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Infrared spectroscopy of supported metal oxide catalysts

Israel E. Wachs

Zettlemoyer Center for Surface Studies and Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015, USA

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Abstract

In situ infrared spectroscopy can provide much fundamental information about the nature of the surface metal oxide species present in supported metal oxide catalysts. The molecular structure of the surface metal oxide species can be obtained from M=O vibrations (number of different species and the number of terminal M=O bonds present in each species). The location of the surface metal oxide species on the oxide supports can be determined by directly monitoring the specific surface hydroxyls of the support being titrated by the surface metal oxide species. The surface coverage of the surface metal oxide species on the oxide supports can only be qualitatively determined by monitoring the surface hydroxyl region and the chemisorption of CO_2 because these measurements vary nonlinearly with surface metal oxide coverage. The nature of surface Lewis and Brönsted acid sites present in supported metal oxide catalysts is readily determined by adsorbing basic probe molecules such as pyridine. Only surface Lewis acid sites are present at low surface coverages and both surface Lewis and Brönsted acid sites can be present at high surface coverages. The appearance of Brönsted acid sites is related to the surface density of the surface metal oxide species. Specific examples are presented for supported rhenium oxide catalysts.

Keywords: Infrared spectroscopy; Location and surface coverage; Molecular structure; Supported metal oxide catalysts; Surface acidity

1. Introduction

Supported metal oxide catalysts find wide application in the petroleum, chemical and pollution control industries [1]. Such catalysts consist of an active metal oxide component (oxides of Re, Cr, Mo, W, V, Nb, etc.) deposited on the surface of a high surface area oxide support (alumina, silica, titania, zirconia, etc.). The deposited metal oxide component may exist as a two-dimensional surface metal oxide overlayer (surface metal oxide species), as a compound with the oxide support (e.g. $Al_2(MoO_4)_3$, $AlVO_4$, etc.) or as a separate crystalline metal oxide phase (e.g. MoO_3, V_2O_5, etc.). Typically, the surface metal oxide species is the active component for many catalytic applications. Infrared spectroscopy has been one of the unique characterization techniques that has provided fundamental information about the surface properties of supported metal oxide catalysts: molecular structure of the surface metal oxide species, location of the surface metal oxide species, surface coverage of the metal oxide overlayer, surface Lewis and Brönsted acid sites, and surface hydroxyl chemistry. The present paper will review the types of information usually reported in the literature for supported metal oxide catalysts from infrared spectroscopic characterization studies. The examples shown will be taken from the author's publications in this area.

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2. Experimental

The supported metal oxide catalysts reported in this paper were synthesized by the incipient-wetness impregnation method [1] and typically calcined at 450–500°C. The oxide supports employed in these studies consisted of: Al_2O_3 (Harshaw, 180 $m^2 g^{-1}$), SiO_2 (Cab-O-Sil, 300 $m^2 g^{-1}$), TiO_2 (Degussa P-25, 55 $m^2 g^{-1}$) and ZrO_2 (Degussa, 39 $m^2 g^{-1}$). The samples were pressed into very thin self-supporting wafers for the in situ IR studies. Several different FT-IR instruments were used for the various measurements and the original articles should be consulted for additional experimental details (references provided below).

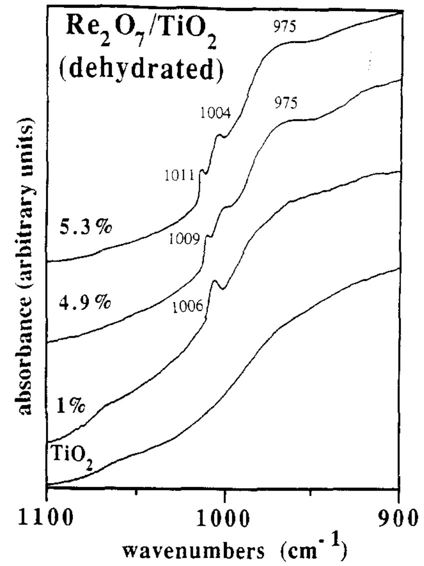

Fig. 1. In situ IR spectra of Re_2O_7/TiO_2 as a function of rhenium oxide coverage on titania. Reproduced from J. Mol. Catal., 76 (1992) 263.

