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Interaction between FeRu Bimetallic Carbonyl Clusters and Oxide Supports. I. Mobility of CO Ligands

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Abstract

Molecular isotope exchange between ^{12}CO ligands in $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $FeRu(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$ supported on Al_2O_3 or on Cab-O-Sil and gaseous ^{13}CO molecules was utilized to study the surface processes that occur after impregnation. It was established that exchange is controlled by the nature of the oxide support and the structure of carbonyl clusters. Disintegration of the cluster framework may be the reason for the formation of CO ligands bonded with different bond strength to the subcarbonyl species on the surface; these CO ligands are characterized by the different rate of exchange. Although kinetic measurements correctly describe these processes, further experimentation is needed to elucidate their full mechanism.

Introduction

Interaction of a molecular transition metal carbonyl cluster with oxide supports is one of the most important processes controlling the preparation of a supported metal catalyst derived from the molecular carbonyl cluster [1]. This interaction can be characterized by the change in bond strength between metal atoms and the CO ligands in the cluster framework.

The initial state of this interaction has been thoroughly investigated. As a first step, the reaction between hydrated alumina or magnesia and the molecular cluster is considered, in which a homonuclear cluster such as $Fe_3(CO)_{12}$ [2], $Ru_3(CO)_{12}$ [3] or $Os_3(CO)_{12}$ [4] forms $[HM_3(CO)_{11}]^-Al^+$ anionic species. The bimetallic Ru–Os molecular cluster has been proved to form similar surface species. $H_2RuOs_3(CO)_{13}$ in hexane solution was brought into contact with Degussa γ-Al_2O_3C, and the formation of a similar complex of $Al^+[HRuOs_3(CO)_{13}]^-$ was identified by IR spectroscopy.

In addition to the IR evidence, these anions were recently prepared by extraction of a CH_2Cl_2 solution of bis-triphenyl phosphine imminium chloride [PPN^+Cl^-]. $H_2FeRu_3(CO)_{13}$ was brought into contact with MgO, and the surface complex was extracted by PPN^+Cl^- solution in the form of $[HFeRu_3(CO)_{13}]^-PPN^+$; the latter was characterized by its IR and NMR spectra [5].

On Cab-O-Sil, only the surface silanol OH groups are utilized in the reaction of metal carbonyl clusters. In this case, these OH groups are generally less reactive than they are on alumina or magnesia; thus in most cases the cluster framework is maintained [6]. After this initial formation stage, decomposition of the surface intermediates may result in the disintegration of the cluster framework, leading to monometallic subcarbonyl species as found for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ supported on alumina [6, 7]. This process may take place even at room temperature after a long contact time [6]. The extent of the disintegration of the molecular cluster is independent of the ambient atmosphere, but it does depend on the support and on the structure of the cluster [8]. The same process also proceeds on bimetallic molecular clusters. IR spectra of $Ru_3(CO)_{12}$, $Fe_2Ru(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$ supported on alumina showed a similar structure after overnight vacuum treatment, which is probably due to the surface process producing the same species [6].

Interaction can be easily monitored by CO evolution, *i.e.* the stronger the interaction, the more CO molecules evolved [6]. However, if the interaction is too strong, CO dissociation can easily take place, leading to carbon deposition which, in turn, can increase metal dispersion [9] of the supported metal catalyst.

Isotope exchange between gas phase CO molecules and the CO ligands in a supported cluster is another important method. Molecular isotope exchange (MIE) occurs when ^{12}CO ligands in the molecular carbonyl cluster or in the subcarbonyl species supported on an oxide surface are replaced by ^{13}CO molecules in the gas phase. This process contrasts with the traditional isotope exchange in which the reaction proceeds between the atoms of different molecules.

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If the metal–CO bonds in the cluster framework are equivalent, MIE can be described by a first order equation. Any deviation clearly indicates the existence of different types of metal–CO bonds, as was observed, for example, for partially decomposed supported rhodium carbonyls [10].

In preliminary experiments the initial rate of exchange between ^{13}CO in the gas phase and ^{12}CO in supported $Fe_3(CO)_{12}$ was measured. It was established that, in agreement with the CO evolution results, the rate of isotope exchange on alumina is higher than that on Cab-O-Sil due to the stronger interaction with Al_2O_3 [8, 11, 13]. It was also determined that the amount of CO dissociated after decomposition increased with increasing pretreatment temperature of alumina. In these experiments, however, no detailed information on the kinetics of MIE was presented. This may be indicative of the number of CO molecules being in different structures on the surface.

