

# Surface Chemistry of Silica-Titania-supported Chromium Oxide Catalysts

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The interaction of chromium oxide with different titania-silica supports has been examined. The oxide supports investigated consisted of  $\text{SiO}_2$ ,  $\text{TiO}_2$ , physical mixtures of  $\text{TiO}_2$  and  $\text{SiO}_2$ , a surface titania overlayer on  $\text{SiO}_2$  (10% of theoretical monolayer) and a surface silica overlayer on  $\text{TiO}_2$  (80% of theoretical monolayer). The supported chromium oxide catalysts were structurally characterized with Raman spectroscopy (RS), diffuse reflectance spectroscopy (DRS) and electron paramagnetic resonance (EPR) and chemically probed by the methanol oxidation reaction. The RS and DRS characterization studies demonstrate that the supported chromium oxide phase is almost exclusively present as a surface  $\text{Cr}^{6+}$  overlayer for 1-3%  $\text{CrO}_3$ , but traces of  $\text{Cr}^{3+}$  and  $\text{Cr}^{5+}$  are also detected. Under ambient conditions, the molecular structures of the surface chromates (monochromates vs. polychromates) are dependent on the net pH at the point of zero charge of the thin aqueous film at the surface of the supports. Under dehydrated conditions, the molecular structures are dependent on the specific support and its composition. Monochromates are dominant on  $\text{SiO}_2$  and the surface silica overlayer on  $\text{TiO}_2$ . Both polychromates and monochromates are present on the surface titania overlayer on  $\text{SiO}_2$ , while surface polychromates are primarily present on  $\text{TiO}_2$  as well as the  $\text{TiO}_2$  and  $\text{SiO}_2$  physical mixtures. These physical mixtures possess mainly polychromates because  $\text{Cr}^{6+}$  and  $\text{Cr}^{5+}$  preferentially migrate and coordinate to the titania phase. The surface chromate and  $\text{Cr}^{5+}$  species also appear to coordinate preferentially to the surface titania sites present in the surface titania overlayer on  $\text{SiO}_2$ . The methanol oxidation probe reaction could not readily discriminate between the different surface chromate coordination sites because of the very similar reactivity and selectivity patterns of all the different surface sites present in the supported chromium oxide catalysts. The reactivity patterns, however, are consistent with the coordination of Cr oxide to the surface titania sites on  $\text{SiO}_2$ .

Supported Cr oxide catalysts are known for their polymerization activity and Cr/ $\text{SiO}_2$  is the famous Phillips polymerization catalyst for the industrial production of high-density polyethylene (HDPE).<sup>1,2</sup> These catalysts have been extensively studied by different spectroscopic techniques: Raman spectroscopy (RS),<sup>3-8</sup> diffuse reflectance spectroscopy (DRS),<sup>8-16</sup> IR spectroscopy,<sup>17,18</sup> and electron paramagnetic resonance (EPR).<sup>19-23</sup> There is now a general consensus that: (1) different oxidation states of Cr ( $\text{Cr}^{n+}$  with  $n = 2, 3, 5$  and  $6$ ) can be present, depending on the pretreatment, and (2) the dispersion of Cr is a function of the support type/composition, the pretreatment and the chromium oxide loading.

To control the molecular weight of the HDPE polymer, Ti oxide is often incorporated into the silica support of Cr/ $\text{SiO}_2$  catalysts which results in a polymer with lower average molecular weight and a broader molecular weight distribution.<sup>24-27</sup> These supported Cr/ $\text{TiO}_2$ / $\text{SiO}_2$  catalysts are prepared by initially depositing a surface layer of titania on the silica support. This is performed by treating the silica support with a titanium ester capable of reacting with the hydroxy groups of the silica support. This  $\text{TiO}_2$ / $\text{SiO}_2$  support is then used for a classic impregnation with a chromium oxide salt. The promotional effect of titania is thought to be due to the formation of Cr-O-Ti-O-Si bridging bonds.<sup>24</sup> However, to our knowledge no systematic spectroscopic study has been devoted to determining the dispersion and molecular structure of these Cr, Ti-supported catalysts. Therefore, the objective of this study is to use RS, DRS and EPR to determine the molecular structure and dispersion of Cr in hydrated and dehydrated silica-titania-supported chromium oxide cata-

lysts. The influence of the Cr loading and preparation method on the surface chemistry of chromium was also investigated. Furthermore, the effect of the surface properties of these catalysts on the catalytic activity and selectivity for methanol oxidation, a sensitive chemical probe reaction of Cr dispersion,<sup>6</sup> was also elucidated.

## Experimental

### Catalyst Preparation

Five types of supported Cr catalysts were prepared and the characteristics and Cr oxide loadings of these samples are summarized in Table 1. The first set of supported chromium oxide catalysts was prepared by the incipient wetness impregnation method with aqueous solutions of chromium nitrate [ $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Allied Chemical Co.]. The support materials used were  $\text{SiO}_2$  (Cab-O-Sil) with a surface area of ca.  $300 \text{ m}^2 \text{ g}^{-1}$ ,  $\text{TiO}_2$  (Degussa P-25, anatase : rutile =

