Pure Appl. Chem., Vol. 80, No. 11, pp. 2397–2403, 2008.
doi:10.1351/pac200880112397

Catalytic behavior of unsupported Co materials in the reformation of ethanol to hydrogen: An in situ diffuse reflectance infrared Fourier transform (DRIFT)-mass spectrometry study*

Salvador Martí, Narcís Homs, Evandro Brum Pereira**, and Pilar Ramírez de la Piscina‡

Department of Inorganic Chemistry and the Institute of Nanoscience and Nanotechnology, University of Barcelona, C/Martí i Franquès 1-11, 08028 Barcelona, Spain

Abstract: New unsupported Co catalysts were studied in the ethanol steam-reforming reaction by in situ diffuse reflectance infrared spectroscopy and on-line mass spectrometry (MS) techniques. The initial ethoxy surface species evolved to surface-acyl species and to acetaldehyde intermediate at temperatures ca. 473 K. The subsequent formation of surface-acetate species occurs at ca. 573 K. Further, the acetate species mainly evolve above 573 K to H_2 and CO_2 products. The route to ketone formation was inhibited on these materials. The presence of surface-hydroxyl groups, which are probably related to the formation of a CoO phase under the reforming conditions, was determined. Alkaline addition shows a beneficial effect on the ethanol steam-reforming over bulk Co catalysts.

Keywords: ethanol-reforming; Co catalysts; hydrogen; surface acetate; surface acyl; in situ DRIFT.

INTRODUCTION

It is now well accepted that hydrogen may constitute a short-term clean source of energy through its use in fuel cell devices. Fuel cells allow a high efficient transformation of chemical energy in electrical energy, and the use of hydrogen only generates water as by-product. Although the hydrogen production is nowadays based in reformation processes of fossil raw materials, the use of ecofriendly feedstock could help to introduce the use of H_2 as energy carrier. At the present time, biomass-derived resources are available and can be used to yield up the hydrogen they contain. In this context, increased production of both bioethanol and biodiesel is now a reality for alternative fuel use in transportation and therefore the use of bioethanol as a H_2 supplier for fuel cells could also be envisaged [1]. The reforming-based processes are well known, and methods for H_2 production from fossil substrates are already well established. In the last few years, many advances have also been made in the study of reforming processes of alcohols. Ethanol is an attractive substrate to be reformed, it is a liquid biofuel, nontoxic, and easy

*Paper based on a presentation at the 3rd International Symposium on Novel Materials and Their Synthesis (NMS-III) and the 17th International Symposium on Fine Chemistry and Functional Polymers (FCFP-XVII), 17–21 October 2007, Shanghai, China. Other presentations are published in this issue, pp. 2231–2563.

**Permanent address: Depto. Fisico-Quimica, Universidade do Estado do Rio de Janeiro (Brazil)
‡Corresponding author: E-mail: pilar.piscina@qi.ub.es

to handle. The steam-reforming of ethanol allows extracting 6 mol of H_2 by each mol of ethanol reacted [1–5]:

$$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 6H_2$$

However, under reaction conditions, usually products other than hydrogen and CO_2 are formed, and the purification of the effluent could be necessary. The requirements of purity of H_2 to be fed in a fuel cell depend on the type of fuel cell used. Solid oxide fuel cells and molten carbonate fuel cells allow the presence of CH_4 and CO, which may be transformed at high temperature in the anode chamber. On the other hand, a CO concentration lower than 0.05 % or 50 ppm is allowed if phosphoric acid fuel cells or polymer electrolyte fuel cells are used. In this context, the main challenge is to develop high-performing catalysts for the steam-reforming reaction and minimize the by-product formation. We have extensively studied new Co-based catalysts for such processes, and we have shown that improvement of the catalysts requires relevant knowledge about their working aspects. In particular, ZnO-supported Co catalysts have been studied by in situ diffuse reflectance Fourier transform–mass spectrometry (DRIFT–MS) techniques. Surface-acetate species involving both the active phase and the support, participate in the evolution of products, determining the catalytic behavior of these materials [6]. We used microcalorimetry studies of chemisorption of ethanol and acetaldehyde to understand the deactivation pathway of these catalysts [7]. In the present paper, we report an in situ DRIFT–MS study of ethanol steam-reforming on unsupported Co, to relate the surface species on the pure active phase and their evolution with the catalytic behavior of the material. The promoter effect of potassium introduction is also reported.