The main goal of this and the other papers planned for this series is to clarify the mechanism of the surface processes which are induced on the oxide surface after the initial interaction of molecular carbonyl clusters and oxide carriers. In this paper the nature of metal–CO bonds in a supported cluster will be studied by MIE between CO ligands of $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Fe_2Ru(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$ supported on Al_2O_3 and on Cab-O-Sil and gaseous ^{13}CO molecules immediately after impregnation. It is intended in subsequent articles to investigate the stability of the surface species by infrared spectroscopy on hydrated alumina support, to clarify the mechanism of this surface rearrangement, and to utilize IR spectroscopy to study the decomposition of bimetallic clusters on hydrated silica.

Experimental

Materials

Commercial $Fe_3(CO)_{12}$ (Strem Chemicals) and $Ru_3(CO)_{12}$ (ICN Pharmaceuticals) were used without further purification. The method given in [12] was used to produce $Fe_2Ru(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$. Alumina and silica were obtained from Degussa (Al_2O_3C) and the Cabot Corporation (Cab-O-Sil HS5), respectively. Labelled carbon monoxide containing 90% ^{13}CO and 10% ^{12}CO analysed mass-spectrometrically was purchased from the USSR. High-purity helium was used.

Apparatus and Method

The experimental set-up for exchange has been described elsewhere [12]. Normally, the oxide support (400 mg) was pretreated overnight in a vacuum at 570 K and then impregnated with a saturated hexane solution of a carbonyl cluster (20 ml) previously degassed by freezing-pumping cycles. The all-glass circulating system was connected to a mass spectrometer (AEI MS 10 C2) via a capillary leak by which the amount of CO initially evolved could be measured. The hexane was distilled back to the original vessel during the determination of CO. After evacuation of CO, ^{13}CO, 90% enriched at 15 mbar, was admitted to the supported cluster which had been placed in a 260 ml reaction vessel. For quantitative measurements, constant pressure must be maintained to ensure the continuous conductance via the capillary leak. For this reason the experimental apparatus was filled with helium up to a pressure of 93 mbar. The change in intensity of the signal of m/e 28 and 29 was monitored by the mass spectrometer, and, with appropriate calibration, the exchange process was calculated on the basis of partial pressure.

Results

Molecular isotope exchange between CO ligands in $Fe_3(CO)_{12}$, $Fe_2Ru(CO)_{12}$, $H_2FeRu_3(CO)_{13}$ and $Ru_3(CO)_{12}$ supported on alumina and on Cab-O-Sil and gaseous ^{13}CO in the temperature range 273 to 350 K has been studied. For most samples the initially high rate of exchange was followed by a very slow process at ambient temperature, and the isotope equilibrium calculated from the initial composition could not be achieved. A typical experimental result for the change in pressure of ^{13}CO and ^{12}CO for $H_2FeRu(CO)_{13}$ on Al_2O_3 measured at 298 K can be seen in Fig. 1.

During the exchange measurement (Fig. 1a) the total amount of CO in the gas phase (Σp) was constant, proving that the only process, as far as the CO ligands were concerned, was the exchange. The quasi-equilibrium state indicated in the Figure after 100

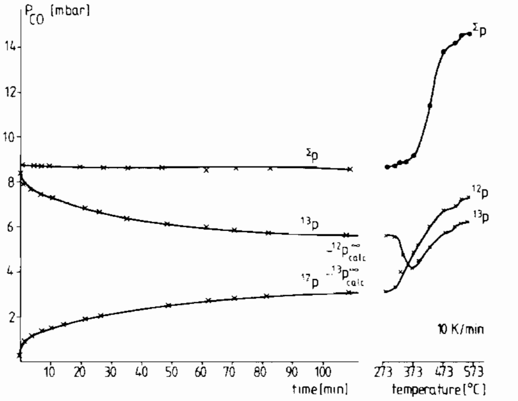


Fig. 1. Plot of ^{12}CO, ^{13}CO and the total CO pressure for $H_2FeRu_3(CO)_{13}$ on Al_2O_3 (a) *vs.* time at 298 K; (b) after equilibrium *vs.* temperature.

min reaction time can be demonstrated by measuring the exchange in the temperature-programmed mode (Fig. 1b). During the initial part of the temperature increase, the total pressure of CO is only slightly changed, but the onset of fast exchange indicates that some of the CO ligands in the supported cluster are strongly bonded to the metal framework; thus, a higher temperature is required for exchange. This clearly shows that the CO ligands are in different environments after being supported on an oxide carrier.

