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Chemistry of dicobalt octacarbonyl on zinc oxide. Homonuclear ion-pairing surface species related to catalytic activity in ethylene hydroformylation

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Abstract

The reaction of $\text{Co}_2(\text{CO})_8$ with partially hydroxylated ZnO has been studied. Formation of $\text{Co}_4(\text{CO})_{12}$ deposited on the surface, and disproportionation of $\text{Co}_2(\text{CO})_8$ to Co^{2+} and $[\text{Co}(\text{CO})_4]^-$ has been evidenced. $[\text{Co}(\text{CO})_4]^-$ has been characterized on the surface by in situ FTIR spectroscopy. Co^{2+} and $[\text{Co}(\text{CO})_4]^-$ were extracted from the surface with $[\text{PPN}]\text{Cl}$. Chemisorption of $[\text{PPN}][\text{Co}(\text{CO})_4]$ on the surface, in presence or not of Co^{2+} ions, suggests that, when $\text{Co}_2(\text{CO})_8$ reacts with ZnO, $\text{Co}^{2+}/[\text{Co}(\text{CO})_4]^-$ homonuclear ion-pairing species on the surface are produced. This supported molecular species is related to the catalytic activity in ethylene hydroformylation with high selectivity to propanal production.

Keywords: Cobalt; Ethylene; Hydroformylation; Octacarbonyl cobalt complex; Organometallic; Surface chemistry; Zinc oxide

1. Introduction

At present there is interest in combining the advantages of homogeneous and heterogeneous catalysis by the use of molecular species supported on inorganic materials as catalysts. One way to obtain these heterogenized-homogeneous catalysts is to support organometallic compounds, which are known to be homogeneous catalysts, on appropriate inorganic oxides. This process could be viewed as the interaction of the organometallic compound with a new ligand being the support. Then, the characteristics of both the organometallic compound and the active surface sites of the

carrier could modulate the reaction of the metallic precursor with the support oxide [1,2].

Many papers have been devoted to the study of the reactivity of transition-metal carbonyls with solid surfaces [3,4]. In particular, the reactivity of cobalt carbonyl compounds with the surfaces of silica, alumina, magnesia and zeolites has been extensively studied [5–10]. However, the chemistry of these systems is complex, and the coexistence of different surface species makes their characterization difficult, so in many cases the new surface species have not been unambiguously determined.

Moreover, interest in the study of these cobalt systems lies not only in understanding the surface reaction but also in the potential use of these new supported cobalt carbonyl species in heterogeneous catalysis [11–13].

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Here we have studied the surface organometallic chemistry of $\text{Co}_2(\text{CO})_8$ on zinc oxide. We report the characterization of the new surface species produced and their catalytic properties in the hydroformylation of ethylene in heterogeneous phase.

2. Experimental section

2.1. Materials

Solvents were distilled and stored over activated molecular sieves under argon. $\text{Co}_2(\text{CO})_8$ (Strem Chemicals Inc.) was stored under argon and kept refrigerated. $\text{Co}_4(\text{CO})_{12}$ was prepared by thermal decomposition of a hexane solution of $\text{Co}_2(\text{CO})_8$. $[\text{PPN}][\text{Co}(\text{CO})_4]$ was synthesized by reaction between $\text{Co}_2(\text{CO})_8$ and NaOH, followed by metathetical exchange with $[\text{PPN}]\text{Cl}$ (PPN = bis(triphenylphosphine)nitrogen(I)) according to literature methods [14]. All carbonyl compounds were checked, prior to use, by IR spectroscopy. Kadox 15-type ZnO with a low impurity content was used as support. Before use, the support was treated in all cases under high vacuum at 473 K for 16 h (ZnO(200)).

