

## Sol-gel synthesis of silicon cobalt mixed oxide nanocomposites

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Silicon cobalt mixed oxide samples, with three different composition: 10 (10Co), 20 (20Co) and 30 (30Co) cobalt wt %, were synthesized using a modified sol-gel method. The materials were characterized in order to correlate their structural and chemical properties to synthesis conditions. TG/DTA measurements and X-ray diffraction (XRD) were used to follow the thermal evolution and the crystallization behaviour of the samples. The textural and red-ox properties were evaluated by N<sub>2</sub> adsorption/desorption isotherms and TPR measurements. Lewis acidity and redox properties of cationic sites were studied by FTIR spectra of samples exposed to NO. It was found that the nature of cobalt oxide species and their interactions with silica matrix depends on the cobalt content. No cobalt oxides were observed in 10 Co sample, while Co<sub>3</sub>O<sub>4</sub> was present as a segregated phase in the samples at higher cobalt loading. TPR measurements strengthen these observations: unless 10 Co sample, the 20Co and 30Co show two TPR peaks in the range 300-400°C, attributed to the two-step reduction of the Co<sub>3</sub>O<sub>4</sub> phase, followed by a signal at about 700°C that is probably due to the reduction of Co<sup>2+</sup> species more strongly bonded to silica. N<sub>2</sub> adsorption-desorption measurements indicate that the Co content affects the micropore and mesopore volumes. FT-IR spectra recorded after NO adsorption at different temperature show two weak acid Lewis sites due to Co<sup>2+</sup> surface. However the presence of NO weakly adsorbed over Co<sup>3+</sup> cannot be excluded.

### 1. Introduction

Composite materials based on transition metal oxides nanoparticles dispersed in high surface area matrix have received a growing interest for their optical, magnetic, adsorptive and catalytic properties. Systems based on cobalt oxide dispersed in amorphous silica matrix have been recently proposed as gas sensors or catalysts for different reactions such as Fischer Tropsch synthesis, selective reduction of NO,

hydrogenation of aromatic compounds (Jozwiak et al. 2004; Backman et al. 2001; Dutta et al. 2004; Koshizaki et al. 2000). The synthesis procedure influences the dispersion of metal oxides particles and generally the surface chemical properties of such systems. The sol-gel method has the advantage of an accurate control of the synthesis condition thus allowing to properly modulate surface chemical properties. In this work cobalt oxide in a silica xerogel matrix were prepared by a modified sol-gel method. The materials were characterized in order to define their structural and chemical properties.

## 2. Experimental

Cobalt doped silica catalysts were prepared by a sol-gel method using cobalt nitrate hexahydrate,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Acros Organics), and tetraethoxysilane,  $\text{Si}(\text{OC}_2\text{H}_5)_4$  (99%, ABCR) (TEOS) as starting materials.

TEOS was hydrolyzed for 1 h at 50°C without any alcoholic solvent using nitric acid (Carlo Erba) as catalyst. The molar ratio employed was  $\text{TEOS} : \text{H}_2\text{O} : \text{HNO}_3 = 1 : 4 : 0.01$ . This solution was cooled to room temperature and a proper amount of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was slowly added under stirring. Three samples with a cobalt content of 10 (10Co), 20 (20Co) and 30 (30Co) cobalt wt % were obtained. After 24 h transparent and pinkish coloured gels were obtained for each composition. The gelled systems were kept 3 days at room temperature before drying. The gels were fully dried in air at 110°C in an electric oven for 12 h. All dried samples were slowly heated up to 400°C and 850°C and kept at these temperatures for 30 min followed by quenching.

Thermogravimetric/differential thermal analyses (TG/DTA) were carried out by using a Netzsch simultaneous thermoanalyzer STA 409C with  $\text{Al}_2\text{O}_3$  as reference material.

The amorphous nature of the dried gels as well as the nature of the crystallizing phases was ascertained by X-ray diffraction with a Philips X'PERT diffractometer by using monochromatized  $\text{Cu-K}\alpha$  radiation with a step width of  $0.02^\circ 2\theta$ , and 1 s data collection per step.