The exchange experiments suggest that at least two types of CO ligand existed on the surface. Since some of the CO cannot be removed in the form of CO due to the dissociation [9], the simple equation which is generally accepted for isotope exchange cannot be applied. Thus, the simplest model has to operate with three different types of CO ligands, distinguished by their rates of exchange, one of which is almost zero at room temeprature. When total CO pressure is constant during the exchange process (Fig. 1a), it is sufficient to follow, for example, the ^{12}CO appearance in the gas phase in accordance with the reaction

$$^{12}CO_{\text{cluster}} + {}^{13}CO_{\text{gas}} \rightleftharpoons {}^{12}CO_{\text{gas}} + {}^{13}CO_{\text{cluster}}$$

The solution of the somewhat complicated system of differential equations with two unknown functions ($^{12}G_1$ and $^{12}G_2$, because the third rate constant of exchange is taken to be zero) can be approached as a sum of two exponential expressions:

$$^{12}G = {}^{12}G_1^{\infty}(1 - e^{-K_1 t}) + {}^{12}G_2^{\infty}(1 - e^{-K_2 t}) \qquad (1)$$

where

$$^{12}G_i^{\infty} = \frac{1 - \dfrac{^{12}G^0}{G}}{1(G+1)\dfrac{x_i C}{n}} \qquad (2)$$

$$K_i = k_i\left(G + \frac{x_i C}{n}\right) \qquad (3)$$

G is the amount of CO in the gas phase (mol); C is the amount of CO in the supported carbonyl cluster (mol); superscripts 0 and ∞ refer to the initial and the equilibrium state, respectively; n is the number of CO ligands per mole of the supported carbonyl cluster (the number of CO ligands evolved during the impregnation has been substracted, *i.e.* $n < 12$ or $n < 13$); x_1 and x_2 are the number of CO molecules per mole of the supported cluster. The exchange is characterized by second order rate constants of k_1 and k_2, respectively, according to the rate equation

$$R_i = k_i G \frac{x_i C}{n}$$

where R_i is the exchange rate which is independent of the actual isotope ratio in the gas phase or in the carbonyl cluster. Equation 1 is valid under the conditions $k_1/k_2 \geqslant 5$, $G = \text{constant}$, $C = \text{constant}$, $^{13}G^0 \gg {}^{12}C^0$ and when no transport phenomenon exists.

For the calculations, the partial pressure of ^{12}CO was plotted against time and a least squares fitting was carried out on the data points according to eqn. 1, if one exponential curve of $^{12}G(1 - e^{-kt})$ did not give an acceptable fit. From the four parameters, $^{12}G_1$, $^{12}G_2$, K_1 and K_2, we calculated x_1, x_2, k_1 and k_2, respectively. (See eqns. 2 and 3). In most cases $^{12}G_1 + {}^{12}G_2 = {}^{12}G_{\text{exp}} \neq {}^{12}G_{\text{calc}}$ from eqn. 2, assuming that all the CO takes part in the process, *i.e.* $x = n$. Additional proof of the existence of strongly bonded CO ligands (numbering x') can be estimated by subtracting $x_1 + x_2$ from the total amount of CO in the supported molecule (n).

Despite the great number of approximations used in the model, Fig. 2 shows that the curve of the type given by eqn. 1 fits the data points well. The numbers of CO ligands (x_1, x_2) with a given metal–CO bond strength and characterized by the second order exchange rate constants (k_1, k_2) are summarized in Table I, where the number of CO ligands evolved (x_0) during impregnation (6) is also shown.

