



# Spectroscopic characterization of cobalt-containing solid catalysts

E. Finocchio<sup>a,b,\*</sup>, T. Montanari<sup>a</sup>, C. Resini<sup>a,c</sup>, G. Busca<sup>a,b</sup>

<sup>a</sup> *Laboratorio di Chimica delle Superfici e Catalisi Industriale, Dipartimento di Ingegneria Chimica e di Processo, Università di Genova, P.le Kennedy, I-16129 Genoa, Italy*

<sup>b</sup> *INSTM, via B. Varchi 59, I-50132 Firenze, Italy*

<sup>c</sup> *INFN, c/o Dipartimento di Fisica, Università di Genova, Via Dodecaneso 33, I-16146 Genoa, Italy*

Received 18 September 2002; received in revised form 24 January 2003; accepted 10 February 2003

Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

## Abstract

The nature of the cobalt centers in oxidized and reduced  $\text{CoO}_x/\text{Al}_2\text{O}_3$  catalysts and in oxidized Co-H-mordenite (Co-H-MOR) have been characterized by UV-Vis spectroscopy and by IR spectroscopy. The UV-Vis spectroscopy of  $\text{CoO}_x/\text{Al}_2\text{O}_3$  catalysts is dominated by the features of divalent cobalt in tetrahedral coordination. These sites can be reduced by hydrogen to cobalt metal centers that have been characterized by IR spectroscopy of adsorbed carbon monoxide. The surface of  $\text{CoO}_x/\text{Al}_2\text{O}_3$  when it is in contact with  $\text{CO}/\text{H}_2$  mixtures and works as the catalyst for hydrocarbon synthesis has also been characterized by IR. Surface formate species were detected that could act as reaction intermediates. The active sites of Co-H-MOR are also constituted by tetrahedrally coordinated  $\text{Co}^{2+}$  that act as medium strong Lewis sites. The presence of Co species seems to cause a slight increase of the average Brønsted acidity of the residual hydroxy groups in Co-H-MOR samples.

© 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** Cobalt-alumina; Co-H-MOR; CO adsorption; Spectroscopic characterization

## 1. Introduction

Cobalt is a very active element in different fields of catalysis. Organometallic cobalt complexes are known since many years as excellent homogeneous catalysts [1] for hydroformylation and different carbonylation, hydrogenation and isomerization reactions [2]. Like for other organometallic complexes, these materials can be supported on solid carriers giving rise to heterogenized homogeneous catalysts [3] or precursors for supported metal catalysts [4]. Alternatively, cobalt-based catalysts can be prepared by

more conventional impregnation, coprecipitation and ion exchange techniques. In any case, supported complexes can be used as models for the surface species observed, in different conditions, over solid catalysts.

Heterogeneous cobalt-based catalysts have several applications in the chemical industry and have been investigated for several different reactions. In fact, due to the redox properties of cobalt species, they can be applied in the reduced state for hydrogenation reactions, but also in the oxidized state for oxidation. In particular, reduced Co catalysts are active for CO hydrogenation to methanol and higher alcohols [5] and to hydrocarbons, in the Fischer–Tropsch synthesis process [6]. In the former case, good selectivities to linear higher alcohols can be obtained, while in the latter case, good activity/selectivity properties in

\* Corresponding author. Tel.: +39-010-3536027;

fax: +39-010-3536028.

E-mail address: [elisabetta.finocchio@unige.it](mailto:elisabetta.finocchio@unige.it) (E. Finocchio).

hydrocarbons synthesis and, at the same time, higher resistance to oxidation and low water-gas shift activity are observed. Deactivation processes, however, are reported, mainly attributed to re-oxidation of metal centers by water [7,8], one of the FT process products. Bartholomew indicated in his review on catalyst deactivation [9] a need for further investigation on partial oxidation on complex oxides for Fischer–Tropsch synthesis. Various studies, applying several analytic techniques, have also been performed over the nature of the interaction between Co ions and the support [10], the reducibility of Co species [11], their dispersion, the influence of calcination temperature [12].

Oxidized cobalt species are active for several oxidation reactions, such as total oxidation of hydrocarbons [13] and of ammonia to NO [14]. Co containing zeolites are active in hydrocarbon ammoxidation [15] and for reducing NO with methane in oxidizing atmosphere [16,17] so allowing the denitrification (DeNOxing) of waste gases.  $\text{Co}^{2+}$  ions exchanging the protons of the protonic zeolites are considered to be the active sites [13,18]. Recently, it has been proposed that a cooperation between the transition metal cations and Brønsted acid sites can occur upon  $\text{CH}_4$ -SCR. According to Yan et al. [19] Co cations act in the oxidation of NO to  $\text{NO}_2$  while Brønsted sites act in the true reduction step by methane. On the contrary, Kauchy et al. [17] suggest that Brønsted sites enhance the activity in oxidizing NO to  $\text{NO}_2$ . Strong drawbacks are the hydrothermal instability of these catalysts [20], their poisoning by  $\text{SO}_x$  [21] and just their strong activity in oxidizing NO to  $\text{NO}_2$  [22].

In the present paper, we report some results of spectroscopic studies carried on two Co-containing catalytic systems: an alumina supported system, 15.5 wt.% Co on  $\text{Al}_2\text{O}_3$ , which is active for hydrocarbon synthesis from CO and hydrogen, and a partially exchanged mordenite (Co-H-MOR) which is active in hydrocarbons oxidation and in the SCR of NO by methane.

## 2. Experimental

### 2.1. Synthesis of catalysts

The sample  $\text{CoO}_x/\text{Al}_2\text{O}_3$  (15.5 wt.% Co) has been prepared by incipient wetness impregnation of

$\gamma\text{-Al}_2\text{O}_3$  support with  $(\text{CH}_3\text{COO})_2\text{Co}\cdot 4\text{H}_2\text{O}$  aqueous solution followed by calcination at 673 K for 3 h. The catalyst has a mean pore diameter of 40 Å and a surface area of 150  $\text{m}^2/\text{g}$ .