MATERIALS AND METHODS

The precursor material of the bulk Co catalyst was prepared by mixing aqueous solutions of $Co(NO_3)_2$ and citric acid (3:2 = Co:citrate molar ratio), as previously described [8,9]. For the preparation of K-promoted catalyst, an aqueous solution of KNO_3 was added simultaneously. Solutions were mixed and heated until water was fully evaporated and a purple gel was formed. After overnight dryness at 363 K under atmospheric conditions, the milled solid was decomposed at 973 K under argon flow (20 mL/min) for 10 h.

Chemical analysis of samples was carried out by inductively coupled plasma using a Perkin Elmer Optima 3200RL apparatus.

Catalytic tests were carried out at atmospheric pressure using Microactivity Reference Equipment (PID Eng & Tech. S.L.) with a fixed-bed reactor. Powdered catalyst (50 mg) was mixed with inactive SiC to obtain a catalytic bed of ca. 0.5 mL; the catalytic bed was in direct contact with a thermocouple for temperature control. A piston pump (Gilson) was used to introduce the water/ethanol (13:1 or 6:1 molar ratio) mixture, and the reactant mixture was vaporized and mixed with He carrier. The He/(EtOH + H_2O) was kept at ca. 3, with a GHSV = 3600 h^{-1}.

In situ DRIFT experiments were carried out using a Nicolet Magna750 spectrophotometer equipped with a Spectra Tech catalytic chamber. Undiluted catalyst (ca. 20 mg) was placed in the catalytic chamber and contacted with flowing He (20 mL/min) saturated with the reactant mixture (water/ethanol = 13/1 molar ratio). The temperature of the catalyst was measured through a thermocouple placed in contact with the sample. The outlet of the chamber was directly connected, through on-line capillary tubing kept at 433 K, to a Balzers–Pfeiffer quadruple mass spectroscopy (QMS) apparatus to continuously monitor the evolved products. The infrared spectra registered at the different temperatures were obtained using the corresponding background of the sample, separately registered under He at the considered temperature.

RESULTS AND DISCUSSION

Two catalysts were prepared: an unpromoted catalyst labeled Co and a K-promoted catalyst labeled Co(K) (4.5 % w/w K).

X-ray diffraction (XRD) analysis evidenced the presence of both cubic and hexagonal phases of metallic Co in the unpromoted Co catalyst, whereas CoO and Co (ccp) phases were detected in the promoted catalyst (see Fig. 1).

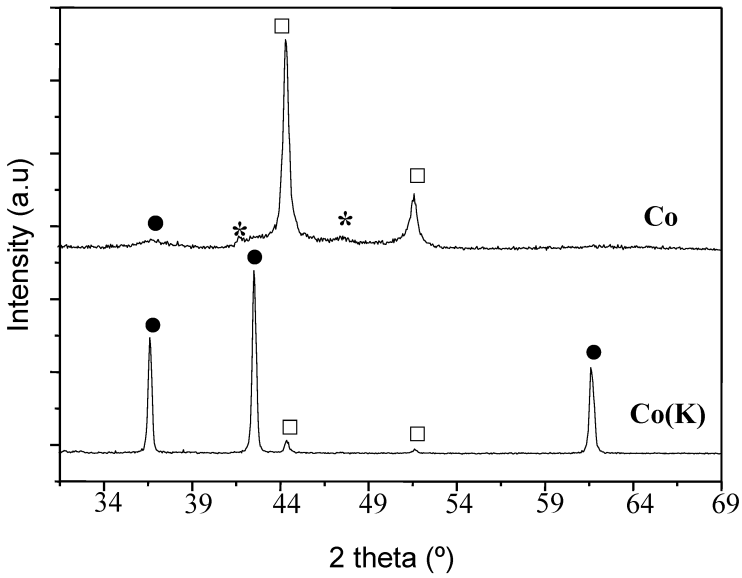

Fig. 1 XRD pattern of Co and Co(K) catalysts. □, Co_{ccp}; *, Co_{hcp}; ●, CoO phases.