3. Results and discussion

3.1. Molecular structure of surface metal oxide species

Many surface metal oxide species on oxide supports terminate with M=O bonds that can be detected with IR spectroscopy in the 1000 cm^{-1} region or in the overtone region at approximately 2000 cm^{-1} [2,3]. It is not always possible to detect the IR vibrations of the surface metal oxide species in the 1000 cm^{-1} region because of strong absorption by the oxide supports below 1000 cm^{-1}, but the overtone region at 2000 cm^{-1} is always observable. The in situ IR spectra of a series of titania supported rhenium oxide catalysts are presented in Fig. 1. The increase in the IR absorption of the titania support below 1000 cm^{-1} is seen in Fig. 1. However, for the titania supported rhenium oxide system it is still possible to detect the Re=O vibrations at about 1000 cm^{-1}. At the highest rhenium oxide loading on titania, two IR vibrations are observed at 1011 and 1004 cm^{-1} due to the symmetric stretches of two different surface rhenium oxide species and a corresponding antisymmetric stretch is observed as a broad band at approximately 975 cm^{-1}. For the alumina supported rhenium oxide catalysts, however, the IR absorption of this alumina support was too strong in the 1000 cm^{-1} to detect Re=O vibrations, and the Re=O IR vibrations were only accessible in the overtone region as shown in Fig. 2. Employing a different alumina support, Wang and Hall [4] have been successful in obtaining the IR vibrations of the surface rhenium oxide species at 1014 and 1006 cm^{-1}. Note that the IR bands in the overtone

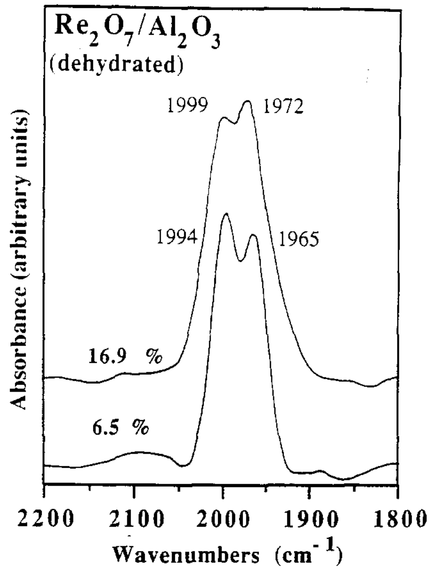

Fig. 2. In situ IR spectra of Re_2O_7/Al_2O_3 showing the overtone region. Reproduced J. Mol. Catal., 76 (1992) 263.

region correspond to approximately doubling of the primary IR vibrations, but usually occur at a few cm^{-1} lower than an exact doubling. Comparison of the IR vibrations of the titania supported and alumina supported rhenium oxide catalysts reveals that the same two surface rhenium oxide species are present in both catalysts. Comparison of the IR vibrations for the supported rhenium oxide catalysts with the IR spectra of rhenium oxide reference compounds suggests that the surface rhenium oxide species are isolated and four-fold coordinated (possessing three terminal Re=O bonds and one bridging Re–O-support bond) [2]. It was also proposed that the difference between the two surface rhenium oxide species is that the species corresponding to the 1011–1016 cm^{-1} vibration probably possessed a proton on the bridging Re–O-support bond [2]. The above structural conclusions are in agreement with additional characterization studies involving in situ Raman spectroscopy [2,5] and in situ X-ray absorption near-edge spectroscopy (XANES) [5].

3.2. Location of surface metal oxide species

Information about the location of the surface metal oxide species on oxide supports can also be obtained from in situ IR spectroscopy investigations that monitor the surface hydroxyl region (3200–4000 cm^{-1}). The alumina support contains different surface hydroxyl groups that vibrate at 3762, 3727, 3676, 3583 and 3460 cm^{-1} (see Fig. 3). The IR band at the highest frequency has been assigned to the most basic hydroxyl group and the decrease in frequency of the surface hydroxyls has been associated with increasing acidity [6]. Deposition of rhenium oxide on alumina reveals that the alumina surface hydroxyls are being consumed and that the consumption of surface hydroxyls proceeds in a sequential fashion (see Fig. 3) [7]. The bands due to the most basic hydroxyls, located at higher frequencies, disappear first with bands due to neutral and more acidic ones disappearing at higher loadings. The broad band centered at about 3590 cm^{-1} is characteristic of residual chemisorbed water. Comparison of the quantity of hydroxyls consumed per surface metal oxide species suggests that titration of the supports' reactive surface hydroxyls is the primary anchoring mechanism of surface metal oxide species [8]. To a lesser extent, however, surface metal oxide species may also become anchored on oxide supports by interacting with exposed Lewis cation sites [9] or