The sample Co-H-MOR was synthesized through an ion exchange process.  $\text{NH}_4\text{-MOR}$  ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$ ;  $S_{\text{BET}} = 480 \text{ m}^2/\text{g}$ ), supplied by Zeolyst was contacted with a 0.02 M  $(\text{CH}_3\text{COO})_2\text{Co}\cdot 4\text{H}_2\text{O}$  aqueous solution (10 g powder for 1 l solution) under stirring at a constant temperature of 353 K for 24 h. The resulting mixture was filtered and washed for three times with bi-distilled water. After centrifugation, the powder was dried at 353 K for 10 h and calcined at 823 K for 4 h (resulting surface area = 430  $\text{m}^2/\text{g}$ ).

### 2.2. Characterization

Diffuse reflectance spectra (DR-UV-Vis-NIR) of pure self-supported sample powder disks have been recorded in the wavenumber range 50,000–4000  $\text{cm}^{-1}$  by a Jasco V-570 at room temperature in air, and after dehydration at 773 K for 5 h by outgassing through a conventional gas manipulation/outgassing ramp connected to a quartz cell. The IR spectra were recorded on a Nicolet Protégé 460 and on a Nicolet Magna 750 Fourier transform instruments. The surface characterization has been performed using pressed disks of pure powders (15 mg), activated by outgassing at 773 or 673 K (cobalt-alumina catalyst) into the IR cell. A conventional manipulation/outgassing ramp connected to the IR cell was used. The adsorption/desorption process of different probe molecules on the catalyst surfaces has been studied through FT-IR spectroscopy. CO was chosen to characterize  $\text{Co}/\text{Al}_2\text{O}_3$ . Before CO adsorption the cobalt-alumina sample has been submitted to an “in situ” reduction pretreatment, i.e. heating in vacuum ( $10^{-2}$  Pa) at 673 K followed by reducing cycles in pure hydrogen at the same temperature. The reducing treatment (critical for the experiment) will be specified in the result section. For Co-H-MOR spectra were collected after activation procedure and after adsorption of acetonitrile (AN), supplied by Aldrich and distilled under vacuum prior to use.

The adsorption procedure involves contact of the activated samples disk with vapors at room temperature

at a pressure of 2 kPa and outgassing in steps at room temperature and increasing temperatures.

### 3. Results and discussion

#### 3.1. UV-Vis spectroscopic characterization: $\text{CoO}_x/\text{Al}_2\text{O}_3$

The UV-Vis spectrum of the  $\text{CoO}_x/\text{Al}_2\text{O}_3$  fresh sample in air shows a very broad absorption centered near  $25,000\text{ cm}^{-1}$ , a sharper one centered near  $15,000\text{ cm}^{-1}$  and a multiple one centered near  $7500\text{ cm}^{-1}$  (Fig. 1a). For comparison we reported in the same figure the UV spectra recorded in air of cobalt aluminate  $\text{CoAl}_2\text{O}_4$  (Fig. 1d) and of the oxide  $\text{Co}_3\text{O}_4$  (Fig. 1c) powder. Note that both  $\text{CoAl}_2\text{O}_4$  and  $\text{Co}_3\text{O}_4$  are essentially normal spinels, so with  $\text{Co}^{2+}$  mainly if not exclusively in tetrahedral coordination and  $\text{Al}^{3+}$  or  $\text{Co}^{3+}$  in octahedral coordination. The

absorption of the support  $\gamma\text{-Al}_2\text{O}_3$  (which is also a defective spinel structure) is negligible in the same region. The spectra are quite close in all cases, however the peaks differ significantly in shape and relative intensity. In particular,  $\text{Co}_3\text{O}_4$  shows the maximum of the broad band at higher energies ( $28,000\text{ cm}^{-1}$ ) and the bond itself is stronger than for  $\text{CoAl}_2\text{O}_4$  and fresh  $\text{CoO}_x/\text{Al}_2\text{O}_3$ . Experimental studies and crystal field calculations [23–25] allow to assign the absorptions near  $25,000$ ,  $15,000$  and  $7500\text{ cm}^{-1}$  to different d–d transitions of tetrahedrally coordinated  $\text{Co}^{2+}$ . The absorption near  $28,000\text{ cm}^{-1}$  which is evident in the spectrum of  $\text{Co}_3\text{O}_4$  could be due to octahedral  $\text{Co}^{3+}$ .

This comparison suggests that the spectrum of fresh  $\text{CoO}_x/\text{Al}_2\text{O}_3$  is dominated too by the absorptions of tetrahedrally coordinated  $\text{Co}^{2+}$  similar to those of cobalt aluminate, while upon further calcinations (Fig. 1b) trivalent cobalt or  $\text{Co}_3\text{O}_4$  are formed.

#### 3.2. UV-Vis spectroscopic characterization: Co-H-MOR

The UV-Vis spectrum of the Co-H-MOR sample, recorded in air, is shown in Fig. 1e. Absorptions due to  $\text{Co}^{n+}$  can be clearly seen also in the spectra of cobalt-containing MOR, as a very strong broad band centered near  $23,000\text{ cm}^{-1}$  and two shoulders near  $28,000$  and  $16,000\text{ cm}^{-1}$ . The spectrum does not give evidence for the presence of massive  $\text{Co}_3\text{O}_4$ , due to the absence of the absorption centered near  $7500\text{ cm}^{-1}$ , present only in traces if any. The main absorption can be associated to octahedrally coordinated  $\text{Co}^{2+}$  aquo or hydroxo ions [23], while the shoulder at higher frequencies could be due to  $\text{Co}^{3+}$  ions. After evacuation at  $773\text{ K}$  for  $5\text{ h}$  the spectrum does not show anymore the very strong and broad adsorption observed in the ambient conditions spectrum. On the contrary, weaker absorptions are found which can be interpreted as a triplet near  $19,000$ ,  $17,000$  and  $15,000\text{ cm}^{-1}$ . The spectrum we observe in this region is closely similar to those reported and deeply discussed by Dedeček and Wichterlová [26] and Drozdova et al. [27] for Co-H-MOR and are also similar to those already observed by Kauchy et al. [28], Dedeček et al. [29] and us [22] for both Co-H-MFI and Co-H-FER. These authors assigned the spectra to bare  $\text{Co}^{2+}$  in three different exchanged positions in the zeolites cavities.

