

In Situ Raman Spectroscopy of Supported Chromium Oxide Catalysts: $^{18}\text{O}_2$ – $^{16}\text{O}_2$ Isotopic Labeling Studies

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The isothermal isotopic exchange reaction of $^{18}\text{O}_2$ with ^{16}O of chromium(VI) oxide supported on zirconia, alumina, and titania has been investigated with *in situ* laser Raman spectroscopy. The isotopic exchange reaction is dependent on the support type, the Cr loading, and the reaction temperature. Complete isotopic exchange of chromium(VI) oxide with $^{18}\text{O}_2$ is difficult to achieve and requires several successive butane reduction– $^{18}\text{O}_2$ oxidation cycles at relatively high temperatures. The efficiency of the isothermal isotopic exchange reaction increases from alumina over titania to zirconia and with increasing Cr loading and reduction temperature. The observed Raman shifts upon isotopic labeling are consistent with a mono-oxo surface chromium oxide(VI) species.

Introduction

Raman spectroscopy (RS) is a powerful characterization technique for studying supported chromium oxide catalysts because it can discriminate between the different molecular structures of surface chromium(VI) oxide species (e.g. monochromate versus dichromate).¹ In previous RS studies, supported chromium oxide catalysts were extensively studied under hydrated and dehydrated conditions as a function of the support type.^{2–7} The characterization studies revealed that under hydrated conditions the molecular structure of the surface chromium oxide species is determined by the iso-electric point of the oxide support. Thus, the monochromate/polychromate ratio increases with the iso-electric point of the support and with decreasing Cr oxide loading. Upon calcination, dehydrated surface chromium(VI) oxide species are formed by reaction with the surface hydroxyl groups of the support. Two surface chromium oxide species were observed on the TiO_2 , ZrO_2 , and Al_2O_3 surfaces: a monomeric species (characterized by a $\text{Cr}=\text{O}$ stretching frequency at $\sim 1030\text{ cm}^{-1}$) and a polymeric species (possessing a $\text{Cr}=\text{O}$ stretching frequency at ~ 1005 – 1010 cm^{-1} and a $\text{Cr}-\text{O}-\text{Cr}$ bending mode at $\sim 880\text{ cm}^{-1}$).⁸

The exact molecular structure of these dehydrated surface chromium oxide species, however, remains unclear.^{1,8} Two tetrahedral structures, as shown in Figure 1 for a monomeric species, were previously proposed from RS data: a mono-oxo species with one terminal $\text{Cr}=\text{O}$ bond and three $\text{Cr}-\text{O}$ –support bonds (structure A) and a di-oxo species with two terminal $\text{Cr}=\text{O}$ and two $\text{Cr}-\text{O}$ –support bonds (structure B). The objective of the present investigation is to resolve this issue by combining *in situ* Raman spectroscopy with oxygen-18 isotopic labeling studies. In addition, the efficiency of the isotopic exchange reaction has been studied as a function of the Cr loading, the support type, and the reaction temperature. The new insights will be used (1) to develop a more detailed understanding of the molecular structures of supported chromium oxides and (2) to obtain knowledge about the surface mobility of oxygen species on the surfaces of supported



Figure 1. Molecular structure of a supported monochromate species: (a) mono-oxo species and (b) di-oxo species.

chromium catalysts. This mobility of oxygen species plays an important role in catalysis, not only in the catalytic cycle itself but also during activation and regeneration treatments of catalysts.⁹

Experimental Section

1. Catalyst Preparation and Characterization. The 1, 3, and 6 wt % $\text{CrO}_3/\text{ZrO}_2$ (Degussa, $39\text{ m}^2/\text{g}$), 5 wt % $\text{CrO}_3/\text{Al}_2\text{O}_3$ (Harshaw, $180\text{ m}^2/\text{g}$), and 3 wt % $\text{CrO}_3/\text{TiO}_2$ (Degussa P-25, $55\text{ m}^2/\text{g}$) catalysts were prepared by the incipient-wetness impregnation method with an aqueous solution of chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Allied Chemical Co.). Additional details about these supported chromium oxide catalysts can be found elsewhere.⁵ After impregnation, the wet samples were initially dried at room temperature for 16 h, further dried at 110 – $120\text{ }^\circ\text{C}$ for 16 h, and then calcined at $500\text{ }^\circ\text{C}$ for 16 h.

