MgO(600), 0.300 g; (c) Co/MgO(1200), 0.300 g

Table 1 Cobalt species in sample(ox), and in sample(red) and cobalt reduction degree

Sample	Co species in sample(ox)	Co species in sample(red)	Co^0 in sample(red) (%)
Co_3O_4	Co_3O_4 cubic	Co^0	100
Co/MgO(600)	Co_3O_4, $MgCo_2O_4$, $Co^{+2}{}_{oct}$	Co^0, $Co^{+2}{}_{oct}$	30
Co/MgO(1200)	$Co^{+2}{}_{oct}$, Co^{+3} [a]	$Co^{+2}{}_{oct}$	–

[a] Trace amount

Table 2 Catalytic activity of Co_3O_4(ox) for ethanol steam reforming

T (°C)	EtOH conversion (%)	$\Delta H_2O/EtOH_{in}$ (mol/mol)	$H_2/EtOH_{in}$ (mol/mol)	$CH_3CHO/EtOH_{in}$ (mol/mol)
250	2.8	−0.2	0.0	0.03
300	6.1	−0.4	0.02	0.04
350	68.1	−0.5	0.4	0.2
400	99.0	−0.3	1.6	0.0
450	100	1.0	5.2	0.0
500	100	1.9	5.4	0.0
550	100	2.0	5.4	0.0

Flow = 25 $cm^3{}_{STP}$ min^{-1}, [EtOH] = 5.8 × 10^{-5} M, H_2O/EtOH = 5.1

In agreement, the reduction pre-treatment in H_2 at 950 °C for 2 h gives rise to a catalytic activity for ethanol SRR. Tables 3–5 show the results on Co_3O_4(red) sample tested with three different experimental conditions. Once more, two temperature ranges have been identified: the first below 350 °C, where the prevailing reaction is the dehydrogenation of ethanol as monitored by the observed products hydrogen and acetaldehyde and by the nil conversion of H_2O; the second, above 350 °C, where hydrogen, methane, carbon monoxide and carbon dioxide are detected, and the catalyst promotes mainly the ethanol SRR with a ratio H_2/CO_2 close to 3. These findings are in agreement with the thermodynamic data [2], which confirm that, already at 250 °C, only the ethanol decomposition may easily occur, because ΔG is sufficiently negative [3]. Finally, it may be added that the carbon balance, in all cases, is below 100% at T < 500 °C, whereas it is above 100% at T > 500 °C.

The efficiency of the overall reaction, reported as H_2/EtOH ratio, is similar to those previously reported for other catalysts [1, 5, 7, 13]. However our ratio increases with the temperature reaching values between 4.1 and 5.4 at 550 °C, depending upon the operative conditions described in the Tables 3–5. In particular, it appears higher in two cases: (i) when the reduction of Co_3O_4 is achieved in reaction condition (Table 2), and (ii) when the reagent mixture is diluted with the inert gas from 25 up to 75 $cm^3{}_{STP}$ min^{-1} (Table 4). In the former case, the comparison of Tables 2 and 3, indicates that the reduction effect in reaction condition, milder with respect to that in pure H_2, would be responsible of a sintering of metallic cobalt in Co_3O_4(ox) lesser that in Co_3O_4(red). In the latter case, the dilution of the reagent mixture and the contemporary increase in the flow rate, increases the H_2 yield, as a possible consequence of different kinetic conditions, as already found for Co/ZnO [4, 7].

Table 3 Catalytic activity of Co_3O_4(red) for ethanol steam reforming

T (°C)	EtOH conversion (%)	H_2/EtOH (mol/mol)	Selectivity (%)				
			H_2	CH_4	CH_3CHO	CO	CO_2
250	27.1	0.2	48.5	0.0	51.5	0.00	0.0
300	55.3	0.7	62.6	1.8	30.1	3.2	2.3
350	98.2	3.1	69.6	3.9	0.0	1.7	24.9
400	100	3.7	69.3	1.8	0.0	5.1	23.7
450	100	3.8	68.2	1.7	0.0	7.4	22.7
500	100	4.1	68.7	1.1	0.0	8.7	21.5
550	100	4.1	65.4	0.80	0.0	13.1	20.8

