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## Characterization of chromium oxide supported on $\text{Al}_2\text{O}_3$ , $\text{ZrO}_2$ , $\text{TiO}_2$ , and $\text{SiO}_2$ under dehydrated conditions

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### Abstract

In the present investigation, Raman and IR spectroscopy were used to study the surface structures of chromium oxide supported on alumina, titania, zirconia, and silica, as a function of the loading under dehydrated conditions. It was found, that the dehydrated surface structures of chromium oxide differ strongly from those previously reported under ambient conditions, in which the surfaces are hydrated. Two species, each possessing one short terminal Cr=O bond, and one (or more) oligomer(s) are proposed to be present on the dehydrated alumina, titania, and zirconia surfaces. The relative concentrations of these different chromium oxide species is independent of the surface coverage. The chromium oxide species present on the dehydrated silica surface are completely different from those observed on the other three supports. The Raman and IR spectra indicate the presence of an isolated chromium oxide species possessing two short Cr=O bonds together with a small amount of surface species possessing a terminal  $\text{CrO}_3$  unit, isolated or not. The gradual disappearance of the surface hydroxyl groups of all four supports upon addition of chromium oxide, as monitored by IR spectroscopy, suggests that the chromium oxide species interacts with the surface by removal of the surface hydroxyl groups.

**Key words:** alumina; chromium; silica; supported catalysts; titania; zirconia

### Introduction

Supported chromium oxide catalysts are known to possess excellent activity for the hydrogenation and dehydrogenation reactions of hydrocarbons, the dehydrocyclization of paraffins, and the polymerization of olefins [1]. It is now well established, that the catalytic properties of these systems are due to surface chromium oxide species, and not to bulk chromium oxides such as crystalline  $\text{CrO}_3$  or  $\text{Cr}_2\text{O}_3$  [2]. This knowledge has led to much interest in the molecular structures of the supported chromium oxide species, and the factors which determine the chromium oxide surface structures [2–21]. Many tech-

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niques have been used to characterize the chromium oxide surface structures, but especially Raman spectroscopy has shown to be a powerful technique to obtain detailed structural information [17-21].

A program has been started by our laboratories to study the support chromium oxide system by Raman spectroscopy as a function of surface coverage, support type, calcination temperature, and presence of moisture [19-21]. These Raman studies showed that after calcination at 500°C and re-exposure to the laboratory atmosphere several hydrated surface chromium oxide species are present on oxide supports such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and SiO<sub>2</sub>. The surface chromium oxide is present as hydrated chromate and dichromate species on alumina, hydrated chromate and possibly dichromate species on titania, and hydrated chromate and oligomeric species (dichromate, trichromate, and tetrachromate) on silica. The monomer/oligomer ratio decreases with increasing surface coverage. Further, it was shown that up to monolayer coverage (ca. 12% CrO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, ca. 6% CrO<sub>3</sub>/TiO<sub>2</sub>, and ca. 3% CrO<sub>3</sub>/SiO<sub>2</sub>) chromium oxide is stabilized as Cr(VI), whereas crystalline Cr<sub>2</sub>O<sub>3</sub> is found above monolayer coverage together with the hydrated chromium(VI) oxide surface species. Crystalline Cr<sub>2</sub>O<sub>3</sub> is not stable at elevated temperatures ( $\geq 800^\circ\text{C}$ ), and was found to react with alumina to form Cr(III) in solid solution with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

In the present paper, the influence of the loading and the support type ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>) on the surface chromium(VI) oxide structures are studied under dehydrated conditions by *in situ* Raman and FTIR spectroscopy. In addition to the investigation of the dehydrated surface chromium oxide structures, the interaction of these species with the support surface hydroxyl groups are also studied by monitoring the change in the OH stretching region by FTIR spectroscopy.

## Experimental

### Sample preparation

The samples were prepared by the incipient-wetness impregnation method with aqueous solutions of Cr(NO<sub>3</sub>)<sub>3</sub> of increasing concentrations. The oxide supports were  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Harshaw, 180 m<sup>2</sup>/g), SiO<sub>2</sub> (Cabot, Cab-O-Sil, 300 m<sup>2</sup>/g), TiO<sub>2</sub> (Degussa P-25, 55 m<sup>2</sup>/g), and ZrO<sub>2</sub> (Degussa, 39 m<sup>2</sup>/g). After the impregnation step, the samples were dried at room temperature and at 110°C overnight. Finally, the CrO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and CrO<sub>3</sub>/SiO<sub>2</sub> samples were calcined at 500°C overnight, while the CrO<sub>3</sub>/TiO<sub>2</sub> and CrO<sub>3</sub>/ZrO<sub>2</sub> samples were calcined at 450°C for 3 hours. The surface coverages were expressed as wt.% of CrO<sub>3</sub>, assuming that the chromium cation was in the +6 oxidation state after calcination at 450-500°C. The +6 oxidation state of the chromium cation for these samples has been determined previously by XPS [19,21]. All samples were recalined for 2 h at 450°C in dry air prior to the Raman analysis to minimize disturbing luminescence.

### Raman studies

The Raman spectra were recorded on a self supporting wafer. The samples were prepared *in situ* cell developed in ca. 1 h and kept in a vacuum oven (Linde gas) until cooled to ca. 50°C in ca. 4 h. The Raman spectra were recorded on a Bruker Raman spectrometer equipped with an Ortec 6615 photomultiplier (operating at -35°C, resolution 10 cm<sup>-1</sup>, Philips) was used with a laser power of 15-40 mW.

### FTIR studies

The FTIR spectra were recorded with a resolution of 2 cm<sup>-1</sup>. The samples were mounted into a Bruker IFS 66 FTIR spectrometer. The experimental conditions were: 4000-400 cm<sup>-1</sup>, self-scanning, 1000 scans were averaged, 4 cm<sup>-1</sup> resolution. For recording the alumina, zirconia, and silica supporting wafers, the samples were pressed into pellets in the overtone region (2000-3000 cm<sup>-1</sup>). The reported samples, however, were baseline-corrected and the IR spectra of the

## Results

### Surface chromium

#### CrO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>

The Raman spectra of the samples are presented in Fig. 1. All samples (0.5-9.5 wt.% CrO<sub>3</sub>) show a shoulder at 935 cm<sup>-1</sup>, 880 cm<sup>-1</sup> increasing coverage. The shoulders are assigned to the Raman bands of the hydrated surface chromium

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### Raman studies

The Raman spectra were recorded from stationary samples pressed into self supporting wafers which were mounted into a modified version of a Raman *in situ* cell developed by Wang and Hall [22]. The wafer was heated to 400°C in ca. 1 h and kept there for 1 h while ultra-high purity, hydrocarbon-free oxygen (Linde gas) was used to purge the cell. Then the sample was cooled down to ca. 50°C in ca. 45 minutes. At this temperature the *in situ* Raman spectrum was recorded on a Triplemate spectrometer (Spex, Model 1877) coupled to an optical multichannel analyzer (Princeton Applied Research, Model 1463) equipped with an intensified photodiode array detector (1024 pixels, cooled to -35°C, resolution 2 cm<sup>-1</sup>). The 514.5 nm line of an argon ion laser (Spectra Physics) was used as the excitation source. The laser power at the sample was 15-40 mW.

