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RAMAN SPECTROSCOPY OF CHROMIUM OXIDE SUPPORTED ON Al_2O_3, TiO_2 AND SiO_2: A COMPARATIVE STUDY

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Summary

The interaction of chromium oxide with Al_2O_3, TiO_2 and SiO_2 supports is investigated with Raman spectroscopy. The influence of the nature of the oxide support, calcination temperature and chromium oxide loading upon the molecular state of the supported chromium oxide is determined. The Raman studies reveal that the oxide supports stabilize the chromium oxide as Cr(VI) in tetrahedral coordination at moderate chromium oxide coverages. The surface chromium oxide is present as monomers and dimers on alumina, monomers and possibly dimers on titania, and monomers and polymers (dimers, trimers and tetramers) on silica. On the alumina support, the ratio of dimers/monomers increases with the chromium oxide coverage. On the silica support, the ratios of trimers/dimers and tetramers/dimers also increase with chromium oxide coverage. The surface chromium(VI) oxide species on titania, however, are not stable to elevated calcination temperatures and appear to be converted to a lower chromium oxide oxidation state. The silica support stabilizes the surface chromium(VI) oxide state at elevated calcination temperatures, but the surface chromium oxide polymers are not stable and convert to isolated surface chromium(VI) oxide monomers. Most of these differences are thought to be related to the differing surface-hydroxyl chemistries of Al_2O_3, TiO_2 and SiO_2 supports.

Introduction

Supported chromium oxide catalysts have found wide application in the petrochemical industry [1]. They have been employed in numerous industrial processes: naphtha reforming, butadiene manufacture, *ortho–para* hydrogen conversion in liquid hydrogen manufacture, automotive exhaust purification, and the production of polyethylene. These applications are a direct consequence of the high activity of supported chromium oxide catalysts in the hydrogenation and dehydrogenation reactions of hydrocarbons, the dehydrocyclization of paraffins, and the polymerization of olefins. The industrial importance of supported chromium oxide catalysts has generated much interest in their physicochemical properties [2 - 4].

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Some of the techniques used to examine supported chromium oxide catalysts include X-ray diffraction, magnetic susceptibility studies, electron spin resonance, nuclear magnetic resonance, optical reflectance spectroscopy and electrical property measurements [2 - 4]. These characterization studies have significantly advanced our understanding of supported chromium oxide catalysts, but a complete molecular picture of these complex and important catalytic materials has not emerged.

The multiple chromium states that can simultaneously be present in the supported chromium oxide phase has led to much confusion in the literature. This confusion has resulted primarily because of the lack of adequate characterization techniques capable of discriminating between these different states.

A technique particularly suited to the study of the molecular structure of supported chromium oxide catalysts is Raman spectroscopy [5]. Raman spectroscopy can discriminate between the different molecular states of supported metal oxides, because each state possesses a unique vibrational spectrum that is related to its structure. Therefore, Raman spectroscopy provides direct information about the structure of each state as well as a method of discriminating between the various molecular states. Only a few Raman investigations, however, have been performed on supported chromium oxide catalysts, and these studies were limited to CrO_3/Al_2O_3 catalysts where the chromium oxide loading was varied [5 - 7]. In the present investigation, we report on the Raman spectroscopy of supported chromium oxide catalysts where the oxide support (Al_2O_3, TiO_2 and SiO_2), calcination temperature and chromium oxide loading are varied. The influence of these three parameters (nature of oxide support, calcination temperature and chromium oxide loading) upon the molecular state of the supported chromium oxide is presented.

Experimental

The supported chromium oxide catalysts were prepared by the incipient-wetness impregnation method with an aqueous solution of $Cr(NO_3)_3$. The oxide supports consist of γ-Al_2O_3 (Harshaw, 180 $m^2\ g^{-1}$), TiO_2 (Degussa P-25, anatase/rutile ~2, 55 $m^2\ g^{-1}$), and SiO_2 (Cab-O-Sil, amorphous, 300 $m^2\ g^{-1}$). The impregnated samples were subsequently dried at room temperature for 16 h, dried at 110 - 120 °C for 16 h, and calcined at 500 °C for 16 h or 700 °C for 2 h to form the supported chromium oxide catalysts.

Raman spectra were obtained with a Spectra-Physics Ar^+ laser (Model 2020-05) delivering 1 - 100 mW incident radiation measured at the sample, where the exciting line was typically 514.5 nm. The scattered radiation was then directed into a Spex Triplemate spectrometer (Model 1877) coupled to a Princeton Applied Research OMA III optical multichannel analyzer (Model 1463) with an intensified photodiode array cooled thermoelectrically to −30 °C. The Raman spectra were recorded using an OMA III dedicated computer and software. The overall resolution was experimentally determined to be better than 3 cm^{-1} in cases where the spectral range was about 800 cm^{-1}. All Raman spectra were obtained at room temperature and under ambient conditions unless otherwise stated. Additional details about the laser Raman apparatus can be found elsewhere [5].

