Nature of the metal–support interface in supported metal catalysts: results from X-ray absorption spectroscopy

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X-ray absorption spectra characterizing the metal–support interface in supported metal complexes and supported metal catalysts are summarized and evaluated. Single-metal-atom transition metal complexes on non-reducible metal oxide supports are bonded with metal–oxygen bonds with metal–oxygen distances of approximately 2.15 Å; the bonding distance is only weakly sensitive to the oxidation state of the metal. Nearly this same metal–oxygen distance is characteristic of the metal–support interface in metal-oxide-supported metal clusters following high temperature reduction in H_2 (HTR: $T > 450°C$). The metals at the interface may be polarized sufficiently that they bond with the oxygen of the support much as the cations in mononuclear complexes bond with it. When the supported metals are treated in H_2 at low temperatures (LTR: $T < 350°C$) or are prepared under He with partially hydroxylated supports, a longer metal–support oxygen distance is observed, typically 2.5–2.7 Å. This distance is suggested to characterize interactions between zero-valent metals and support oxygen. Changes in the performance of supported metal catalysts resulting from differences in the temperature of pretreatment in H_2 are attributed to changes in the electronic properties and/or morphology of the metal clusters, which are suggested to be related to the concomitant changes in the structure of the metal–support interface.

Keywords: Nature metal–support interface; hydrogen pretreatment; EXAFS

1. Introduction

Extensive research has been done to characterize metal–support interactions in catalysis by supported metal clusters and particles [1,2]. Only in the preceding

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few years, however, has quantitative information about the nature and structure of the metal–support interface begun to appear. The information has been obtained by X-ray absorption spectroscopy of metal clusters on metal oxide and zeolite supports. X-ray absorption spectroscopy is particularly successful with these materials because the supported metal clusters are so small (in our usage, having less than about 10 atoms) that a large fraction of the metal atoms are in contact with the support and a significant part of the X-ray absorption spectrum is determined by the contribution of the metal–support interface. Because the spectra determine average structural data, the most reliable characterizations are obtained with supported metals that have nearly uniform structures.

Our goals here are to summarize key results characterizing the metal–support interface by X-ray absorption spectroscopy and to state some implications for catalysis and raise questions that may indicate research opportunities.

2. Structural data from X-ray absorption spectroscopy (EXAFS)

2.1. MONONUCLEAR TRANSITION METAL COMPLEXES ON METAL OXIDES

Quantitative characterizations of metal–support interfaces by extended X-ray absorption fine structure (EXAFS) spectroscopy have been reported for mononuclear (single-metal-atom) complexes on metal oxide supports [3]. Table 1 is a summary of average metal–support oxygen distances in metal subcarbonyls; the metals, present as cations (typically with a formal charge of +1) are Ru, Rh, Re, and Os, and the supports are SiO_2, γ-Al_2O_3, and MgO. The distance between the metal ion and the oxygen of the support is typically in the range 2.1–2.2 Å. EXAFS data characterizing rhenium subcarbonyls on MgO indicate that the Re–O distance is virtually the same for an almost fully hydroxylated support as for a largely dehydroxylated support; evidently, the O^{2-} and OH^- ligands of the support surface bond to the metal at essentially the same distance [9].

Table 1
Metal–support oxygen distances determined by EXAFS spectroscopy

Metal	Support	Proposed surface structure [a]	Average metal–support oxygen distance (Å)	Ref.
$Ru_3(CO)_{12}$	γ-Al_2O_3	$Ru(CO)_2\{OAl\}_2$	2.17	[4]
$Ru_3(CO)_{12}$	SiO_2	$Ru(CO)_2\{OSi\}_n$	2.08	[5]
$RhCl_3$	γ-Al_2O_3	$Rh(CO)_2\{OAl\}_3$	2.12	[6]
$Rh_4(CO)_{12}$	γ-Al_2O_3	$Ru(CO)_2\{OAl\}_3$	2.04	[5]
$H_3Re_3(CO)_{12}$	MgO	$Re(CO)_3\{OMg\}\{HOMg\}_2$	2.15	[7]
$HRe(CO)_5$	MgO	$Re(CO)_3\{OMg\}\{HOMg\}$	2.13	[3]
$Os_3(CO)_{12}$	γ-Al_2O_3	$Os(CO)_{2-3}\{OAl\}_3$	2.17	[8]

[a] The braces refer to groups terminating the metal oxide support.