All experiments for isotope exchange were carried out immediately after impregnation. Even under these conditions, depending on the support (Al_2O_3 or Cab-O-Sil) and on the structure of the initial cluster, interaction developed to different extents. Consequently, instead of the expected uniformity of the CO bond strength to the cluster framework, CO molecules were transferred into different environments, indicated by the difference in the rate of exchange which seems to be characteristic of the cluster-support interaction. This process, however,

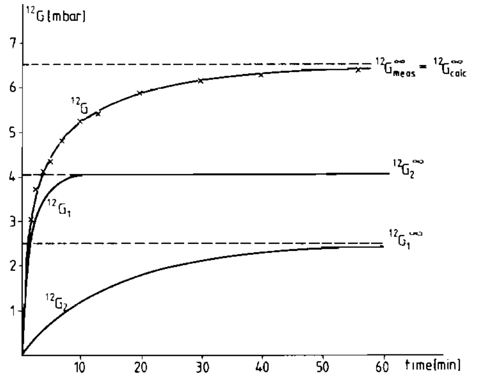


Fig. 2. Data points and fitted curves for the system of $Fe_2Ru(CO)_{12}$ on Al_2O_3 measured at 298 K. Parameters of eqn. 1 are: $^{12}G_1 = 4.08$ mbar, $^{12}G_2 = 2.45$ mbar, $K_1 = 0.54$ min^{-1} and $K_2 = 0.07$ min^{-1}. The corresponding values of x_1, x_2, k_1 and k_2 are given in Table I.

TABLE I. The Average Number of Different Metal–CO Bonds (Mol Carbonyl Cluster (x_i) Characterized by Second Order Rate Constants (k_i))

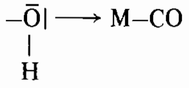
Exchange rate constants (25 °C)	$Fe_3(CO)_{12}$	$Fe_2RuCO)_{12}$		$H_2FeRu_3(CO)_{13}$		$Ru_3(CO)_{12}$
	Al_2O_3	Al_2O_3	SiO_2	Al_2O_3	SiO_2	Al_2O_3
k_1(l/mol s)[a]	120	40	0.3[c]	50	13	1[c]
k_2(l/mol s)[b]	13	5		1	0.4	
x_0(mol CO/mol cluster)[d]	1.0	1.2	0.5	0.1	0.05	0.5
x_1(mol CO/mol cluster)	1.0	6.5	8.3[c]	3.5	1.5	10.5[c]
x_2(mol CO/mol cluster)	9.5	3.5		4.5	11.5	
x' [e]	–	–	3.2	5.0	–	1.0
$F\%$ [f]	1.03	1.07	1.40	1.53	1.68	1.8

[a] ±20%, $k' = 0$ (see the text). [b] x_0 is the number of CO/mol carbonyl cluster stripped off during impregnation [6]. [c] One $^{12}G(1 - e^{-kt})$ expression was enough to describe the exchange. [d] ±1 mol CO/mol cluster. [e] The number of CO ligands most strongly bonded to the metal frame/mol carbonyl cluster. [f] $F = \sum_{j=1}^{1} {}^{12}G_j - {}^{12}G_j \Big/ \sum_{j=1}^{m} {}^{12}G_j$ where m is the number of data points, $^{12}G_j$ is the calculated pressure of ^{12}CO according to eqn. 1 at the j-th data point ($^{12}G_j$).

progresses in time, as shown by the lack of exchange at room temperature after remaining in a vacuum overnight.

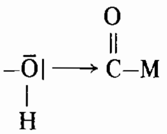
Discussion

Since O^{2-} and OH^- groups are present on the Al_2O_3 and the Cab-O-Sil surfaces during interaction between the oxide support and the molecular cluster, different types of surface reactions between OH^-, O^{2-} and the cluster framework should be considered. Of these, the most important are



$$\underset{\mathrm{H}}{\underset{|}{-\bar{\mathrm{O}}|}} \longrightarrow \mathrm{M{-}CO} \qquad \text{(I)}$$

$$-\mathrm{OH}\cdots\cdots\mathrm{O{-}C{-}M} \qquad \text{(II)}$$



$$\underset{\mathrm{H}}{\underset{|}{-\bar{\mathrm{O}}|}} \longrightarrow \overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}M} \qquad \text{(III)}$$

We have suggested [6] that CO evolution is acceptable as a measure of $\underset{\mathrm{H}}{\underset{|}{-\bar{\mathrm{O}}|}} \rightarrow \mathrm{M{-}CO}$ (I) type interaction. On the other hand, this kind of interaction surely has an effect on the exchange rate between the CO ligands in the supported cluster and ^{13}CO; presumably the stronger the interaction, the faster the exchange. Table I shows that for every carbonyl cluster supported on the stronger electron donor alumina, the rate constants are higher than for Cab-O-Sil-supported clusters, in agreement with the results of CO evolution [6].