2.2. Procedures

In the impregnation process, an n-hexane solution of $\text{Co}_2(\text{CO})_8$ was reacted with ZnO(200) surface under deoxygenated and dry argon. After two hours, the gases evolved were analysed by mass spectrometry and the impregnation solution was removed. The solid was washed with hexane until no more carbonylic species passed into the solution and then dried under high vacuum at room temperature. To extract the surface species, the solid was treated with a CH_2Cl_2 solution of $[\text{PPN}]\text{Cl}$ at room temperature. After two hours the solution was removed and the solid and the solution were characterized. Samples for IR experiments were prepared in situ, by adsorption of a solution of the metallic precursor in hexane onto ZnO(200) wafers (10 mg), in the strict

absence of oxygen and water, using vacuum-gas-line and break-seal techniques. All IR experiments were carried out in special greaseless vacuum Pyrex cells with CaF_2 windows, which allowed thermal treatment. Hydroformylation reactions were carried out in an 80 ml magnetically stirred stainless-steel autoclave. In a typical procedure, the reactor was first purged and loaded with 0.3–0.4 g of catalyst, then pressurized with the reaction gases at 54 bar, and heated to 433 K. Two series of experiments were performed with $\text{C}_2\text{H}_4/\text{CO}/\text{H}_2 = 1/1/1$ and $2/1/1$ molar ratios. After the reaction time (6 h), the reaction products were collected by bubbling the gases through toluene kept at 194.5 K, characterized by mass spectrometry and analysed by gas chromatography. No cobalt lost from the catalyst was detected in any case.

2.3. Instrumentation

Infrared spectra were obtained with a Nicolet 520 Fourier transform spectrophotometer. Gas chromatography analyses were performed on a Hewlett-Packard 5890 A GC instrument with a 50 m Ultra-2 capillary column. Mass spectrometry was achieved by GC-MS on a Hewlett-Packard chromatograph with a 5971 mass-selective detector. UV-Vis spectra were recorded on a Shimadzu UV-160 A spectrophotometer.

3. Results

3.1. $\text{Co}_2(\text{CO})_8$ adsorption on ZnO and extraction of surface species

After treatment of ZnO(200) with a hexane solution of $\text{Co}_2(\text{CO})_8$, the IR spectrum of the solution showed the presence of $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ as the only carbonyl species (see Fig. 1). During the process an evolution of 7.7 mol CO/mol of cobalt in ZnO was found, and no other gaseous products were detected. In contrast, a hexane solution of $\text{Co}_4(\text{CO})_{12}$ did not react with ZnO(200) under similar experimental conditions.

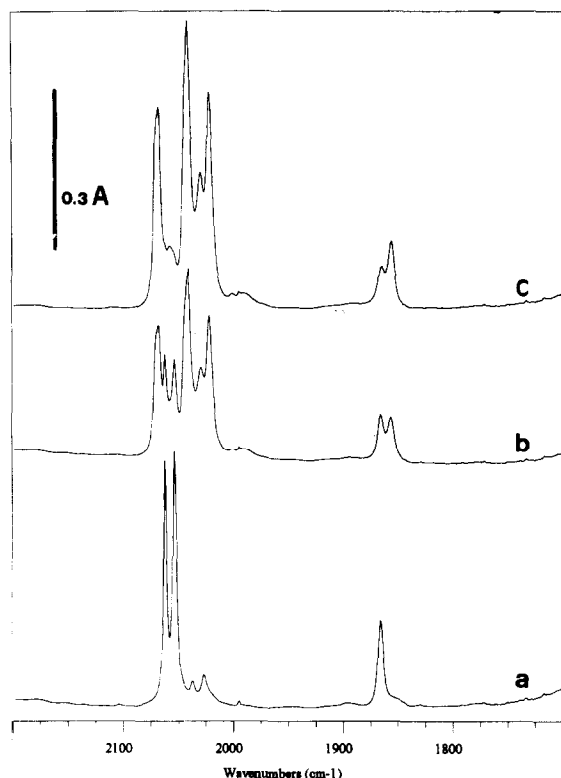


Fig. 1. Infrared spectra in the $\nu(\text{CO})$ region. (a) $\text{Co}_2(\text{CO})_8$ impregnating hexane solution. (b) $\text{Co}_2(\text{CO})_8$ impregnating hexane solution after reaction with $\text{ZnO}(200)$. (c) $\text{Co}_4(\text{CO})_{12}$ in hexane.

When the solid, after $\text{Co}_2(\text{CO})_8$ impregnation and washing, was treated with a CH_2Cl_2 solution of $[\text{PPN}]\text{Cl}$ the only carbonyl species extracted from the surface was $[\text{Co}(\text{CO})_4]^-$, characterized by a single IR absorption band at 1889 cm^{-1} [15]. $[\text{CoCl}_4]^{2-}$ was also identified in the solution (characterized by UV–Vis absorptions at 632, 667, 692 nm [16]). Cobalt contents in the sample before and after extraction of surface species were 0.163 and 0.083 wt%, respectively.