Results and discussion

The Raman spectrum of a metal oxide contains detailed structural information because the Raman vibrational modes are determined by the symmetry and structure of the coordinated compound. The relationship between the metal oxide structures and the corresponding Raman vibrational spectra of several chromium oxide reference compounds are presented below prior to discussion of the supported chromium oxide catalysts.

Chromium oxide reference compounds

The aqueous chemistry of chromium oxide has been widely investigated [8]. Chromium(VI) is extensively hydrolyzed in water, giving only neutral or anionic species. The species are $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$; with some evidence for the formation of H_2CrO_4 in relatively concentrated acid. All the equilibria occur rapidly, with $Cr_2O_7^{2-}$ dominating in acidic solutions at concentrations above 0.01 M and CrO_4^{2-} dominating in basic solutions. More recent studies have shown that, under extreme conditions of acidity and high chromium concentrations, chromium oxide trimers, $Cr_3O_{10}^{2-}$, and tetramers, $Cr_4O_{12}^{2-}$, are also present in aqueous solutions [9].

The Raman spectra of CrO_4^{2-}, $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ ions are schematically illustrated in Fig. 1 as free ions in aqueous solution (reproduced from [9]). The vibrational assignments for these ions are presented in Table 1 [9, 10]. In general, chromium(VI) oxide compounds possess strong Raman bands in the 800 - 1000 cm^{-1} region due to Cr—O stretching modes, and bands of moderate intensity in the 300 - 400 cm^{-1} region due to the Cr—O bending modes. These Raman band positions are consistent with the tetrahedral coordination assigned to the chromates. Tetrahedrally coordinated molecules of the type CrO_4 possess four Raman-active fundamental modes of vibration: symmetric and antisymmetric stretching modes, and two bending modes (846, 904, 371 and 348 cm^{-1} for the isolated chromate ion, respectively). In the case of dimers, trimers and tetramers (see Fig. 1 and Table 1), bands appear in the Raman spectrum which have been assigned to Cr—O—Cr linkages (772 - 844 cm^{-1}, 525 - 557 cm^{-1} and 209 - 217 cm^{-1}) and CrO_2 chain moieties (956 - 987 cm^{-1}), both resulting from polymerization of the monomeric chromate units [9, 10]. Similar Raman spectra are observed for solid chromium(VI) oxide compounds possessing monomers, dimers, trimers and tetramers, but the Raman spectra for the solid compound contain additional Raman bands due to the slight distortion of the chromium oxide units in the solid state [11].

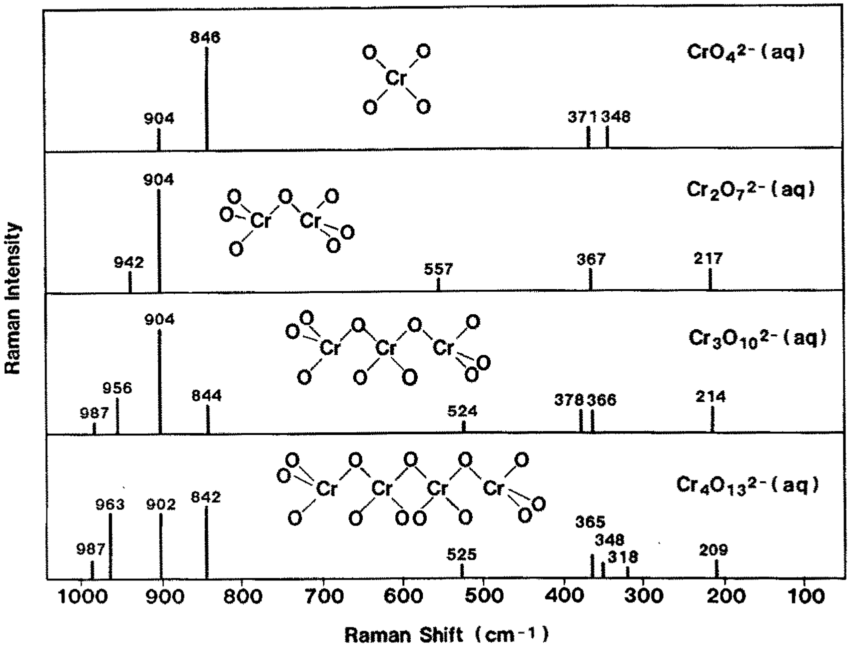

Fig. 1. Raman spectra of aqueous chromium(VI) oxides.

