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Raman spectroscopy of supported chromium oxide catalysts

Determination of chromium—oxygen bond distances and bond orders

Bert M. Weckhuysen*,† **and Israel E. Wachs**
Zettlemoyer Center for Surface Studies, Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015, USA

An empirical correlation is described for relating Raman stretching frequencies of chromium—oxygen (Cr—O) bonds to their bond lengths in chromium oxide reference compounds. An exponential fit of crystallographically determined Cr—O bond lengths to Cr—O Raman symmetric stretching frequencies (800–1300 cm^{-1}) is presented along with a relation between Cr—O bond strengths and Raman stretching frequencies. These empirical correlations have led to a systematic method for determining the coordination and bond lengths of chromates. The developed method is illustrated for chromates with unknown local structure in $Bi_2O_3 \cdot K_2CrO_4$ sillenite and for different supported chromium oxide catalysts. The obtained results are compared with those previously obtained by X-ray absorption spectroscopy.

Raman spectroscopy is an excellent technique for the elucidation of molecular structures of complex transition metal oxides present as either bulk phases or as two-dimensional surface phases.[1–3] This is because Raman spectroscopy directly probes the structure and bonding of a metal oxide complex by its vibrational spectrum. Therefore, this technique can be successfully used to discriminate between different molecular structures on oxide surfaces. For example, mono-, di-, tri- and tetrachromate surface species were found to be present on hydrated surfaces of supported chromium oxide catalysts and the polymerization degree of the surface chromate species was found to depend on the specific iso-electric point of the inorganic support.[4–6]

Vibrational spectroscopy has also proven useful in the characterization of simple diatomic molecules. For many years there has been considerable interest in deriving expressions relating crystallographically determined bond lengths to observed vibrational frequencies for diatomic molecules. The most common empirical expression relating harmonic force constant and interatomic distance for diatomic molecules is Badger's rule, which has been extended to many families of molecules but does not adequately relate bond distances to force constants in polyatomic molecules.[7–9] Recently, the diatomic approximation was used by our group to justify the observed relationship between molybdenum–oxygen,[10] vanadium–oxygen,[11] niobium–oxygen,[12] bismuth–oxygen[13] and, tungsten–oxygen[14] bond lengths and their corresponding Raman stretching frequencies. However, a chromium–oxygen correlation does not exist in the literature and is required for better structural determination of Cr—O compounds and supported chromium oxide catalysts.

In the present study, the diatomic approximation is used to establish empirical relationships between Cr—O bond lengths and Raman stretching frequencies of chromium oxide reference compounds in the solid state, the gas phase and in solution. An exponential function was found to most reasonably describe the empirical dependence between the Cr—O bond length and Raman stretching frequency. The presented correlation is an invaluable tool for structural characterization of a chromium oxide compound because its Raman spectrum may be interpreted in terms of Cr—O bond lengths. This is illustrated for supported chromium oxide catalysts and the results are compared with those previously obtained by X-ray absorption spectroscopy.[5]

Experimental

Chromium oxide reference compounds and supported chromium oxide catalysts

The Raman spectra of the following chromium oxide reference compounds were collected in our laboratory: K_2CrO_4, $K_2Cr_2O_7$ and CrO_3. The Raman band positions of CrO_2Cl_2, $CrO_4{}^{2-}$, $Cr_2O_7{}^{2-}$, $Cr_3O_{10}{}^{2-}$, $Cr_4O_{13}{}^{2-}$, $K_2Cr_3O_{10}$ and $K_2Cr_4O_{10}$ were taken from the literature.[15–17] The investigated chromium oxide catalysts were: Cr/SiO_2, Cr/Al_2O_3, Cr/Nb_2O_3, Cr/TiO_2 and Cr/ZrO_2. Details about the preparation and the characteristics of these supported chromium oxide catalysts can be found elsewhere.[4–6,18–24] The bismuth chromate compound was prepared by mixing stoichiometric amounts of Bi_2O_3 (99.9%) with K_2CrO_4 (with Bi : Cr = 18 : 1). The mixture was ground in acetone with an agate mortar and pestle, dried in air overnight, and then heated at *ca.* 600 °C for 72 h in air. The obtained sample was orange. The exact stoichiometry of this compound is unknown but can be denoted as a $Bi_2O_3 \cdot K_2CrO_4$ compound. A reference sample without Cr, treated in identical conditions was made for comparison and had a yellow colour.