Both promoted and unpromoted Co catalysts were tested in the ethanol-reforming reaction at increasing temperatures from 623 to 673 K, representative catalytic data are compiled in Table 1. Over unpromoted Co catalyst under a water/ethanol = 6 ratio, total ethanol conversion was not achieved in the temperature range studied; acetaldehyde, methane, and carbon monoxide were obtained as by-products. If previously reported results for supported Co catalysts were assumed, ethanol dehydrogenation to acetaldehyde could be applied, and then the acetaldehyde reforming to H_2 and CO_2 would complete the total process over the Co active phase. Furthermore, acetaldehyde decomposition to CH_4 and CO seems to be favored over the unpromoted Co catalyst. Co catalyst progressively deactivates under reaction conditions, and the selectivity pattern changes; the selectivity to acetaldehyde increases whereas ethanol conversion continuously decreases. As to the effect of the water/ethanol ratio, catalytic behavior is improved when the ratio increases, and over this material it is possible to achieve total ethanol conversion and selectivity to carbon monoxide below 1 % at 648 K. However, a deactivation process is apparent under these conditions, and the selectivity to acetaldehyde and CO increases with the reaction time.

The presence of K promoter in the bulk Co catalyst has a beneficial effect. Table 1 shows the results for the Co(K) catalyst under a water/ethanol = 6 ratio. Even under these conditions, total ethanol conversion can be achieved at 648 K with selectivity to CO ca. 1 %, and no variations in the catalytic behavior were determined after 10 h of reaction under these conditions. Moreover, no acetaldehyde was produced at temperature above 623 K and with selectivity to CH_4 kept around 2 %. These facts clearly show a positive effect of the alkaline addition on these materials, similar to that which has been reported for sodium addition to supported Co catalysts [10].

Table 1 Catalytic behavior of unsupported Co catalysts on the ethanol steam-reforming at atmospheric pressure.

Catalyst	H_2O/EtOH (molar ratio)	Reaction temperature (K)	EtOH conversion (%)	Time at each temperature (h)	Selectivity (%)*				
					H_2	CO	CO_2	CH_4	CH_3CHO
Co	6	623	87	0.25	57.4	1.2	19.2	9.8	12.4
		648	95	3.0	60.9	1.6	23.4	10.9	3.2
		648	86	15.0	59.3	1.2	21.4	8.2	9.9
		673	84	2.0	56.9	2.4	23.6	7.7	9.4
Co	13	623	93	2.0	64.7	2.9	19.8	5.8	6.8
		648	100	4.0	69.0	0.6	25.1	5.2	0.1
		648	97	15.0	69.4	1.2	22.8	4.6	2.0
		673	100	4.0	69.9	1.1	24.5	4.5	0.0
Co(K)	6	623	82	2.0	61.8	0.4	21.4	1.8	14.6
		648	100	3.5	70.9	1.0	25.8	2.3	0.0
		648	100	10.0	71.7	1.1	24.7	2.5	0.0
		673	100	3.5	72.4	1.8	24.3	1.5	0.0