3.2. In situ infrared characterization of surface species

When a hexane solution of $\text{Co}_2(\text{CO})_8$ reacted with the surface of $\text{ZnO}(200)$, new surface carbonyl species were produced. In Fig. 2, spectra in the CO stretching region of the solid obtained are shown. Fig. 2a corresponds to the solid after impregnation. When the sample was evacuated at

room temperature for 16 h, the elimination of residual $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ on the surface was observed, and the new surface carbonyl species remained, giving Sample 1 (Fig. 2b).

In order to clarify whether $[\text{Co}(\text{CO})_4]^-$ extracted from the surface was responsible for the IR bands shown by Sample 1, two different experiments were carried out:

The first experiment was the impregnation of a CH_2Cl_2 solution of $[\text{PPN}][\text{Co}(\text{CO})_4]^-$ on $\text{ZnO}(200)$ to give Sample 2. A single IR absorption band centered at 1888 cm^{-1} was obtained corresponding to the tetrahedral $[\text{Co}(\text{CO})_4]^-$ species deposited on the ZnO surface. After evacuation at room temperature, the presence of shoulders at 1896 and 1875 cm^{-1} (Fig. 3a) is related to the distortion of this tetrahedral species [5].

In the second experiment, the impregnation of a CH_2Cl_2 solution of $[\text{PPN}][\text{Co}(\text{CO})_4]^-$ in the

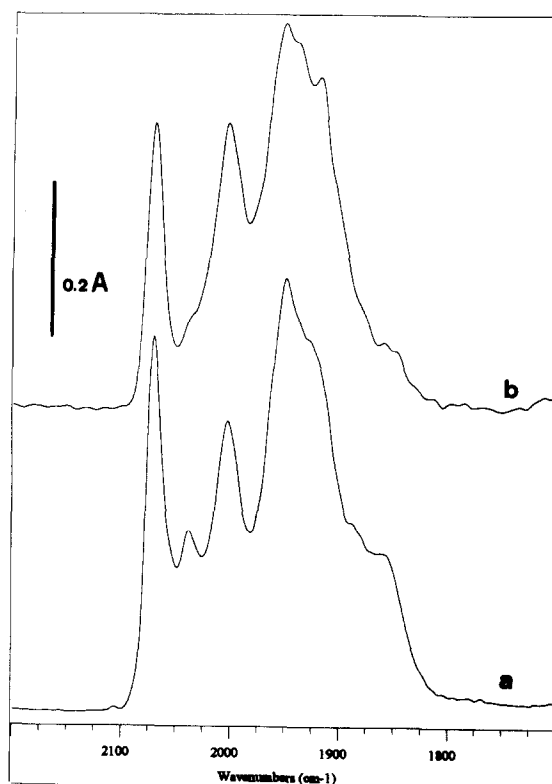


Fig. 2. Infrared spectra in the $\nu(\text{CO})$ region. (a) $\text{ZnO}(200)$ after impregnation with a hexane solution of $\text{Co}_2(\text{CO})_8$. (b) After spectrum (a) solid evacuated under high vacuum at room temperature for 16 h (Sample 1).