Another factor which influences the interaction is the carbonyl cluster itself. Generally, higher exchange rates, *i.e.* stronger interaction, are experienced for clusters with higher iron content (see Table I). As a result of this stronger interaction, the metal cluster framework is easily decomposed, as indicated by the data obtained by Mössbauer spectroscopy [8, 11, 13]. The appearance of high spin Fe^{3+} and Fe^{2+} in the spectrum is a clear indication of the oxidation of the iron atoms.

The sequence of the decreasing exchange rate coincides with the order of interatomic CO scrambling in these carbonyl clusters:

$Fe_3 \sim Fe_2Ru > H_2FeRu_3 > Ru_3$

revealing the importance of intramolecular CO mobility in the exchange [14].

The effects of both the support and the structure of the molecular cluster on the isotope exchange are well supported by Mössbauer and infrared spectroscopy [11, 16]. Infrared data show that the structure of the cluster is completely changed on alumina, whereas on Cab-O-Sil the original structure is partly retained but the bands are broadened, thereby indicating weaker interaction. These effects are even more pronounced in the Mössbauer spectra. On Cab-O-Sil the $H_2FeRu_3(CO)_{13}$ retains its structure, but on the same support $Fe_3(CO)_{12}$ disintegrates. A similar observation was reported by Choplin *et al.* [5] for $H_2FeOs_3(CO)_{13}$ on a silica surface where the molecular cluster was first physisorbed at impregnation, as shown by IR and Raman spectroscopy. On the other hand, the same bimetallic cluster which proved stable on Cab-O-Sil is fully decomposed on Al_2O_3. These findings are in complete agreement with the data obtained from isotope exchange, and they lend credibility to the usefulness of this method.

We still need to find an explanation as to why the metal–CO bonds, which are equivalent in an unsupported cluster due to the scrambling [14], become different in the supported state even at room temperature. Although the data obtained by isotope exchange alone are not able to provide this explanation (a detailed discussion will be given in a subsequent paper), some speculations are in order, *viz.*

(i) There may be different types of metal–CO bonds in each supported cluster, but these are stabilized by the oxide carrier and scrambling is prevented.

(ii) Carbonyl clusters may be attached to different sites of the surface and, even though each molecule has uniform metal–CO bonds (because of the scrambling), several types of metal–CO bonds would be experienced.

(iii) The most plausible explanation is that a carbonyl cluster reacts with the surface groups producing metal subcarbonyls with different metal–CO bond strengths. Deviation from simple exchange certainly indicates that the CO ligand is in different environments.

The validity of the third assumption also seems to be supported by the experimental fact that the extent of the surface process increases over time. After overnight standing most of the clusters are found to be in a strongly bonded environment, indicated by the lack of exchange at room temperature when using an alumina support. Thus, one has to be careful about judging the interaction from isotope exchange alone, because the appearances of interactions that are too weak or too strong are very similar. Nevertheless, a very strong interaction leads to dissociation of CO ligands, which means that CO is not able to participate in the molecular CO exchange process, and appears as the CO retained by the support or metal on support [8, 9]. Isotope exchange experiments should, therefore, always be complemented by other techniques such as IR or Mössbauer spectroscopy or even by stability investigations using temperature-programmed spectroscopy [18] to gain information on the mechanism of this surface process.

Conclusions

There must be at least two (in some cases three) different types of metal–CO bonds in alumina- and Cab-O-Sil-supported $Fe_3(CO)_{12}$, $Fe_2Ru(CO)_{12}$, $H_2FeRu_3(CO)_{13}$ and $Ru_3(CO)_{12}$; *i.e.*, there is no uniformity in bond strength.

The amount of CO involved in molecular isotope exchange processes with different rates depends on the support. Normally, on Cab-O-Sil nearly all CO ligands have the same rate of exchange, whereas on Al_2O_3, due to the stronger interaction, not only is the rate of exchange higher, but a higher proportion of the impregnated cluster is transferred to surface species to which CO ligands are attached with different bond strength.

The rate constant for exchange is higher (and interaction is stronger) for supported carbonyl clusters having originally more mobile CO ligands (*i.e.* clusters with higher Fe content).

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