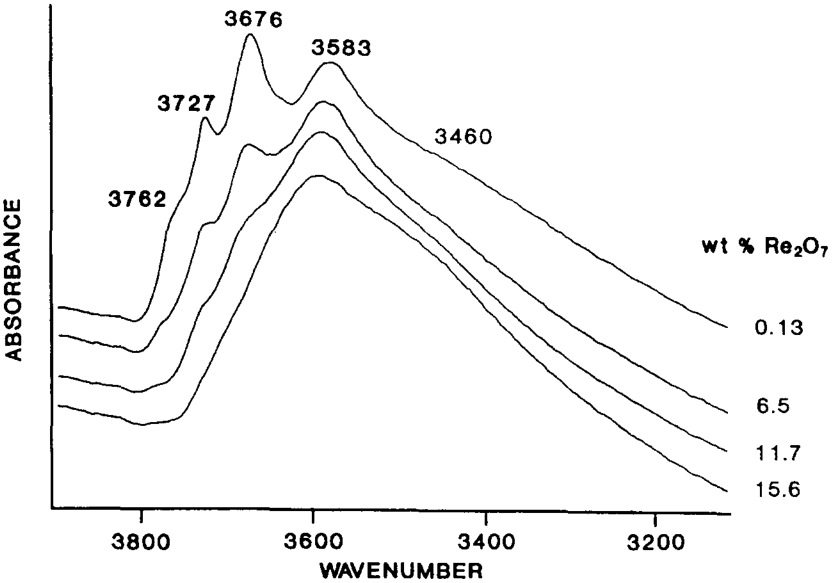

Fig. 3. In situ IR spectra of the hydroxyl region of Re_2O_7/Al_2O_3 as a function of rhenium oxide coverage on alumina. Reproduced from J. Phys. Chem., 96 (1992) 5000.

by breaking M–O–M bonds of the oxide support [10]. Thus, in situ IR studies directly demonstrate that the surface metal oxide species primarily anchor to the oxide supports by titrating the surface hydroxyl sites and, consequently, the surface metal oxide species are located on the surface of the oxide supports.

3.3. Surface coverage of the surface metal oxide species

In principle, it should be possible to determine monolayer coverage of the surface metal oxide species from IR experiments since complete consumption of surface hydroxyls of the oxide support by the surface metal oxide species should correspond to monolayer coverage. However, maximum coverage of surface rhenium oxide on alumina corresponds to 16.7% Re_2O_7 [2], and the IR spectra of the alumina supported rhenium oxide catalysts in Fig. 3 exhibit very few remaining surface hydroxyls at 11.7% Re_2O_7 and essentially no surface hydroxyls remaining at 15.6% Re_2O_7. Thus, it appears that the IR signal of the surface hydroxyls decreases somewhat more rapidly than the increasing surface rhenium oxide coverage. This trend may be due to broadening of the surface hydroxyls at high surface metal oxide coverages which makes it more difficult to detect their IR signals. Similar observations were made for other supported metal oxide catalyst systems [3,7]. CO_2 chemisorption also generally provides qualitative information about the surface metal oxide coverage on the oxide support. The IR spectra of CO_2 chemisorbed on a series of alumina supported rhenium oxide catalysts are presented in Fig. 4. At very low loadings of surface rhenium oxide, five different forms of chemisorbed CO_2 surface species are detected [7,11]: bicarbonate (1646, 1469 and 1232 cm^{-1}), "free" carbonate (1446 cm^{-1}), monodentate carbonate (1537 and 1074 cm^{-1}), bidentate carbonate (1269 cm^{-1}) and bridged carbonate (1755, 1711 and 1204 cm^{-1}). The most abundant surface carbonates are bicarbonates, which coordinate with basic surface hydroxyls, and "free carbonates" and these are the surface carbonate species which are primarily detected at high surface coverages. The decrease in the IR intensities of the surface bicarbonate and "free" carbonate species with rhenium oxide loading is more rapid than the