TABLE 1

Raman band assignments for chromium(VI) oxide compounds [9 - 11]

Band assignments[a]	Monomer	Dimer	Trimer	Tetramer
as (CrO_2)			987	987
ss (CrO_2)			956	963
as (CrO_3)	904	942	942[b]	942[b]
ss (CrO_3)	846	904	904	902
as (CrOCr)		772 (vw)	844	842
ss (CrOCr)		557	524	525
b (CrO_3)	371	367	378	365
	348		366	348
				318
b (CrOCr)		217	214	209

[a] as = antisymmetric stretch, ss = symmetric stretch, b = bending.
[b] Estimated Raman frequencies.

The Raman spectra of crystalline Cr_2O_3 and $Cr_{0.25}Al_{1.75}O_3$ which contain Cr(III) are presented in Fig. 2. The $Cr_{0.25}Al_{1.75}O_3$ reference material contains Cr(III) in solid solution with α-Al_2O_3 (corundum). The Cr(III) reference compounds exhibit Raman bands in the 500 - 600 cm^{-1} region due to their lower oxidation state relative to the Cr(VI) compounds that exhibit Raman bands in the 800 - 1000 cm^{-1} region. The Raman spectra reveal that

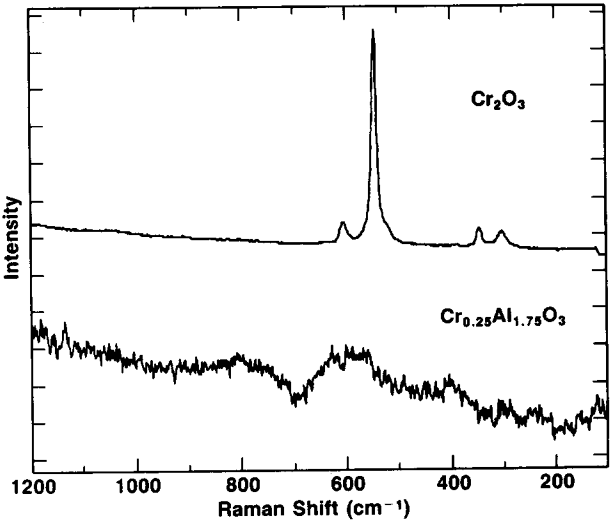

Fig. 2. Raman spectra of solid chromium(III) oxides.

the different molecular states of chromium oxide, especially Cr(VI) compounds, can be discriminated with Raman spectroscopy.

Chromium oxide supported on alumina

The Raman spectra of a series of chromium oxide on alumina catalysts are presented in Fig. 3 as a function of chromium oxide coverage and after

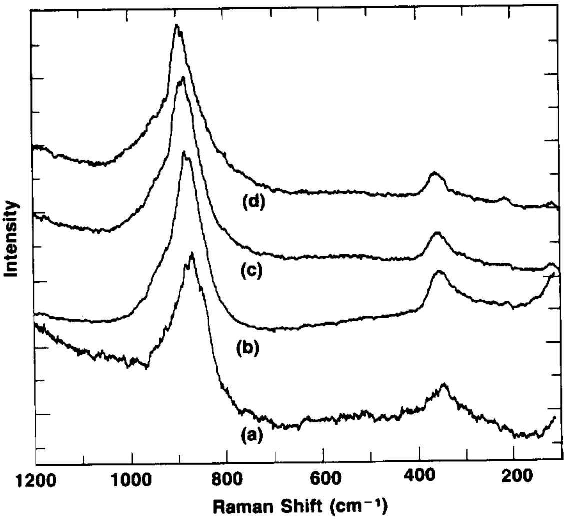

Fig. 3. Raman spectra of chromium oxide supported on alumina, calcined at 500 °C, as a function of chromium oxide coverage; (a) 0.5% CrO_3, (b) 1% CrO_3, (c) 3% CrO_3, (d) 5% CrO_3.

calcination at 500 °C. The Raman band positions are indicative of Cr(VI) oxides, and the oxidation state is further confirmed by X-ray photoelectron spectroscopy measurements. The 0.5% CrO_3/Al_2O_3 sample possesses Raman bands at ~880 and ~350 cm^{-1}. These bands are assigned to the symmetric stretching and bending modes, respectively, and are consistent with an isolated tetrahedral surface-chromate species that is distorted by its interaction with the oxide support surface (shift from 846 to 880 cm^{-1}) [9, 10].