Laser Raman spectroscopy

Raman spectra were obtained by using a Spectra-Physics (Mountain View, CA, USA) Model 171 Ar^+ laser, where the exciting line was 514.5 nm. The laser power at the samples was maintained at 10–20 mW. The scattered radiation was then directed into a Spex Triplemate (Edison, NJ, USA) Model 1877 spectrometer coupled to a Princeton Applied Research OMAIII Model 1463 optical multichannel analyser equipped with an intensified photodiode array detector cooled thermoelectrically to −35 °C. Under ambient conditions, the laser beam was focused on the sample illuminator, where the sample typically spins at about 2000 rpm to avoid local heating. The scattered Raman light was reflected into the spectrometer by a 90° angle with the incident light, and was collected and analysed by the optical multichannel analyser. The overall spectral resolution was determined to be better than 2 cm^{-1}. The catalysts were dehydrated at 500 °C for 1 h

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† Present address: Centrum voor Oppervlaktechemie en Katalyse, Katholieke Universiteit Leuven, Kardinaal Mercierlaan 92, 3001 Heverlee, Belgium.

in flowing oxygen and the corresponding Raman spectra were collected at room temperature by using a special designed cell. The reference compounds were measured as such. Ultrahigh-purity hydrocarbon-free oxygen (Linde gas, Union Carbide, PA, USA) was purged through this cell during the acquisition of the Raman spectra of the dehydrated samples. The characteristics of this cell have been described elsewhere.[19,22]

Theory

Diatomic approximation

Several types of approximations may be made in order to more easily interpret the Raman spectrum of a complex transition metal oxide species. First, it is commonly assumed that the internal and external modes of the crystal are independent of one another. The internal modes of a molecular unit occur in the high-frequency region and constitute the normal vibrations of the molecular unit. The external modes occur at lower frequency and correspond to translations and vibrations of the molecular units within the crystal. Such a separation of the internal modes of the molecular unit contained within the crystal from the external modes of the crystalline lattice is an assumption of the site symmetry approximation.[25]

The site symmetry approach begins by assigning a high degree of symmetry at each site within a unit cell (usually, the actual symmetry at these sites is lower than that assigned). As the site symmetries within the crystalline lattice must be assigned beforehand, a detailed knowledge of the structure of the crystal is a prerequisite. The site symmetry approach leads to the total number of infrared- and Raman-active modes and allows the vibrational spectrum of a confined, distorted molecule within the crystal to be directly compared to that of a similar molecule in free space or in solution. Thus, although the site symmetry approach is useful in allowing the observed Raman bands to be assigned to symmetry species, it does not directly yield structural information about metal oxide species contained within the crystalline lattice.

In the present study, another type of approximation is used, called the diatomic approximation. Such an approximation is necessary for justifying the direct relationship observed between metal–oxygen bond lengths and Raman stretching frequencies in transition metal oxide compounds. Whereas the site symmetry approximation assumes that each metal oxide polyhedron is separated from the crystalline lattice, the diatomic approximation assumes that each distinct metal–oxygen is vibrationally independent of the crystalline lattice. Thus, to a first approximation, the Raman spectrum of a crystalline metal oxide is a superposition of the stretching frequencies from an assembly of metal–oxygen diatomic oscillators. Each oscillator has a unique vibrational bond. If the metal–oxygen bond is assumed to act like a harmonic oscillator, then the stretching force constant may be found from its square-root dependence on vibrational frequency. In the present study, the diatomic approximation is shown to be justified for chromium oxide reference compounds within the experimental accuracy afforded by the measurement of Raman stretching frequencies and crystallographically determined Cr—O bond lengths.