### FTIR studies

The FTIR spectra were recorded on a Biorad FTS-7 spectrometer (resolution 2 cm<sup>-1</sup>). The samples were pressed into self-supporting wafers, and mounted into a modified version of an *in situ* IR cell developed by Xu [23]. The experimental conditions were exactly the same as those used for the Raman experiments. For monitoring the surface hydroxyl stretching region (4000-3000 cm<sup>-1</sup>), self-supporting wafers of 8 mg (ca. 10 mg/cm<sup>2</sup>) were used and 1000 scans were averaged. These spectra were smoothed to improve the S/N ratio. For recording the chromium-oxygen stretching region (1100-800 cm<sup>-1</sup>), the alumina, zirconia, and titania supported samples were pressed into self-supporting wafers of ca. 5 mg (ca. 6 mg/cm<sup>2</sup>), while the silica supported samples were pressed into wafers of 2 mg (ca. 2.5 mg/cm<sup>2</sup>). The chromium-oxygen overtone region (2150-1850 cm<sup>-1</sup>) was scanned for alumina and titania supported samples, having a weight of 20 mg (ca. 25 mg/cm<sup>2</sup>). The latter spectra were baseline-corrected, to eliminate the sloping background, by subtracting the IR spectra of the alumina and titania support, respectively.

## Results

### Surface chromium oxide species

#### CrO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>

The Raman spectra of a series of dehydrated chromium oxides on alumina samples are presented in Fig. 1 as a function of the chromium oxide coverage. All samples (0.5-9% CrO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) reveal the same Raman bands at 1005, ca. 935 (shoulder), 880, ca. 770 (shoulder), ca. 600, 400, and ca. 300 cm<sup>-1</sup>. With increasing coverage, the strong 880 cm<sup>-1</sup> band broadens, and thereby overshadows the shoulders at ca. 935 and ca. 770 cm<sup>-1</sup>. The relative intensities of all the Raman bands, however, do not seem to change significantly with increasing surface coverage. At very low loadings (0.5 and 1%) additional weak Ra-

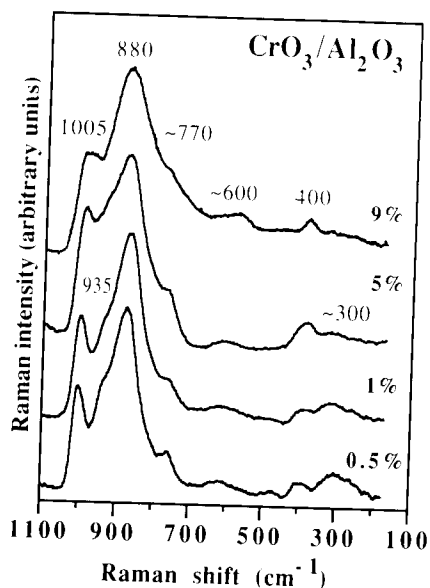


Fig. 1. Raman spectra of  $\text{CrO}_3/\text{Al}_2\text{O}_3$  under dehydrated conditions. The chromium oxide loading increases from 0.5 to 9%.

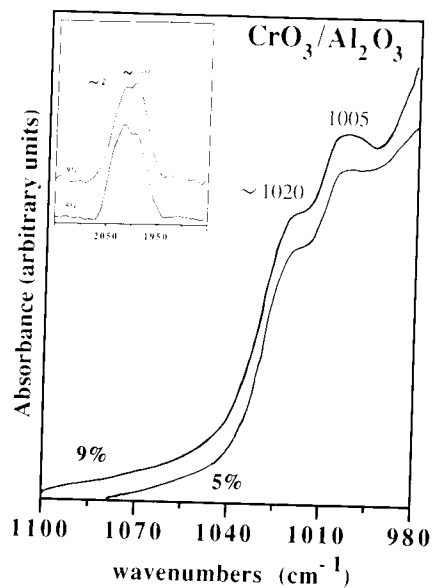


Fig. 2. IR spectra of 5 and 9%  $\text{CrO}_3/\text{Al}_2\text{O}_3$  under dehydrated conditions. The Cr=O overtone region is also shown.

man bands are observed in the 500-1000  $\text{cm}^{-1}$  window of the *in situ* IR spectra of the 5 and 9%  $\text{CrO}_3/\text{Al}_2\text{O}_3$  samples. Both samples reveal a broad band in the 500-1000  $\text{cm}^{-1}$  region, and two sharp bands in the 1000-1100  $\text{cm}^{-1}$  region. IR bands of the 5% sample are not obscured by strong  $\text{Al}_2\text{O}_3$  bands. The 1%  $\text{CrO}_3/\text{Al}_2\text{O}_3$  sample shows a broad band in the 500-1000  $\text{cm}^{-1}$  region, and two sharp bands in the 1000-1100  $\text{cm}^{-1}$  region. IR bands of the 0.5%  $\text{CrO}_3/\text{Al}_2\text{O}_3$  sample are not obscured by strong  $\text{Al}_2\text{O}_3$  bands.

#### $\text{CrO}_3/\text{TiO}_2$

The Raman spectra of  $\text{CrO}_3/\text{TiO}_2$  are shown in Fig. 3. The Raman spectra of  $\text{CrO}_3/\text{TiO}_2$  are similar to those of  $\text{CrO}_3/\text{Al}_2\text{O}_3$  since titania exhibits a broad band in the 500-1000  $\text{cm}^{-1}$  region, and two sharp bands in the 1000-1100  $\text{cm}^{-1}$  region. IR spectra are similar to those of  $\text{CrO}_3/\text{Al}_2\text{O}_3$ .