As the chromium oxide surface coverage is increased, the symmetric stretching and bending modes shift upward to 896 and 362 cm^{-1}, respectively. In addition, a new band appears at 217 cm^{-1} due to the presence of Cr—O—Cr linkages. The upward shift in frequency of the Raman bands and the appearance of the new band at 217 cm^{-1} are indicative of chromium oxide dimers which have also formed on the alumina surface at higher chromium oxide coverages. The chromium oxide trimers and tetramers are characterized by the appearance of additional Raman bands at ~990 and ~840 cm^{-1} due to the presence of non-terminal chromate units (*i.e.* bridging CrO_2 moieties) [9, 10]. The absence of Raman bands in these regions reveals that only surface chromium oxide monomers $[CrO_4]_{ads}$, and dimers, $[Cr_2O_7]_{ads}$, are present in CrO_3/Al_2O_3 samples.

The influence of calcination temperature upon a 3% CrO_3/Al_2O_3 sample was also examined. The Raman spectra of 3% CrO_3/Al_2O_3 calcined at 500 and 700 °C are shown in Fig. 4. There does not appear to be any significant difference between the two Raman spectra. Similar results were obtained with other CrO_3/Al_2O_3 catalysts. This demonstrates that the surface chromium oxide species on alumina, $[CrO_4]_{ads}$ and $[Cr_2O_7]_{ads}$, are stable to elevated calcination temperatures.

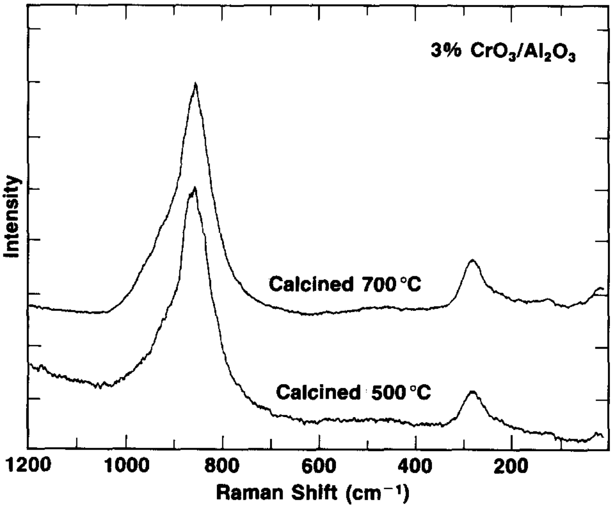

Fig. 4. Raman spectra of 3% CrO_3/Al_2O_3 as a function of calcination temperature.

The supported metal oxides have been shown to contain adsorbed water from the ambient environment which is readily desorbed by thermal treatments (*in situ* or laser-induced dehydration) [5, 12]. The effect on the Raman spectrum of heating the 3% CrO_3/Al_2O_3 samples by increasing the laser power is shown in Fig. 5. The dehydration causes the Raman band at 887 cm^{-1} to split into two bands located at ~883 and ~1016 cm^{-1}. The band at ~1016 cm^{-1} originates from dehydrated surface chromium oxide species [5, 12], and the band at ~883 cm^{-1} is due to the surface chromium oxide species that are interacting with the surface hydroxyls of the alumina support. Similar results were observed with the other CrO_3/Al_2O_3 catalysts, and with *in situ* experiments [6] where the temperature and environment of the CrO_3/Al_2O_3 catalysts were controlled.

The CrO_3/Al_2O_3 Raman studies reveal that the alumina support stabilizes the supported chromium oxide as Cr(VI) in tetrahedral coordination. The surface chromium oxide is present as monomers and dimers, and the relative ratio of dimers/monomers increases with increasing chromium oxide coverage on the alumina support. The surface chromium oxide species are stable to elevated calcination temperatures and upon dehydration. Essentially the same observations and conclusions were made by Wang [6].

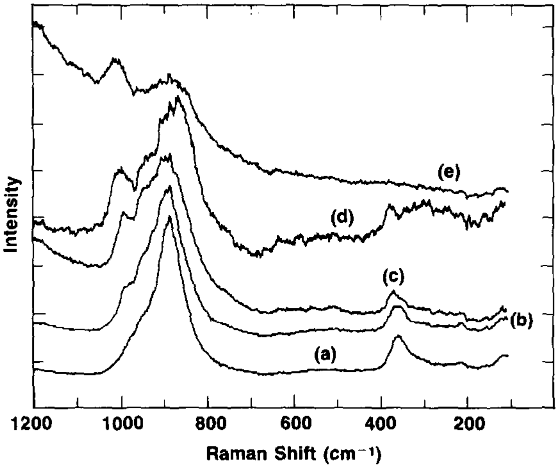

Fig. 5. Raman spectra of laser-induced dehydration of 3% CrO_3/Al_2O_3: increasing laser power from (a) to (e).