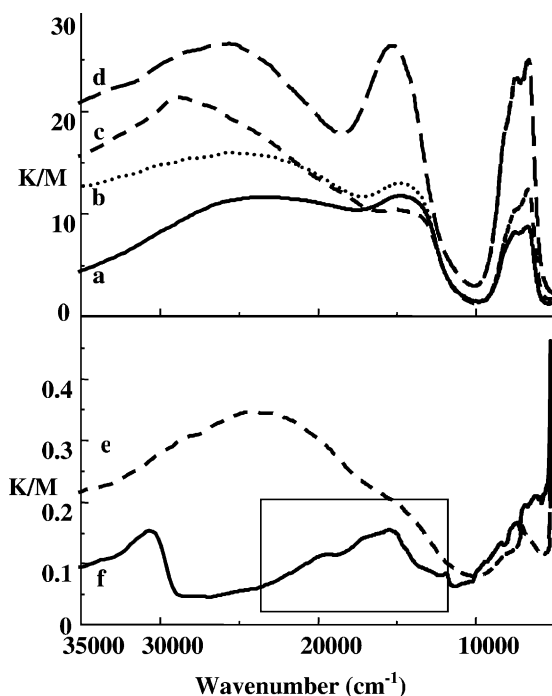


Fig. 1. DR-UV-Vis-NIR spectra recorded at room temperature: (a)  $\text{CoO}_x/\text{Al}_2\text{O}_3$ ; (b)  $\text{CoO}_x/\text{Al}_2\text{O}_3$  further calcined at  $673\text{ K}$ ; (c) commercial  $\text{Co}_3\text{O}_4$ ; (d)  $\text{CoAl}_2\text{O}_4$ ; (e) Co-H-MOR; (f) Co-H-MOR spectrum recorded after outgassing at  $773\text{ K}$ .

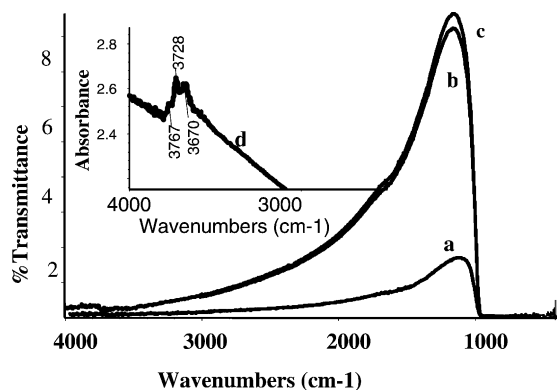


Fig. 2. FT-IR spectra of the  $\text{CoO}_x/\text{Al}_2\text{O}_3$  sample after activation in vacuum ( $10^{-2}$  Pa) at: (a) 473 K; (b) after reduction in hydrogen at 673 K and still in the presence of hydrogen; (c) after reduction in hydrogen at 673 K and following outgassing. Inset: FT-IR spectra of the  $\text{CoO}_x/\text{Al}_2\text{O}_3$  sample outgassed at 673 K (d), OH stretching region.

### 3.3. IR characterization: $\text{CoO}_x/\text{Al}_2\text{O}_3$ pure powder spectra

In Fig. 2, the IR spectra of pressed disks of the pure  $\text{CoO}_x/\text{Al}_2\text{O}_3$  sample after activation by outgassing (a) and after reduction with hydrogen 400 Torr at 673 K for 2 h (b and c) are reported. Activation by outgassing and by reduction causes the disappearance of bands at 1552 and  $1309\text{ cm}^{-1}$  due to residual carbonates. Reduction with hydrogen causes a strong increase of the transmittance of the sample. This has already been observed for cobalt oxide [30] and it can be due to the reduction of the semiconductivity behavior of this material. Both activation procedures cause the appearance of sharp bands at 3767, 3728 and  $3670\text{ cm}^{-1}$  (Fig. 2, inset) typically observed also on activated  $\gamma\text{-Al}_2\text{O}_3$  [31] due to free surface hydroxy groups bonded to Al ions. No evidence is found of bands due to OH coordinated over Co ions.

### 3.4. IR study of CO adsorption over oxidized $\text{CoO}_x/\text{Al}_2\text{O}_3$ catalyst

The spectra of the surface species arising from CO adsorption at room temperature over the fresh  $\text{CoO}_x/\text{Al}_2\text{O}_3$  catalyst are reported in Fig. 3a. Immediately after CO adsorption two main bands are detected at 2190 and at  $2130\text{ cm}^{-1}$ , the latter being broad and complex, with a shoulder at  $2170\text{ cm}^{-1}$ .

If contact with CO gas is carried out longer at room temperature (Fig. 3b), the band at higher wavenumbers decreases in intensity until it disappears while the complex band at lower wavenumbers is better defined into three components, the last one being shifted towards lower frequencies. The band at  $2190\text{ cm}^{-1}$ , decreasing with time, is likely due to CO coordinated over surface  $\text{Co}^{3+}$  [30]. The simultaneous growth of bands at  $2350\text{ cm}^{-1}$ , due to adsorbed  $\text{CO}_2$ , and at 1620, 1437 and  $1227\text{ cm}^{-1}$  due to bicarbonate species is certainly associated to CO oxidation over  $\text{Co}^{3+}$  ions which are partially reduced. The complex band around  $2130\text{ cm}^{-1}$  can also be assigned to CO coordinated over ionic Co (likely  $\text{Co}^{2+}$ ) [30,32]. The evidence of different components in the IR absorption bands can be due to the presence of cobalt ions in different environment.