2. Raman Spectroscopy and Sample Treatment. Raman spectra of the supported chromium oxide catalysts were obtained with a laser Raman apparatus with the 514.5 nm line of an Ar^+ laser (Spectra Physics, Model 171) as the excitation source. The laser power at each sample was about 40 mW . The scattered radiation from the sample was directed into a Spex Triplemate spectrometer (Model 1877) coupled to a Princeton Applied Research (Model 1463) OMA III optical multichannel photodiode array detector (1024 pixels). The detector was cooled thermoelectronically to $-35\text{ }^\circ\text{C}$ to decrease the thermal noise. The Raman scattering in the 600 – 1100 cm^{-1} region was collected, and the spectra were recorded using an OMA III computer and software. The instrument resolution was experimentally determined to be better than 2 cm^{-1} . About 0.2 g of each supported chromium oxide catalyst was pressed into a thin wafer of about 1 mm thickness. The catalyst samples were calcined in dry air at $500\text{ }^\circ\text{C}$ for 2 h before the Raman measurements in order to minimize possible sample fluores-

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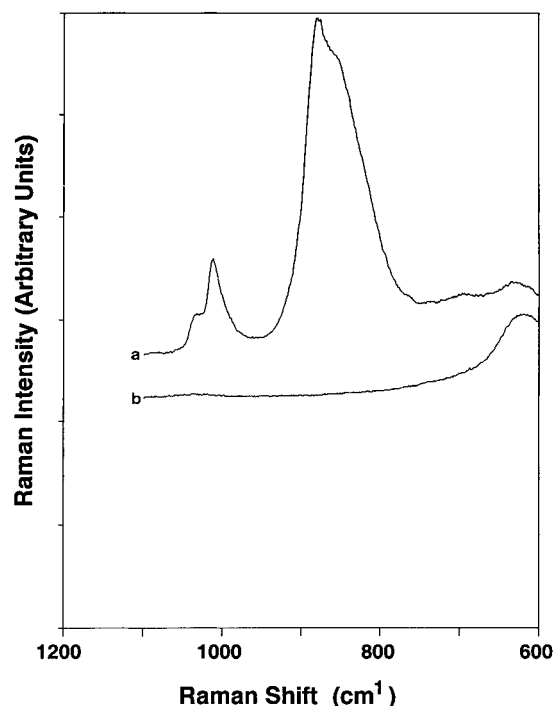


Figure 2. *In situ* Raman spectra of the 6% $\text{CrO}_3/\text{ZrO}_2$ catalyst after calcination (a) and after butane reduction at 450 °C (b).

cence. The *in situ* Raman spectra were obtained with the following procedure. The samples were placed into the cell and heated up to 500 °C for 2 h in a flow of pure oxygen gas (Linde Specialty Grade, 99.99% purity). The Raman spectra of the dehydrated samples were then collected after cooling the sample to 200 or 350 °C in a flow of pure oxygen gas for 30 min. Flowing of pure $^{18}\text{O}_2$ only gives rise to small changes in the Raman spectra of the calcined Cr catalyst. Thus, a reduction step is crucial to incorporate ^{18}O in the supported chromium oxide species. Therefore, butane (Air Products and Chemicals, mixture of 98.7% He and 1.3% butane) was dynamically introduced at high temperature into the cell, and the Raman spectra were collected. The reduced samples were then reoxidized in $^{18}\text{O}_2$ (JWS Technologies, Inc., Matheson, and $^{18}\text{O}_2/\text{He} = 3/97$). This reduction–reoxidation cycle for each catalyst was repeated until the extent of oxygen-18 isotopic exchange was maximized.¹⁰ The maximum number of reduction–reoxidation cycles for complete isotopic exchange of the supported chromium oxides decreases with increasing reduction and reoxidation temperature. The optimal reduction and reoxidation temperatures were determined to be 450 °C.