Relating Raman stretching frequency to bond length and bond order

Many empirical and semi-empirical formulae are present in the literature of simple diatomic molecules. These formulae relate physical parameters such as bond distances, force constants and bond valences.[26–28] Efforts have also been directed at extending force constant/bond distance relationships to polyatomic molecules. Perhaps the most common expression relating bond lengths to force constants in diatomic molecules is Badger's rule. A general form of Badger's rule is expressed as:

$$k^{-1/3} = (a_{ij} - d_{ij})^{-1}(R - d_{ij}) \tag{1}$$

where k (mdyn Å^{-1}) is the force constant for a particular bond, R (Å) is the equilibrium bond length, and d_{ij} and a_{ij} are constants (fixed for designated bonds between atoms from rows i and j of the periodic table). Recently, Badger's rule has been used to correlate uranium—oxygen bond lengths with both symmetric and antisymmetric stretching frequencies for dioxo functionalities (UO_2) in uranium oxide compounds.[29] In previous studies[10–14] and in the course of the present work, it was found that Badger's rule does not adequately correlate bond distances to stretching frequencies or force constants. This is because $k^{-1/3}$ is not a linear function of R but exhibits a slight curvature. Herschbach[9] encountered a similar problem in fitting cubic anharmonic force constants to internuclear distances for diatomic molecules. Consequently, Herschbach applied an exponential fit to conveniently account for the slight curvature in the data.[9] Numerical fits of the present Cr—O bond length/stretching frequency data have also led to a simple exponential dependence between Raman stretching frequencies and Cr—O bond lengths. Thus, in accordance with Herschbach's treatment, an exponential function of the form:

$$\nu = A\exp(BR) \tag{2}$$

is applied in the present work as the most convenient method of relating Cr—O stretching frequencies and bond distances in bulk, solution and gas phase chromium oxide reference compounds where ν is the Cr—O stretching frequency, R is the Cr—O interatomic distance, and A and B are fitting parameters. If we assume that each Cr—O bond can be modelled after a harmonic oscillator, then the stretching frequency is directly proportional to the square root of the force constant.

The Pauling bond strengths (in valence units), also referred to as bond orders or bond valences, of the Cr—O bonds and the calculated valence state of the chromium cation are also useful in discussing the plausibility of proposed structures.[30] The bond valence reflects the relative strength of a chemical bond and shows the distribution of available valence electrons in the chemical bonding of a molecular species. Furthermore, according to Pauling's valence sum rule, there is a conservation of valency associated with the metal cation. Hence, the calculated valence state can be compared to the formal oxidation state of the chromium cation and serves as a bookkeeping device for the distribution among the available Cr—O bonds.

A general relationship has been developed by Brown and Wu[31] that relates the cation–oxygen bond valence s to the interatomic distance R. The empirical expression for relating a Cr—O bond length to its bond valence is:

$$s(\mathrm{Cr{-}O}) = (R/1.787)^{-5.0} \tag{3}$$

where 1.787 Å is the estimated bond length for a Cr—O bond of unit valency. The empirical parameters of eqn. (3), 1.787 and 5.0, were determined based on data from 23 Cr^{6+} environments.[31] The valence sum rule, as discussed by Brown,[30] is extremely useful in estimating valence states of chromium cations in chromate structures. The valence state of a chromium cation is calculated by adding the contributions from each Cr—O bond as determined by eqn. (3). For example, any deviation of a calculated valence state that lies outside 6.0 ± 0.2 valence units suggests a source of error in the bond length data. Common sources of error may be attributed to a misassigned oxidation state or erroneously determined bond lengths. In the course of the present work we have found some research papers on the structural determination of chromium oxide compounds, which show unreasonable Cr—O distances. For example, a crystallographic study