Flow = 25 $cm^3{}_{STP}$ min^{-1}, [EtOH] = 5.8 × 10^{-5} M, H_2O/EtOH = 5.1

Table 4 Catalytic activity of Co_3O_4(red) for ethanol steam reforming

T (°C)	EtOH conversion (%)	$H_2/EtOH_{in}$ (mol/mol)	Selectivity (%)				
			H_2	CH_4	CH_3CHO	CO	CO_2
250	19.6	0.1	69.6	3.6	26.8	0.0	0.0
300	25.9	0.4	68.8	2.3	25.0	2.0	2.0
350	84.4	0.9	58.9	8.2	22.9	2.6	7.5
400	99.1	2.6	59.6	3.6	0.0	5.8	30.9
450	100	3.9	69.7	2.1	0.0	5.8	22.4
500	100	4.8	70.2	1.2	0.0	8.3	20.3
550	100	5.4	71.3	0.6	0.0	8.6	19.5

Flow = 75 cm^3_{STP} min^{-1}, [EtOH] = 1.9 × 10^{-5} M, H_2O/EtOH = 5.5

Table 5 Catalytic activity of Co_3O_4(red) for ethanol steam reforming

T (°C)	EtOH conversion (%)	$H_2/EtOH_{in}$ (mol/mol)	Selectivity (%)				
			H_2	CH_4	CH_3CHO	CO	CO_2
250	25.8	0.2	45.1	1.9	41.7	11.2	0.0
300	59.4	0.8	54.2	2.2	22.9	15.8	5.0
350	85.0	1.9	58.2	2.7	10.7	20.7	7.6
400	98.7	3.1	63.4	3.1	1.7	16.4	15.3
450	100	3.8	68.1	2.1	0.0	7.5	22.3
500	100	4.9	69.0	1.1	0.0	6.6	23.2
550	100	5.2	70.2	0.9	0.0	7.5	21.4

Flow = 75 cm^3_{STP} min^{-1}, [EtOH] = 1.9 × 10^{-5} M, H_2O/EtOH = 12

The effect of the stream velocity on efficiency of reaction was tested at 500 °C in the range 10–100 cm^3_{STP} min^{-1}, corresponding to GHSV of 23,600–2,36,000 h^{-1}. The ethanol supplied increased from 0.6 × 10^{-6} mol min^{-1} up to 6.0 × 10^{-6} mol min^{-1}, with 5.8 × 10^{-5} M concentration. The H_2/EtOH ratio was found to be 4.1–4.5 in the whole flow range. Literature data are not available for Co_3O_4, but results on Co supported catalysts show a decrease in activity as the GHSV increases [12, 13]. An ethanol concentration higher than that presently investigated, and a dehydrating activity of the support, might be responsible for a larger coke deposition and a decay in activity in the above mentioned works. However, an analysis of the carbon balance for Co_3O_4(red) shows that some carbon is deposited on the surface in all the kinetic conditions and its amount decreases with increasing temperatures, giving values over the 100% at T > 500 °C as a result of the possible reaction of surface coke with water ($\Delta H°_{298}$ = 131 kJ mol^{-1}). The presence of coke was confirmed by evolution either of CO_2, by flowing O_2 at 500 °C (O_2 10% 20 cm^3_{STP} min^{-1}), or of CH_4, by flowing H_2 above 600 °C (H_2 5% 20 cm^3_{STP} min^{-1}) on aged samples. The present results, in spite of the beneficial effect of the reagent mixture dilution, and of the H_2O/EtOH ratio increase on efficiency of the reaction, are clear indications of the existence of centers on Co_3O_4(red) with an intrinsic selectivity to products leading to coke, and of the difficulty of avoiding coke deposition even at very low reagent concentration, irrespective of the GHSV.

The H_2 selectivity, S_{H_2}, is nearly independent on temperature above 350 °C, with a value of 60–70%, in good agreement with the published data [8, 14]. By contrast the CO selectivity, S_{CO}, increases with the temperature, reaching values between 8.3 and 13.1% at 500–550 °C, with a H_2O/EtOH ratio 5.1–5.5 (Tables 3, 4). This behaviour appears in contrast with that reported for pure Co_3O_4 [8, 14], but in reasonable agreement for cobalt containing catalysts [3, 7, 9, 11, 12]. However, when the H_2O/EtOH ratio increases to 12, the S_{CO} decreases with temperature (Table 5). The water excess may be thought to favour the methane steam reforming reaction $CH_4 + H_2O \rightarrow CO + 3H_2$ and the WGS reaction $CO + H_2O \rightarrow CO_2 + H_2$. The role of water was found to improve the CO_2/CO ratio above 450 °C by Sahoo et al. [12] for Co supported on alumina, even if it did not improve significantly the catalytic performances.