**Table 1** Overview of the characteristics of the Cr supported catalysts

Cr catalysts	$\text{CrO}_3$ content (wt.%)	characteristics
$\text{CrO}_3/3\% \text{ TiO}_2/\text{SiO}_2$	1, 2, 3	prepared from $\text{SiO}_2$ (Cab-O-Sil) with $300 \text{ m}^2 \text{ g}^{-1}$
$\text{CrO}_3/3\% \text{ SiO}_2/\text{TiO}_2$	1	prepared from $\text{TiO}_2$ (Degussa) with $55 \text{ m}^2 \text{ g}^{-1}$
$\text{CrO}_3/(\text{TiO}_2-\text{SiO}_2)$	1	prepared from $\text{SiO}_2$ (Cab-O-Sil) and $\text{TiO}_2$ (Degussa)
$\text{CrO}_3/\text{TiO}_2$	1	Degussa with $55 \text{ m}^2 \text{ g}^{-1}$
$\text{CrO}_3/\text{SiO}_2$	1	Cab-O-Sil with $300 \text{ m}^2 \text{ g}^{-1}$

66 : 34) with a surface area of  $55 \text{ m}^2 \text{ g}^{-1}$  and a mixture of both supports (85%  $\text{TiO}_2$  and 15%  $\text{SiO}_2$ ). The second set was prepared using 3%  $\text{TiO}_2/\text{SiO}_2$  and 3%  $\text{SiO}_2/\text{TiO}_2$ . These supports were prepared starting from the pure  $\text{TiO}_2$  and  $\text{SiO}_2$  supports by a two-stage incipient wetness impregnation method. In the first stage, titanium isopropoxide (Aldrich) in a toluene solution was impregnated onto the  $\text{SiO}_2$  support under a nitrogen environment to avoid the decomposition of the air-sensitive precursor. The sample was initially dried at room temperature for 2 h, followed by drying at  $120^\circ\text{C}$  for 16 h under flowing nitrogen. After drying, the sample was calcined at  $550^\circ\text{C}$  for 16 h in air to form a 3%  $\text{TiO}_2/\text{SiO}_2$ . The 3%  $\text{SiO}_2/\text{TiO}_2$  support was prepared by the same procedure, but  $\text{TiO}_2$  was used as the starting support. A tetraethylorthosilicate (TEOS)-methanol solution was used as a precursor for the impregnation step. After impregnation, the material was calcined at  $500^\circ\text{C}$  for 2 h in dry air. In a second stage, the samples were impregnated by the incipient wetness technique with a chromium nitrate solution (Allied Chemical Co.). After impregnation, all the samples were subsequently dried at room temperature for 16 h, further dried at  $120^\circ\text{C}$  for 16 h, and calcined at  $500^\circ\text{C}$  for 16 h. Only the Cr/3%  $\text{SiO}_2/\text{TiO}_2$  catalyst was calcined for 2 h in dry air. The Cr loadings are expressed as wt.%  $\text{CrO}_3$ . Physical mixtures were made by using pure silica (Cab-O-Sil), titania (Degussa) and alumina (home-made, for details see ref. 10).

#### Laser Raman Spectroscopy

Raman spectra were obtained with a Spectra Physics Model 171  $\text{Ar}^+$  laser where the exciting line was 514.5 nm. The laser power at the sample was maintained at 10–20 mW. The scattered radiation was then directed into a Spex Triplemate Model 1877 spectrometer coupled to a Princeton Applied Research OMAIII Model 1463 optical multichannel analyser equipped with an intensified photodiode array detector cooled thermoelectrically to  $-35^\circ\text{C}$ . Under ambient conditions, the laser beam was focused on the sample illuminator, where the sample typically spins at about 2000 rpm to avoid local heating. The scattered Raman light was reflected into the spectrometer by a  $90^\circ$  angle with the incident light, and was collected and analysed by the optical multichannel analyser. The overall spectral resolution was determined to be better than  $2 \text{ cm}^{-1}$ . The samples were dehydrated at  $500^\circ\text{C}$  for 1 h in flowing oxygen and the corresponding Raman spectra were collected at room temperature by using a specially designed cell. Ultrahigh-purity hydrocarbon-free oxygen (Linde gas) was purged through this cell during the acquisition of the Raman spectra of the dehydrated samples. The characteristics of this cell have been described elsewhere.<sup>4,5</sup>

#### Diffuse Reflectance Spectroscopy

DR spectra were taken on a Cary 5 spectrometer (Varian) in the UV-VIS-NIR region at room temperature. The spectra were recorded against a Halon white standard in the range 200–2200 nm. The samples were first granulated and the size fraction 0.25–0.40 mm was loaded into a quartz flow cell with a suprasil window for DRS and a side arm for EPR (see later). The samples were then calcined at  $500^\circ\text{C}$  in oxygen ( $3600 \text{ ml h}^{-1}$ ) for 1 h and DR spectra were measured of these dehydrated samples. Then, the samples were rehydrated with a water saturated air stream at room temperature over 30 min and spectra were recorded. The computer processing of the spectra consisted of the following steps: (1) subtraction of the baseline; (2) conversion to wavenumber and (3) calculation of the Kubelka-Munk (KM) function. Some spectra

were deconvoluted with a commercial computer package Spectra Calc (Galaxies Industries Corp.). Details about this deconvolution procedure are described elsewhere.<sup>9,10</sup>

#### Electron Paramagnetic Resonance

EPR spectra were recorded on a Bruker ESP300E spectrometer in X-band (9.5 GHz) between 120 and 300 K using a double rectangular TE104 cavity.