Table 1 Bond lengths and observed stretching frequencies for Cr—O bonds in chromium oxide reference compounds*

compound	R/Å	site symmetry	ref.	ν_s/cm^{-1}	s(valence units)	VS
$CrO_2Cl_{2\,(g)}$	1.580	C_{2v}	33	984	1.85	nd
$CrO_4{}^{2-}{}_{(aq)}$	1.660	T_d	34	847	1.45	5.78
$Cr_2O_7{}^{2-}{}_{(aq)}$	1.630	C_{2v}	35	904	1.58	nd
$Cr_3O_{10}{}^{2-}{}_{(aq)}$	1.598	C_{2v}/C_{3v}	36	956	1.75	nd
$Cr_4O_{13}{}^{2-}{}_{(aq)}$	1.587	C_{2v}/C_{3v}	36	963	1.81	nd
$K_2CrO_{4(s)}$	1.650	T_d	37	874	1.49	5.96
$K_2Cr_2O_{7(s)}$	1.630	C_{2v}	35	902	1.59	nd
$K_2Cr_3O_{10(s)}$	1.593	C_{2v}/C_{3v}	38	945	1.78	nd
$K_2Cr_4O_{10(s)}$	1.587	C_{2v}/C_{3v}	36	957	1.81	nd
$CrO_{3(s)}$	1.578	nd	39	975	1.86	nd

* g = gas phase; aq = aqeous phase; and s = solid phase.

of $KCrO_3Cl$ crystals revealed a bond length $R(Cr{=}O) = 1.53$ Å.[32] According to eqn. (3), this bond length corresponds to a bond valence of 2.17, which is rather unlikely.

Results

The chromium—oxygen bond lengths were obtained from several chromium oxide reference compounds in the solid state, in solution and in the gas phase, and correlated with their corresponding Raman stretching frequencies.[33–39] The reference chromium oxide compounds are listed in Table 1, together with their crystallographically determined bond lengths, literature references, assigned Raman stretching frequencies, bond strengths [from eqn. (3)] and calculated Cr^{6+} valence states (valence sum rule). The valence sum rule can, of course, only be applied about the chromium oxides which have four identical Cr—O bonds (*i.e.* monochromate structure).

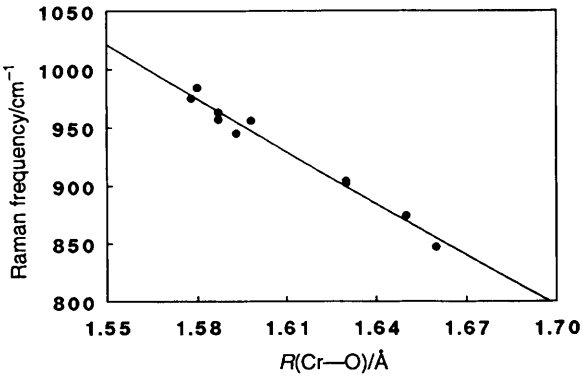

Fig. 1 Correlation plot relating Cr—O bond lengths (Å) to Cr—O stretching frequencies (cm^{-1}). The data points are fit to an exponential function [eqn. (4)].

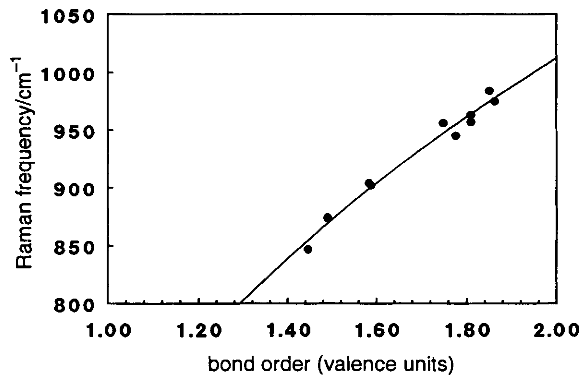

Fig. 2 Correlation plot relating Cr—O bond strength (in valence units) to Cr—O stretching frequencies (cm^{-1}), according to eqn. (5)