Table 2
Metal–support oxygen distances in supported metal catalysts determined by EXAFS spectroscopy

Metal	Support	Precursor	Pretreatment	Metal–oxygen distance [a] (Å)		Ref.
Pd	X zeolite	$(NH_3)_4PdCl_2$	O_2, 350°C; H_2, 150°C	2.28	2.80	[11]
Pt	Y zeolite	$(NH_3)_4PtCl_2$	O_2, 360°C; H_2, 360°C	ND	2.65	[12]
			O_2, 550°C; H_2, 550°C	ND	2.65	
Pt	BaKL zeolite	$(NH_3)_4Pt(NO_3)_2$	H_2, 450°C	2.14	2.71	[13]
Pt	γ-Al_2O_3	$(NH_3)_4Pt(OH)_2$	O_2, 400°C; H_2, 400°C	2.05 [b]	2.65	[14]
Pt	KL	$(NH_3)_4Pt(NO_3)_2$	H_2, 300°C	ND	2.72	[15]
Rh	γ-Al_2O_3	$RhCl_3$	H_2, 300°C	ND	2.74	[16]
Rh	γ-Al_2O_3	$Rh(NO_3)_3$	O_2, 350°C; H_2, 200°C	2.05 [b]	2.68	[17]
			O_2, 350°C; H_2, 400°C	ND	2.68	
Rh	TiO_2	$Rh(NO_3)_3$	O_2, 350°C; H_2, 200°C	2.08 [b]	2.78	[18]
			O_2, 350°C; H_2, 450°C	ND	2.61	
Ir	γ-Al_2O_3	$IrCl_3$	H_2, 350°C	2.16	2.55	[19]
			vacuum, 350°C	2.19	ND	[20]
Ir	γ-Al_2O_3	$Ir_4(CO)_{12}$	vacuum, 200°C; H_2, 350°C	–	2.58	[21]
Os	MgO	H_2OsCl_6	He, 300°C; H_2, 300°C	2.09	2.63	[22]
Re	MgO	$[H_2Re_3(CO)_{12}]$	H_2, 500°C	2.06 [b]	2.60	[7]

[a] ND none detected.
[b] Sample not fully reduced.

X-ray diffraction crystallographic data characterizing numerous transition metal complexes with various oxygen-containing ligands show that this metal–oxygen distance is generally characteristic of compounds of transition metals that lie to the right of Mo and W in the periodic table [3]. Compounds such as polyoxometallates (Keggin ions, which are metal oxide clusters) with metal subcarbonyls bonded at their surfaces are characterized by essentially this same metal–oxygen distance [10]. The polyoxometallates seem to be precise models of the metal–support interface when the metals in the bound complexes are cationic and the complexes are mononuclear [3].

2.2. HIGHLY DISPERSED TRANSITION METALS ON METAL OXIDE SUPPORTS

EXAFS spectroscopy has been used to characterize the metal–support interface in highly dispersed supported metals (table 2). The metals are Ni, Rh, Pd, Re, Os, Ir, and Pt, and the supports are SiO_2, γ-Al_2O_3, TiO_2, MgO, and L and X zeolites. The following pattern has been observed: When the EXAFS data were collected with samples in the presence of H_2 after reduction at relatively low temperatures (< 350°C, designated as LTR, low-temperature reduction), metal–support oxygen distances of 2.5–2.7 Å were generally observed. The shorter metal–support oxygen distances (about 2.15 Å) mentioned above were also generally observed. The relative intensities of the EXAFS signals indicating these two different distances depend on the type of support and the metal.

Table 3
Metal–support oxygen distances in supported Pt catalysts after high-temperature reduction

Support	Precursor	Treatment	Metal–oxygen distance (Å)	Ref.
γ-Al_2O_3	H_2PtCl_6	H_2, 480°C	2.07 [a]	24
SiO_2	H_2PtCl_6	H_2, 500°C	1.91 [a]	25
KL	$(NH_3)_4Pt(NO_3)_2$	H_2, 600°C	2.24	15

[a] Samples may not have been fully reduced.

(Metal–oxygen distances less than about 2.05 Å are indicative of oxidic structures present in less than fully reduced catalysts, including some listed in table 2 that were calcined before treatment in H_2.)

An example of a catalyst characterized by both the long and shorter metal–support oxygen distances is Ir/γ-Al_2O_3 after treatment in H_2 at 350°C; the metal–support oxygen distances are 2.16 and 2.55 Å, with the EXAFS signal for the former being very low in intensity [19]. However, after this sample had been evacuated, the longer metal–oxygen distance was no longer detectable; only a short metal–support oxygen distance (2.19 Å) was observed [20]. It was suggested [20] that the nearly hemispherical metal particles formed as a result of reduction of the sample in H_2 and that these were transformed upon evacuation into raft-like structures that wetted the support surface as a result of a stronger interaction with it. When O_2 was admitted to this evacuated sample at liquid nitrogen temperature, there was an increase in the intensity of the EXAFS contribution corresponding to this shorter distance [20].

The longer metal–support oxygen distance is also characteristic of some samples that had not been treated in H_2 at relatively low temperatures. These samples were synthesized from Pt precursors on partially hydroxylated MgO [23].

Pt supported in KL zeolite that had been fully reduced in H_2 at high temperature (a HTR catalyst) is characterized by a metal–support oxygen distance of 2.24 Å (table 3). Even shorter metal–oxygen distances than about 2.1 Å have also been observed (table 3). We speculate that these are indications of oxidic species in less than fully reduced samples, possibly those that had been brought in contact with trace amounts of O_2 during the EXAFS experiments. Longer metal–support oxygen distances were not observed in the HTR catalysts (table 3). The reduction temperature required to cause removal of the longer metal–support oxygen distance depends on the metal and the support.