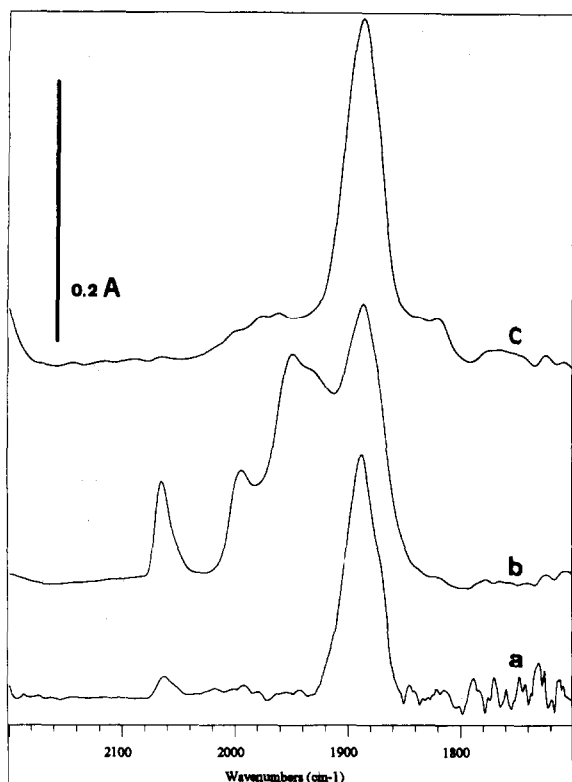


Fig. 3. Infrared spectra in the $\nu(\text{CO})$ region. (a) $\text{ZnO}(200)$ after impregnation with a CH_2Cl_2 solution of $\text{PPN}[\text{Co}(\text{CO})_4]$ and subsequent treatment under high vacuum at room temperature for 6 h (Sample 2). (b) $\text{ZnO}(200)$ after impregnation with a CH_2Cl_2 solution of $\text{PPN}[\text{Co}(\text{CO})_4]$ in the presence of $[\text{CoCl}_4]^{2-}$ and subsequent treatment under high vacuum at room temperature for 6 h. (c) After spectrum (b), solid in the presence of CH_2Cl_2 vapor at room temperature.

presence of Co^{2+} ions was carried out. After evacuation at room temperature carbonyl species gave the infrared spectrum shown in Fig. 3b. If CH_2Cl_2 vapor was allowed to contact the solid, the IR spectrum changed, and only the band centered at 1888 cm^{-1} , assigned to non-distorted tetrahedral $[\text{Co}(\text{CO})_4]^-$ was observed (Fig. 3c).

3.3. Decarbonylation and recarbonylation of surface species

After $\text{Co}_2(\text{CO})_8$ impregnation on $\text{ZnO}(200)$, evacuation of Sample 1 at 373 K indicated the existence of carbonyl species stable even at this temperature under vacuum (Fig. 4a). A subsequent CO treatment at room temperature regen-

erated the carbonyl species of Sample 1 (Fig. 4b). All carbonyl species disappeared after hydrogen treatment at 673 K and subsequent evacuation at 473 K (Fig. 4c). After this, CO treatment at room temperature produced the recarbonylation of surface species (Fig. 4d); simultaneously, the formation of CH_4 was detected. The spectrum corresponding to the recarbonylated species differed from the spectrum of Sample 1 mainly on the relative intensity of the band at 2072 cm^{-1} . The intensity increase of this band may be due to CO linearly chemisorbed on cobalt metal particles, which in turn may be responsible for the formation of CH_4 from strongly chemisorbed hydrogen, which was not eliminated after evacuation.

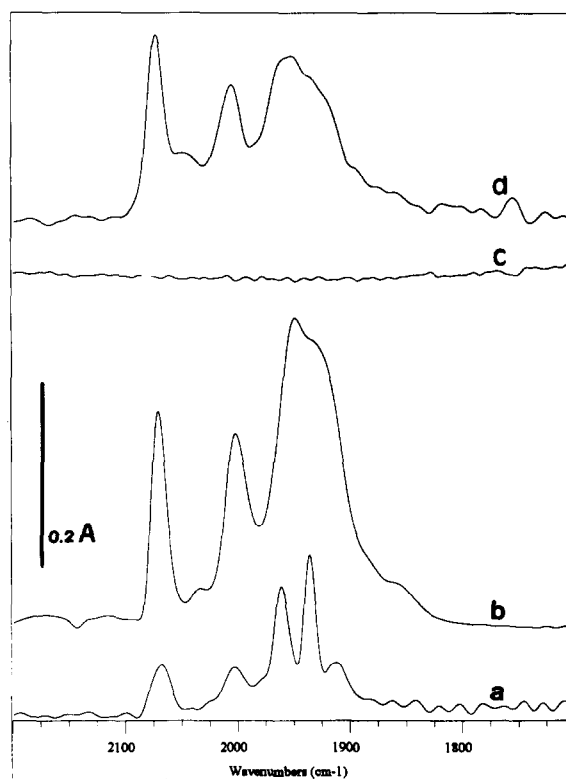


Fig. 4. Infrared spectra corresponding to the decarbonylation and recarbonylation of surface species. (a) Sample 1 after high vacuum treatment at 373 K for 16 h. (b) After spectrum (a), sample treated under 300 mbar of CO for 16 h at room temperature. (c) After spectrum (b), sample treated with 300 mbar of H_2 at 673 K for 16 h and evacuated at 473 K for 16 h. (d) After spectrum (c), sample treated with CO (300 mbar) at room temperature for 16 h.