$\text{N}_2$  adsorption-desorption isotherms at -196°C were obtained with a Micromeritics Gemini II 2370 apparatus. The isotherms were elaborated by BET and  $\alpha$ -plot methods, using the  $\text{N}_2$  adsorption isotherm of non-porous silica as reference (Gregg and Sing, 1967).

Cobalt catalysts were characterized using temperature programmed reduction (TPR). TPR studies were performed using 2%  $\text{H}_2/\text{Ar}$  as the reducing gas. The consumption of  $\text{H}_2$  was measured by a TCD with a KOH trap to remove moisture formed during reduction. Catalyst sample weight of 100mg and a temperature ramp of  $10^\circ \text{C}/\text{min}$  from room temperature to 800°C were used for all the experiments.

FT-IR spectra were performed with a Nicolet Protegè 460 Fourier Transform spectrometer ( $4 \text{ cm}^{-1}$  resolution). NO was taken from commercial cylinder from SIAD (Milano, Italy) at  $5 \cdot 10^6 \text{ Pa}$ .

## 3. Results and discussion

### 3.1 Structural characterization

Gels were prepared hydrolysing TEOS in a solely aqueous acid environment according to a modified sol-gel method previously proposed (Aronne et al., 2005). According to

our experimental conditions the probability of the formation of Co-O-Si bridges is very low therefore all wet gels will be formed by a siloxane network in which the cobalt species are physically trapped as suggested by Ortega-Zarzosa et al., 2002. This hypothesis is confirmed by the pinkish colour of all wet gels as well as by the fact that all studied compositions exhibit the same gelation time (24 h) independently of the cobalt loading. The annealing temperature of the prepared samples were selected on the bases of the thermal analysis results.

The total weight losses given by the TG curves were: 24 wt % (10Co), 33 wt % (20Co) and 42 wt % (30Co). In each case, the majority of the weight loss takes place from room temperature to about 300°C. In this range, the evaporation of the solvents and the subsequent pyrolysis and/or burning of residual organic molecules are overlapped to the decomposition of the  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $T_d = 242^\circ\text{C}$ ).

Cobalt loading has a strong influence on the crystallization behaviour of the gels. XRD patterns of 10, 20 and 30 Co samples heat treated at 400°C are reported in Fig. 1a. Whereas the 10Co keeps an amorphous nature, the crystallization of the mixed valence cobalt oxide,  $\text{Co}_3\text{O}_4$ , (JCPDS card 42-1467) is detected at higher cobalt loading. On annealing at 850°C the formation of  $\text{Co}_2\text{SiO}_4$  crystallites (JCPDS card 15-0865) occurs in all samples, Fig. 1b. even if the  $\text{Co}_3\text{O}_4$  phase is still present in 20 and 30 Co samples. These results strongly suggest that the gel composition and temperature of calcination play an important role to determine the nature of cobalt species and their interactions with the silica matrix.

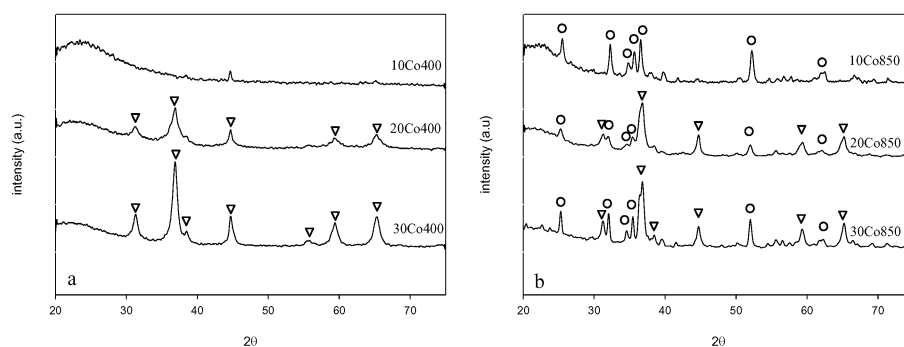


Fig.1 XRD patterns of gel derived samples at 400 °C (a) and 850 °C (b).  $\circ$   $\text{Co}_2\text{SiO}_4$  (JCPDS card 15-0865).  $\nabla$   $\text{Co}_3\text{O}_4$ , (JCPDS card 42-1467).