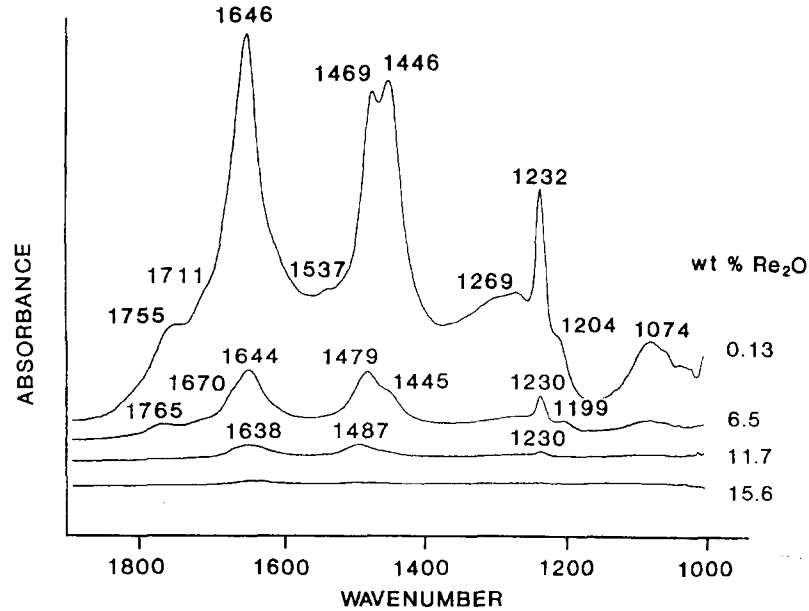

Fig. 4. In situ IR spectra of CO_2 chemisorbed on Re_2O_7/Al_2O_3 as a function of rhenium oxide coverage on alumina. Reproduced from J. Phys. Chem., 96 (1992) 5000.

increasing surface rhenium oxide coverage (see Fig. 4). Maximum surface rhenium oxide coverage corresponds to 16.7% Re_2O_7, but very little chemisorbed CO_2 is present for the 11.7% Re_2O_7 sample and no chemisorbed CO_2 is present for the 15.6% Re_2O_7 sample. This nonlinear behavior is a consequence of the preferential titration of the surface hydroxyls of the support by the surface rhenium oxide species with coverage (see Fig. 3 and discussion above). Similar observations have been made for other alumina supported metal oxide systems [7,12], but a linear relationship appears to exist for some titania supported metal oxide systems (e.g., MoO_3/TiO_2) [1]. Thus, only qualitative information about the surface coverage of surface metal oxide species on oxide supports can generally be obtained from in situ IR experiments. Quantitative determination of the surface coverage of the metal oxide species on oxide supports can usually be obtained from Raman spectroscopy, XPS or structure insensitive reactions such as methanol oxidation [1].

Typically, monolayer coverage for surface metal oxide species on alumina corresponds to approximately 4–5 metal atoms nm^{-2} for Cr, Mo, W and Nb [7]. However, the surface vanadium oxide species is able to pack more densely and monolayer coverage corresponds to about 7–8 atoms nm^{-2}. In contrast, monolayer coverage for surface rhenium oxide on alumina corresponds to only 2.3 atoms nm^{-2} because of the ability of surface rhenium oxide species to form volatile dimeric Re_2O_7 at high surface coverages. The maximum surface densities of surface rhenium oxide species on different oxide supports are presented in Table 1 [2]. Similar maximum surface densities, 2–3 atoms nm^{-2}, are found for alumina, zirconia and titania. The significantly lower maximum surface density of rhenium oxide on silica, approximately 0.5 atoms nm^{-2}, is due to the lower number of surface hydroxyls on silica as well as their lower reactivity compared to other oxide supports (alumina, titania, zirconia, niobia, etc.). Similar trends with the specific oxide support are found for the other surface metal oxide species (Cr, Mo, W, V and Nb): the same maximum surface metal oxide densities are found on alumina, titania, zirconia and niobia supports for each oxide, and significantly lower maximum surface metal oxide densities are found on silica.

Table 1
Maximum surface density of surface rhenium oxide species

Catalyst support	Maximum surface density (atoms/nm^2)
Alumina	2.3
Zirconia	3.3
Titania	2.4
Silica	0.5

3.4. Surface Brönsted and Lewis acid sites

Chemisorption of basic probe molecules followed by in situ IR is usually an informative approach to determine the nature of surface Lewis and Brönsted acid sites present on oxide surfaces [13]. Pyridine is a typical probe molecule in such studies since its ring-stretching vibrational modes (originally at 1439 and 1583 cm^{-1}) are affected by becoming coordinatively bonded to surface Lewis acid sites (PyL: observed at 1440–1460 and 1600–1635 cm^{-1}) or forming a pyridinium ion at surface Brönsted acid sites (PyH^+: observed at 1535–1550 and about 1640 cm^{-1}). The concentration of surface Lewis and Brönsted acid sites can also be determined from the intensities of the PyL and PyH^+ IR bands and their extinction coefficients after saturation of all the surface sites [9]. Pyridine adsorption was used to determine the nature of surface Lewis and Brönsted acid sites present for alumina supported rhenium oxide catalysts (see Table 2) [7].