#### Catalytic Reactions

The partial oxidation of methanol was carried out in an isothermal fixed-bed continuous-flow reactor at atmospheric pressure and a temperature of  $230^\circ\text{C}$ . The reactor was held in a vertical position and made of a 6 mm od Pyrex glass tube, and the catalyst was held between two layers of quartz wool. About 5–15 mg of catalyst sample were employed to obtain low conversions (below 10%). Prior to the reaction, the catalyst was typically treated with flowing oxygen at  $500^\circ\text{C}$  for 1 h, and then the temperature was reduced to the reaction temperature. Thermogravimetric (TG) analysis shows that the pretreatment conditions used in this study are sufficient for the formation of dehydrated catalysts. The gas mixture,  $\text{CH}_3\text{OH}-\text{O}_2-\text{He}$ , was 6 : 13 : 81 (mol%) at 1 atm pressure, and flowed from the top to the bottom of the reactor; the reaction products were analysed by an on-line gas chromatograph (HP 5840A) equipped with two columns (Poropak R and Carbosive SII) and an FID and two TCD detectors. The catalytic activity, defined as turnover frequency (TOF), was calculated from the number of mol of methanol converted per mol of surface chromium atom  $\text{s}^{-1}$ . The catalytic activity and selectivity were measured at steady state which was reached about 3 h after the initialization of the catalytic reaction.

### Results

#### Spectroscopic Characterization

The assignments of the observed bands can be made by considering the Raman and DRS bands of some relevant chromium oxide reference compounds. These bands are presented in Table 2. The assignments of the reported bands are discussed in previous publications.<sup>3–10</sup> Note that the colour of the samples reflects the presence of the majority of the species. A yellow colour is characteristic for chromate, orange for polychromate (dichromate, *etc.*) and the presence of  $\text{Cr}^{3+}$  is revealed by a greenish shade.

#### Oxide Supports

The characteristics of the oxide supports employed in this study are listed in Table 1. The Raman spectrum of the  $\text{TiO}_2$  support is dominated by the strong Raman bands of the anatase phase at 640, 520, 399 and  $144 \text{ cm}^{-1}$ . The  $\text{SiO}_2$  support possesses Raman features at 452 and  $803 \text{ cm}^{-1}$  (siloxane linkages), 605 and  $488 \text{ cm}^{-1}$  (three- and four-fold siloxane rings) and  $979 \text{ cm}^{-1}$  (surface silanol linkages). Deposition of 3%  $\text{TiO}_2$  onto the  $\text{SiO}_2$  support results in a weak and broad Raman band at  $960 \text{ cm}^{-1}$  under ambient conditions and the appearance of weak Raman bands at 920 and  $1060 \text{ cm}^{-1}$  under dehydrated conditions. The absence of strong Raman bands of crystalline  $\text{TiO}_2$  phases and the sensitivity of the Raman bands in the  $900\text{--}1200 \text{ cm}^{-1}$  region to moisture reveals that the 3%  $\text{TiO}_2$  phase is present as a surface titania overlayer of the  $\text{SiO}_2$  support surface. Higher concentrations of  $\text{TiO}_2$  result in the formation of  $\text{TiO}_2$  (anatase) particles on the  $\text{SiO}_2$  support with the current preparation method. Corresponding Raman studies with 3%  $\text{SiO}_2/\text{TiO}_2$  could not reveal any information about the state

**Table 2** Survey of DRS and RS bands of reference chromium oxide compounds

reference compound	colour	DRS bands/cm <sup>-1</sup> <sup>a</sup>	RS bands/cm <sup>-1</sup>
K <sub>2</sub> CrO <sub>4</sub> (solid)	yellow	21 800 (s); 29 400 (s); 37 700 (s); 43 600 (s)	350; 386; 394; 850; 867; 878; 906
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (solid)	orange-red	19 000 (s, br); 30 100 (s); 38 200 (s); 43 600 (s)	217; 370; 560; 770; 902; 945
CrO <sub>3</sub> (solid)	purple-brown	— <sup>b</sup>	208; 338; 375; 404; 497; 563; 975; 1001
Cr <sub>2</sub> O <sub>3</sub> (solid)	green	14 000 (sh); 15 500 (sh); 16 800 (s); 21 700 (s); 28 500 (s); 36 500 (s)	298; 350; 550; 610
CrO <sub>4</sub> <sup>2-</sup> (solution)	yellow	22 700 (sh, vw); 27 000 (s); 36 350 (s)	348; 371; 846; 904
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> (solution)	orange	22 700 (sh, w); 28 400 (s); 39 200 (s)	217; 367; 557; 904; 942
Cr <sub>3</sub> O <sub>10</sub> <sup>2-</sup> (solution)	dark orange	— <sup>b</sup>	214; 366; 378; 524; 844; 904; 956; 987
Cr <sub>4</sub> O <sub>13</sub> <sup>2-</sup> (solution)	orange-red	— <sup>b</sup>	209; 318; 348; 365; 525; 842; 902; 963; 987

<sup>a</sup> s, strong; m, medium; w, weak; vw, very weak; sh, shoulder and br, broad. <sup>b</sup> Not measured.

of the deposited silica because of the very strong Raman bands of the titania support and the very weak Raman features of the silica phase. However, the methanol reactivity pattern of the 3% SiO<sub>2</sub>/TiO<sub>2</sub> support suggests that the 3% SiO<sub>2</sub> is present as a surface silica overlayer on the TiO<sub>2</sub> support which is estimated to cover about 80% of the TiO<sub>2</sub> support. Thus, the characterization studies demonstrate that the deposited titania and silica phases on the SiO<sub>2</sub> and TiO<sub>2</sub> supports, respectively, are present as surface metal oxide overlayers.