The shoulder at 1010  $\text{cm}^{-1}$  of the broad *ca.* 870  $\text{cm}^{-1}$  band is more pronounced in the 6%  $\text{CrO}_3/\text{TiO}_2$  sample. The unresolved band between 870 and 1010  $\text{cm}^{-1}$  is more pronounced in the 6% chromium oxide bands are more pronounced in the corresponding IR spectra. The 1010  $\text{cm}^{-1}$  band is not detected in the 1%  $\text{CrO}_3/\text{TiO}_2$  sample. Figure 4 also shows the IR spectra of  $\text{CrO}_3/\text{TiO}_2$ .

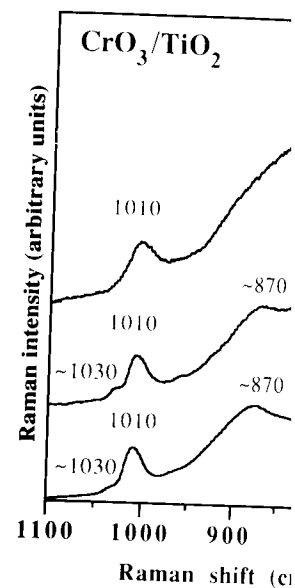


Fig. 3. Raman spectra of  $\text{CrO}_3/\text{TiO}_2$  under dehydrated conditions. The chromium oxide loading increases from 1 to 6%.

man bands are observed at *ca.* 480 and 310  $\text{cm}^{-1}$ , which are due to the quartz window of the *in situ* Raman cell used in this study [24]. Figure 2 shows the IR spectra of the 5 and 9%  $\text{CrO}_3/\text{Al}_2\text{O}_3$  samples under dehydrated conditions. Both samples reveal two bands at 2010 and 1986  $\text{cm}^{-1}$  in the first Cr=O overtone region, and two bands at *ca.* 1020 and 1005  $\text{cm}^{-1}$  in the Cr=O stretching region. IR bands of the surface chromium oxide species below 980  $\text{cm}^{-1}$  are obscured by strong absorptions of the alumina, while IR bands of the 0.5, and 1%  $\text{CrO}_3/\text{Al}_2\text{O}_3$  samples are too weak to be detected in both regions.

$\text{CrO}_3/\text{TiO}_2$

The Raman spectra of the dehydrated 1, 3, and 6%  $\text{CrO}_3/\text{TiO}_2$  samples are shown in Fig. 3. The spectra are presented in the 1100-700  $\text{cm}^{-1}$  region, since titania exhibits strong Raman bands below 700  $\text{cm}^{-1}$ , which prevents the detection of chromium oxide bands in the lower frequency region. All Raman spectra are similar with bands at *ca.* 1030 (shoulder), 1010, and *ca.* 870  $\text{cm}^{-1}$ .

The shoulder at *ca.* 800  $\text{cm}^{-1}$ , which is located at the low frequency side of the broad *ca.* 870  $\text{cm}^{-1}$  band, is the second-order feature of  $\text{TiO}_2$  [25]. This shoulder is more pronounced in the 6%  $\text{CrO}_3/\text{TiO}_2$  sample, resulting in a broad unresolved band between 750 and 900  $\text{cm}^{-1}$ . The two high frequency chromium oxide bands are also observed at *ca.* 1030 and *ca.* 1012  $\text{cm}^{-1}$  in the corresponding IR spectra (Fig. 4). Chromium oxide bands below 980  $\text{cm}^{-1}$  could not be detected in the IR due to the increase in the background of the spectrum. Figure 4 also shows the chromium-oxygen overtone region for the three titania

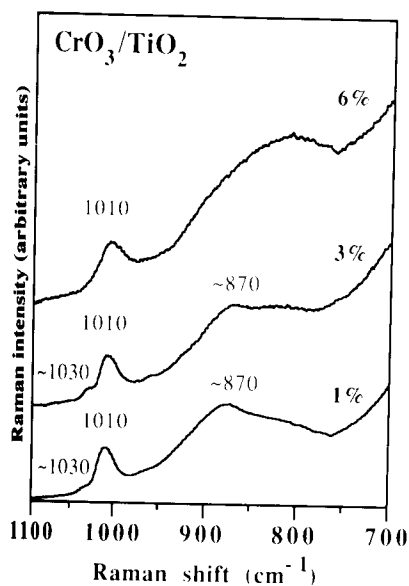


Fig. 3. Raman spectra of  $\text{CrO}_3/\text{TiO}_2$  under dehydrated conditions. The chromium oxide loading increases from 1 to 6%.

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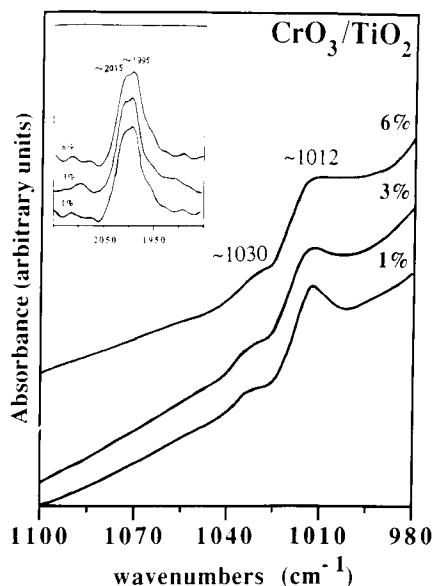


Fig. 4. IR spectra of  $\text{CrO}_3/\text{TiO}_2$  under dehydrated conditions. The chromium oxide loading increases from 1 to 6%. The Cr=O overtone region is also included.

supported samples. Two bands, similar to those detected for the  $\text{CrO}_3/\text{Al}_2\text{O}_3$  samples (see Fig. 2), are observed at 2015 and 1995  $\text{cm}^{-1}$  for all three titania samples.