The alumina support only possesses Lewis acid sites and low concentrations of surface rhenium oxide do not appear to alter the number of such

Table 2
Results of pyridine adsorption

Catalyst	Amount of PyL (μmol/g)	Amount of PyH^+ (μmol/g)
Al_2O_3	199	0
6.5% R_2O_7/Al_2O_3	194	0
15.6% Re_2O_7/Al_2O_3	120	39

sites. At high loadings of surface rhenium oxide on alumina, however, the number of surface Lewis acid sites appreciably decreases and surface Brönsted acid sites are present. In situ IR studies revealed that two surface rhenium oxide species are present on the alumina surface with the second surface rhenium oxide species becoming more dominant at high coverages (see Section 3.1.). It was proposed that the second surface rhenium oxide species possesses the Brönsted acid site on the bridging Re–O–Al bond of the second surface rhenium oxide species on alumina [2]. Similarly, surface Brönsted acid sites were also detected on titania supported rhenium oxide catalysts at high surface coverages [14]. The presence of only surface Lewis acid sites at low surface coverages and the additional presence of surface Brönsted acid sites only at high surface coverages are a general pattern for supported metal oxide catalysts (Re, Cr, Mo, W, V, Nb, etc.) [7,9,15]. This acidity pattern does not appear to be related to changes in the coordination of the surface metal oxide species, but is related to surface density of the metal oxide overlayers [7]. The origin of this coverage effect is not entirely understood at present, but it has been proposed that the surface Brönsted acid proton may be stabilized by two adjacent bridging M–O-support bonds at high surface coverages [7].

The relative strength of the Lewis acid sites present on the different oxide supports can be determined from thermodesorption experiments and the shift of the 1450 cm^{-1} PyL IR band. Such measurements reveal that the strength of the Lewis acid sites decreases in the order: Al ≫ Ti > Zr, and no Lewis acid sites are present on silica [9]. The influence of these surface Lewis acid sites upon the reaction selectivity during the oxidation of methanol over 1% Re_2O_7 supported catalysts is presented in Table 3 [16]. The surface Lewis acid sites are responsible for the conversion of methanol to dimethylether and the selectivity towards this acid catalyzed product very closely follows the relative acid strengths of the surface Lewis acid sites: Al ≫ Zr, Ti and Si. Thus, the surface Lewis acid sites compete with the surface rhenium oxide redox sites during oxidation reactions and, consequently, influence the overall reaction selectivity. The same selectivity trends with oxide supports have also been found for other supported metal oxide catalysts possessing surface redox sites (V, Mo and Cr) [17–19]. At high surface coverages, the influence of the Lewis acid sites is diminished because they are covered by the surface metal oxide species and the selectivity to dimethyl ether is diminished. The Brönsted acid sites present at high surface coverage generally do not affect the selectivity since they are associated with the surface metal oxide species which become reduced, and consequently lose their Brönsted acidity.

4. Conclusions

In situ infrared spectroscopy characterization of supported metal oxide catalysts provides much fundamental information about the nature of the surface metal oxide species in such catalyst systems. IR monitors the terminal M=O vibrations of the surface metal oxide species and can provide information about the number of surface metal oxide species as well as the number of terminal M=O bonds in each species (especially with the aid of oxygen-18 isotopes and complementary Raman

Table 3
Influence of surface Lewis sites upon reaction selectivity

Catalyst support	Selectivity during mechanol oxidation over 1% Re_7O_7 supported catalysts				
	$HCHO$	$HCOOCH_3$	$(CH_3O)_2CHa$	CH_3OCH_3	CO/CO_2
Al_2O_3	0	0	0	100.0	0
TiO_2	68.2	24.0	1.2	0.9	5.7
ZrO_2	21.4	62.3	0	2.4	13.9
SiO_2	9.8	0	0	1.0	89.2

spectroscopy experiments). The surface metal oxide species coordinate to the oxide supports by titrating the surface hydroxyls of the supports and, consequently, are located on the surface of the supports. The surface coverages of the surface metal oxide species on the oxide supports can only be qualitatively determined with IR because the hydroxyl signal and the chemisorption of CO_2 diminish more rapidly than the increase in surface coverage of the surface metal oxide species. This nonlinearity is due to the selective interaction of the surface metal oxide species with the hydroxyls of the support as a function of coverage and the possible broadening of the IR bands of the surface hydroxyls at high coverages. The nature of surface Lewis and Brönsted acid sites can be determined by the chemisorption of basic probe molecules such as pyridine. Only surface Lewis acid sites are present for low surface metal oxide coverages on oxide supports. At high surface coverages of the surface metal oxide species, both surface Lewis and Brönsted acid sites may coexist for supported metal oxide catalysts. The nature of surface acidity may be more complex in mixed metal oxide supports (e.g., silica-alumina, titania-silica, etc.) and the above acidity conclusions are based on single component oxide supports (alumina, silica, titania, etc.)

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