The procedure for making assignments of the Raman stretching frequencies to Cr—O bond lengths for the chromium oxide reference compounds is straightforward. The shortest Cr—O bonds of the reference compounds were correlated with the highest symmetric stretching frequencies [$\nu_s(CrO_2)$; $\nu_s(CrO_3)$ or $\nu_s(CrO_4)$] and are typically associated with the terminal Cr=O bonds of the chromate structures. The obtained results are plotted in Fig. 1, which shows the relation between the crystallographic Cr—O bond lengths and corresponding Cr—O stretching band positions, summarized in Table 1. A least square fit of the data to the exponential function, described by eqn. (2), yields the following expression for the bond length–stretching frequency correlation:

$$\nu = 13055 \exp(-1.6419{*}R) \qquad (4)$$

where ν is in cm^{-1} and R is in Å. The precision in the calculation of a Cr—O bond length R from a measured Raman frequency using the bond length–stretching frequency correlation is 0.030 Å. The standard deviation in the estimate of a Raman stretching frequency from an absolute Cr—O bond length is 46 cm^{-1}.

Bond order–stretching frequency correlations are also useful in the determination of chromate structures because the Cr—O bond order is representative of the strength of the chemical bond. The combined use of the empirical relation of Brown and Wu, eqn. (3), and the above bond length–stretching frequency correlation yields the following relation between the Pauling Cr—O bond strength (in valence units) and Raman stretching frequency:

$$s(\mathrm{Cr{-}O}) = \left[0.3408 \ln\left(\frac{13055}{\nu}\right)\right]^{-5.0} \qquad (5)$$

The bond strength–stretching frequency correlation is plotted in Fig. 2.

Discussion

Evaluation of the bond length–strength frequency correlation

The Cr—O correlation is derived from an exponential fit of the crystallographically determined bond distances and observed Raman stretching frequencies. Such a direct relationship between these two experimental observables is justified under the assumptions of the diatomic aproximation. The basic assumption behind this correlation is that each distinct Cr—O bond is entirely separated from its crystalline lattice. Such a separation means that there are no vibrational interactions between neighbouring Cr—O bonds in the lattice. Each isolated Cr—O bond exhibits a stretching frequency which is characteristic of its bond length. To a first approximation, the Raman spectrum is a superposition of these Cr—O stretching frequencies. We have limited our analysis to the symmetric stretching frequency because this is the most intense high frequency band and consequently easy to measure. However, because the diatomic approximation ignores the point symmetry of a molecule, symmetric and antisymmetric stretching frequencies cannot be distinguished and a particular assignment must be handled with care.

There are both advantages and disadvantages of using the diatomic approximation to derive a correlation between Cr—O bond distances and stretching frequencies. The advantage of the technique lies in its simplicity. Within the limits of experimental error (± 46 cm^{-1}), the diatomic approximation immediately provides a good estimate of Cr—O bond distances (± 0.030 Å) from observed stretching frequencies. These spectroscopically determined bond distances can be expressed in terms of bond valences and evaluated to determine the plausibility of proposed structures. Conversely, if the bond distances of a metal oxide are already known, then the stretching frequencies corresponding to these bonds may be predicted. The disadvantage of the diatomic approximation, but itself, does not lead to an assignment of the symmetry species of the Raman vibrational modes.