*Water not included

In situ DRIFT–MS study

In separate experiments, the ethanol steam-reforming reaction was studied on the unpromoted Co sample placed in the catalytic DRIFT chamber at atmospheric pressure and up to 673 K. For such purposes, the reaction mixture was first contacted with the sample at 298 K, and then the temperature progressively rose to 673 K. The evolved products were continuously monitored by on-line MS and the evolution of surface species with the temperature was evidenced by infrared spectroscopy (DRIFT). Upon contact with the reactant mixture at 298 K, characteristic υ(C–O) infrared band was seen appearing at 1063 cm^{-1}, and this is ascribed to the formation of coordinate bidentate ethoxy species (see Fig. 2, spectrum A) [11,12]. Moreover, a low-intensity band at 1285 cm^{-1} evolves with time (Fig. 2, spectrum B). This feature, together the increased broadness of other bands which may contain those bands ascribed to $\delta(CH_3)$ and υ(C–C), could be indicative of the formation of η^2-acetaldehyde species [6]. As the temperature rose to 373 K, the main spectral features assigned to ethoxy species remained unchanged, but those corresponding to the η^2-acetaldehyde species disappeared (Fig. 2, spectrum C). Moreover, a new band (not shown) in the υ(OH) region appeared at 3685 cm^{-1}, and we propose that this band is related to hydroxyl groups of CoO surface species [13] formed upon oxidation of Co centers. This band is visible up to 573 K under the reaction mixture. However, from 473 K, the collected spectra changes progressively. Figure 3 shows the corresponding spectra in the 1400–2400 cm^{-1} region. Initially, a very low intensity absorption at ca. 1660 cm^{-1} and which can be ascribed to acyl species was observed (Fig. 3, spectrum A). Simultaneously, a broad band at 1760–1700 cm^{-1} which intensity grew with time was evidenced (see Fig. 3, spectra A and B); this band is characteristic of physisorbed acetaldehyde. During this process, MS analysis only gives indication of the evolution of acetaldehyde, hydrogen, and minor amounts of CO and CO_2, the latter also being visible in the infrared spectra. These facts can be related with the decomposition of η^2-acetaldehyde species through acyl species as has been proposed to occur over supported metal catalysts at low temperature [14]. At 573 K, a huge amount of CO_2 and CH_4 is formed and is also visible in the infrared spectra; hydrogen and minor amounts of acetaldehyde were also detected. On the other hand, only additional absorptions in the 1590–1540 cm^{-1} region were detected (see spectrum C in Fig. 3); these probably indicate the presence of different surface-acetate species [15,16]. Further raising of temperature up to 673 K does not allow further information from the infrared spectra; the MS analysis indicated the main evolution of H_2, CO_2, and CH_4. It is worth men-

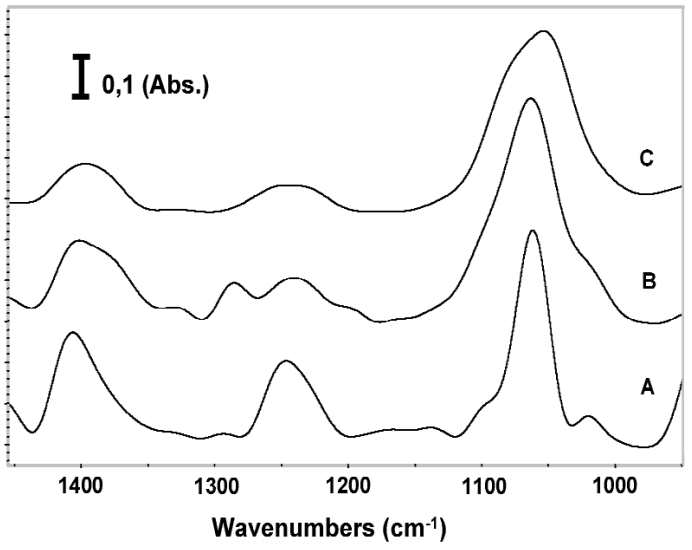

Fig. 2 DRIFT spectra after contact of Co catalyst with the reaction mixture (EtOH:H_2O = 1:13 molar ratio) under several experimental conditions; (A) initial spectrum at 298 K; (B) after spectrum A, catalyst was contacted with the reactant mixture at 298 K for 30 min; (C) after increasing temperature up to 373 K.