Chromium oxide supported on titania

The Raman spectra of 1% and 3% CrO_3 supported on titania are presented in Fig. 6 for calcination at 500 °C. The strong TiO_2 Raman features below 700 cm^{-1} prevent the acquisition of chromium oxide Raman bands in this region [12]. Thus, only chromium oxide symmetric and antisymmetric stretching modes in the 800 - 1000 cm^{-1} region can be obtained for the CrO_3/TiO_2 system. The 1% and 3% CrO_3/TiO_2 catalysts exhibit bands at ~880 cm^{-1}, similar to those observed for CrO_3/Al_2O_3 and consistent with

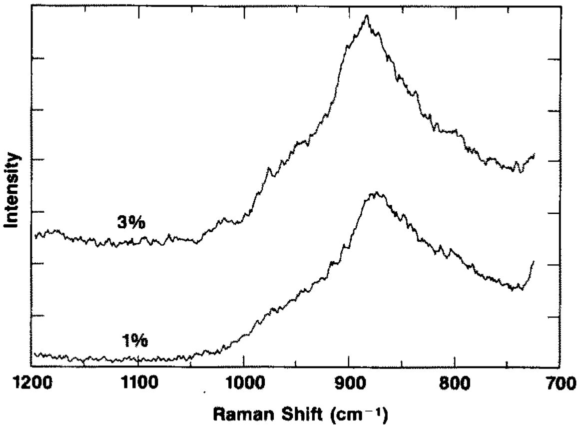

Fig. 6. Raman spectra of chromium oxide supported on titania, calcined at 500 °C, as a function of chromium oxide coverage.

the presence of an isolated tetrahedral surface chromium(VI) oxide species distorted by interaction with the oxide support surface. It is not possible to determine if surface chromium oxide dimers are also present on the alumina support at high coverages because of the inability to observe the Cr—O—Cr bending modes which occur at ~217 cm^{-1}. The absence of Raman bands at ~990 and ~842 cm^{-1}, which originate with non-terminal chromate units [9, 10], reveals that surface chromium oxide trimers and tetramers are not present in the CrO_3/TiO_2 catalysts.

The calcination temperature dependence of a 1% CrO_3/TiO_2 catalyst is presented in Fig. 7. The thermal response of the 1% CrO_3/TiO_2 is very unlike that observed for the corresponding CrO_3/Al_2O_3 sample. The 1% CrO_3/TiO_2 catalyst calcined at 500 °C exhibits a Raman band at ~880 cm^{-1} due to the symmetric stretch of the surface chromate species and a weaker shoulder at ~800 cm^{-1} which originates from a second-order transition of

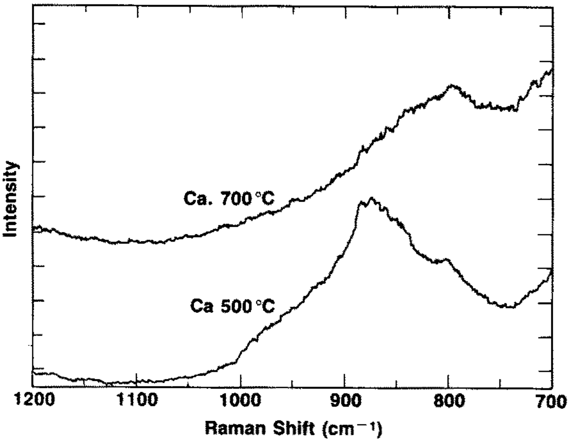

Fig. 7. Raman spectra of 1% CrO_3/TiO_2 as a function of calcination temperature.

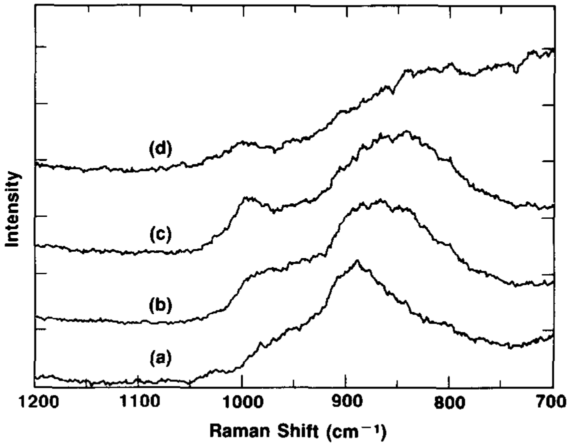

Fig. 8. Raman spectra of laser-induced dehydration of 4% CrO_3/TiO_2 calcined at 500 °C; increasing laser power from (a) to (d).

the TiO_2 (anatase) support [12]. Upon heating the 1% CrO_3/TiO_2 sample to 700 °C, the surface chromate Raman band at ~880 cm^{-1} disappears.