Results

As an example we will discuss the *in situ* Raman spectra of the 6 wt % $\text{CrO}_3/\text{ZrO}_2$ catalyst in great detail. The spectrum obtained after calcination in $^{16}\text{O}_2$ is shown in Figure 2. The spectrum is dominated by three strong Raman peaks at 1030, 1010, and 880 cm^{-1} , which were previously assigned to terminal $\text{Cr}=\text{O}$ vibrations of monochromate (1030 cm^{-1}) and terminal $\text{Cr}=\text{O}$ and bridging $\text{Cr}-\text{O}-\text{Cr}$ vibrations of polychromate species (1010 and 880 cm^{-1}), respectively.⁸

After calcination, the samples were cooled down and contacted with butane gas in the absence of oxygen at 450 °C. The corresponding RS spectrum is included in Figure 2. The Raman active surface Cr^{6+} species is reduced to surface Cr^{3+} and Cr^{2+} species. The stretching modes of $\text{Cr}^{2+}-\text{O}^{2-}$ or $\text{Cr}^{3+}-\text{O}^{2-}$ peaks are Raman active, but are much less intense with respect to those of $\text{Cr}^{6+}-\text{O}^{2-}$. They are also located at lower

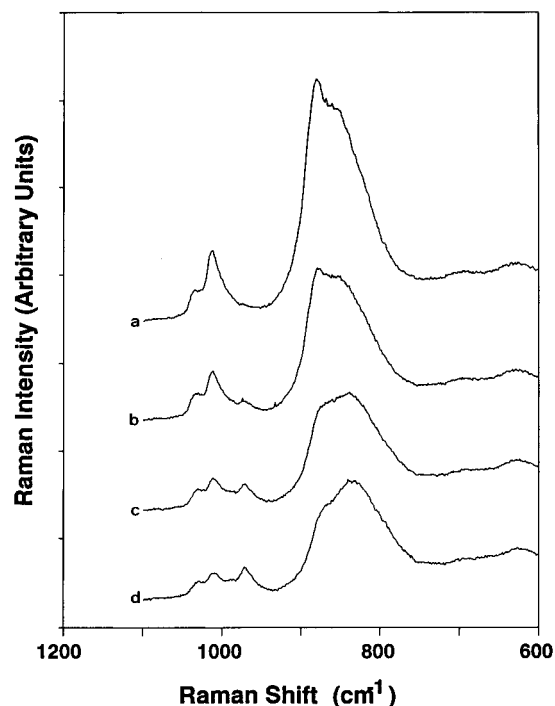


Figure 3. *In situ* Raman spectra of the 6% $\text{CrO}_3/\text{ZrO}_2$ catalyst as a function of the number of butane reduction– $^{18}\text{O}_2$ reoxidation cycles (X) with X = (a) 1; (b) 3; (c) 6; and (d) 9.

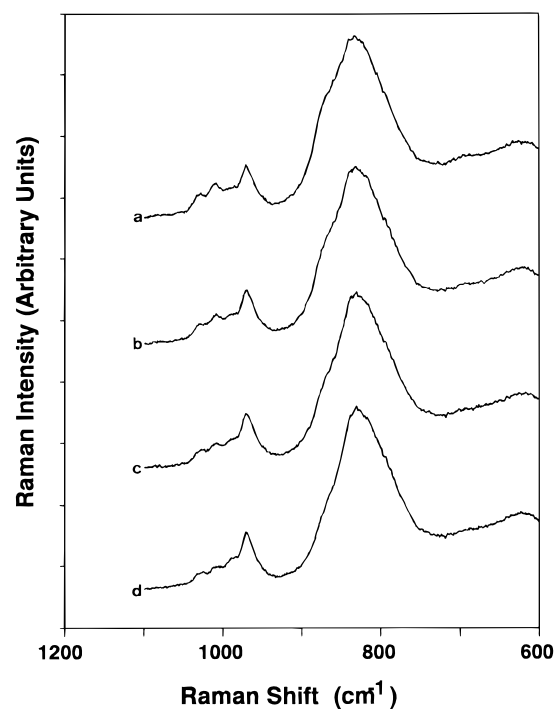


Figure 4. *In situ* Raman spectra of the 6% $\text{CrO}_3/\text{ZrO}_2$ catalyst as a function of the number of butane reduction– $^{18}\text{O}_2$ reoxidation cycles (X) with X = (a) 11; (b) 15; (c) 17; and (d) 19.

frequencies and are therefore masked by the vibrational modes of the support.