#### Supported Chromium Oxide Catalysts

DRS and RS bands of the Cr catalysts depend on the pretreatment, the support composition, the preparation method and Cr oxide loading. Tables 3 and 4 summarize the

DRS absorption bands (as well as the related colours) and the RS bands of the samples, respectively. The DR spectrum of hydrated CrO<sub>3</sub>/SiO<sub>2</sub> is characterized by two intense bands at 27 000 and 37 700 cm<sup>-1</sup> and one shoulder around 21 800 cm<sup>-1</sup>. These bands are typical for O → Cr<sup>6+</sup> charge-transfer (CT) bands due to monochromates and polychromates.<sup>9,10</sup> The additional band at 17 000 cm<sup>-1</sup> is the first d-d absorption band of Cr<sup>3+</sup> and is due to the formation of some chromia (Cr<sub>2</sub>O<sub>3</sub>) (Table 2). After calcination essentially the same bands are observed for the dehydrated CrO<sub>3</sub>/SiO<sub>2</sub>. The DR spectra of the CrO<sub>3</sub>/TiO<sub>2</sub> sample are more complicated because of the absorption of the titania support in the UV region at around 33 000 cm<sup>-1</sup>, which masks the Cr<sup>6+</sup> CT bands. RS shows dichromate on hydrated silica, and after dehydration monochromate is the dominant species on silica.

**Table 3** Overview of the DRS absorption bands of Cr supported catalysts

sample	pretreatment	colour	absorption bands/cm <sup>-1</sup>
1% CrO <sub>3</sub> /3% TiO <sub>2</sub> /SiO <sub>2</sub>	hydrated	yellow	16 400 (w); 21 500 (sh); 26 800 (s); 34 000 (s)
	dehydrated	orange-yellow	14 900 (m); 21 500 (s); 27 800 (s); 37 600 (s)
2% CrO <sub>3</sub> /3% TiO <sub>2</sub> /SiO <sub>2</sub>	hydrated	orange-yellow	15 700 (m); 21 500 (sh, m); 26 300 (s, br); 34 700 (s)
	dehydrated	deep orange	15 500 (m); 21 500 (s); 27 400 (s); 37 500 (s)
3% CrO <sub>3</sub> /3% TiO <sub>2</sub> /SiO <sub>2</sub>	hydrated	dark green	16 700 (m); 22 700 (sh); 27 000 (s); 35 000 (s)
	dehydrated	dark green	16 700 (s); 21 600 (s); 27 900 (s); 38 100 (s)
1% CrO <sub>3</sub> /TiO <sub>2</sub>	hydrated	yellow	23 000 (sh, w); > 30 000 (s, br)
1% CrO <sub>3</sub> /SiO <sub>2</sub>	dehydrated	yellow-orange	23 000 (sh, m); > 30 000 (s, br)
	hydrated	light green-yellow	17 000 (i); 21 800 (sh); 27 000 (i); 37 700 (s)
1% CrO <sub>3</sub> /3% SiO <sub>2</sub> /TiO <sub>2</sub>	dehydrated	light green-yellow	16 300 (m); 21 500 (sh, m); 27 700 (s); 37 700 (s)
	hydrated	yellow	— <sup>a</sup>
1% CrO <sub>3</sub> /(TiO <sub>2</sub> -SiO <sub>2</sub> )	dehydrated	yellow-orange	— <sup>a</sup>
	hydrated	yellow	— <sup>a</sup>
	dehydrated	yellow-orange	— <sup>a</sup>

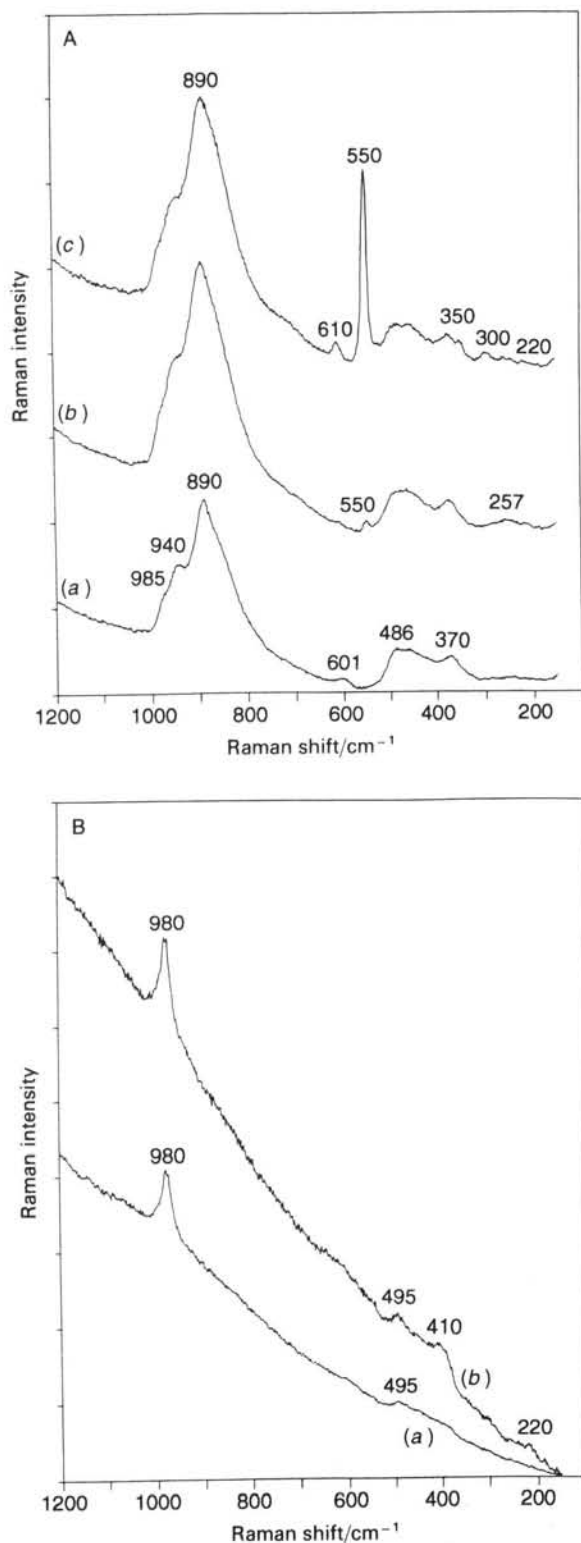
<sup>a</sup> Difficult to measure.