#### $\text{CrO}_3/\text{ZrO}_2$

Figures 5 and 6 present the Raman and IR spectra of the  $\text{CrO}_3/\text{ZrO}_2$  samples, respectively, under dehydrated conditions as a function of the surface coverage. Detection of chromium oxide bands below *ca.* 700  $\text{cm}^{-1}$  is not possible in both the Raman and IR spectra due to strong zirconia bands. The observed spectra are quite similar as a function of the loading with Raman bands at *ca.* 1030 (shoulder), 1010, 875, and *ca.* 850 (shoulder)  $\text{cm}^{-1}$ , and IR absorptions at 1030, 1010, *ca.* 920 (shoulder), *ca.* 870 (shoulder), and *ca.* 850  $\text{cm}^{-1}$ . The intensity ratio of the 875 and 850  $\text{cm}^{-1}$  bands is reversed in the Raman and IR spectra but this could be due to a rapid increase of the baseline below 800  $\text{cm}^{-1}$  in the infrared. The weak band at *ca.* 920  $\text{cm}^{-1}$  observed in the IR spectra could not be resolved in the Raman spectra, and is most probably hidden under the broad and intense 875  $\text{cm}^{-1}$  band. The intensity ratio of the 1030 and 1010  $\text{cm}^{-1}$  bands is similar in both the Raman and IR spectra, but the 875  $\text{cm}^{-1}$  band is more pronounced in the Raman than in the IR spectra compared to the 1030 and 1010  $\text{cm}^{-1}$  bands. IR absorptions in the chromium-oxygen overtone stretching region (2150–1850  $\text{cm}^{-1}$ ) could not be detected for the  $\text{CrO}_3/\text{ZrO}_2$  samples because of strong zirconia absorptions in this region.

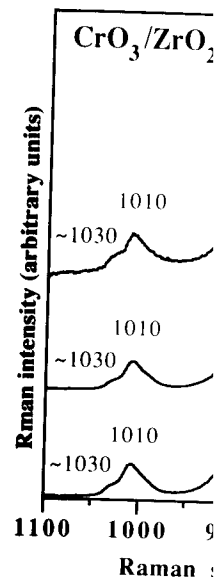


Fig. 5. Raman spectra of  $\text{CrO}_3/\text{ZrO}_2$  under dehydrated conditions. The chromium oxide loading increases from 1 to 6%.

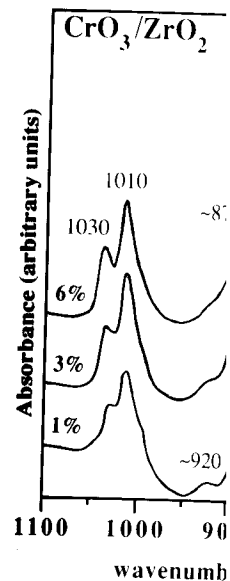


Fig. 6. IR spectra of  $\text{CrO}_3/\text{ZrO}_2$  under dehydrated conditions. The chromium oxide loading increases from 1 to 6%.

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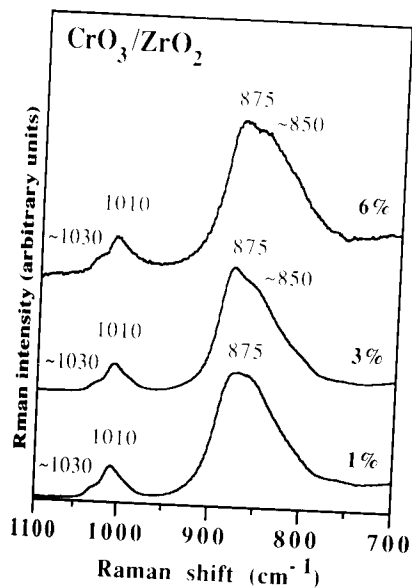


Fig. 5. Raman spectra of  $\text{CrO}_3/\text{ZrO}_2$  under dehydrated conditions. The chromium oxide loading increases from 1 to 6%.

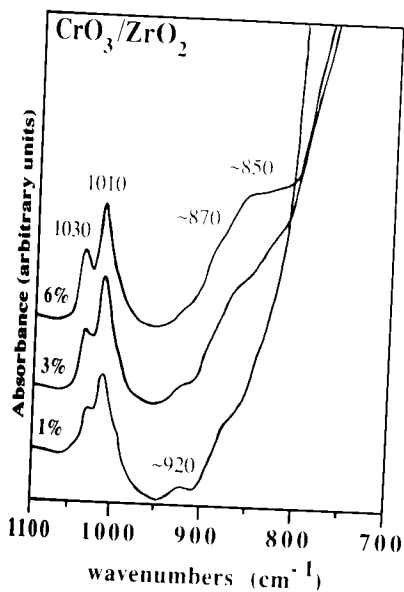


Fig. 6. IR spectra of  $\text{CrO}_3/\text{ZrO}_2$  under dehydrated conditions. The chromium oxide loading increases from 1 to 6%.

$\text{CrO}_3/\text{SiO}_2$

The Raman spectra of the dehydrated 1 and 3%  $\text{CrO}_3/\text{SiO}_2$  samples are

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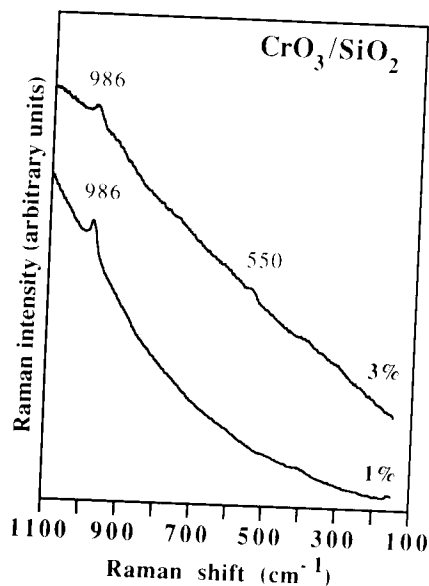


Fig. 7. Raman spectra of 1 and 3%  $\text{CrO}_3/\text{SiO}_2$  under dehydrated conditions.

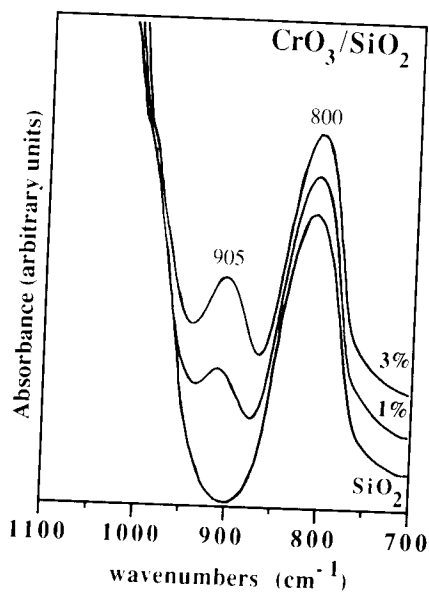


Fig. 8. IR spectra of 1 and 3%  $\text{CrO}_3/\text{SiO}_2$  under dehydrated conditions. The IR spectrum of silica is also shown.

shown in Fig. 7. The rapidly increasing baseline at higher wavenumber is due to fluorescence, and could not be reduced by standard procedures such as prolonged calcination at  $500^\circ\text{C}$  or irradiation with high laser power. Due to this