Similar behavior was observed for the 3% CrO_3/TiO_2 sample. The disappearance of the chromium oxide Raman band at ~880 cm^{-1} suggests that the chromium oxide is being transformed from a Cr(VI) surface species to a chromium species with a lower oxidation state which would be expected to have Raman bands below 700 cm^{-1} (see Fig. 2 for Cr(III) oxides).

The influence of dehydration upon the Raman spectrum of the 4% CrO_3/TiO_2 catalyst is shown in Fig. 8. The response is similar to that seen with CrO_3/Al_2O_3, where bands at ~1016 cm^{-1}, due to the dehydrated surface chromium oxide species, and at ~883 cm^{-1}, due to the surface chromium oxide species that are interacting with the surface hydroxyls of the titania support, are produced. Similar results were obtained with the 1% CrO_3/TiO_2 catalyst.

The CrO_3/TiO_2 Raman studies reveal that the titania support, as the alumina support, also stabilizes the supported chromium oxide as Cr(VI) in tetrahedral coordination. The surface chromium oxide is present as monomers and possibly dimers. The titania support, unlike the alumina support, does not stabilize the surface Cr(VI) oxide species at elevated calcination temperatures, such as 700 °C. Additional studies are needed in order to determine if the chromium oxide on TiO_2 remains as a surface species or undergoes a solid-state reaction with the titania support at 700 °C. The findings do show, however, that surface chromium oxide interacts more strongly with the alumina support surface than the titania support surface.

Chromium oxide supported on silica

The Raman spectra of a series of chromium oxide on silica catalysts are presented in Fig. 9 as a function of chromium oxide coverage for calcination at 500 °C. The 0.2% CrO_3/SiO_2 catalyst possesses Raman bands that originate

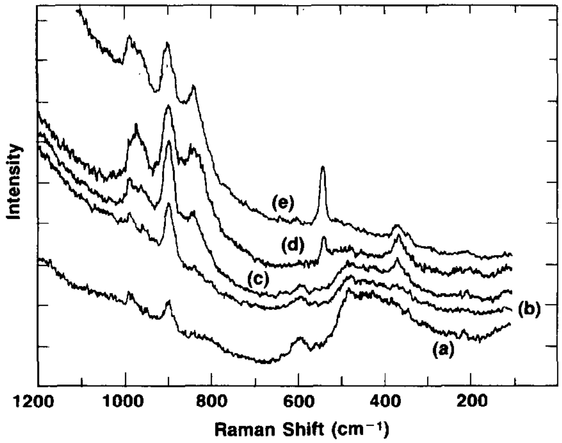

Fig. 9. Raman spectra of chromium oxide supported on silica, calcined at 500 °C, as a function of chromium oxide coverage; (a) 0.2%, (b) 0.5%, (c) 1%, (d) 3%, (e) 4% CrO_3.

with the supported chromium oxide phase as well as the silica support. The broad band centered at 432 cm^{-1} and the sharper bands at 492 and 607 cm^{-1} are characteristic Raman features of the SiO_2 support [13]. The SiO_2 Raman features decrease in intensity as the CrO_3 coverage increases, due to the increased coloration of the sample by the supported chromium oxide (yellowish color). The Raman band positions are indicative of Cr(VI) oxides and in agreement with other measurements on CrO_3/SiO_2 containing moderate amounts of chromium oxide [4]. The 0.2% CrO_3/SiO_2 sample exhibits Raman bands at 898 and 991 cm^{-1} as well as weak bands at 217, 840 and 962 cm^{-1}. The 991 cm^{-1} band is related to sample dehydration, since its relative intensity increased with increasing laser power. The relative intensity of the 898 cm^{-1} band is consistent with surface chromium oxide possessing both monomers and dimers, the 840 and 962 cm^{-1} bands are consistent with surface chromium oxide trimers, and the 217 cm^{-1} band is representative of Cr—O—Cr bonds.

As the chromium oxide coverage is increased to 1% CrO_3/SiO_2, the Raman bands at 962 and 840 cm^{-1} increase relative to the band at 898 cm^{-1}. The relative intensity ratio of these peaks is very similar to that obtained for chromium oxide trimers (see Fig. 1) and suggests that surface chromium oxide trimers predominate on the silica catalyst surface at this coverage and calcination temperature.