Finally it is worthy of mention that, at temperatures below 350 °C, acetaldehyde, methane, and carbon monoxide are simultaneously present, but, at temperatures above 350 °C, the acetaldehyde is absent. This finding is consistent with the results of Guil et al. [15] on the ethanol adsorption on cobalt supported catalysts, that reported the

presence of acetaldehyde as reaction intermediate. Hence, the decomposition of acetaldehyde, to CO and CH_4, which in turn react with water, may be thought as the main reaction pathway leading to the hydrogen production.

3.2 Co/MgO

The system CoO/MgO has been deeply investigated in the past and an exhaustive introduction on bulk and surface properties is given in the review by Cimino and Stone [22]. Therefore the characterization is restricted to the check of the system reproducibility and to additional information gained with TPR analysis.

X-ray diffraction pattern of Co/MgO(1200) as prepared confirms the diffraction lines characteristic of MgO cubic phase only (JCPDS card. No. 87-0653). The UV-Vis-DRS spectrum (Fig. 1, spectrum c), shows a small band at about 510 nm, characteristic of $^4T_{1g}(F)-^4T_{2g}(P)$ transition of Co^{+2} ions in octahedral symmetry [17, 23]. XRD and UV-Vis analysis confirm that, in Co/MgO(1200), all cobalt is present as Co^{+2} in MgO solid solution with the absence of segregated Co_3O_4. The fraction of cobalt dissolved as solid solution in MgO depends on the calcination temperature of the sample, and, already at 900 °C, the solid solution Co(Mg)O is the only Co-containing phase present [24]. In fact, X-ray diffraction pattern of Co/MgO(600) shows, in addition to MgO lines, weak peaks of Co_3O_4 phase at $2\theta = 31°$ e 37° and the UV-Vis-DRS spectrum (Fig. 1, spectrum b), two broad bands, at about 416 and 713 nm, indicative of the presence of Co_3O_4 clusters [16, 21].

The H_2-TPR analysis shows that the MgO support is stable in a reduction treatment up to 950 °C. As far as the Co/MgO(1200)(ox) sample is concerned, the TPR profile (Fig. 2, profile c) shows a very small peak at about 290 °C in the region of $Co^{+3} \rightarrow Co^{+2}$ reduction, but it is not possible to measure accurately the H_2 consumption. The inspection of the literature data suggests that the O_2 pretreatment may be responsible for the oxidation of a small fraction of surface Co^{+2} to Co^{+3}, without a noticeable Co_3O_4 segregation [22, 25, 26].

The TPR profile of Co/MgO(600) sample (Fig. 2, profile b) shows peaks at about 193, 322, 394, 463 and 797 °C, all associated or assigned to various cobalt species. Several studies reported that the reduction temperature of supported Co_3O_4 is strongly influenced by the particle size, which in turn depends on interactions with the support and on pretreatment temperatures, but such a dependence has not been clearly established. In fact, on increasing particles size, either an increase [21] or a decrease [27] in the reduction temperature have been observed. The comparison of profiles a and b (Fig. 2) allows to attribute the peaks at 322, 394, 463 °C to the reduction of Co_3O_4 particles with different particle sizes to metallic cobalt [21, 24, 27, 28]. The intense and broad peak at 798 °C is assigned to reduction of $MgCo_2O_4$ to metallic Co [24]. The shoulder at low temperature (195 °C), might be associated with the reduction of oxygen chemisorbed on cobalt, as reported for cobalt supported on ZrO_2 [28, 29], or exchanged in ZSM-5 [30].

The total H_2 consumption allowed us to evaluate an e/Co = 0.8, which, on the basis of an average oxidation number of cobalt in Co/MgO(600)(ox) equal to 2.7, corresponds to a reduction of 30% of analytical cobalt to metallic cobalt.

Results of characterization by XRD, UV-Vis-DRS and TPR are summarized in Table 1.