### 3.5. IR study of CO adsorption over reduced $\text{Co}/\text{Al}_2\text{O}_3$ catalyst

CO adsorption has also been performed over the “mildly” reduced catalyst with 400 Torr of hydrogen at 473 K and at increasing contact time (Fig. 3c and d). A quite strong doublet due to CO stretching modes are detected at 2168 and  $2157\text{ cm}^{-1}$ , associated to terminal carbonyls formed over cobalt ions [33]. Other weak features are detectable at lower frequencies, immediately after CO adsorption, around 2080 and  $1995\text{ cm}^{-1}$ , together with a component around  $1790\text{ cm}^{-1}$ . Increasing contact time leads to the progressive decrease of the higher frequency bands, and to the broadening of the band around  $1800\text{ cm}^{-1}$ . Following literature data [34–37], the two bands at 2080 and  $1995\text{ cm}^{-1}$  are ascribed to terminal carbonyls on reduced Co centers like  $\text{Co}^{\delta+}\text{-CO}$  and  $\text{Co}^0\text{-CO}$ , while the band at  $1800\text{ cm}^{-1}$  is assigned to bridging CO species over metallic Co.

The sample has also been submitted to a eight cycles of reduction and outgassing at 673 K in order to limit the contact between water (formed by reduction with hydrogen) and cobalt at the surface. After this treatment the surface is almost completely dehydroxylated. The spectrum we obtained after contact with CO (Fig. 3e and f) clearly shows the presence of reduced metal centers according to the presence of terminal carbonyls absorbing at 2037 and  $2004\text{ cm}^{-1}$ . Bands due to hydrogencarbonate species are also detected.

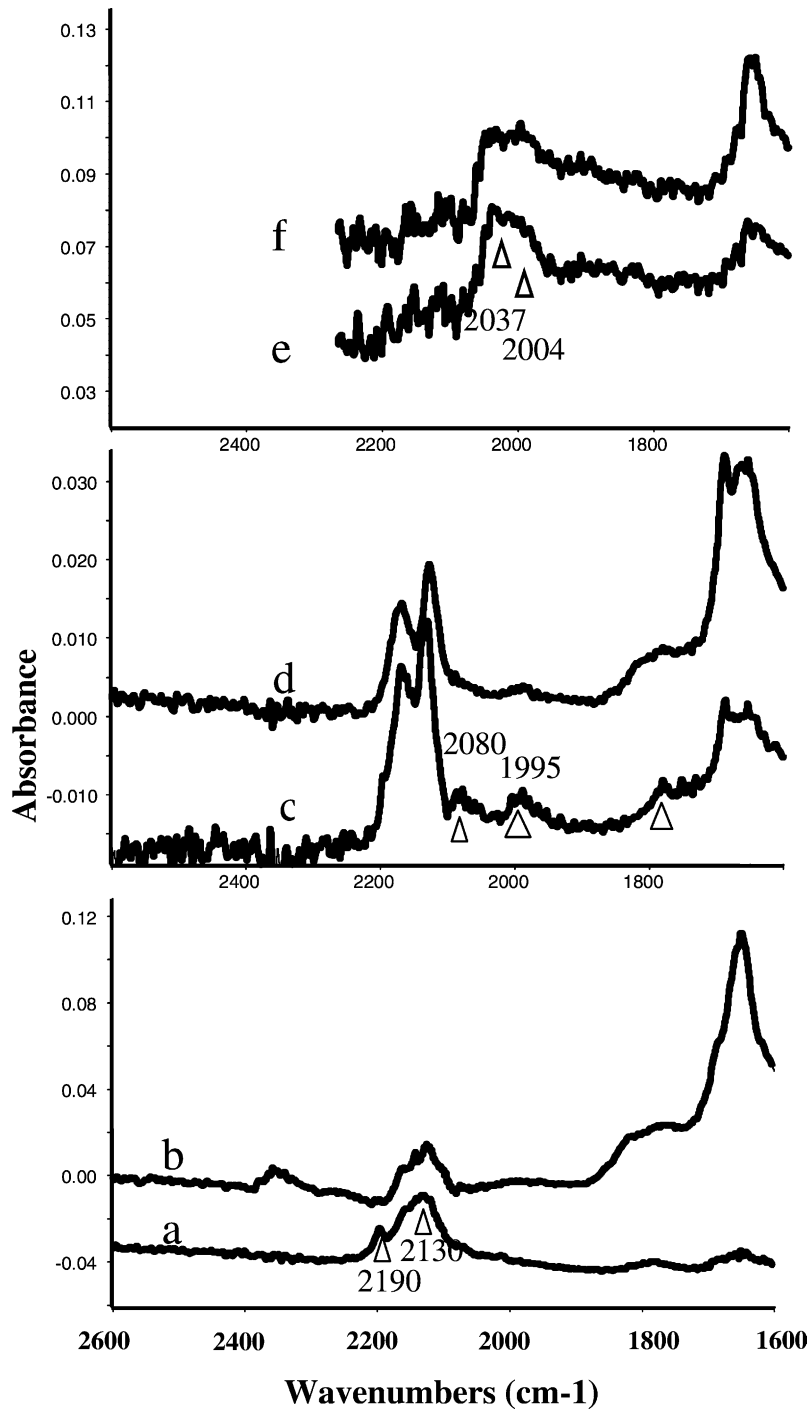


Fig. 3. FT-IR spectra of the surface species arising from CO adsorption over  $\text{CoO}_x/\text{Al}_2\text{O}_3$  catalyst: CO adsorbed at room temperature over the oxidized catalyst (a), after 10 min in CO (b); CO adsorbed at 473 K over the mildly reduced catalyst (c) (see text), after 10 min in CO (d); CO adsorbed at room temperature over the reduced catalyst (e) (see text), after 10 min in CO (f). Gas phase and activated surface spectra have been subtracted.