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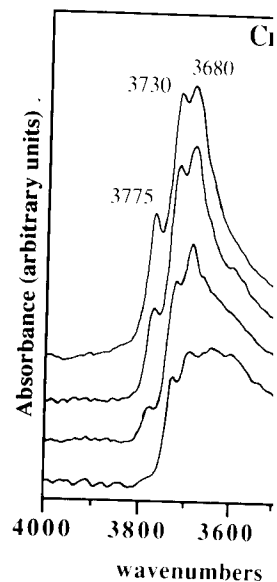


Fig. 9. IR spectra of hydroxyl support is also shown.



fluorescence, it is difficult to observe well resolved chromium-oxygen vibrations, but a Raman band at  $986\text{ cm}^{-1}$  is observed for both the 1 and 3%  $\text{CrO}_3/\text{SiO}_2$  samples. The Raman spectrum of the 3%  $\text{CrO}_3/\text{SiO}_2$  samples further shows a weak band at  $550\text{ cm}^{-1}$ , which points to the presence of a small amount of crystalline  $\text{Cr}_2\text{O}_3$  on the dehydrated surface [19]. Figure 8 shows the IR spectrum of  $\text{SiO}_2$  in addition to the IR spectra of the 1 and 3%  $\text{CrO}_3/\text{SiO}_2$  samples under dehydrated conditions. The IR spectra are characterized by a moderately intense peak at  $800\text{ cm}^{-1}$  due to the silica. On either side of this peak the background spectra increase toward regions of total absorption above *ca.*  $1000\text{ cm}^{-1}$  and below *ca.*  $600\text{ cm}^{-1}$ . Consequently, it was not possible to obtain IR data for the  $986\text{ cm}^{-1}$  band observed in the Raman spectrum. In the so called 'silica window', a band at  $905\text{ cm}^{-1}$  becomes more pronounced with increasing surface coverage, and this band is assigned to a dehydrated chromium oxide surface species. The  $2150\text{--}1850\text{ cm}^{-1}$  region does not present structural information, since the silica support exhibits numerous bands in this region.

#### Support hydroxyl groups

##### $\text{CrO}_3/\text{Al}_2\text{O}_3$

The OH stretching region of  $\text{Al}_2\text{O}_3$ , 1, 5, and 9%  $\text{CrO}_3/\text{Al}_2\text{O}_3$  after standard oxygen pretreatment are shown in Fig. 9. Pure alumina exhibits three major IR bands at  $3775$ ,  $3730$ , and  $3680\text{ cm}^{-1}$ , which have been assigned to basic, neutral, and acidic OH groups, respectively [26]. The intensities of these hydroxyl stretching bands, especially those of the basic and neutral hydroxyl

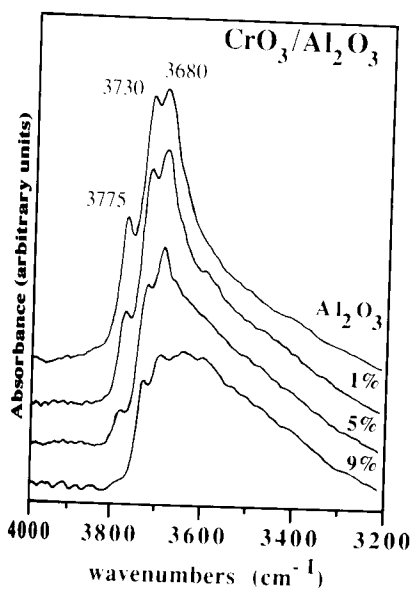


Fig. 9. IR spectra of hydroxyl region of the  $\text{CrO}_3/\text{Al}_2\text{O}_3$  samples. The IR spectrum of the alumina support is also shown.

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groups, are seen to decrease upon addition of chromium oxide to the alumina. The deposition of chromia on alumina, however, does not remove all the original alumina OH bands, since at 9%  $\text{CrO}_3$  coverage alumina hydroxyl bands can still be observed.

#### $\text{CrO}_3/\text{TiO}_2$

The IR spectrum of titania (Fig. 10) reveals bands at 3740, 3690, 3670, and 3640  $\text{cm}^{-1}$ , which is in agreement with the results of Busca *et al.* [27]. The 3740  $\text{cm}^{-1}$  band has been assigned to a small amount of SiOH impurities, while the other three bands were identified as Ti-OH groups in different coordinative situations. The band positions for anatase and rutile hydroxyl groups have been reported to be similar [28]. There has been no agreement in the literature on the assignment of the  $\text{OH}_{\text{Ti}}$  bands. Some authors attributed the 3690, 3670  $\text{cm}^{-1}$  bands to a bridged and isolated hydroxyl group [29], respectively, while others assign the 3690 and 3640  $\text{cm}^{-1}$  bands to two types of bridged hydroxyls [30]. Upon deposition of 1% chromia, all hydroxyl bands decrease slightly, while adding 3% and 6% chromia mainly removes the 3740, 3690, and 3670  $\text{cm}^{-1}$  bands. The 3640  $\text{cm}^{-1}$  band remains present even at monolayer coverage (ca. 6%  $\text{CrO}_3/\text{ZrO}_2$ ).

#### $\text{CrO}_3/\text{ZrO}_2$

Zirconia possesses three types of hydroxyl groups with IR bands at 3770  $\text{cm}^{-1}$  (OH group bonded to one Zr ion), 3670  $\text{cm}^{-1}$  (OH group bonded to

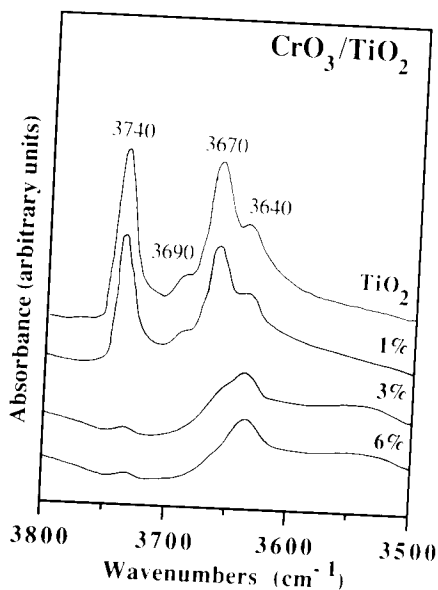


Fig. 10. IR spectra of hydroxyl region of the  $\text{CrO}_3/\text{TiO}_2$  samples. The IR spectrum of the titania support is also shown.



