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SUPPORTED TETRANUCLEAR CARBONYL CLUSTERS: 1. FRAMEWORK DISTORTION AND CATALYTIC ACTIVITY IN HYDROFORMYLATION *

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In comparison with the structural data determined by EXAFS, the catalytic activities of supported clusters $Co_4(CO)_{10}$ $(PPh)_2/SiO_2$ and $PhCH_2(CH_3)_3NFeCO_3(CO)_{12}$/polystyrene have been investigated. Consistent increase (or decrease) between Co-Co bond distance and catalytic activity in hydroformylation suggests that the cleavage of the metal-metal bond is the first step towards the formation of the catalyst center and the cluster framework distortion is beneficial to the catalyst in raising the catalytic activity in hydroformylation.

1. Introduction

The cleavage and reformation of metal-metal bonds are usually related to the metal cluster catalytic activity [1]. A transition metal carbonyl cluster as catalytic precursor added to the reaction has shown various features. Many studies have demonstrated that the cluster fragment to the mononuclear complex was the active catalyst in the reaction. Some workers have, however, clearly demonstrated that it is the metal cluster and not the mononuclear fragment which catalyzes the reaction, such as $Co_4(CO)_{10}(PPh)_2$ in 1-pentene hydroformylation [2]. The questions that arise from these results are (i) whether the metal-metal bond cleavage is the first step to the formation of the active site, and (ii) whether the evidence of bond cleavage can sufficiently confirm that the active catalyst must be the fragment. However, the bond opening and closing in homogeneous reactions are experimentally difficult to observe. The bound clusters may have distinct properties unlike those of free clusters [4].

The cobalt cluster chemically bonded to silica, Co_4/SiO_2 $[Co_4(\mu_2\text{-}CO)_2(CO)_8(PPh)_2/SiO_2]$ was first investigated by Y. Wang and his co-workers [3]. The results showed that the supported cluster Co_4/SiO_2 presented higher catalytic activity in hydroformylation than the unsupported pure cluster. However, when $FeCo_3(CO)_{12}^-$, a heteronuclear cluster with relatively higher activity, was supported, the catalytic activity in hydroformylation obviously decreased [7].

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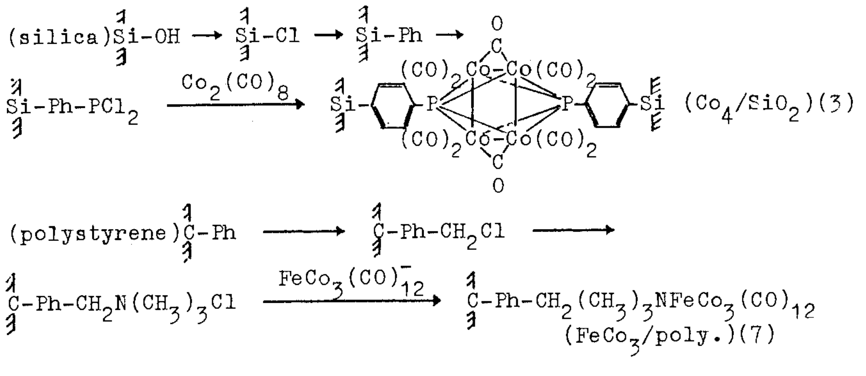
We describe herein the structural characterization of Co_4/SiO_2 and $FeCo_3$/poly. $[PhCH_2(CH_3)_3NFeCo_3(CO)_{12}$/polystyrene 1 determined by in-house EXAFS analysis, and explain the changes of these immobilized clusters in catalytic activities through the cluster framework distortion.

2. Experiments

X-ray absorption spectra were taken at the Institute of Physics, Academia Sinica, Beijing, with a double detector EXAFS spectrometer using a 60 kW rotating anode X-ray generator (Rigaku-1000). The typical available photon flux near the K-edge of cobalt was about 3×10^4 photons/s through a 20×1 mm area. Each point was recorded in 20 seconds. Computational work was done on an IBM PC/AT computer with the Program Library for EXAFS Data Processing written and published by the Institute of Physics, Academia Sinica.