### 3.6. Study of the surface species and gas phase product under CO/H<sub>2</sub> mixture

After reduction in hydrogen, the sample has been put in contact with 86 kPa of a CO/H<sub>2</sub> (1:2) mixture. The catalyst has been heated at increasing temperature and the spectra of both the catalyst surface (Fig. 4, bottom) and the gas phase (Fig. 4, top) have been recorded at each temperature. In the gas phase, reaction products can be detected starting from 473 K: at this temperature, it is possible to detect weak and sharp bands at 3016 and 1305 cm<sup>-1</sup> due to CH stretching and deformation of methane gas. Their intensity increases at increasing temperatures reaching a “plateau” at 673 K, where these bands are predominant in the spectrum. The careful study of the low

frequency region of the gas phase spectra also reveals the presence of new sharp bands (see the enlargement in the inset of Fig. 4, top). At 473 K bands at 989 cm<sup>-1</sup> (very weak, CH<sub>2</sub> twisting mode of propene), 949 cm<sup>-1</sup> (CH<sub>2</sub> wagging mode of ethylene) and 912 cm<sup>-1</sup> (CH<sub>2</sub> wagging mode of propene) are detected. At increasing temperature (523 K) the band of ethylene at 949 cm<sup>-1</sup> becomes predominant while new bands at 890 cm<sup>-1</sup> (CH<sub>2</sub> wagging mode of isobutene) and at 923 cm<sup>-1</sup> (CH<sub>2</sub> wagging mode of 1-butene) are present, whose intensity is constant even following a further increase of temperature. The high frequency region of the spectra shows complex but weak bands around 2800 and 2900 cm<sup>-1</sup>, partially masked by the strong absorption of methane, associated to several hydrocarbons. Carbon dioxide and water are also

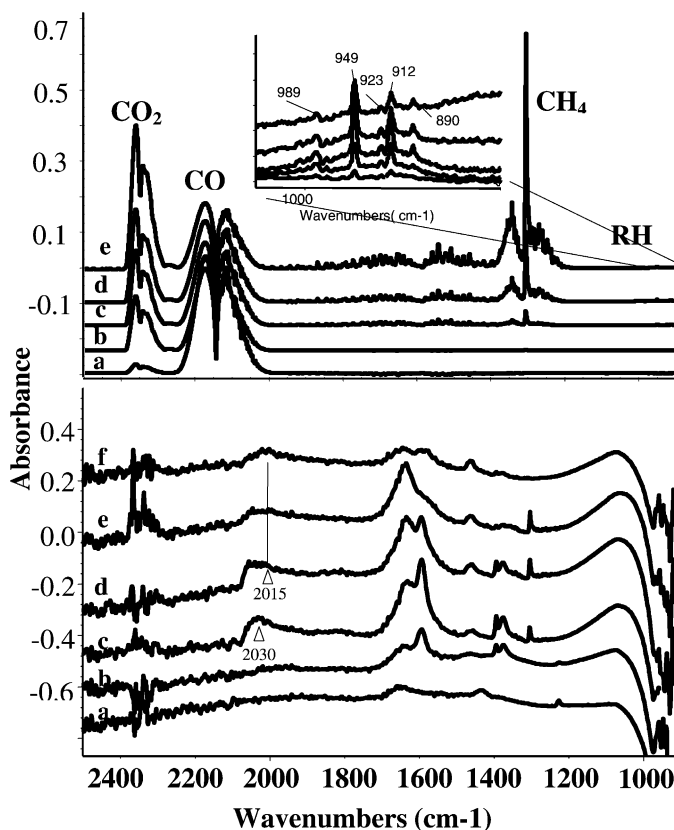


Fig. 4. Top: FT-IR spectra of the gas phase species arising from CO/H<sub>2</sub> (excess) interaction with the pre-reduced CoO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst at: (a) 373 K; (b) 473 K; (c) 523 K; (d) 573 K; (e) 673 K. Bottom: FT-IR spectra of the surface species arising from CO/H<sub>2</sub> (excess) interaction with the pre-reduced cobalt-alumina catalyst at: (a) 373 K; (b) 473 K; (c) 523 K; (d) 573 K; (e) 673 K; (f) after outgassing at 673 K. Gas phase and activated surface spectra have been subtracted.



observed. This shows that the material is now working as a catalyst for the synthesis of hydrocarbons.

Looking at the catalyst (Fig. 4, bottom), at room temperature weak bands due to hydrogenocarbonate species are the only features after the contact of  $\text{CO} + \text{H}_2$ . At 473 K bands at 1630, 1593, 1394 and  $1376\text{ cm}^{-1}$  have been detected, indicating the presence of adsorbed water (broad band at  $1630\text{ cm}^{-1}$ ) and, in agreement with Khassin et al. [38], formate species (asymmetric and symmetric COO stretchings at 1593 and  $1376\text{ cm}^{-1}$ , CH deformation at  $1394\text{ cm}^{-1}$ ) likely interacting with reduced cobalt. Formate adsorbed over  $\text{Co}_3\text{O}_4$  [13] or on the alumina [39] support have been reported at slightly different wavenumbers. The band intensity increases reaching a maximum at 523 K, then these bands disappear between 523 and 573 K. The weak and sharp band at  $1305\text{ cm}^{-1}$  is due to physisorbed methane, still evident in the spectra recorded in the presence of methane in the gas phase even after the subtraction of the corresponding gas phase spectra. The negative band centered below  $1000\text{ cm}^{-1}$  is a common feature in the case of reactants adsorption over alumina surface and is due to Al–O bands perturbation with respect to the same bands in the activated surface spectrum.