Fig. 11. IR spectra of the hydroxyl region of the  $\text{CrO}_3/\text{ZrO}_2$  samples. The IR spectrum of the zirconia support is also shown.

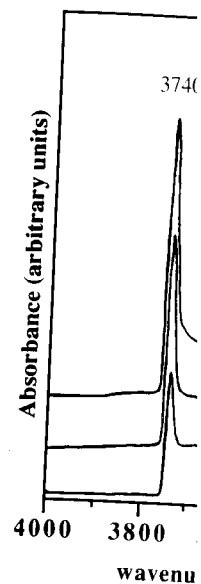


Fig. 12. IR spectra of the hydroxyl region of the  $\text{CrO}_3/\text{ZrO}_2$  samples. The IR spectrum of the zirconia support is also shown.

to the alumina.  
 over all the orig-  
 hydroxyl bands

3740, 3690, 3670,  
 isca et al. [27].  
 OH impurities,  
 in different co-  
 hydroxyl groups  
 reement in the  
 attributed the  
 p [29], respec-  
 types of bridged  
 bands decrease  
 3740, 3690, and  
 at monolayer

bands at 3770  
 up bonded to

um of the titania

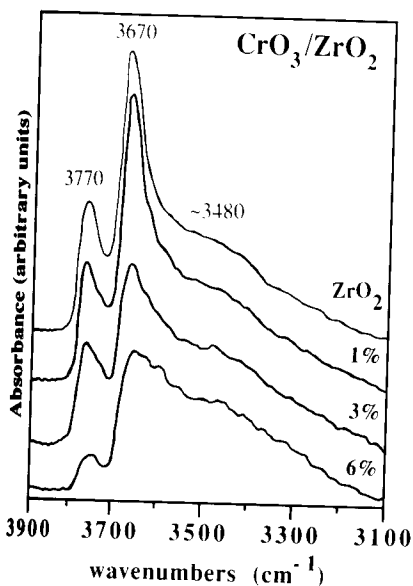


Fig. 11. IR spectra of hydroxyl region of the  $\text{CrO}_3/\text{ZrO}_2$  samples. The IR spectrum of the zirconia support is also shown.

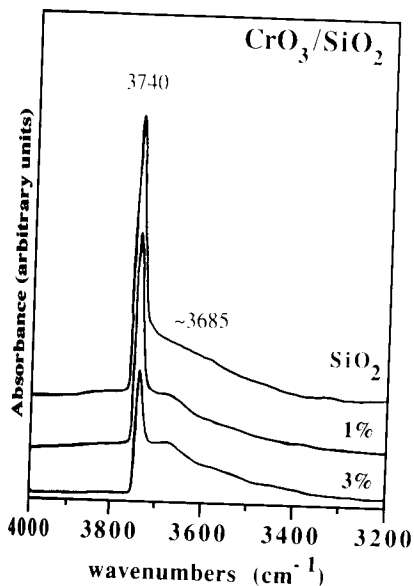


Fig. 12. IR spectra of hydroxyl region of the  $\text{CrO}_3/\text{SiO}_2$  samples. The IR spectrum of the silica support is also shown.

multiple Zr ions), and *ca.* 3480  $\text{cm}^{-1}$  (hydrogen-bonded hydroxyl groups) (see Fig. 11) [30]. The deposition of chromium oxide on zirconia removes part of the OH groups bonded to one or multiple Zr ions (bands at 3770 and 3670  $\text{cm}^{-1}$ , respectively), but does not appear to titrate the hydrogen-bonded hydroxyl groups (band at *ca.* 3480  $\text{cm}^{-1}$ ). At monolayer coverage (6%  $\text{CrO}_3/\text{ZrO}_2$ ) the IR spectrum still shows the presence of a small amount of OH groups bonded to one or more multiple Zr ions.

#### *CrO<sub>3</sub>/SiO<sub>2</sub>*

The hydroxyl region of  $\text{SiO}_2$  is presented in Fig. 12 in addition to the spectra of 1 and 3%  $\text{CrO}_3/\text{SiO}_2$ . The IR spectrum of silica shows a sharp band at 3740  $\text{cm}^{-1}$  and a broad shoulder at *ca.* 3685  $\text{cm}^{-1}$ , which have been assigned to an OH group bonded to one Si ion and a hydrogen-bonded (vicinal) hydroxyl group, respectively [26]. The isolated hydroxyl groups are partly removed by addition of chromium oxide, while the vicinal surface silanol groups do not seem to be influenced, as revealed by the disappearance of the 3740  $\text{cm}^{-1}$  band compared to the broad *ca.* 3685  $\text{cm}^{-1}$  band.

## Discussion

### *Surface chromium oxide structures*

Recently, Deo and Wachs proposed a model to predict the molecular structures of surface metal oxide species on different oxide supports ( $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ , and  $\text{SiO}_2$ ) under ambient conditions [31]. It was found, that under ambient conditions the support surface is hydrated and that the surface metal oxide species are basically in an aqueous medium. Consequently, the hydrated surface metal oxide structures are similar to the structures observed in aqueous solutions. The hydrated surface metal oxide molecular structures were found to be dependent on the net pH at which the surface possesses zero surface charge. The net pH at point of zero surface charge is determined by the combined pH of the oxide support and the metal oxide overlayer. Applying this model to the chromium oxide system, explains the several hydrated chromium oxide structures observed on different oxide supports as reported in several previous articles and summarized in the Introduction [19-21].

The adsorbed moisture on the oxide support, present under ambient conditions, desorbs upon heating and the surface metal oxide overlayer becomes dehydrated. As a consequence of the model proposed by Deo and Wachs, the molecular structures of the surface metal oxide phases must generally be altered upon dehydration since the surface pH can only exert its influence via and aqueous environment. This has been confirmed experimentally by the present investigation, since the observed Raman spectra, recorded under dehydrated conditions, differ strongly from those obtained under ambient conditions [19-21]. The Raman and IR band positions of the dehydrated chro-

mium oxide species in Table 1. The first and IR bands of a species or have to be a series of all bands in favour of the assignment, since it has been determined oxide for example of the loading [24] reported in which same CO) atmospheres at 1030, 1018, 1010, *ca.* treatment at 650°C. to Cr(V) species, at the milder temperature known that heating atures can cause reaction with our data, tion, the intensities of same rate [14,16]. Treatment, strongly dependent of each other independence of the surface complex, which suggests the presence is yet not possible to