Applications

Determining stretching frequencies for ideal structures: CrO_4 and CrO_6. An interesting application of the developed Cr—O correlation is the prediction of Raman stretching frequencies for proposed chromate structures. The stretching frequencies for the perfect CrO_4 tetrahedron and CrO_6 octahedron can be estimated from the developed Cr—O correlation. These ideal structures have a high degree of point-group symmetry (T_d and O_h, respectively). Consequently, vibrational interactions between bonds are expected to be significant. In spite of these significant vibrational interactions, the diatomic approximation may be used to provide an excellent estimate of the frequency of the totally symmetric Cr—O stretching mode for each of these structures. This is because the magnitude of the vibrational interactions constants between neighbouring Cr—O bonds is of the same order as the error associated with the experimental measurements of crystallographic Cr—O bond distances and Raman stretching frequencies. The stretching frequencies of the regular CrO_4 and CrO_6 structures are estimated by first equally dividing the six valence units of bond order between the four bonds of the tetrahedron and the six bonds of the octahedron. This results in R(Cr—O) = 1.648 Å for CrO_4 and R(Cr—O) = 1.787 Å for CrO_6 by eqn. (3). If these bond distances are considered absolute (without error), then the Cr—O correlation [eqn. (4)] yields symmetric stretching frequencies of 873 cm^{-1} for the perfect CrO_4 tetrahedron and 694 cm^{-1} for the perfect CrO_6 octahedron.

A comparison of the predicted stretching frequency of the perfect CrO_4 structure with those of existing chromate compounds suggests that a perfect CrO_4 tetrahedron may exist. On the other hand, octahedral CrO_6 structures (with oxidation state 6) are not reported up to now[40] and the calculated value must be only regarded as a prediction. The most perfect CrO_4 tetrahedron listed in Table 1 is present in K_2CrO_4 which has a symmetric stretching frequency of 874 cm^{-1}. Thus, the CrO_4 tetrahedron present in K_2CrO_4 probably contain a perfect T_d structure. The $CrO_{4(aq)}{}^{2-}$ is believed to have also a perfect T_d symmetry. However, the value is 26 cm^{-1} lower than 873 cm^{-1}, predicted for the perfect tetrahedron, and is indicative for some irregularities, although the observed value lies within the standard deviation. All the other structures with four coordinated chromium, reported in Table 1, have a lower point symmetry and consequently their bond length deviates from 1.649 Å.

Determining the structure of a crystalline compound of unknown local structure: $Bi_2O_3 \cdot K_2CrO_4$. The Raman spectrum of the orange $Bi_2O_3 \cdot K_2CrO_4$ sample (Bi : Cr = 18 : 1) is presented in Fig. 3. One single band is observed at 818 cm^{-1}. According to eqn. (4), this stretching frequency corresponds with a R(Cr—O) = 1.687 Å, only slightly higher than for a perfect CrO_4 tetrahedron. This is indicative for the presence of a Cr^{6+} site in the $Br_2O_3 \cdot K_2CrO_4$ compound with a slightly distorted T_d coordination.

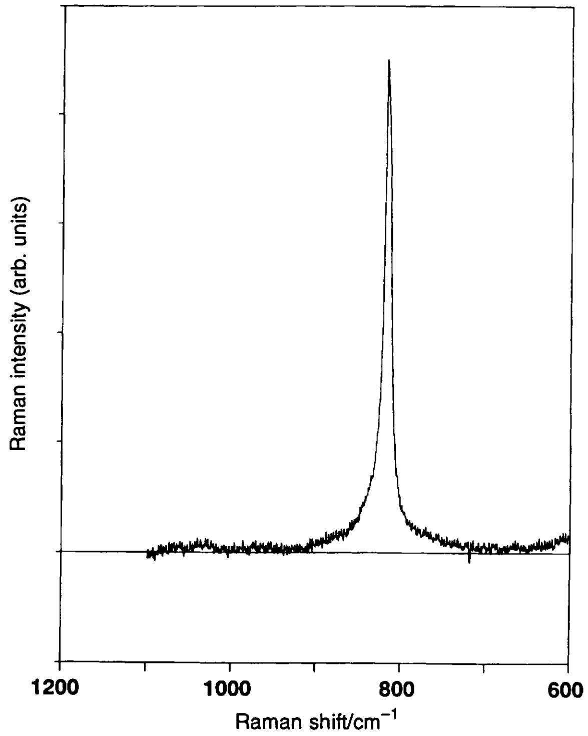

Fig. 3 Raman spectrum of the $Bi_2O_3 \cdot K_2CrO_4$ compound

Determining the structure of supported chromium oxides. The determination of bond distances from Raman stretching frequencies is of most benefit when diffraction techniques are unable to detect oxygen positions because of the absence of long-range order. Such is the case for supported metal oxides which are present as two-dimensional metal oxide overlayers on high surface area oxide substrates. Consequently, diffraction techniques are not suitable for studying the structures of surface metal oxides. One example of surface metal oxides is the surface chromium oxide species supported on different inorganic supports, which is known to be active in oxidation, dehydrogenation–hydrogenation and polymerization reactions.[6]