**Table 4** Overview of the RS bands of Cr supported catalysts

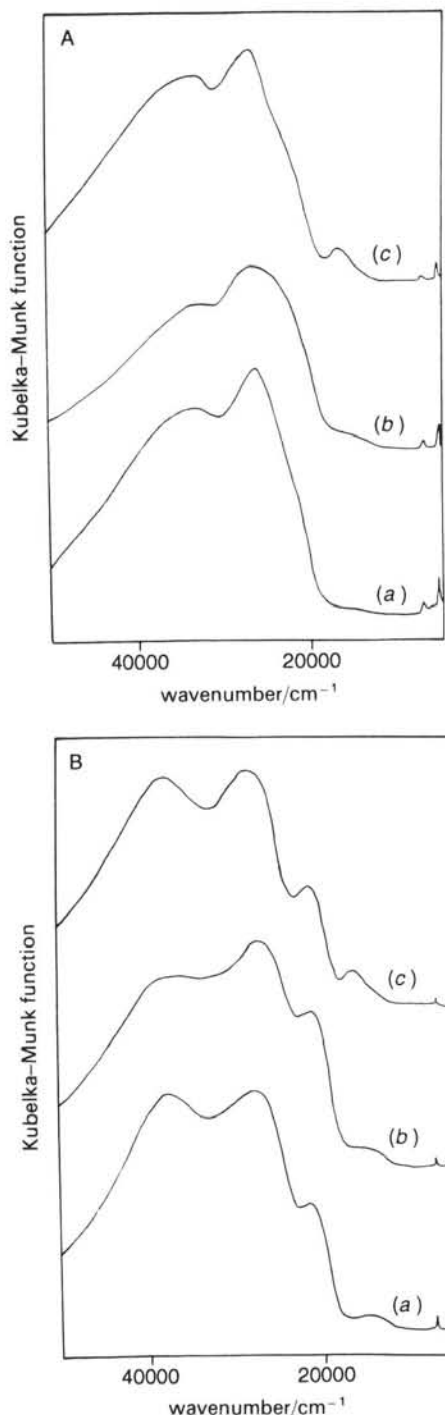
sample	pretreatment	RS bands/cm <sup>-1</sup>
1% CrO <sub>3</sub> /3% TiO <sub>2</sub> /SiO <sub>2</sub>	hydrated	370; 486; 601; 890; 940; 985
	dehydrated	495; 980
2% CrO <sub>3</sub> /3% TiO <sub>2</sub> /SiO <sub>2</sub>	hydrated	257; 370; 486; 550; 890; 940; 985
	dehydrated	220; 410; 495; 980
3% CrO <sub>3</sub> /3% TiO <sub>2</sub> /SiO <sub>2</sub>	hydrated	220; 300; 350; 486; 550; 610; 890; 940; 985
	dehydrated	300; 495; 552; 610; 890; 984
1% CrO <sub>3</sub> /TiO <sub>2</sub>	hydrated	880; 940
	dehydrated	870; 1010; 1030
1% CrO <sub>3</sub> /SiO <sub>2</sub>	hydrated	217; 380; 840; 898; 962
	dehydrated	986
1% CrO <sub>3</sub> /3% SiO <sub>2</sub> /TiO <sub>2</sub>	hydrated	940; 850
	dehydrated	1000; 982; 830
1% CrO <sub>3</sub> /(TiO <sub>2</sub> -SiO <sub>2</sub> )	hydrated	940; 986
	dehydrated	980

On hydrated titania, monochromate is the only species detectable by RS, but after dehydration polychromate is the dominant species for RS.

Typical Raman and DR spectra of hydrated  $\text{CrO}_3/3\% \text{TiO}_2/\text{SiO}_2$  catalysts with increasing Cr loadings are shown in Fig. 1A and 2A, respectively. At low loadings, the sample is yellow and the colour changes from orange-yellow to dark green with increasing Cr loading, indicative of increasing amounts of  $\text{Cr}^{3+}$ . The Raman spectra are dominated by one strong, broad band at  $890 \text{ cm}^{-1}$  and shoulders around  $850$ ,



**Fig. 1** Raman spectra of  $\text{CrO}_3/3\% \text{TiO}_2/\text{SiO}_2$  catalysts under A, hydrated conditions B, dehydrated conditions for increasing  $\text{CrO}_3$  loading: (a) 1%  $\text{CrO}_3$ , (b) 2%  $\text{CrO}_3$ , (c) 3%  $\text{CrO}_3$



**Fig. 2** DR spectra of  $\text{CrO}_3/3\% \text{TiO}_2/\text{SiO}_2$  catalysts under A, hydrated conditions and B, dehydrated conditions for increasing  $\text{CrO}_3$  loading [(a)–(c) as Fig. 1]