TABLE 1

Raman and IR band positions  
conditions

$\text{CrO}_3/\text{Al}_2\text{O}_3$

Raman	IR
	2010
	1986
	1020
1005	1005
935	
880	
770	
600	
400	
300	

yl groups) (see removes part of 3770 and 3670 hydrogen-bonded hydroxyl groups (6% CrO<sub>3</sub>/t of OH groups

on to the spec- sharp band at been assigned (vicinal) hydroxyl groups are partly re-silanol groups e of the 3740

molecular struc- (MgO, Al<sub>2</sub>O<sub>3</sub>, and, that under surface metal the hydrated ed in aqueous s were found zero surface by the com- plying this ed chromium ed in several

ambient con- yer becomes Wachs, the erally be al- nfluence via tally by the d under de- mbient con- trated chro-

mium oxide species supported on the different oxide supports are summarized in Table 1. The first question that needs to be addressed is whether all Raman and IR bands of a particular sample are due to different chromium oxide species or have to be attributed to one surface complex. The fact that the intensities of all bands do not vary as a function of the surface coverage argues in favour of the assignment of these bands to one chromium oxide surface complex, since it has been reported, for supported vanadium, tungsten and molybdenum oxide for example, that different surface structures exist as a function of the loading [24]. Recently, however, an IR study on CrO<sub>3</sub>/ZrO<sub>2</sub> has been reported in which samples were studied under oxygen and under reducing (NO, CO) atmospheres at elevated temperatures [14,16]. IR bands were found at 1030, 1018, 1010, ca. 1004 (shoulder), ca. 920, 889, and 865 cm<sup>-1</sup> after oxygen treatment at 650°C. The bands at 1018 and ca. 1004 cm<sup>-1</sup>, which were assigned to Cr(V) species, are not observed in our spectra. This is most probably due to the milder temperature treatment employed in this study (400°C), since it is known that heating of supported chromium oxide samples at elevated temperatures can cause reduction of Cr(VI) [7,8,19]. All other bands are in agreement with our data, and are assigned to surface Cr(VI) species. Upon reduction, the intensities of all the IR bands were reported to decrease but not at the same rate [14,16]. The fact that their relative intensities can vary with sample treatment, strongly suggests that the bands at 1030 and 1010 cm<sup>-1</sup> are independent of each other and of those in the 930-850 cm<sup>-1</sup> region. Thus, the independence of the band intensities on loading argues for assignment to one surface complex, while the dependence of the IR bands on sample treatment suggests the presence of different surface chromium oxide species. Although it is yet not possible to make a clear choice between these two options, we are in

TABLE 1

Raman and IR band positions (in cm<sup>-1</sup>) of surface chromium oxide species under dehydrated conditions

CrO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>		CrO <sub>3</sub> /TiO <sub>2</sub>		CrO <sub>3</sub> /ZrO <sub>2</sub>		CrO <sub>3</sub> /SiO <sub>2</sub>	
Raman	IR	Raman	IR	Raman	IR	Raman	IR
	2010		2015				
	1986		1995				
	1020	1030	1030	1030	1030		
1005	1005	1010	1012	1010	1010	986	
935					930		
880		870		875	875		905
770				850	850		
600							
400							
300							





The intense 880–870  $\text{cm}^{-1}$  Raman band is assigned to the stretching mode of OCrO groups with the two oxygens making a bridge to other chromium cations. The presence of oligomeric species is supported by the *ca.* 770, *ca.* 600, 400, and *ca.* 300  $\text{cm}^{-1}$  bands observed in the Raman spectra of  $\text{CrO}_3/\text{Al}_2\text{O}_3$ , which are assigned to  $\nu_{\text{as}}(\text{CrOCr})$ ,  $\nu_{\text{s}}(\text{CrOCr})$ ,  $\delta(\text{CrO}_2)$ , and  $\delta(\text{OCrO})$ , respectively. The shoulder at *ca.* 935  $\text{cm}^{-1}$  may be attributed to the symmetric stretching mode of  $\text{CrO}_2$  units, which terminate the polymer. This latter band is very weak in the spectra of  $\text{CrO}_3/\text{ZrO}_2$ , which points to rather long chain structure on the zirconia support. This is in agreement with the relative high intensity of the 875  $\text{cm}^{-1}$  band compared to the alumina supported system. The shoulder at 850  $\text{cm}^{-1}$  in the spectra of  $\text{CrO}_3/\text{ZrO}_2$  indicates the presence of another polymer on the zirconia surface with slightly different OCrO bond distances or indicates the presence of different OCrO bond distances within the same polymer. In fact the broadness of the 880–850  $\text{cm}^{-1}$  bands in all the spectra indicates a wide range of OCrO bond distances. Thus, two Cr=O species with bands at 1030 (1020) and 1010 (1005)  $\text{cm}^{-1}$ , and one (or more) polymer(s) with the strongest band at 880–850  $\text{cm}^{-1}$  are present on the dehydrated alumina, titania, and zirconia surfaces. The relative ratio of these different chromium oxide structures is essentially independent of loading up to monolayer coverage, since the Raman and IR band positions and relative intensities do not change significantly as a function of loading. Recently, similar conclusions were reached for the  $\text{CrO}_3/\text{Nb}_2\text{O}_5$  system under dehydrated conditions, which showed a strong Raman band at 890  $\text{cm}^{-1}$  and a weak band at 1010  $\text{cm}^{-1}$  [35].

The dehydrated surface chromium oxide species present on silica differ strongly from those observed on the other three supports, and are characterized by a Raman band at 986  $\text{cm}^{-1}$  and an IR band at 905  $\text{cm}^{-1}$ . Based upon the band positions and relative intensities in the Raman and IR spectra, both bands cannot be assigned to one surface chromium oxide species and are, therefore, attributed to two different species. The position of the 986  $\text{cm}^{-1}$  band is consistent with the symmetric stretching mode of a terminal  $\text{CrO}_2$  unit (see *e.g.*,  $\text{CrO}_2\text{Cl}_2$ , Table 2). This surface species should be isolated, since no strong Raman bands due to Cr–O–Cr or O–Cr–O linkages are observed in the 820–880  $\text{cm}^{-1}$  region. The 906  $\text{cm}^{-1}$  band is typical for the presence of terminal  $\text{CrO}_3$  units, isolated or not, as can be concluded from the reference spectra in Table 2. This latter band is not observed in Raman spectra of this study, but has been detected as a weak band in a previous Raman study under laser-induced dehydrated conditions with a much cleaner background signal [19]. If the Raman cross-sections are comparable, this indicates that the species possessing a terminal  $\text{CrO}_3$  unit is present as a minority species compared to the surface species having an isolated structure with two terminal Cr=O bonds. Thus, the present study suggests that the monomeric surface chromium oxide species is the predominant surface chromate species on silica support [2,12].