Table 1
Vapor phase hydroformylation of ethylene on $\text{Co}_2(\text{CO})_8/\text{ZnO}$ catalysts^a

Catalyst precursor ^b	$\text{C}_2\text{H}_4:\text{CO}:\text{H}_2$ molar ratio	mol product/mol Co	Product selectivities (%)			CO conversion (%)
			$\text{C}_2\text{H}_5\text{CHO}$	$\text{C}_3\text{H}_7\text{OH}$	$(\text{C}_2\text{H}_5)_2\text{CO}$	
$\text{Co}_2(\text{CO})_8$	1:1:1	526	99.2	0.4	0.4	5.6
	2:1:1	165	96.6	0.9	2.5	5.0
$[\text{PPN}][\text{Co}(\text{CO})_4]$	1:1:1	0.5	51.0	49.0	–	$<10^{-2}$

^aReaction conditions: $P_{\text{total}} = 78$ bar, $T = 433$ K, Reaction time = 6 h.

^bMetal loading: Co 0.16 wt.%. Catalyst charge: 0.3–0.4 g.

3.4. Catalytic activity

Sample 1 was active in the hydroformylation of ethylene to propanal, at temperature higher than 393 K. The results of catalytic activity at different reaction conditions are shown in Table 1. It is worth mentioning that Sample 1 gave a high selectivity to propanal and no hydrogenation products were found.

For comparative purposes, Sample 2 was also tested in the hydroformylation of ethylene under the same reaction conditions, and a negligible catalytic activity for this reaction was found.

In Fig. 5 the IR spectra of Samples 1 and 2 exposed to air after catalytic reaction are shown.

4. Discussion

Cobalt carbonyl disproportionation by the action of Lewis bases in solution is a well established reaction [17,18]. In a previous study, by the Basset research group, a disproportionation of $\text{Co}_2(\text{CO})_8$ or $\text{Co}_4(\text{CO})_{12}$ when interacted with the MgO surface was established as the only reaction taking place, and the presence of $[\text{Co}(\text{CO})_4]^-$ anions in association with Mg^{2+} cations on the surface was evidenced [7]. On the other hand, the transformation of $\text{Co}_2(\text{CO})_8$ into $\text{Co}_4(\text{CO})_{12}$ has been established by the reaction of non-basic oxides, like SiO_2 , with $\text{Co}_2(\text{CO})_8$ [5].

The results obtained here indicate that the interaction of $\text{Co}_2(\text{CO})_8$ with the ZnO(200) surface produces both reactions:

- (i) A disproportionation reaction to yield $[\text{Co}(\text{CO})_4]^-$ and Co^{2+} on the support surface, shown by extraction of surface species and FTIR study.
- (ii) A transformation of $\text{Co}_2(\text{CO})_8$ into $\text{Co}_4(\text{CO})_{12}$, which does not react to an appreciable extent with the ZnO(200) surface under our experimental conditions.

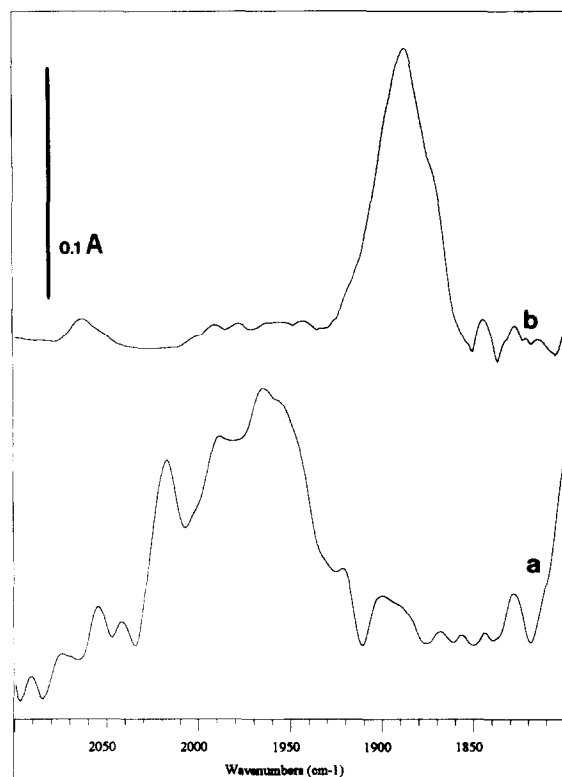


Fig. 5. Infrared spectra in the $\nu(\text{CO})$ region of the catalysts exposed to air. (a) Sample 1 (b) Sample 2.