Table 2. Surface area, total pore volume and micropore volume of samples treated at 400°C.

Sample	Surface area m <sup>2</sup> g <sup>-1</sup>		Pore volume cm <sup>3</sup> g <sup>-1</sup>	Micropore volume cm <sup>3</sup> g <sup>-1</sup>
	BET	$\alpha$ -plot		
SiO <sub>2</sub> -400	401	151	0.193	0.129
10Co	409	322	0.198	0.036
20Co	314	291	0.171	0.016
30Co	411	413	0.288	0.009

### 3.2 Textural and redox properties

The N<sub>2</sub> adsorption-desorption isotherms are obtained and subsequently elaborated using, besides the conventional BET method, the  $\alpha$ -plot one that is more advisable for materials containing micropores (Gregg and Sing, 1967).

Micropore volumes and surface areas calculated from  $\alpha$ -plots are reported in Table 1 together with BET surface areas and total pore volumes. It can be observed that surface areas determined by  $\alpha$ -plot are generally lower than those calculated by BET because they exclude the contribution of micropores, with the exception of 30Co. For this sample BET and  $\alpha$ -plot give same values indicating that microporosity is negligible. All the materials have BET surface areas close to that of pure silica, with the exception of 20Co samples that show lower values. These data indicate that the presence of Co has the main effect of modifying the pore size distribution of silica, by reducing the micropore volume even with low Co content and adding some mesoporosity with the highest Co content. The segregated Co<sub>3</sub>O<sub>4</sub> phase gives a contribution to mesoporosity of the material, because a mesoporous oxide is generally formed from decomposition of the Co nitrate at low temperature (Van de Loosdrecht et al., 1997). This explains the mesoporous texture of samples 30Co. Therefore the dependence of surface area on Co content, with a minimum at 20 Co, can be explained with two opposite effects: a decrease of microporosity of silica due to the strong interaction of Co<sup>2+</sup> with the siloxane matrix and an increase of mesoporosity due to the formation of the Co<sub>3</sub>O<sub>4</sub> phase.

The H<sub>2</sub> reduction profiles of Co/SiO<sub>2</sub> catalysts treated at 400°C are presented in Fig. 2. The spectra show two main signals in the range 330-400°C and a weaker signal at about 700°C. The first and the second peaks located at about 330 °C and 400°C are due to the two step reduction of Co<sub>3</sub>O<sub>4</sub> (Co<sub>3</sub>O<sub>4</sub> → CoO → Co) (Li and Coville, 2001). The third peak located at about 700°C may be due to the reduction of cobalt oxide species (Co<sup>+2</sup>, Co<sup>+3</sup>) which interact strongly with the support and are difficult to be reduced.

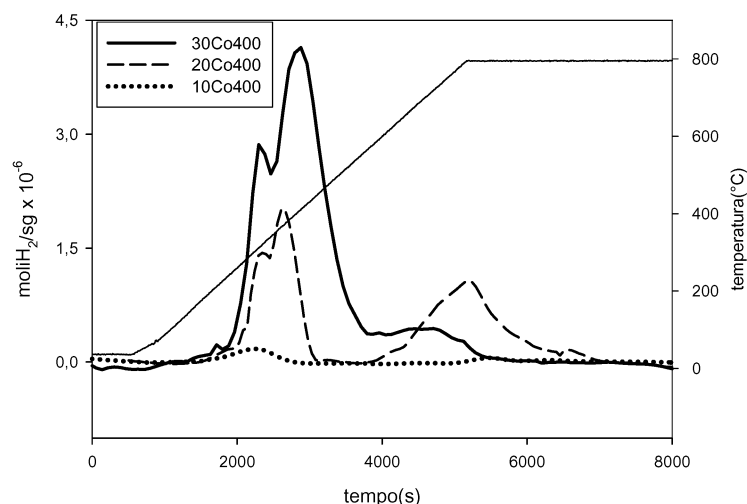


Fig.2 Temperature Programmed Reduction profiles of gel derived samples at 400°C.