In the  $2500\text{--}1700\text{ cm}^{-1}$  region, a complex band with a maximum at  $2030\text{ cm}^{-1}$  appears at 523 K, together with a weak broad absorption near  $1800\text{ cm}^{-1}$ . The position of these band is typical of linear and bridging carbonyls over Co metal species, as discussed in previous paragraph. It is worth to note that these reduced Co surface sites become detectable at this temperature, i.e. higher than the temperature at which methane starts to be observed in the gas (473 K) and their appearance parallels the formation of ethylene and propene in gas phase and the detection of maximum of formate species at the surface.

At increasing temperature (i.e. between 523 and 573 K) a component seems to grow at  $2015\text{ cm}^{-1}$ , simultaneously to the decrease of the component at  $2030\text{ cm}^{-1}$ . This could be the result of the evolution of the morphology of the Co metal particles.

### 3.7. IR study of the residual Brønsted sites on Co-H-mordenite

The IR spectrum of the OH stretching bands of hydroxyl groups of the activated Co-containing zeolite

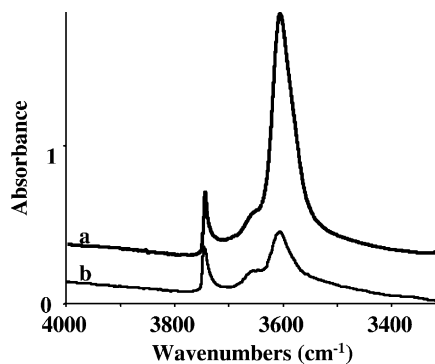


Fig. 5. FT-IR spectra recorded after outgassing at 773 K, OH stretching region: (a) H-MOR; (b) Co-H-MOR.

is compared to that of the corresponding H-zeolite in Fig. 5. As discussed elsewhere [40], the spectrum of H-MOR shows a very sharp band at  $3745\text{ cm}^{-1}$  which is due to the terminal silanol groups located on the external surface and weakly acidic; at least another broad component is present roughly centered at  $3730\text{ cm}^{-1}$ . The very strong band at  $3605\text{ cm}^{-1}$ , is due to the bridging Si–OH–Al groups that are exclusively on the inner surface and possess a strong Brønsted acidity. Such band is characterized by a tail towards lower frequencies, due to the bridging OHs located in the so-called side-pockets [40]. The component near  $3650\text{ cm}^{-1}$  is due to extraframework species. The Co-exchanged MOR sample shows the same bands but with a loss of intensity, apart from the extraframework species bands that seems not to be affected by the ion exchange process. The absolute intensity of the band of the external silanol groups is near 89% with respect to that of the unexchanged material, while concerning the band of the internal bridging the residual OHs band is just 33% of the original one. This suggests that Co exchange has been only partial although nearly 66% of the internal OHs has been actually exchanged.

### 3.8. IR study of CO adsorption over oxidized Co-H-MOR

CO adsorption at room temperature over the oxidized catalysts provide evidence for the existence of  $\text{Co}^{2+}$  ions (band centered at  $2205\text{ cm}^{-1}$  in the IR spectrum), thus confirming UV data. Moreover, following recent literature results [41], we have been able to

detect bands due to polycarbonyl species over  $\text{Co}^+$ , possibly  $\text{Co}^+(\text{CO})_3$ . The contemporary presence of a band due to adsorbed  $\text{CO}_2$  points out the  $\text{CO}$  oxidation over cobalt ions, which are partially reduced.

### 3.9. IR study of the adsorption of acetonitrile on Co-H-MOR

To test whether the partial exchange with cobalt modified the acidity of the residual OHs and if Co sites are actually accessible, we investigated the adsorption of AN on them (Fig. 6). This is a weak base which cannot, in contrast to  $\text{CO}$ , reduce cobalt centers.

Fig. 6 shows the subtraction spectra of H-MOR (spectrum a) and Co-H-MOR (spectrum b) after the adsorption of AN, and evacuation at room temperature for 10 min in order to eliminate the excess vapor (the spectra of the activated samples have been subtracted). After the interaction with AN, both the band at  $3745\text{ cm}^{-1}$  and the one at  $3605\text{ cm}^{-1}$  have disap-

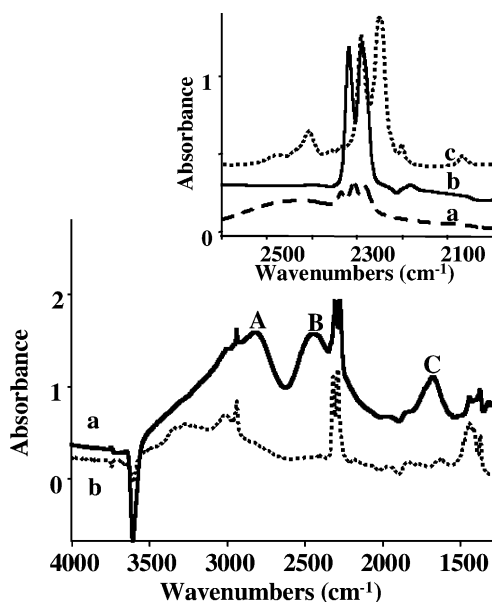


Fig. 6. FT-IR subtraction spectra recorded after adsorption of AN and evacuation at room temperature, ABC pattern region: (a) H-MOR; (b) Co-H-MOR. Inset: spectra recorded after adsorption of AN and evacuation step at 473 K, CN stretching region: (a) H-MOR; (b) Co-H-MOR; (c) liquid AN recorded at room temperature for comparison.