Pure clusters were prepared in our laboratory following the literature [5,6]. The immobilizations completed through chemical bonding were described as follows:



Infrared spectra were obtained on a Specord 75 IR double beam spectrophotometer with a resolution of 2 cm^{-1}. Longer scan time was used when a better resolution or signal/noise ratio was required.

3. Results and discussion

3.1. FOURIER TRANSFORM FEATURE

Almost all of the Fourier transforms of transition metal carbonyl clusters show the same permanent spectral features: the strongest peak appearing near 2 Å can be assigned to the strong backscattering between metal atoms, preference of which with a middle strength is to the terminal carbon atoms and/or bridging

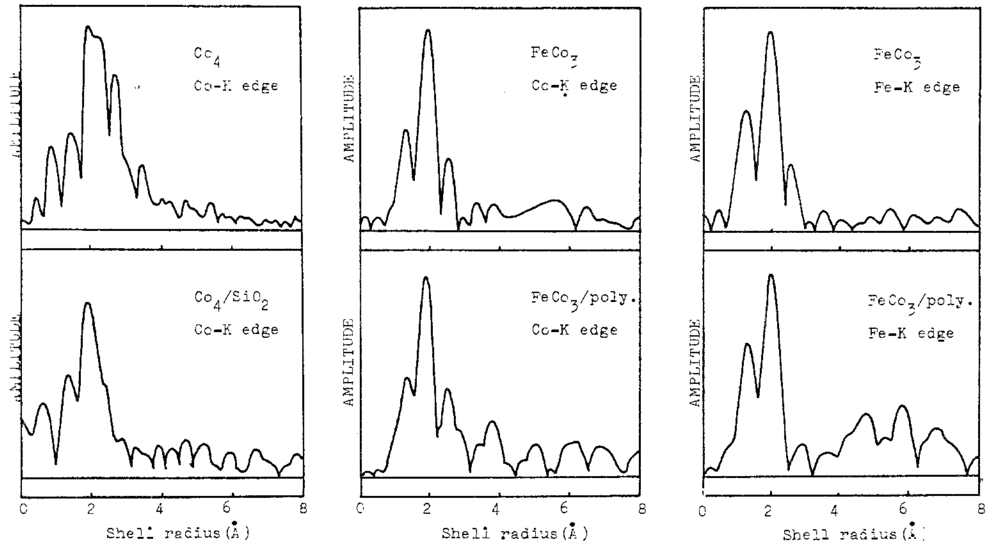


Fig. 1. Fourier transforms of pure and supported carbonyl clusters. Transform range: 4–12 $Å^{-1}$, k^1 scaling for Co_4 and Co_4/SiO_2, k^2 for rest.

carbons, followed by a usually sharp peak with an uncertain strength assigned to the oxygen backscattering due to colinear atomic arrays [8].

It was found that the features remained through immobilization by chemical bonding, shown in fig. 1, with slight differences from the pure clusters merely in the position of each peak. For the pure cluster $FeCo_3$, as an example, the cobalt backscattering appeared at 1.97 Å (peak value in transform, similarly hereinafter) with iron as the central atom. In the case of cobalt as the central atom, the peak of cobalt and iron backscattering appeared at 1.97 Å also. For the immobilized clusters Co_4/SiO_2 and $FeCo_3$/poly., however, both peaks appeared at 1.94 Å.

A unique feature of the heteronuclear cluster is the breakage of the original cluster framework, which, if taking place, is made known by a couple of the peaks. For example, the $FeCo_3$ to $FeCo_2$ can still give a certain peak at the Fe-K edge, but at the Co-K edge, as a result of the difference between Co-Co and Co-Fe bond lengths, the iron and cobalt backscatterings, each of which were assumed to follow the Gauss distribution will be separated more obviously than before.

For a mononuclear cluster, at least in principle, one can also find the similarly distinct feature of backscattering to determine the change of the framework. For instance, Co_4 and $Co_3(CO)_9PR$ almost have the same coordination environment. The Co_4 to Co_3, however, would lead to the disappearance of diagonal cobalt backscattering at 3.4 Å in Fourier transform. It should be noticed that the distortion along the diagonal of Co_4 framework can lead to the same phenomenon since the carbonyl stretching vibration of Co_4/SiO_2 (2008, 1980, 1850 cm^{-1}) has confirmed the existence of carbonyl cluster Co_4. Therefore, it can be concluded that the chemical bonding method can effectively keep the designed cluster framework on the support surface after immobilization.