Taking into account the population of the surface hydroxyl groups of ZnO(200) [19], the evolved CO referred to the final cobalt content on the sample indicates that only a small fraction of the surface OH groups have basicity enough to carry out the disproportionation of $\text{Co}_2(\text{CO})_8$.

After the reaction of $\text{Co}_2(\text{CO})_8$ with the ZnO surface, Sample 1 shows an IR spectrum that could reasonably be assigned to the surface species $[\text{Co}(\text{CO})_4]^-$, the symmetry of which has decreased from T_d to C_{2v} due to the interaction with the cations on the surface. As no low-frequency $\nu(\text{CO})$ bands were observed the interaction through a carbonyl ligand can be ruled out [20]. When impregnation of $[\text{PPN}][\text{Co}(\text{CO})_4]$ on ZnO was carried out the IR spectrum showed the presence of tetrahedral $[\text{Co}(\text{CO})_4]^-$ only slightly distorted. However, when the impregnation of $[\text{PPN}][\text{Co}(\text{CO})_4]$ was carried out in the presence of Co^{2+} ions, the surface species, besides a broad adsorption at 1889 cm^{-1} , showed a similar IR spectrum to that of Sample 1 (see Fig. 3b). Thus, the interaction of $[\text{Co}(\text{CO})_4]^-$ with Co^{2+} ions on the surface may be the responsible for this lowered symmetry, giving the infrared pattern of Sample 1, which shows all $\nu(\text{CO})$ bands at higher wavenumbers than that of unperturbed $[\text{Co}(\text{CO})_4]^-$. This may indicate the existence of a covalent interaction between Co^{2+} and $[\text{Co}(\text{CO})_4]^-$, electron density being donated to Co^{2+} by $[\text{Co}(\text{CO})_4]^-$ [18].

These surface species may be reduced to small particles of cobalt by hydrogen treatment at 673 K, and the IR spectra after a CO treatment (Fig. 4d) suggest that some of them reacted with CO to give $\text{Co}_2(\text{CO})_8$, which quickly disproportionates to $[\text{Co}(\text{CO})_4]^-$ and Co^{2+} .

It is reasonable to compare the formation of these surface species involving homonuclear ion-pairing species with similar ones in molecular chemistry. In fact, after addition of moderate amounts of pyridine to a $\text{Co}_2(\text{CO})_8$ solution the formation of $\text{Co}^{2+}/[\text{Co}(\text{CO})_4]^-$ homonuclear ion pairing species is produced [21].

On the other hand Sample 1, which gave good activity in the heterogeneous hydroformylation of

ethylene, showed on exposure to air after the reaction (Fig. 5a) an IR spectrum that resembles the pattern for the $[\text{Co}_3(\text{CO})_{10}]^-$ cluster. This anionic cluster had been found after reaction in solution of ion-pair activated $[\text{Co}(\text{CO})_4]^-$ with traces of oxygen [22].

Sample 2, prepared by impregnation of $\text{PPN}[\text{Co}(\text{CO})_4]$ on ZnO(200), that was not active in hydroformylation, showed, exposed to air after reaction, no other carbonyl species than tetrahedral $[\text{Co}(\text{CO})_4]^-$ (Fig. 5b). This is in good agreement with the finding in homogeneous phase that symmetrical $[\text{Co}(\text{CO})_4]^-$ with a PPN^+ counterion is inert towards substitution reactions, and reacts only slowly with air [22].

Our results suggest that the catalytic behaviour of Sample 1 is due to the existence of $[\text{Co}(\text{CO})_4]^-/\text{Co}^{2+}$ activated homonuclear ion-pairing species on the support surface.

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