The catalytic activity of Co/MgO was performed over a portion of samples containing the same number of Co atoms as in pure Co_3O_4. In particular, 0.300 g of Co/MgO was compared with 0.050 g of pure Co_3O_4. The experiments were carried out after reduction at 950 °C for 2 h (5% H_2/Ar mixture 10 cm^3_{STP} min^{-1}).

At first, the investigation of pure MgO showed the formation of H_2, CO, CO_2, CH_3CHO and CH_4, with small quantities of ethane, ethene and other hydrocarbons. The ethanol conversion reaches 100% at 500 °C with a H_2/EtOH ratio equal to 0.8 (Fig. 3). It is confirmed that, over pure MgO, the main reaction is the ethanol dehydrogenation to acetaldehyde [31]. However, the formation of small quantities of ethane and water points out some dehydration reaction.

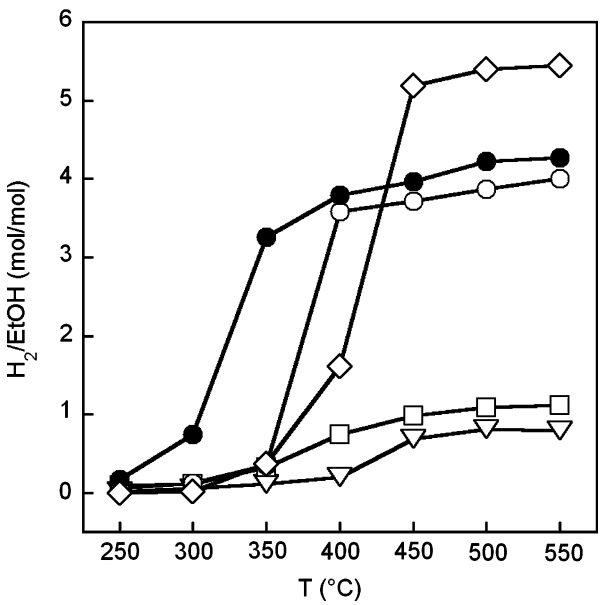

Fig. 3 Efficiency of ethanol steam reforming over different samples. H_2/EtOH molar ratio versus temperature. (◇) Co_3O_4(ox), (●) Co_3O_4(red), (○) Co/MgO(600)(red), (□) Co/MgO(1200)(red), (▽) MgO. The experimental conditions for Co_3O_4 are reported in Tables 2 and 3; those for MgO and Co/MgO systems in Table 6

The addition of Co^{+2} in the MgO solid solution improves the H_2 production. In fact, over Co/MgO(1200)(ox) and on Co/MgO(1200)(red), the H_2/EtOH increases with temperature, reaching 1.1 at 550 °C (Fig. 3), with a H_2O production similar to that found on pure MgO. It is concluded that the addition of Co^{+2} in MgO solid solution, enhanced the ethanol dehydrogenation, as also reported for isopropanol decomposition on the same system [32], but it is unable to promote the ethanol SRR.

Turning now to Co/MgO(600)(red), it is found active for the ethanol SRR (Table 6); the activity and the selectivities are similar to those of Co_3O_4(red). However, the coke deposition appears higher as a result of the ethene formation on the support. The ethanol conversion reaches 100% at 400 °C and the H_2O conversion starts at 350 °C. The efficiency in H_2 production increases with temperature and reaches H_2/EtOH = 4.0 at 550 °C. These results are in reasonable agreement with the presence of metallic cobalt due to the reduction of segregated Co_3O_4, as found by the characterization analysis.

The H_2 production as H_2/EtOH, observed over Co_3O_4(ox), Co_3O_4(red), MgO and Co/MgO(red) samples, is reported in Fig. 3.