Another interesting point arising from the Fourier transform of $FeCo_3$/poly. at the Fe-K edge is the disappearance of oxygen backscattering which exists at 2.7 Å in pure cluster. A reasonable explanation is that the curved Fe-C-O angle favours the achievement of a good spatial arrangement.

3.2. DATA ANALYSIS

Details of the parameters obtained from the curve fitting the experimental EXAFS spectra with the Herman-Skillman wave function and a comparison with those from X-ray diffraction are given in table 1. The experimental and theoretical scattering curves for the second shell of Co_4/SiO_2 and $FeCo_3$/poly. are shown in fig. 2. The parameters confirm the cluster frameworks of Co_4 on silica and $FeCo_3$ on polystyrene and show that almost all of the coordination numbers are similar to pure clusters except that of bridging carbonyl in Co_4/SiO_2, which was double. Perhaps the latter can be considered to be the formation of $Co_4(\mu_2\text{-}CO)_4(CO)_8(PPh)_2$ on the silica surface, however, further research is needed to study this unexpected result.

The Debye-Waller factors for each atom in supported samples were closer than those of pure samples, 0.0026 to 0.0030 for the terminal carbon atom, 0.0009 to 0.0030 for the bridging carbon and 0.0010 to 0.0014 for cobalt. An exception was anticipated only for the iron atom from 0.0013 to 0.0099 through immobilization.

The changes of bond distances are summarized in table 2. The results indicate that for Co_4/SiO_2, the Co-Co bond increased 0.01 Å and both the bonds between cobalt and the terminal carbon and the cobalt and the bridging carbon decreased 0.04 Å. Since the quantity of EXAFS only gives an average distance [9], the reduced Co-C_b (bridging carbon) bond suggests that the Co-Co bond linked by the bridging carbonyl must be shorter than average and the Co-Co bond unlinked by the bridging carbonyl must be longer. Referring to the basal cobalts in

Table 1
EXAFS spectroscopically derived bond distances (BD, Å) and coordination numbers (CN) for pure and supported clusters with mean X-ray diffraction values [5] in parentheses.

	Co-C_t		Co-C_b		Co-Co		Co-Fe	
	BD	CN	BD	CN	BD	CN	BD	CN
$Co_4(CO)_{10}(PPh)_2$	1.88 (1.800)	2.0	2.08 (1.944)	1.0	2.55 (2.608)	2.0		
Co_4/SiO_2	1.84	1.91	2.04	2.50	2.56	1.54		
$FeCo_3(CO)_{12}^-$	1.72	2.0	2.13	2.0	2.49	2.0	2.59	1.0
$FeCo_3$/poly.	1.75	2.07	2.09	1.93	2.44	1.99	2.67	1.02

Abbreviations: C_t for terminal carbon, C_b for bridging carbon.

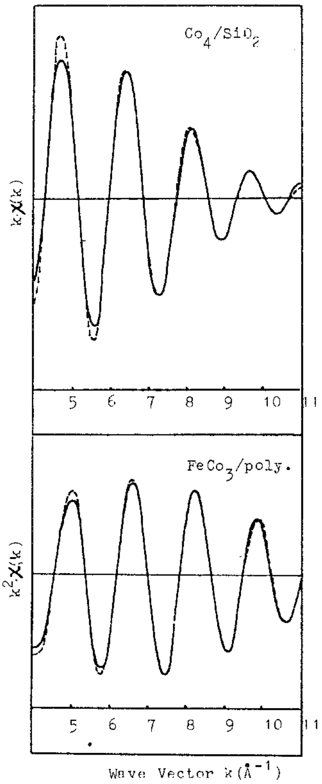


Fig. 2. Second-shell fits for structure determination. The solid lines are theoretical fits, and the dashed lines are filtered experimental EXAFS.

$FeCo_3$/poly., the reasonable data is a decrease of 0.05 Å for the bridging carbonyl linked Co-Co bond and an increase of 0.06 Å for the unlinked one.