The catalysts were not completely reduced in experiments with 800°C as the maximum temperature. This fact is maybe due to a fraction of cobalt that is contained in the inner cavities of the silica support and that is inaccessible to  $H_2$  or to the necessity of working using temperature higher than 800°C to completely reduce the cobalt silicate. The adsorption of NO has been extensively investigated in the literature over catalytic systems active in several reaction. In principle, NO can be adsorbed in a molecular form, with a lone pair of the N atom to the surface metal cationic centers, and can be oxidized by oxide surfaces. So nitrogen oxide is a probe molecule which provides detailed information about Lewis acidity and redox properties of cationic sites. The interaction of NO with supported cobalt-oxides and supported cobalt-silica is very complex and gives a number of different species. Bands below  $1800\text{ cm}^{-1}$  are characteristic of transformation products of NO, while molecularly adsorbed NO bands can be found only in the spectral range  $1900\text{--}1800\text{ cm}^{-1}$ . NO is a diatomic molecule giving rise in the IR spectrum to a single band at  $1875\text{ cm}^{-1}$  in the gas. The adsorption of NO at different temperature over 10Co, gives rise to the complex spectra, Fig. 3. A band at  $1803\text{ cm}^{-1}$  and a stronger absorption at  $1882\text{ cm}^{-1}$ , that resist at evacuation at r.t., but disappeared after outgassing at higher temperatures, are observed indicating that NO is adsorbed in two different cationic sites. The position of the weaker band is shifted to lower frequencies as compared to that of NO gas. This red shift of the NO stretching band of adsorbed nitrogen monoxide characterises terminal surface nitrosyl species, probably adsorbed over  $Co^{2+}$  cation toward the  $\pi^*$  antibonding orbitals of NO. A band, probably coupled, is also observed near  $2224\text{ cm}^{-1}$ . A band, probably coupled, is also observed near  $2224\text{ cm}^{-1}$ . This couple of bands, that disappears by outgassing at increasing temperature, can be assigned to N-bonded and O-bonded species of adsorbed  $N_2O$  either formed on the surface from NO or present as an impurity in the gas. In the spectral region below  $1800\text{ cm}^{-1}$  the complex absorption in the  $1600\text{--}1450\text{ cm}^{-1}$  is due

mainly to different forms of bridged nitrates although presence of adsorbed  $\text{NO}_2$  cannot be excluded. These species should be produced by NO oxidation. The adsorption of NO at different temperature over cobalt-silica at higher cobalt loading gives rise to very similar spectra. The main difference is due to the reduced transparency of the sample and the consequent lower resolution of the spectra. However all the bands observed over 10Co are still detectable. Only a small change in the relative intensities of same bands can be detected.

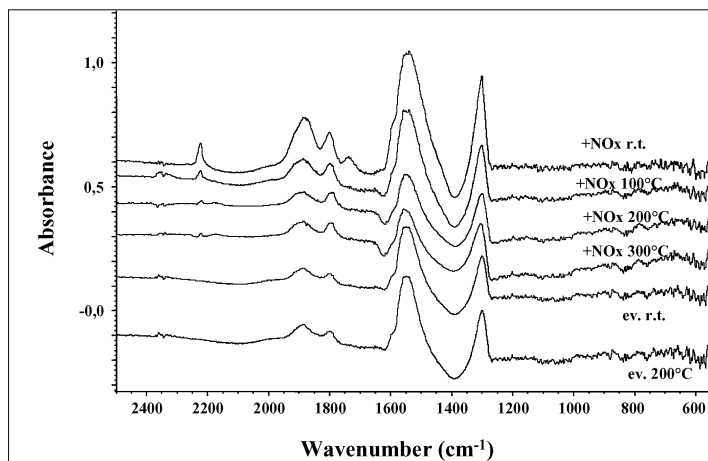


Fig. 3 FTIR spectra of adsorbed NOx species on 10Co samples annealed at 400°C collected at different temperatures.

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