A further increase in the chromium oxide coverage to 4% CrO_3/SiO_2 increases the intensities of the 963 and 844 cm^{-1} bands relative to the 902 cm^{-1} band. These changes suggest that surface chromium oxide tetramers predominate on the silica support surface at this coverage and calcination temperature (see Fig. 1). The slight shift in wavenumber of the 898 cm^{-1} band to 902 cm^{-1} indicates that the ratio of dimers/monomers increases with chromium oxide coverage. The 989 cm^{-1} band, assigned to a dehydrated chromium oxide surface species, is also observed to increase in relative

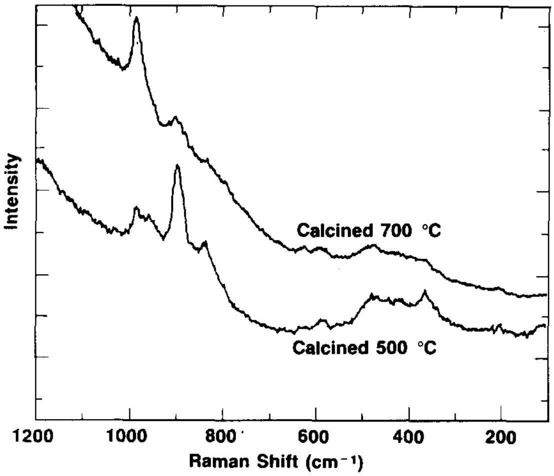

Fig. 10. Raman spectra of 1% CrO_3/SiO_2 as a function of calcination temperature.

intensity with chromium oxide coverage. The 3% and 4% CrO_3/SiO_2 samples also exhibit the appearance of a new band at 543 cm^{-1} which is due to the presence of Cr_2O_3 crystallites.

The influence of calcination temperature upon 1% CrO_3/SiO_2 is shown in Fig. 10. Calcination at 700 ℃ dramatically changes the Raman spectrum of CrO_3/SiO_2 and is related to the known dehydroxylation of the SiO_2 support at these temperatures [4]. The appearance of a strong Raman band at 989 cm^{-1} and a very weak Raman band at 907 cm^{-1} is consistent with the extensive dehydroxylation of the silica support surface by the calcination treatment [5, 12]. The strong band at 989 cm^{-1} is associated with the dehydrated surface chromium oxide species and the weak band at 907 cm^{-1} is due to surface chromium oxide species interacting with the remaining surface hydroxyls of the silica support. The decrease in the number of Raman bands in the 800 - 1000 cm^{-1} region for the 1% CrO_3/SiO_2 sample upon calcination at 700 ℃ and the upward shift to a single strong Raman band at 989 cm^{-1}, similar to that observed for the CrO_3/Al_2O_3 and CrO_3/TiO_2 samples upon dehydration, suggest that the surface chromium oxide is converted primarily to a monomer upon calcination at elevated temperatures. Essentially the same results were obtained by laser-induced dehydration of 3% CrO_3/SiO_2, as shown in Fig. 11. The same results were also observed for the other CrO_3/SiO_2 catalysts. These results suggest that surface chromium(VI) oxide polymers (dimers, trimers and tetramers) are not stable on the SiO_2 support under conditions that cause surface dehydration/dehydroxylation, and that they convert to isolated surface chromium(VI) oxide monomers, $[CrO_4]_{ads}$.

The CrO_3/SiO_2 Raman studies reveal that the silica support, as the alumina and titania supports, also stabilizes the supported chromium oxide as Cr(VI) in tetrahedral coordination. This only holds for moderate coverages of chromium oxide on silica because Cr_2O_3, possessing Cr(III), is formed

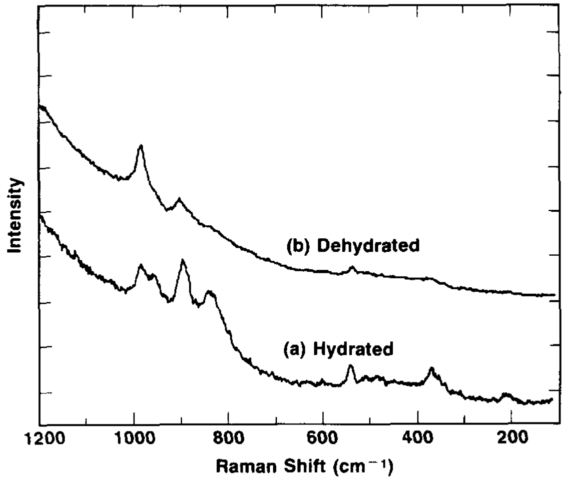

Fig. 11. Raman spectra of laser-induced dehydration of 3% CrO_3/SiO_2 calcined at 500 °C.

above ~3% CrO_3/SiO_2. The surface chromium oxide on silica is present as chromium oxide polymers (dimers, trimers and tetramers). The silica support, as the alumina support, stabilizes the surface Cr(VI) oxide state toward elevated calcination temperatures such as 700 °C. The surface chromium oxide polymers are not stable on the SiO_2 support under conditions that cause surface dehydration/dehydroxylation, and are converted to isolated surface chromium(VI) oxide monomers. The very different behavior of the CrO_3/SiO_2 interaction compared to CrO_3/Al_2O_3 and CrO_3/TiO_2 interactions is related to the surface density of the surface hydroxyls and their surface chemistry [4, 14]. Silica has a low surface concentration of hydroxyls relative to Al_2O_3 and TiO_2 supports.