After recalcination in $^{18}\text{O}_2$ at 450 °C, the following spectra features are observed: (1) decrease of the Raman peaks at 1030, 1010, and 880 cm^{-1} ; (2) broadening of the 880 cm^{-1} Raman peak; and (3) formation of a new Raman peak at around 970 cm^{-1} . After repeating this reduction–reoxidation cycle 18 times, the RS spectra change drastically, as illustrated in Figures 3–4: (1) the intensity of the Raman peak at 970 cm^{-1} further increases; (2) the Raman peaks at 1030 and 1010 cm^{-1} further

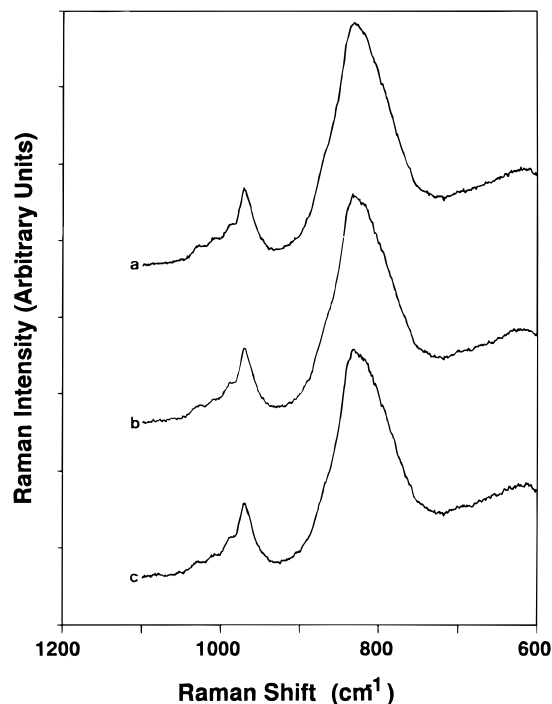


Figure 5. *In situ* Raman spectra of the 6% CrO₃/ZrO₂ catalyst as a function of the number of butane reduction–¹⁸O₂ reoxidation cycles (X) with X = (a) 21; (b) 23; and (c) 25.

decrease with respect to the initial intensity as obtained after calcination in pure oxygen; (3) the Raman peak at 880 cm⁻¹ shifts to lower energy; and (4) a new weak band at around 990 cm⁻¹ is formed. After 25 reduction–reoxidation cycles, almost complete oxygen-18 isotopic exchange is achieved and the Raman spectrum is characterized by absorptions at 1030, 1010, 990, 970, and 840 cm⁻¹ (see Figure 5). The Raman peaks at 1030 and 1010 cm⁻¹, however, are very weak. It appears that the 990, 970, and 840 cm⁻¹ Raman peaks are formed at the expense of the 1030, 1010, and 880 cm⁻¹ Raman peaks from the oxygen-18 isotope exchange.

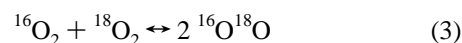
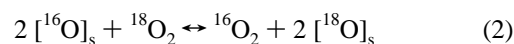
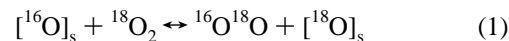
The same results were obtained for the 1 and 3 wt % CrO₃/ZrO₂ catalysts; however, more reduction–reoxidation cycles were necessary to achieve complete oxygen-18 isotopic exchange. It seems that the efficiency of the isotopic exchange reaction increases with increasing Cr loading.