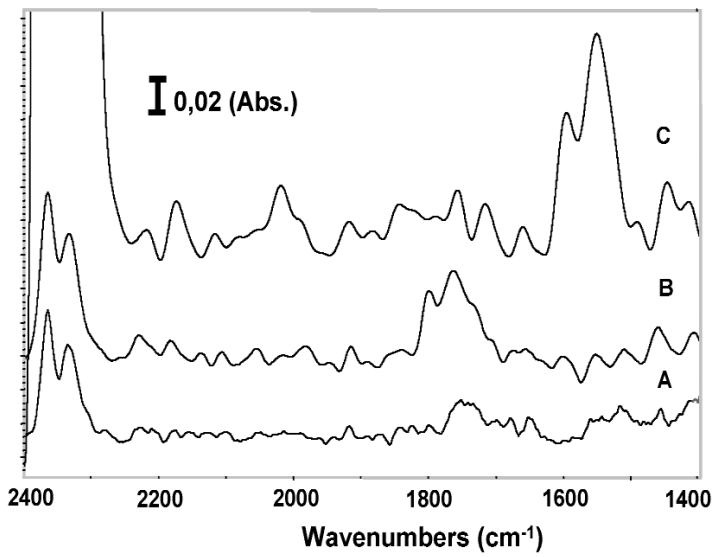

Fig. 3 DRIFT spectra under steam-reforming conditions: (A) initial spectrum at 473 K; (B) after spectrum A, 20 min at 473 K; (C) at 573 K.

tioning that no dimethyl ketone is obtained as by-product in this experiment or in the catalytic test carried out with these materials, contrary to previous results obtained over ZnO-supported Co catalysts [6]. The evolution of surface-acetate species on unsupported Co catalyst differs from that occurring on ZnO-supported catalysts; a C–C scission route is favored on Co. On the other hand, on ZnO-supported catalysts, ZnO surface-acetate species have been previously detected, and the ketonization route was operative over these systems. DRIFT experiment under reaction conditions evidenced the development of a CoO phase on the unsupported Co catalyst, thus indicating a possible oxidation of Co which was ap-

parent at least up to 573 K. At the 473–573 K temperature range, evolution of acetaldehyde occurs as detected by MS. These facts can be related with a preferential dehydrogenation of ethanol on CoO to give acetaldehyde and H_2. However, as temperature increased, H_2 could be further used into the partial reduction of the CoO phase, as reported for the Co_3O_4 phase [17,18]. To verify that Co^0 centers exists under reaction conditions above 573 K, CO was co-fed with the reactant mixture at 673 K. Figure 4 shows the recorded spectra. Apart from the infrared bands due to gas phase (CO_2 and CO), a band at ca. 2069 cm^{-1} is observed (Fig. 4, spectrum A). After cooling down under He flow, the residual chemisorbed CO evidenced low-intensity bands remaining between 2010 and 2050 cm^{-1} at 298 K (Fig. 4, spectra B and C). For comparison, Fig. 4 also shows the spectrum of CO chemisorbed on the unsupported Co catalyst registered in a Fourier transform–infrared (FT–IR) separate experiment (spectrum D), using a gas-vacuum cell. The bands centred at 2049 and 1879 cm^{-1} are respectively assigned to linear and bridge-coordinated CO on metallic Co, which confirms the presence of reduced-surface Co under steam-reforming conditions. On the other hand, from the DRIFT experiment, the presence of surface-oxidized Co species cannot be ruled out, as is revealed by the shoulder located at ca. 2200 cm^{-1} (see Fig. 4, spectra B and C).

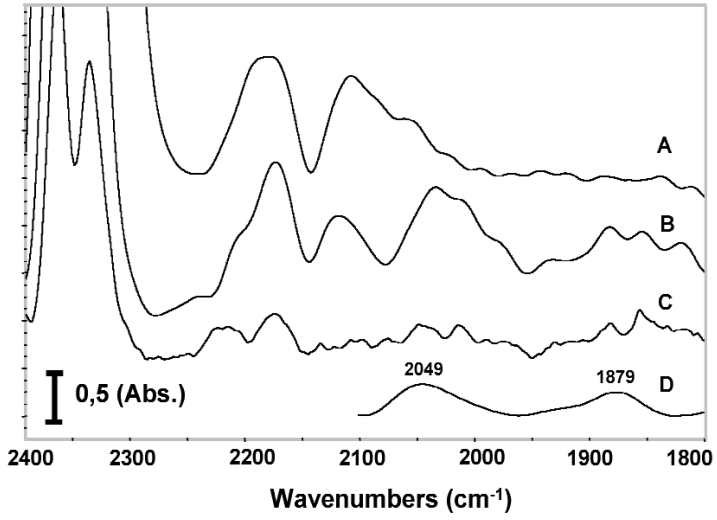

Fig. 4 (A) DRIFT spectrum under steam-reforming at 673 K with co-fed CO; (B) after flushing with He at 298 K; (C) after spectrum (B), 15 min at 298 K. (D) FT–IR spectrum of chemisorbed CO at 298 K on the unsupported Co catalyst.