$940$  and  $985 \text{ cm}^{-1}$ . The band at  $890 \text{ cm}^{-1}$  is typical for dichromate, while the shoulders are due to monochromate and trichromate (polychromates), respectively. The bands at  $220$ ,  $300$  and  $350 \text{ cm}^{-1}$  are also attributed to these Cr oxide species. In any case, the amount of polymerized Cr oxide is much less than on the pure silica support. Increasing the Cr oxide loading results in an overall increase of the intensity of the bands, and a new band at  $550 \text{ cm}^{-1}$  becomes clearly visible. The latter is due to  $\text{Cr}_2\text{O}_3$  and accounts for the greenish colour of the 3%  $\text{CrO}_3$  loaded sample. The related DR spectra show two broad bands at  $26200$  and  $33300 \text{ cm}^{-1}$ . The former band broadens with increasing Cr oxide loading and is due to the presence of monochromate, while the band broadening suggests the presence of dichromate (or

polychromates). The  $33\,300\text{ cm}^{-1}$  band is due to the  $\text{TiO}_2$  phase and masks the second absorption band around  $37\,000\text{ cm}^{-1}$  of monochromate. The absorption in the region  $15\,000\text{--}18\,000\text{ cm}^{-1}$  is due to some clustered  $\text{Cr}^{3+}$ , which increases in concentration with increasing Cr oxide loading (Table 2) and this correlates also with the  $550\text{ cm}^{-1}$  Raman band.

The Raman and DR spectra of  $\text{CrO}_3/3\% \text{TiO}_2/\text{SiO}_2$  catalysts for increasing Cr oxide loading under dehydrated conditions are shown in Fig. 1B and 2B, respectively. The dehydrated samples possess a deep orange colour, while the Raman bands are less intense owing to fluorescence. The Raman spectra possess a band around  $980\text{ cm}^{-1}$ , which is ascribed to the terminal  $\text{Cr}=\text{O}$  bond of a highly distorted tetrahedral monochromate species<sup>4</sup> and is also observed on dehydrated  $\text{Cr}/\text{SiO}_2$  catalysts. However, the presence of polymeric species such as dimers, trimers and tetramers cannot be ruled out, as they may be submerged in the fluorescent background. The weak bands observed at around  $495$  and  $410\text{ cm}^{-1}$  are characteristic Raman bands of the silica support<sup>8</sup> and no peaks typical for  $\text{Cr}_2\text{O}_3$  could be observed. The DR spectra are dominated by intense bands at around  $38\,000$ ,  $27\,700$  and  $21\,500\text{ cm}^{-1}$ . These bands are typical for monochromate and polychromate ( $21\,500\text{ cm}^{-1}$ ) species. The latter species increases in concentration and Cr oxide loading and explains the orange colour of the samples with higher Cr oxide loadings. The chromate: polychromate ratio, as calculated from the DR spectra by a previously published method,<sup>9,10</sup> is 0.75 for the  $1\% \text{CrO}_3/\text{TiO}_2/\text{SiO}_2$  sample instead of 2.82 for the corresponding  $1\% \text{CrO}_3/\text{SiO}_2$  system. Besides the chromate and polychromate absorptions, an absorption at  $15\,000\text{ cm}^{-1}$  is visible which increases in intensity and shifts to higher energies ( $17\,200\text{ cm}^{-1}$ ) with increasing Cr loading. This absorption band can be assigned to octahedral  $\text{Cr}^{3+}$ , in an oxidic form. The shift to higher energies is due to the formation of crystalline  $\text{Cr}_2\text{O}_3$  clusters on the surface.

The Raman spectra of Cr oxide on various  $\text{TiO}_2\text{--SiO}_2$  catalysts under hydrated and dehydrated conditions as a function of preparation method are shown in Fig. 3A and B, respectively. The catalysts differ only in the  $1200\text{--}700\text{ cm}^{-1}$  region and so only this region will be discussed. Under hydrated conditions, the  $\text{CrO}_3/3\% \text{TiO}_2/\text{SiO}_2$  sample shows one Raman band at  $890\text{ cm}^{-1}$  and three shoulders at  $850$ ,  $940$  and  $985\text{ cm}^{-1}$ , which are already assigned. For  $\text{CrO}_3/3\% \text{SiO}_2/\text{TiO}_2$  a broad Raman band at  $850\text{ cm}^{-1}$  is visible and this band broadens to higher energies, suggesting the presence of at least two species. This spectrum is typical for Cr oxide on hydrated  $\text{TiO}_2$  and is due to the presence of monochromate and some dichromate, which is indicative of the prevalence of Cr oxide on the  $\text{TiO}_2$  component of the catalyst. Cr loaded on a physical mixture of  $\text{TiO}_2$  with  $\text{SiO}_2$  ( $85\% \text{TiO}_2$  and  $15\% \text{SiO}_2$ ) gives rise to two Raman bands at  $896$  and  $940\text{ cm}^{-1}$  which are due to dichromate and some trichromate.<sup>9</sup> This spectrum is similar to that for  $\text{CrO}_3/\text{TiO}_2$ .

After calcination, the Raman spectra are drastically changed as shown in Fig. 3B. The Raman spectrum of  $\text{CrO}_3/3\% \text{TiO}_2/\text{SiO}_2$  was already discussed above and is similar to that of  $\text{CrO}_3/\text{SiO}_2$ . For  $\text{CrO}_3/3\% \text{SiO}_2/\text{TiO}_2$  three bands are visible at  $830$  (broad),  $982$  and  $1000\text{ cm}^{-1}$ , suggesting the presence of two species. The  $830$  and  $1000\text{ cm}^{-1}$  bands can be attributed to polymeric Cr oxide on  $\text{TiO}_2$ , while the  $982\text{ cm}^{-1}$  band is due to monochromate on the  $\text{SiO}_x$  phase. The spectrum of  $1\% \text{CrO}_3/(\text{TiO}_2\text{--SiO}_2)$  is dominated by a broad band at around  $877\text{ cm}^{-1}$  and a smaller band at  $1002\text{ cm}^{-1}$ . Such a spectrum is similar to those of  $\text{CrO}_3/\text{TiO}_2$  and is due to the presence of polymeric Cr oxide mainly on the  $\text{TiO}_2$  phase.