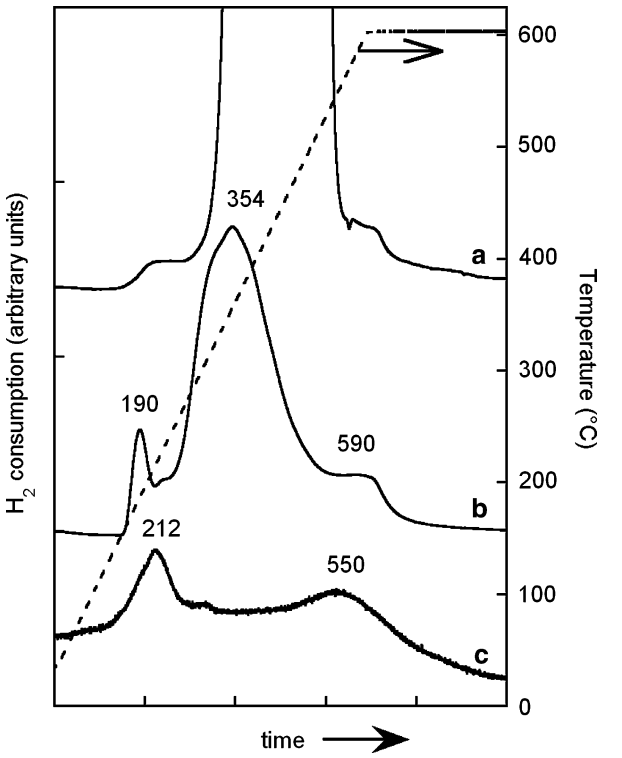

Fig. 4 TPR profiles of: (a) Co_3O_4(ox), as reference; (b) Co_3O_4(red) after H_2O at 500 °C for 1 h; (c) Co_3O_4(red) after ethanol SRR at 550 °C for 30 h

3.3 TPR Characterization After Catalysis

In order to investigate the oxidation state of the cobalt in reaction conditions, TPR experiment were performed on Co_3O_4 and on Co/MgO(600) after catalysis. In addition the role of H_2O alone on the oxidation state of cobalt was investigated.

In Fig. 4 (profile a, c) H_2-TPR profile of Co_3O_4(red) after ethanol steam reforming at 550 °C and the reference TPR profile of Co_3O_4(ox) are reported. Co_3O_4(red) shows a weak peak at 550 °C assigned to reduction of CoO clusters to Co^0 [21, 27, 28], with e/Co = 0.014, corresponding to about 1% of analytical cobalt. The weak peak at 212 °C, according to other authors [28, 29], is assigned to the reduction of trace of chemisorbed oxygen. Similarly, TPR profile of Co/MgO(600)(red) after ethanol steam reforming (not reported), shows a main peak at 515 °C assigned to CoO clusters reduction, with e/Co = 0.034 corresponding to about 2% of analytical cobalt. These results confirm the oxidation of metallic cobalt to CoO during ethanol steam reforming, as reported by Llorca et al. [8].

In order to investigate the role of H_2O, the TPR profile of Co_3O_4(red) previously treated in a flow of H_2O at 500 °C for 1 h (Fig. 4, profile b), shows a peak at 354 °C assigned to reduction of Co_3O_4 to Co^0, with a shoulder at 590 °C assigned to reduction of CoO to Co^0, with total

Table 6 Catalytic activity of Co/MgO(600)(red) for ethanol steam reforming

T (°C)	EtOH conversion (%)	$H_2/EtOH_{in}$ (mol/mol)	Selectivity (%)				
			H_2	CH_4	CH_3CHO	CO	CO_2
250	28.4	0.1	23.9	0.5	35.3	33.5	6.9
300	55.0	0.1	19.1	8.1	37.0	30.5	5.3
350	89.5	0.4	23.9	12.2	11.2	35.7	17.0
400	100	3.6	64.0	1.6	0.0	7.8	26.6
450	100	3.7	59.9	0.8	0.0	14.8	24.5
500	100	3.9	58.2	0.7	0.0	19.5	21.7
550	100	4.0	64.8	0.6	0.0	14.2	20.4

Flow = 25 cm^3_{STP} min^{-1}, [EtOH] = 5.8 × 10^{-5} M, H_2O/EtOH = 3.5

e/Co = 0.13, and a peak at 190 °C attributed to chemisorbed oxygen. Similarly, the TPR profile of Co/MgO (600)(red), pre-treated in a flow of H_2O at 500 °C for 1 h (not shown), presents H_2 consumption in the range 200–800 °C, with a main peak at 360 °C due to Co_3O_4 reduction, with total e/Co = 0.12. In both samples the consumed H_2 corresponds to the reduction of about 5% of analytical cobalt.