Similar oxygen-18 isotopic exchange results are obtained for the 3 wt % CrO₃/TiO₂ catalyst (not shown for brevity). The initial RS spectrum after calcination in ¹⁶O₂ is also characterized by three Raman peaks at 1030, 1010, and 880 cm⁻¹. These Raman peaks decrease in intensity after reducing the sample with butane, followed by recalcination in ¹⁸O₂ at 450 °C. In addition, the band at 880 cm⁻¹ shifts to lower energy values. After applying 25 reduction–reoxidation cycles, a RS spectrum almost identical to the 6 wt % CrO₃/ZrO₂ catalyst is obtained, but the Raman peak intensities are always much weaker. The oxygen-18-exchanged RS spectra of the 5 wt % CrO₃/Al₂O₃ catalyst, obtained after successive butane reduction–¹⁸O₂ oxidation cycles are also very similar (not shown for brevity). The initial RS spectrum after calcination in ¹⁶O₂ is dominated by three Raman peaks at around 1005, 990, and 800 cm⁻¹. The Raman peaks at around 1005 and 990 cm⁻¹ decrease in intensity at the expense of a new Raman peak at 970 cm⁻¹ after the reduction–reoxidation cycles at 450 °C. Thus, essentially the same main spectral features are observed for CrO₃/Al₂O₃ as for the CrO₃/ZrO₂ and CrO₃/TiO₂ catalysts; however, the CrO₃/Al₂O₃ Raman spectra are always noisy and more difficult to interpret.

Discussion

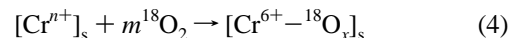
1. Isotopic Exchange Reaction: Efficiency and Mechanism. Our experiments clearly show that a high number of redox cycles and severe reduction conditions are necessary for an almost complete oxygen-18 isotopic exchange reaction. The efficiency of the isotopic exchange reaction seems to be support and treatment dependent, and this observation suggests that the oxygens of the support are playing an important role in the exchange process. This merits a more detailed discussion.

Isotopic exchange studies on oxides have been done in the 1950s and 1960s by Nováková, Winter, and Boreskov.^{11–16} They have shown that the oxygen atoms of the inorganic oxides such as ZrO₂, TiO₂, and Al₂O₃ undergo isotopic labeling with ¹⁸O₂ at relatively high temperatures. According to Boreskov^{15,16} and Nováková,^{11,12} three types of exchange reactions could occur on oxide surfaces:



s indicating support and reaction 1 always dominant for the supports under investigation.

In addition, ¹⁸O₂ reoxidizes the reduced Crⁿ⁺ species (obtained after reduction with butane) on the support, according to



with n indicating oxidation state (n < 6) and s, surface.

Our experiments show that reactions 1 and 4 take place because (a) an increase of the oxide coverage by CrO₃ (increasing Cr oxide loading) and (b) an increase of the reduction temperature (more [Crⁿ⁺]_s) result in a reduction of the number of reduction–reoxidation cycles necessary for complete isotopic exchange. In other words, reaction 4 becomes dominant over reaction 1 for increasing Cr oxide loading and reduction temperature.

It is clear that supports with a lower surface area (i.e. ZrO₂ and TiO₂) give rise to better resolved RS spectra after isotopic exchange because they are more covered by CrO₃. The presence of some fluorescence for the CrO₃/Al₂O₃ catalyst may originate from the residual hydrocarbon on the alumina surface due to the strong Lewis acid sites present on this support. The necessity of a large number of reduction–reoxidation cycles for complete isotopic labeling also implies that the surface oxygens of the support and the supported chromium oxides are highly mobile and can be interchanged. Direct evidence for such a spillover effect comes from a recent study of Martin and Duprez for Rh supported catalysts.⁹

2. Molecular Structure of Supported Chromium Oxide Species. The present oxygen-18 isotopic exchange experiments provide fundamental information about the number of terminal Cr=O bonds, mono-oxo versus di-oxo (see Figure 1), present in the isolated and polymerized surface chromium oxide species. For the supported chromium oxide catalysts containing comparable amounts of the two oxygen isotopes, a mono-oxo should give rise to two strong vibrations, Cr=¹⁶O and Cr=¹⁸O, and a di-oxo structure should exhibit three strong vibrations, ¹⁶O=Cr=¹⁶O, ¹⁸O=Cr=¹⁸O, and ¹⁶O=Cr=¹⁸O, the latter is expected to be predominant. Furthermore, a Raman peak

characteristic of a Cr–O simple oscillator will lead to an isotopic ratio calculated as