The preference of chromium oxide species for the  $\text{TiO}_2$

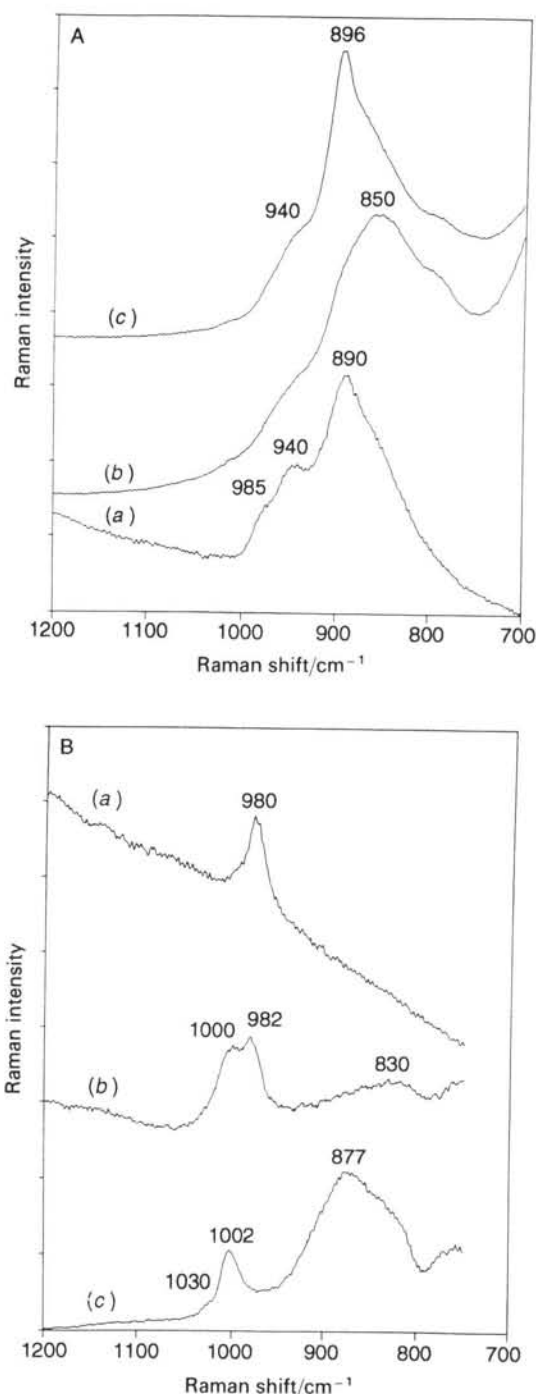
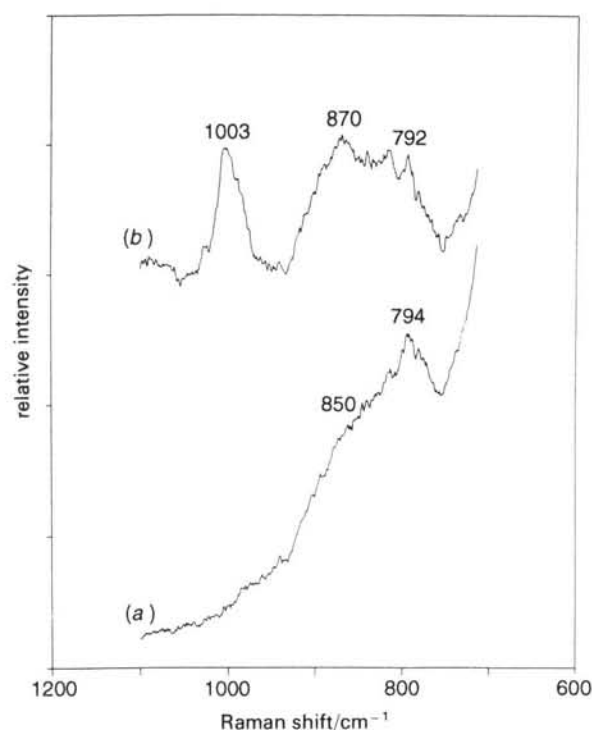


Fig. 3 Raman spectra of Cr, Ti catalysts on different titania-silica supports under A, hydrated conditions and B, dehydrated conditions: (a)  $1\% \text{CrO}_3/3\% \text{TiO}_2/\text{SiO}_2$ , (b)  $1\% \text{CrO}_3/3\% \text{SiO}_2/\text{TiO}_2$ , (c)  $1\% \text{CrO}_3/(\text{TiO}_2\text{--SiO}_2)$

support over the  $\text{SiO}_2$  support was demonstrated by making a physical mixture of  $\text{Cr}/\text{SiO}_2$  and  $\text{TiO}_2$  which was subsequently calcined at  $500^\circ\text{C}$  for 2 h. The resulting Raman spectrum is shown in Fig. 4 and reveals that all the surface chromate initially present on  $\text{SiO}_2$  migrated to the  $\text{TiO}_2$  support: note the absence of the  $986\text{ cm}^{-1}$  band characteristic of  $\text{Cr}/\text{SiO}_2$  and the presence of the  $1002$  and  $877\text{ cm}^{-1}$  bands characteristic of  $\text{Cr}/\text{TiO}_2$ . A similar experiment can be performed with DRS; however, because of the titania absorptions in the UV region we have chosen alumina as a substitute for titania because it has no absorption in the UV region (at least up to  $45\,000\text{ cm}^{-1}$ ). Physically mixing  $\text{Cr}/\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , followed by calcination, results in a DR spectrum