3. Implications of the structure data

Many supported metal clusters and particles are characterized by a metal–support oxygen distance in the range 2.1–2.2 Å. This metal–oxygen distance, observed for supported metal clusters and particles after they have been treated in H_2 at high temperature, or after they have been evacuated following low-temperature reduction, is indistinguishable from the metal–oxygen distances observed for the monocular metal complexes mentioned above. This comparison suggests that the metals in clusters at the metal–metal oxide interface may be sufficiently polarized to bear slight but significant positive charges and to bond to the oxygen of the support, helping to anchor the metal clusters and stabilize their dispersion. This polarization and bonding might be especially pronounced for metals in raft-like structures.

The crystallographic data [3] characterizing transition metal complexes with oxygen-containing ligands suggest that in complexes with the metals in low positive oxidation states the metal–oxygen distance is only weakly sensitive to the metal oxidation state [3,9]. It is thus tempting to suggest that the metal–oxygen distance of about 2.15 Å pertains with some generality to transition metals that (1) are in low, positive oxidation states, (2) are relatively noble and not strongly oxyphilic (i.e. are to the right of Mo and W in the periodic table), and (3) are present on nonreducible metal oxide supports [3].

The EXAFS results show that the metal–oxygen distance of 2.5–2.7 Å is observed when hydrogen is chemisorbed on the metal and/or when the metal oxide surface is sufficiently hydroxylated. Perhaps hydrogen reduces the charge on the metal sufficiently to increase the distance characteristic of the interaction with the support oxygen. Thus, the metal–support oxygen distance in these samples may be characteristic of pure metallic species in direct contact with the metal oxide support. For example, the radius of Pt^0 is approximately 1.4 Å and that of O^{2-} is approximately 1.3 Å; the sum of these is nearly the observed longer metal–oxygen distance.

It is also possible that hydrogen is present at the interface between the metal and oxygen atoms, thereby increasing the metal–oxygen distance. There are several limiting cases for the nature of hydrogen at the metal–oxygen interface: (1) it may be present essentially as protons in hydroxyl groups that interact with metal atoms; (2) it may be adsorbed on the metal as hydride ligands, as in metal hydride complexes; and (3) it may be adsorbed in the interface as a neutral atomic species, resembling hydrogen on the surface of a metal.

The nature of the postulated interfacial hydrogen remains to be determined, but we speculate that the limiting cases are too simplified and the hydrogen interacting with both the metal and the oxygen at the interface has an intermediate character; theory may help to elucidate its nature.

4. Implications for catalysis

The degree of reduction of the metal atoms at the interface or hydrogen that is postulated to exist at the metal–support interface may influence the electronic properties of metal clusters and thus their reactivity for adsorption of hydrocarbons and other reactants and their catalytic properties. The cluster morphology may also depend on the degree of reduction and the presence of hydrogen, and hydrogen present at the metal–metal oxide interface may have a different reactivity from that present elsewhere, thus influencing the catalytic properties.

Consistent with these hypotheses, there is a mass of experimental evidence indicating that the conditions of pretreatment of supported metals with H_2 influence the catalytic activity for reactions of H_2. Examples of catalytic results that show the influence of the H_2 pretreatment are the following: den Otter and Dautzenberg [26] and Menon and Froment [27] reported large decreases in the hydrogenolysis activity of a $Pt/\gamma\text{-}Al_2O_3$ catalyst as the temperature of reduction was increased to temperatures higher than 500°C. Margitfalvi et al. [28] observed that high-temperature treatment of $Pt/\gamma\text{-}Al_2O_3$ in H_2 resulted in a significant change in the selectivity for hydrocarbon aromatization relative to that observed after lower-temperature pretreatment. Kramer and Fischbacher [29] showed the effects of H_2 pretreatment temperature on the methylcyclopentane hydrogenolysis activity of Pt catalysts with various dispersions prepared by deposition on amorphous silica and alumina films; pretreatment in H_2 at 400°C led to a lower activity and a lower selectivity for *n*-hexane formation than reduction at 275°C.

We infer from the results stated above that these changes in catalytic performance resulting from changes in the conditions of pretreatment in H_2 may be related to concomitant changes in the nature and structure of the metal–support interface. The nature of the interaction of the metal clusters with the support is expected to influence both the electronic properties and the morphology of the clusters and thus their catalytic properties. We recommend investigations of the relationships between the structure of the metal–support interface (including the amount and nature of the interfacial hydrogen), the electronic properties and morphology of the metal clusters, and the catalytic properties of supported metals. Experiments might be done with EXAFS spectroscopy, temperature programmed reduction and desorption, and infrared spectroscopy in combination with chemisorption and catalytic activity measurements. Understanding of these effects may also be expected to help clarify the issues of structure sensitivity in catalysis by supported metals.

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