The highest observed Raman stretching frequencies of series of supported chromium oxide catalysts are summarized in Tables 2 and 3, together with the calculated bond lengths and bond orders. Table 2 shows that for all dehydrated supported chromium oxide catalysts the bond order is near 2 and one can calculate a stretching frequency of 1015 cm^{-1} for a perfect Cr=O bond ($s = 2$). On the other hand, the hydrated catalysts have frequencies in the range 880–960 cm^{-1} and, conse-

Table 2 Bond length–stretching frequency correlation applied to dehydrated chromium oxide catalysts

catalyst	ν/cm^{-1}	R/Å	s(valence units)
Cr/Al_2O_3*	1005	1.562	1.9598
	1030	1.547	2.0567
Cr/SiO_2	986	1.573	1.8923
Cr/TiO_2*	1010	1.559	1.9789
	1030	1.547	2.0567
Cr/ZrO_2*	1010	1.559	1.9788
	1030	1.547	2.0567
Cr/Nb_2O_5	991	1.570	1.9104

* Two chromium oxide species, differing in their highest stretching frequency are present after dehydration.

Table 3 Bond length–stretching frequency correlation applied to hydrated chromium oxide catalysts

catalyst	ν/cm^{-1}	R/Å	s(valence units)	R/Å *via* EXAFS*
Cr/Al_2O_3	870	1.650	1.490	1.65
Cr/SiO_2	953	1.594	1.771	1.58
Cr/TiO_2	880	1.643	1.522	nd
Cr/ZrO_2	880	1.643	1.522	nd
Cr/Nb_2O_5	880	1.643	1.522	nd

* According to reference 5.

quently, lower bond orders or high bond lengths are observed than for the dehydrated counterparts. Therefore, hydrated monochromate is dominant on alumina, titania, zirconia and niobia, whereas on a silica surface mainly dichromate is observed. Furthermore, the calculated bond lengths for hydrated Cr/SiO_2 and Cr/Al_2O_3 catalysts agree with those previously obtained on the same samples by X-ray absorption spectroscopy.[5] This confirms that the derived Cr—O correlation is physically meaningful and applicable for structure determination.

In summary, the Cr—O correlation provides a powerful tool in the interpretation of Raman spectra of chromium oxide species on inorganic surfaces. In cases where diffraction techniques fall short of providing oxygen positions, Raman spectroscopy may be used to determine Cr—O bond distances for the chromate species. Knowledge of the bond distances of a chromate species can lead to information concerning its coordination and structure. Such an approach should popularize Raman spectroscopy as a complementary technique to diffraction methods in the structural studies of complex transition metal oxide systems.

Conclusions

An empirical correlation was established between Cr—O Raman stretching frequency and bond length. The correlation is based on Raman symmetric stretching frequencies and previously reported crystallographic Cr—O bond lengths. The obtained correlation was further combined with Brown's empirical correlation between Cr—O bond length and bond strength (in valence units) to derive a relation between stretching frequency and bond strength. The developed relationships are expected to be of high importance to gain insight into structures of surface chromium oxide species, especially for those chemical systems which are not amenable to analysis by diffraction or other spectroscopic techniques. In this work, Raman stretching were predicted for the perfect CrO_4 and CrO_6 structures. The Cr—O bond distances of different supported chromium oxide catalysts were determined from their Raman spectra. The Cr—O correlation is expected to aid in the determination of the structure of chromium oxide species on various oxide supports, which are heterogeneous catalysts for many industrially important reactions.

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