In general, the dispersed chromium oxide species anchor to the oxide supports by reacting with the surface hydroxyls. The absence of a significant population of surface hydroxyls on SiO_2 is responsible for the formation of crystalline Cr_2O_3 at low surface coverages of chromium oxide, ~3% CrO_3/SiO_2 on a SiO_2 support possessing ~300 $m^2\ g^{-1}$. In contrast, it is possible to disperse 13 - 15% CrO_3 on an Al_2O_3 support containing ~180 $m^2\ g^{-1}$ before crystalline Cr_2O_3 is formed [15]. The capacity of the TiO_2 support to maintain dispersed surface chromium oxide is ~4% CrO_3/TiO_2, but this is related to the lower surface area of the titania support, ~55 $m^2\ g^{-1}$, and not to a significantly different hydroxyl surface density relative to alumina. The surface chromium oxide density is comparable on Al_2O_3 and TiO_2 supports when normalized to surface area. In the presence of a high concentration of surface hydroxyls, as found on the Al_2O_3 and TiO_2 supports, chromium oxide chains cannot grow very long before encountering surface hydroxyls. The surface hydroxyls appear to serve as chain terminators. Thus for Al_2O_3 and TiO_2 only surface chromium oxide monomers and dimers are observed, and the monomers appear to predominate.

The much lower surface hydroxyl concentration of SiO_2 allows the surface chromium oxide to polymerize to trimers and tetramers before surface hydroxyls are encountered. The lower surface hydroxyl population on SiO_2 accounts for both the formation of crystalline Cr_2O_3 at low chromium oxide coverage on silica and the formation of chromium oxide trimers and tetramers on silica.

The different hydroxyl surface chemistry of silica and alumina is also responsible for the different behavior of the CrO_3/Al_2O_3 and CrO_3/SiO_2 systems towards calcination at elevated temperatures. The surface hydroxyl concentration on the Al_2O_3 support does not change much between calcination at 500 and at 700 °C, and the surface is readily rehydrated upon exposure to moisture [14]. Thus, the CrO_3/Al_2O_3 catalysts examined under ambient conditions, before and after calcination, are similar. By contrast, the surface hydroxyl concentration on the SiO_2 support is not as stable and significantly decreases between calcination at 500 and at 700 °C [4]. Furthermore, the dehydroxylated silica is very slow to rehydrate upon exposure to moisture. Thus, the CrO_3/SiO_2 catalysts examined under ambient conditions, before and after calcination, are very different, the post-calcined CrO_3/SiO_2 catalysts being indistinguishable from dehydrated CrO_3/SiO_2 catalysts. Prolonged exposure to moisture, however, will rehydroxylate the CrO_3/SiO_2 surface and give similar Raman results. But, even under conditions of very low laser power, a dehydrated surface chromium oxide species is still detected. The different hydroxyl surface chemistry was also reflected in the laser-induced dehydration experiments. The CrO_3/Al_2O_3 samples exhibited a large population of dehydrated and hydroxylated surface chromium oxide species. The CrO_3/SiO_2 sample possessed a large population of dehydrated surface chromium oxide species, and a very small population of hydroxylated surface chromium oxide species.

Conclusion

The interaction of chromium oxide with Al_2O_3, TiO_2 and SiO_2 supports was investigated with Raman spectroscopy. The influence of the nature of the oxide support, calcination temperature and chromium oxide loading upon the molecular state of the supported chromium oxide was determined. The Raman studies reveal that the oxide supports stabilize the supported chromium oxide as Cr(VI) in tetrahedral coordination at moderate chromium oxide coverage. The surface chromium oxide is present as monomers and dimers on alumina, monomers and possibly dimers on titania, and monomers and polymers (dimers, trimers and tetramers) on silica. On the alumina support, the ratio of dimers/monomers increases with the chromium oxide coverage. On the silica support, the ratios of trimers/dimers and tetramers/dimers also increase with chromium oxide coverage. The surface chromium(VI) oxide species on titania, however, are not stable to elevated calcination temperatures and appear to be converted to a lower chromium oxide oxidation state. The silica support stabilizes the surface chromium(VI) oxide state at elevated calcination temperatures, but the surface chromium oxide polymers are not stable and convert to isolated surface chromium(VI) oxide monomers. Most of these differences are thought to be related to the differing surface-hydroxyl chemistries of Al_2O_3, TiO_2 and SiO_2 supports.

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