peared. As previously reported [36], the adsorption of AN on the surface of H-MOR and of many other protonic zeolites [42] perturbs entirely the OH groups; the perturbation of the bridging hydroxyl groups, in particular, gives rise to the so-called ABC pattern: two intense and broad bands at around  $2800$  and  $2400\text{ cm}^{-1}$ , a less intense one at around  $1600\text{ cm}^{-1}$  and a window with a minimum at around  $2600\text{ cm}^{-1}$ , corresponding to  $\sim 2\delta\text{OH}$ . Such pattern has been assigned to very strong quasi-symmetrical hydrogen bonding where the proton is partially but not completely transferred to the base. It arises from the Fermi resonance between  $\nu\text{OH}$ , and the  $\delta\text{OH}$  and  $\gamma\text{OH}$  overtones when the acidic bridging OH groups strongly interact with bases. It is evident that the ABC spectrum is very strong in the case of H-MOR and corresponds to the strong negative band at  $3605\text{ cm}^{-1}$ . Both these features are by far weaker for Co-H-MOR in the subtraction spectra just because most of the internal OHs have been exchanged. Additionally, the exchange with Co in the zeolite seems to have caused a small ( $5\text{--}10\text{ cm}^{-1}$ ) but significant shift down of the overall ABC spectrum. This should correspond to an increased average acidity of the residual hydroxyl groups, either due to a direct effect of  $\text{Co}^{2+}$  species on the acidity of the residual OHs or to a easier exchange of the weaker acidic OHs.

In the inset of Fig. 6, the spectra of adsorbed species arising from AN adsorption on the catalysts are shown in the  $2600\text{--}2000\text{ cm}^{-1}$  region: the spectra of activated samples have been subtracted. The spectra have been collected after evacuation step at 473 K, to reveal quite strongly adsorbed species; the analyses of the exchanged and not exchanged mordenite are compared also with the spectrum of liquid AN. At 473 K, the presence of water eventually adsorbed should be negligible and not interfering with the analysis.

In the  $2600\text{--}2000\text{ cm}^{-1}$  range of wavenumbers, liquid acetonitrile shows a strong doublet at  $2294$  and  $2254\text{ cm}^{-1}$ ; the latter band is definitely stronger than the former. They are due to Fermi resonance between the  $-\text{CN}$  stretching and a  $\delta\text{CH}_3 + \nu\text{C}-\text{C}$  combination. This characteristic pattern changes when the  $-\text{CN}$  group adsorbs on an acidic surface: the stronger the electron-withdrawal effect of either Brønsted or Lewis site to which the N lone pair interacts the larger the shift upwards of the components and their relative intensity inversion, as previously reported [43].



AN adsorbed on H-zeolite gives rise to a quite complex and weak group of bands in these conditions. The doublet at 2335 and 2306  $\text{cm}^{-1}$  has been assigned to the AN interacting with extraframework Al Lewis sites, which are very strong Lewis acids. Actually, part of the component at 2306  $\text{cm}^{-1}$  and the further band at 2290  $\text{cm}^{-1}$  arise from the doublet due to AN strongly H-bonded with surface OHs, and still present in part after outgassing at 473 K.

The spectrum relative to Co-H-MOR appears significantly different from that of the H-precursor. It shows a single very strong doublet at 2319 and 2290  $\text{cm}^{-1}$ , which resists outgassing at 473 K, characterized by a comparable intensity of the two components. This doublet is certainly due to AN interacting with the naked Co sites typical of the Co-exchanged zeolites as already reported by our group for Co-H-FER and Co-H-MFI [22]. This spectrum characterizes the  $\text{Co}^{2+}$  of Co-H-MOR as medium strong Lewis acid sites.

#### 4. Conclusions

The results reported in this paper allow to draw some conclusions on the chemistry of cobalt at the surface of two different supports of catalytic interest, i.e. alumina and the mordenite zeolite. Our data show that surface of oxidized  $\text{CoO}_x/\text{Al}_2\text{O}_3$  presents Co in both divalent and trivalent states. However, the UV-Vis spectra are dominated by the absorptions of tetrahedrally coordinated  $\text{Co}^{2+}$  similar to that of  $\text{CoAl}_2\text{O}_4$ . By calcination the amount of  $\text{Co}^{3+}$  seems to increase. On the contrary, treatment in hydrogen shows the progressive reduction of Co centers, up to  $\text{Co}^0$  that can produce both linear and bridging carbonyls by adsorption of CO. Data obtained under  $\text{CO}/\text{H}_2$  mixtures suggest that extended Co metal is necessary for the formation of the olefins ethylene, propene, *n*-butene and isobutene, while methane, which is formed in big amounts, is possibly formed also on only partially reduced surfaces. The detection of formate species under reaction conditions can suggest that these species are intermediates in the reaction. In fact, these species are per se thermally labile at the temperature at which they are detected in the presence of CO and hydrogen.

UV-Vis spectra show that octahedrally coordinated  $\text{Co}^{2+}$  aquo or hydroxo ions are likely predominant on

Co-H-MOR under ambient conditions. These species convert into tetrahedrally coordinated Lewis acidic  $\text{Co}^{2+}$  species by outgassing. These species are characterized by a typical UV-Vis spectrum (probably due to three different spectra related to three different exchange positions) but also by the formation, after adsorption of acetonitrile, of a strongly bonded and well characterized acetonitrile- $\text{Co}^{2+}$  complex. The presence of cobalt is also likely to cause an increase of the average Brønsted strength of the residual hydroxy groups. The coupling of UV-Vis and FT-IR spectroscopy techniques allows a detailed characterization of the active sites of these catalysts and also the study of the catalyst in working conditions.