$$\frac{\nu(\text{Cr}^{-16}\text{O})}{\nu(\text{Cr}^{-18}\text{O})} = \left[\left(\frac{1}{52} + \frac{1}{18} \right)^{1/2} \left/ \left(\frac{1}{52} + \frac{1}{16} \right) \right. \right] \quad (5)$$

of 0.9566. For the polymerized surface chromium oxide species, only two strong Raman peaks are observed after oxygen-18 isotopic exchange at 1010 and 970 cm^{-1} , and the third strong band expected at around 990 cm^{-1} for a di-oxo structure is not observed. The observed isotopic shift of 40 cm^{-1} is close to the theoretical shift of 44 cm^{-1} . The weak Raman peak present at 990 cm^{-1} is associated with the isolated surface chromium oxide species. It is always possible that if the bond angle in a CrO_2 group is near 90° and for an appropriate interaction force constant between the two Cr=O groups, then only one new Raman peak would be observed on total oxygen-18 isotope exchanged Cr systems. However, it seems rather unlikely that this would arise together on ZrO_2 , TiO_2 , and Al_2O_3 surfaces. For the isolated surface chromium oxide species, two weak Raman peaks are observed at 1030 and 990 cm^{-1} , and the third band for a di-oxo structure would be expected at around 1010 cm^{-1} . However, the strong 1010 cm^{-1} Raman peak for the polymeric surface chromium oxide species occurs at this location and prevents discrimination between mono-oxo and di-oxo structures for the isolated surface chromium oxide species based on isotopic oxygen exchange experiments. The observed isotopic shift of the 1030 cm^{-1} Raman peak (40 cm^{-1}), however, is close to the expected shift of 45 cm^{-1} .

Summarizing, the isotopic oxygen exchange experiments reveal that the polymeric surface chromium oxide species possesses a mono-oxo structure. Additional experiments are required for the structural determination of the isolated surface chromium oxide species because of its weak Raman signal, but such experiments will be possible only if one can selectively reduce the polymeric species so that Raman spectroscopy shows only the isolated species. This, however, will be a difficult task.

Additional evidence for the proposed molecular structures can be found in an earlier publication of our group, in which dehydrated Raman and IR spectra of supported chromium oxide catalysts are compared.⁵ The relative intensities of the 1030 and 1010 cm^{-1} Raman and IR bands are the same, which is consistent with mono-oxo structures since di-oxo structures would give rise to more intense Cr=O symmetric vibrations in the Raman and more intense Cr=O antisymmetric vibrations in the IR.¹⁷ Furthermore, the IR overtone region only exhibits two bands due to Cr=O vibrations, 1986–1995 and 2010–2015 cm^{-1} , which is only consistent with two mono-oxo surface chromium oxide species since di-oxo species would give rise to three combination bands (symmetric, antisymmetric, and a combination mode).¹⁷ Thus, the oxygen-18 isotopic exchange experiments and the corresponding *in situ* Raman/IR measurements are consistent with the mono-oxo structure for the isolated as well as polymerized surface chromium oxide species. Such detailed structural information is new and could not be obtained in the past by other spectroscopic techniques, like diffuse reflectance spectroscopy.^{18–21} It is also important to mention here that the presence of mono-oxo surface species is also revealed by a combination of IR spectroscopy and oxygen-18 isotopic exchange experiments in Cr_2O_3 , $\text{MoO}_3/\text{SiO}_2$, $\text{SO}_4/\text{Al}_2\text{O}_3$, and SO_4/TiO_2 , and $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts.^{22–25}

Conclusions

Combined *in situ* laser Raman spectroscopy and oxygen-18 labeling studies is a powerful technique for the elucidation of the molecular structure of chromium oxide structures supported on ZrO_2 , TiO_2 , and Al_2O_3 . The present investigation reveals that supported chromium oxide species possess, independent of their polymerization degree, a mono-oxo structure. Complete isotopic exchange with $^{18}\text{O}_2$ is difficult to achieve and several successive butane reduction– $^{18}\text{O}_2$ oxidation cycles at relatively high temperature are required. The support oxide, the reaction temperature, and the Cr loading seem to have a strong influence on the efficiency of the isotopic exchange process.

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