**Support hydro**

The observed chromium–oxygen are isolated or support interactions, which served in the R vibrations have terms, *e.g.*, support [24]. The absence of the Cr–O–support are much more obscured in the

Some information interaction with surface hydroxyl group on  $\text{Al}_2\text{O}_3$ , Ti disappearance of chromium oxide surface by titrating even at coverage are removed. In frequency position affected by the presence yet completely characterized as has been reported reason could be corresponding surface supports reveals hydroxyl group is only one type of on the  $\text{Al}_2\text{O}_3$ , TiC are observed, which however, also be with alumina, titanic surface chromate were observed as reported for support support mainly characterized. Furthermore, it should be noted that part of the chromium (coordinated unsaturated surface hydroxyl group



the stretching mode  
to other chromium  
the ca. 770, ca. 600,  
ra of  $\text{CrO}_3/\text{Al}_2\text{O}_3$ ,  
and  $\delta(\text{OCrO})$ , re-  
to the symmetric  
r. This latter band  
rather long chain  
the relative high  
supported system.  
ates the presence  
erent OCrO bond  
distances within  
bands in all the  
two Cr=O species  
(or more) poly-  
on the dehydrated  
of these different  
ling up to mono-  
relative intensities  
7, similar conclu-  
rated conditions,  
ak band at 1010

on silica differ  
d are character-  
 $1^{-1}$ . Based upon  
IR spectra, both  
species and are,  
of the  $986\text{ cm}^{-1}$   
minal  $\text{CrO}_2$  unit  
olated, since no  
observed in the  
esence of termi-  
ference spectra  
f this study, but  
dy under laser-  
nd signal [19].  
hat the species  
es compared to  
al Cr=O bonds.  
chromium oxide  
upport [2,12].

### Support hydroxyl groups

The observed chromium oxide vibrations reveal which type of terminal chromium-oxygen bonds the surface species possess, or whether these species are isolated or polymerized, as discussed above. Information about the Cr-O-support interaction, however, has not been obtained since Cr-O-support vibrations, which are expected to be found below  $800\text{ cm}^{-1}$ , have not been observed in the Raman spectra. This is not unique, since metal-oxygen-support vibrations have also not been observed for other supported metal oxide systems, e.g., supported rhenium oxide, molybdenum oxide, and tungsten oxide [24]. The absence of this Raman mode indicates (partly) ionic character of the Cr-O-support bond, which results in a very low Raman intensity because of the decrease of polarizability. Vibrations of bonds with more ionic character are much more visible in the infrared, however, bands below  $800\text{ cm}^{-1}$  are obscured in the infrared by the strong support bands.

Some information on the nature of the oxide support surface, and its interaction with surface metal oxide species can be provided by examining the surface hydroxyl structures. The various types of surface hydroxyl groups present on  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{SiO}_2$  have been discussed in Results. The gradual disappearance of the surface hydroxyl groups of all four supports upon addition of chromium oxide suggests that the chromium oxide species bonds to the surface by titrating the surface hydroxyl groups. It has been found, however, that even at coverages approaching monolayer, not all the surface hydroxyl groups are removed. In fact, the hydroxyl groups of  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{SiO}_2$  with frequency positions at  $3640$ , ca.  $3480$ , and ca.  $3685\text{ cm}^{-1}$ , respectively, are not affected by the presence of surface chromium oxide. The reason for this is not yet completely clear, but could be due to inaccessible positions on the surface as has been reported for the vicinal hydroxyl groups of  $\text{SiO}_2$  [26]. Another reason could be that these hydroxyls are very strongly bonded to the corresponding surfaces and, therefore, not easily removed. A comparison of the four supports reveals that on  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ , more than one type of surface hydroxyl group is removed by addition of chromium oxide, whereas on silica only one type of hydroxyl group is titrated. This difference may explain why on the  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ , various types of surface chromium oxide species are observed, whereas on silica mainly isolated species are present. It should, however, also be noted that apparently the interactions of chromium oxide with alumina, titania, or zirconia surface sites have little influence on the specific surface chromium oxide structures, since the same Raman and IR bands were observed as discussed above. A similar observation has recently been reported for supported vanadium and rhenium oxide, and it was argued that the support mainly controls the metal-oxygen-support bond strength [36,37]. Furthermore, it should be noted that our data cannot exclude the possibility that part of the chromium oxide species interact with support Lewis acid sites (coordinated unsaturated sites), since this reaction would not effect the surface hydroxyl groups, and, thus, it was not observed in our IR spectra.

## Conclusions

The present combined Raman and IR spectroscopic investigation reveals that the dehydrated surface chromium oxide structures supported on  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{SiO}_2$  differ strongly from those previously reported under ambient conditions. Two species possessing one terminal Cr=O bond (mono-oxo) with bands at 1030 (1020) and 1010 (1005)  $\text{cm}^{-1}$ , and one (or more) polymer(s) possessing a strong band at 880–850  $\text{cm}^{-1}$ , are proposed to be present on the dehydrated alumina, titania, and zirconia surfaces. The relative ratio of these different chromium oxide species appeared to be essentially independent of chromium oxide loading, since the Raman and IR band positions and relative intensities do not change significantly as a function of loading. The chromium oxide species present on the dehydrated silica surface differ drastically from those observed on the other three supports under study. The Raman and IR spectra indicate the presence of an isolated chromium oxide species possessing two short Cr=O bonds (dioxo) together with a small amount of surface species possessing a terminal  $\text{CrO}_3$  unit, isolated or polymerized. The gradual disappearance of the surface hydroxyl groups of all four supports upon addition of chromium oxide suggests that the chromium oxide species bond to the surface mainly by titrating the surface hydroxyl groups. The surface chromium oxide, however, selectively reacts with specific support hydroxyl groups, since even at coverages approaching monolayer coverage some specific hydroxyls remain intact.

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Investigation reveals supported on  $\text{Al}_2\text{O}_3$ , supported under am-bond (mono-oxo) (or more) poly-posed to be present the relative ratio of ally independent positions and rela-loading. The chro-differ drastically. The Raman and oxide species pos-amount of surface ized. The gradual rts upon addition bond to the sur-face chromium xyl groups, since specific hydroxyls

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