As a conclusion, the reaction mixture is able to oxidize to a limited extent metallic cobalt to Co^{+2}, thus excluding any presence of Co^{+3}, as also recently reported by other authors [14]. About the role of Co^{+2} and Co^0 in the steam reforming, it may be suggested that in our conditions the dehydrogenation reaction is due to the presence of Co^{+2}, either present on sample (ox), or created on sample (red) by the oxidizing action of the water in reaction conditions, whereas Co^0 is thought to be mainly responsible of WGS and of methane steam reforming.

4 Conclusions

The high H_2 selectivity of Co_3O_4 is in line with that reported in literature, but it is not confirmed the low level of CO production. It appears that samples containing metallic cobalt are active for the steam reforming of ethanol, whereas Co^{+2} stabilized in MgO solid solution, is able for ethanol dehydrogenation. Finally it has been evidenced that coke deposition is always present in spite of different kinetic conditions and of low ethanol concentration.

References

1. Haryanto A, Fernando S, Murali N, Adhkari S (2005) Energy Fuels 19:2098
2. Vayda PD, Rodriguez AE (2006) Chem Eng J 117:39
3. Haga F, Nakajima T, Miya H, Mishima S (1997) Catal Lett 48:223
4. Llorca J, Homs N, Sales J, de la Piscina PR (2002) J Catal 209:306
5. Llorca J, Dalmon J-A, de la Piscina PR, Homs N (2003) Appl Catal A 243:261
6. Batista MS, Santos RKS, Assaf EM, Assaf JM, Ticianelli EA (2003) J Power Sources 124:99
7. Llorca J, de la Piscina PR, Dalmon J-A, Sales J, Homs N (2003) Appl Catal B 43:355
8. Llorca J, de la Piscina PR, Dalmon J-A, Homs N (2004) Chem Mater 16:3573
9. Batista MS, Santos RKS, Assaf EM, Assaf JM, Ticianelli EA (2004) J Power Sources 134:27
10. Batista MS, Assaf EM, Assaf JM, Ticianelli EA (2006) Int J Hydrogen Energy 31:1204
11. Zhang B, Tang X, Li Y, Cai W, Xu Y, Shen W (2006) Catal Commun 7:367
12. Sahoo DR, Vajpai S, Patel S, Pant KK (2007) Chem Eng J 125:139
13. Cavallaro S, Mondello N, Freni S (2001) J Power Sources 102:198
14. de la Pena O'Shea VA, Homs N, Pereira EB, Nafria R, de la Piscina PR (2007) Catal Today 126:148
15. Guil J, Homs N, Llorca J, Ramirez de la Piscina P (2005) J Phys Chem B 109:10813
16. Lo Jacono RL, Cimino A, Schuit GCA (1973) Gazz Chim Ital 103:1281
17. Yan J, Kung MC, Satchler WMH, Kung H (1997) J Catal 172:178
18. Sexton BA, Hughes AE, Turney TW (1986) J Catal 97:390
19. Lin HY, Chen YW (2004) Mater Chem Phys 85:171
20. Potoczna-Petru D, Kępiński L (2001) Catal Lett 73:41
21. Okamoto Y, Nagata K, Adachi T, Imanaka K, Inamura K, Takyu T (1991) J Phys Chem 95:310
22. Cimino A, Stone F (2002) Adv Catal 47:141 and references therein
23. Pepe F, Schiavello M, Minelli G, Lo Jacono M (1979) Z Phys Chem Neue Folge 115:7
24. Wang HY, Ruckenstein E (2001) Appl Catal A 209:207
25. Cimino A, Pepe F (1972) J Catal 25:362
26. Cordischi D, Indovina V, Occhiuzzi M, Arieti A (1979) J Chem Soc Faraday Trans I 75:533
27. Saib AM, Borgna A, van de Loosdrecht J, van Berge PJ, Geus JW, Niemantsverdriet JW (2006) J Catal 239:326
28. Todorova S, Kadinov G, Tenchev K, Kalvachev Y, Kostov-Kytin V (2007) J Mater Sci 42:3315
29. Milt VG, Ulla MA, Lombardo EA (2001) J Catal 200:241
30. Wang X, Chen H-Y, Sachtler WMH (2000) Appl Catal B 26:L227–L239
31. Lorca J, de la Piscina PR, Sales J, Homs N (2001) Chem Commun 641
32. Pepe F, Stone FS (1979) J Catal 56:160