CONCLUSIONS

The initial interaction of ethanol on bulk Co material under steam-reforming conditions produces bidentate ethoxy surface species. Surface acyl species and physisorbed acetaldehyde are evidenced at 473 K. At 573 K, surface-acetate species are present and undergo C–C scission to H_2 and CO_2, dimethyl ketone did not form. It is proposed that under the reaction conditions used, CoO formation occurs on the surface of the material that promotes the ethanol dehydrogenation. Above 573 K, the coexistence on the surface of both reduced and oxidized Co centers could exist. Potassium addition largely improves the catalytic behavior of unsupported Co catalysts for ethanol reformation.

ACKNOWLEDGMENTS

Financial support from the Spanish CICYT (MAT2005-03456) and from the Generalitat de Catalunya (SGR2005-00184) is acknowledged. EBP is grateful to the Universidade do Estado do Rio de Janeiro and CNPq (Brazil).

REFERENCES

1. P. Ramírez de la Piscina, N. Homs. *Chem. Soc. Rev*. In press.
2. P. Ramírez de la Piscina, N. Homs. "Ethanol reformation to hydrogen", in *Alcoholic Fuels*, S. Minteer (Ed.), Chap. 13, Taylor & Francis (2006).
3. J. Rass-Hansen, C. H. Christensen, J. Sehested, S. Helveg, J. R. Rostrup-Nielsen, S. Dahl. *Green Chem.* **9**, 1016 (2007).
4. G. A. Deluga, J. R. Salge, L. D. Schmidt, X. E. Verykios. *Science* **303**, 993 (2004).
5. T. Ioannides. *J. Power Sources* **92**, 17 (2001).
6. J. Llorca, N. Homs, P. Ramírez de la Piscina. *J. Catal.* **227**, 556 (2004).
7. J. M. Guil, N. Homs, J. Llorca, P. Ramírez de la Piscina. *J. Phys. Chem. B* **109**, 10813 (2005).
8. G. Saracco, G. Scibilia, A. Iannibello, G. Baldi. *Appl. Catal. B: Environ.* **8**, 229 (1996).
9. H. Taguchi, S. Yamada, M. Nagao, Y. Ichikawa, K. Tabata. *Mater. Res. Bull.* **37**, 69 (2002).
10. J. Llorca, N. Homs, J. Sales, J. L. G. Fierro, P. Ramírez de la Piscina. *J. Catal.* **222**, 470 (2004).
11. P. Y. Sheng, A. Yee, G. A. Bowmaker, H. Idriss. *J. Catal.* **208**, 393 (2002).
12. M. Nagao, T. Morimoto. *J. Phys. Chem.* **84**, 2054 (1980).
13. A. A. Tsyganenko, V. N. Filimonov. *Spectrosc. Lett.* **5**, 477 (1972).
14. C. J. Houtman, M. A. Barteau. *J. Catal.* **130**, 528 (1991).
15. A. Yee, S. J. Morrison, H. Idriss. *J. Catal.* **186**, 279 (1999).
16. G. B. Deacon, R. J. Phillips. *J. Coord. Chem. Rev.* **33**, 227 (1980).
17. J. Llorca, P. Ramírez de la Piscina. J. A. Dalmon, N. Homs. *Chem. Mater.* **16**, 3573 (2004).
18. V. A. de la Peña O'Shea, N. Homs, E. B. Pereira, R. Nafria, P. Ramírez de la Piscina. *Catal. Today* **126**, 148 (2007).