#### References

- [1] R. Ugo, Aspects of Homogeneous Catalysis, vol. 5, Reidel, Dordrecht, 1984.
- [2] G.F. Pregaglia, A. Andreetta, G.F. Ferrari, R. Ugo, J. Organomet. Chem. 30 (1971) 387.
- [3] R. Ugo, Catal. Rev. 11 (1975) 225.
- [4] R. Ugo, C. Dossi, R. Psaro, J. Mol. Catal. A 13 (1996) 22.
- [5] Ph. Courty, A. Forestiere, N. Kawata, T. Ohno, C. Raimbault, M. Yoshimoto, in: D.R. Fahey (Ed.), Industrial Chemicals via C1 Processes, American Chemical Society, Washington, 1987, p. 42.
- [6] R.B. Anderson, The Fischer-Tropsch Synthesis, Academic Press, New York, 1984.
- [7] A.M. Hilmen, D. Schanke, K.F. Hanssen, A. Holmen, Appl. Catal. A: Gen. 186 (1999) 169.
- [8] P.J. van Berge, J. van de Lossdrecht, S. Barradas, A.M. van der Kraan, Catal. Today 58 (2000) 321.
- [9] C.H. Bartholomew, Appl. Catal. A: Gen. 212 (2001) 17.
- [10] D. Schanke, A.M. Hilmen, E. Bergene, K. Kinnari, E. Rytter, E. Adnanes, A. Holmen, Energy Fuels 10 (1996) 867.
- [11] P. Arnoldy, J.A. Mouljin, J. Catal. 93 (1985) 38.
- [12] A. Lapidus, A. Krylova, V. Kazanskii, V. Borokov, A. Zaitsev, J. Rathousky, A. Zukal, M. Jancalkova, Appl. Catal. 73 (1991) 65.
- [13] E. Finocchio, G. Busca, V. Lorenzelli, V. Sanchez Escribano, J. Chem. Soc., Faraday Trans. 92 (1996) 1587.
- [14] W.W. Scott, W.D. Leech, Ind. Eng. Chem. 19 (1972) 170.
- [15] R. Bulánek, K. Novoveská, B. Wichterlová, Appl. Catal. A: Gen. 235 (2002) 181.
- [16] J.N. Armor, Catal. Today 26 (1995) 147.
- [17] D. Kauchy, A. Vondrová, J. Dedeček, B. Wichterlová, J. Catal. 194 (2000) 318.
- [18] M.C. Campa, S. De Rossi, G. Ferrarsi, V. Indovina, Appl. Catal. B: Environ. 8 (1996) 315.
- [19] J.-Y. Yan, H.H. Kung, W.M.H. Schtler, M.C. Kung, J. Catal. 175 (1998) 294.
- [20] M. Shelef, Chem. Rev. 95 (1995) 209.

- [21] Z. Li, M. Flytzani-Stephanopoulos, *Appl. Catal. B: Environ.* 22 (1999) 35.
- [22] C. Resini, T. Montanari, L. Nappi, G. Bagnasco, M. Turco, G. Busca, F. Bregani, M. Notaro, G. Rocchini, *J. Catal.* 214 (2003) 179.
- [23] B.M. Weckhuysen, R.A. Schoonheydt, in: B.M. Weckhuysen, P. van der Voort, G. Catana (Eds.), *Spectroscopy of Transition Metal Ions on Surfaces*, Leuven University Press, Leuven, 2000, p. 221.
- [24] M. Zayat, D. Levy, *Chem. Mater.* 12 (2000) 2763.
- [25] A.E. Palomares, J.M. Lopez-Nieto, F.J. Lazaro, A. Lopez, A. Corma, *Appl. Catal. B: Environ.* 20 (1999) 257.
- [26] J. Dedechek, B. Wichterlová, *J. Phys. Chem. B* 103 (1999) 1462.
- [27] L. Drozdova, R. Prins, J. Dedechek, Z. Sobalik, B. Wichterlová, *J. Phys. Chem. B* 106 (2002) 2240.
- [28] D. Kauchy, J. Dedechek, B. Wichterlová, *Microporous Mesoporous Mater.* 31 (1999) 75.
- [29] J. Dedechek, D. Kauchy, B. Wichterlová, *Microporous Mesoporous Mater.* 35–36 (2000) 483.
- [30] G. Busca, R. Guidetti, V. Lorenzelli, *J. Chem. Soc., Faraday Trans.* 86 (1990) 989.
- [31] C. Morterra, G. Magnaccia, *Catal. Today* 27 (1996) 497.
- [32] A.Yu. Khodakov, J. Lynch, D. Bazin, B. Rebours, N. Zanier, B. Moisson, P. Chaumette, *J. Catal.* 168 (1997) 16.
- [33] J.G. Choi, H.K. Rhee, S.H. Moon, *Appl. Catal.* 13 (1985) 269.
- [34] L.E.S. Rygh, O.H. Ellestad, P. Klæboe, C.J. Nielsen, *Phys. Chem. Chem. Phys.* 2 (2000) 1835.
- [35] L.E.S. Rygh, C.J. Nielsen, *J. Catal.* 194 (2000) 401.
- [36] G. Kadinov, Ch. Bonev, S. Todorova, A. Palazov, *J. Chem. Soc., Faraday Trans.* 94 (1998) 3027.
- [37] G.A. Beitel, C.P.M. deGroot, H. Oosterbeek, J.H. Wilson, *J. Phys. Chem.* 101 (1997) 4035.
- [38] A.A. Khassin, T.M. Yurieva, V.V. Kaichev, V.I. Bukhtiyarov, A.B. Budneva, E.A. Paukshtis, N. Parmon, *J. Mol. Catal. A: Chem.* 175 (2001) 189.
- [39] G. Busca, J. Lamotte, J.-C. Lavalley, V. Lorenzelli, *J. Am. Chem. Soc.* 109 (1987) 5197.
- [40] M. Bevilacqua, G. Busca, *Catal. Commun.* 3 (2002) 497.
- [41] K. Hadjiivanov, B. Tsyntsarski, Tz. Venkov, M. Daturi, J. Saussey, J.-C. Lavalley, *Phys. Chem. Chem. Phys.* 5 (2003) 243.
- [42] A.G. Pelmenschikov, G.H.M.C. van Wolput, J. Jänchen, R.A. van Santen, *J. Phys. Chem.* 99 (1995) 3612.
- [43] G. Busca, *Phys. Chem. Chem. Phys.* 1 (1999) 723.