The tendency of $FeCo_3$/poly. was contrary to that of Co_4/SiO_2. Namely, the Co-Co bond was shorter and the Co-C_t (terminal carbon) was longer than those in pure cluster. If the increase of Co-C_t bond length were known to be advantageous to CO insertion and migration, the catalytic activity of $FeCo_3$/poly. would be beneficial and the activity of Co_4/SiO_2 would go down through immobiliza-

Table 2

The major changes of bond distances of tetranuclear clusters throughout immobilization (compared with pure clusters)

Samples	Changed value of bond distances (Å)			
	Co-C_t	Co-C_b	Co-Co	Co-Fe
$Co_4(CO)_{10}(PPh)_2/SiO_2$	−0.04	−0.04	+0.01	
$FeCo_3(CO)_{12}^{-1}$/poly.	+0.03	−0.04	−0.05	+0.08

Abbreviations: C_t for terminal carbon, C_b for bridging carbon.

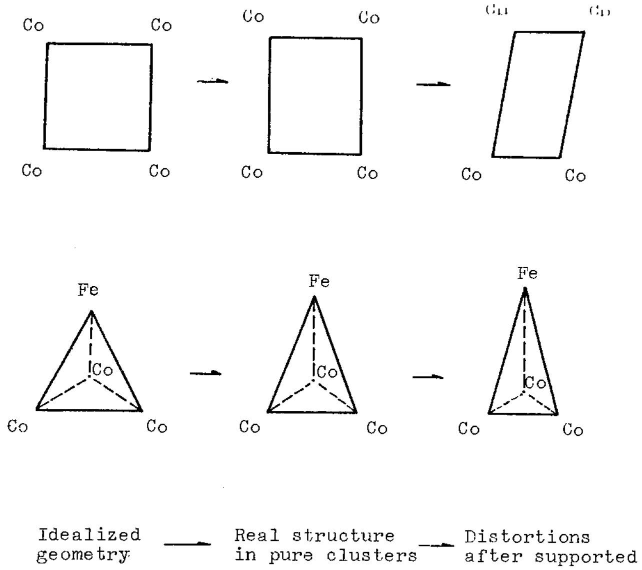


Fig. 3. Illustrative framework distortions of tetranuclear clusters (the ligands have been omitted for clarity).

tion. Therefore, the decreased activity of $FeCo_3$/poly. and the increased activity of Co_4/SiO_2, consistent with the changes in the Co-Co bond, is direct experimental evidence to demonstrate that, at least for the cobalt clusters, the cleavage of the metal-metal bond is the first step of the sequence to form a catalyst center.

The changes of the metal-metal bond distances in both clusters, i.e. the framework distortion, of course depend on the steric requirement of immobilizations, but also show the effect of symmetry from the cluster cores. The structural data suggests that the highly symmetrical framework of a tetrahedron is so stable that $FeCo_3$/poly. has to distort along the threefold symmetrical axis to reduce the immobilization effect. In this case, the basalt cobalts still kept in idealized geometry but turn closer to each other than before, as illustrated in fig. 3. However, because of low symmetry, the rectangle framework of Co_4/SiO_2 can "freely" distort to adapt to two fixed phosphine ligands, also shown in fig. 3. The IR result which shows the strength of the bridging carbonyl stretching vibration in Co_4/SiO_2 increases 1.4 times as much as in pure cluster [10] also indicates that the framework tends to asymetry.

4. Conclusion

It can be concluded that in order to achieve high catalytic activity in hydroformylation, from the viewpoint of symmetry, it is necessary to make the framework of the cobalt clusters deviate from idealized geometry so that the metal-metal bond can be much more easily broken down under reaction conditions.

Note added

Based on the above discussion, Prof. Hongxiang Fu and his colleagues have recently prepared several other supported carbonyl clusters, namely, fixing one of the cobalt atoms in $Co_4(CO)_{10}(PPh)_2$ or in $R_4NFeCo_3(CO)_{12}$ through chemical bonding. The results from these catalysts in hydroformylation have however shown the poor stability. The problem is that the chemical bonding effects the distortion of cluster framework so strongly that the catalysts cannot be kept for a longer time, and the precursor under the reaction cannot be recovered after one cycle. Therefore, finding a "soft" method to distort the cluster framework has to be considered in further research.

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