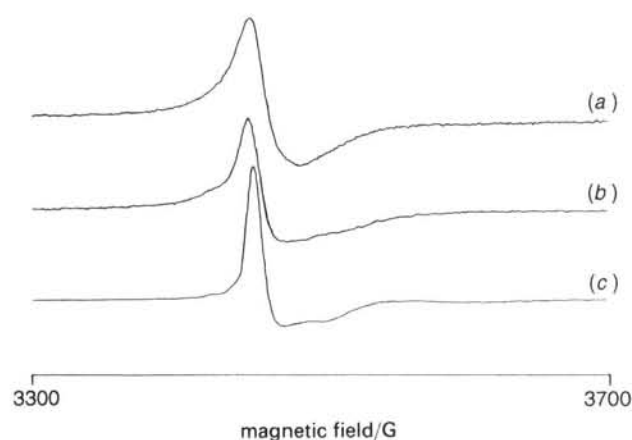
**Fig. 4** Raman spectra of a physical mixture of 50% of 3%  $\text{CrO}_3/\text{SiO}_2$  and 50%  $\text{TiO}_2$  under hydrated (a) and dehydrated (b) conditions after treatment of ca.  $500^\circ\text{C}$  for 2 h

typical for alumina,<sup>9,10</sup> proving the low preference of the silica support for chromium oxide.

Fig. 5 shows the EPR spectra of 1%  $\text{CrO}_3$  on  $\text{SiO}_2$ ,  $\text{TiO}_2$  and 3%  $\text{TiO}_2/\text{SiO}_2$  after calcination (dehydration). The spectra are typical for surface  $\text{Cr}^{5+}$  complexes and the spectra of Cr on silica and titania are well reported in the literature.<sup>19–23</sup> On titania only a square-pyramidal  $\text{Cr}^{5+}$  is observed, while on silica tetrahedral  $\text{Cr}^{5+}$  can also be formed. However, in any case both spectra are different, and this allows us to determine where  $\text{Cr}^{5+}$  is located in the mixed support. The spectra of  $\text{CrO}_3/3\% \text{TiO}_2/\text{SiO}_2$  and  $\text{CrO}_3/(\text{SiO}_2 + \text{TiO}_2)$  samples resemble that of Cr on titania, suggesting preferential coordination onto the titania overlayer. Although the amount of  $\text{Cr}^{5+}$  is low (<2% of the total Cr content), and therefore not representative of the majority, it does show a preference of Cr for the  $\text{TiO}_x/\text{TiO}_2$  phase.

### Catalytic Characterization

In general, the methanol oxidation reaction is very sensitive to the nature of the surface sites present in oxide catalysts



**Fig. 5** EPR spectra of 1%  $\text{CrO}_3/3\% \text{TiO}_2/\text{SiO}_2$  (a); 1%  $\text{CrO}_3/\text{TiO}_2$  (b) and 1%  $\text{CrO}_3/\text{SiO}_2$  (c) after calcination (measurement at 120 K after He treatment)

and, therefore, this reaction was used for the characterization of the  $\text{SiO}_2/\text{TiO}_2$  supported Cr oxide catalysts. Surface redox sites (sites that are capable of being reduced and oxidized) primarily form formaldehyde (FM) as well as methyl formate (MF) and dimethoxy methane (DMM) as the reaction products. Surface acid sites, Lewis as well as Brønsted, result in the formation of dimethyl ether (DME). Basic surface sites yield CO and  $\text{CO}_2$  as the reaction products. In order to determine the influence of the support material and the dispersion of Cr oxide on the reactivity and selectivity of the surface chromium oxide species, the methanol oxidation reaction over different catalysts was carried out at  $230^\circ\text{C}$ .

The product selectivity for the methanol oxidation reaction over the various oxide catalysts employed in this investigation, together with those of the pure supports and the Cr supported silica and titania, is presented in Table 5. The activities of the pure supports ( $\text{TiO}_2$ ,  $\text{SiO}_2$ , 3%  $\text{TiO}_2/\text{SiO}_2$ , 3%  $\text{SiO}_2/\text{TiO}_2$  and  $\text{SiO}_2\text{-TiO}_2$ ) are very low and are minimal in comparison with the reactivity of the supported chromium oxide catalysts under the same reaction conditions.

The  $\text{SiO}_2$  support primarily yielded  $\text{CO}_x$  as reaction products and the absence of FM/MF reflects the absence of redox sites on this surface. Introduction of surface titania to silica, 3%  $\text{TiO}_2/\text{SiO}_2$ , introduces surface redox sites: significant selectivity to FM/MF and decrease in  $\text{CO}_x$  selectivity. Deposition of surface chromia species on either  $\text{SiO}_2$  or 3%  $\text{TiO}_2/\text{SiO}_2$  significantly increases the selectivity towards formaldehyde production. Thus, the silica-supported chromia catalysts possess high selectivity towards FM production, which reflects the surface chemistry of the surface chromium

**Table 5** Activity and selectivity for methanol oxidation over supported Cr and Cr, Ti catalysts

catalyst	TOF <sup>a</sup> /s <sup>-1</sup>	selectivity				
		formaldehyde	methyl formate	dimethoxymethane	dimethyl ether	$\text{CO}_x$
$\text{SiO}_2$	—	—	—	—	15	85
1% $\text{CrO}_3/\text{SiO}_2$	$2.0 \times 10^{-1}$	68.7	20.4	—	2.6	8.3
$\text{TiO}_2$	—	—	—	—	91	9
1% $\text{CrO}_3/\text{TiO}_2$	$1.4 \times 10^{-1}$	60.5	11.5	1.5	0.8	25.7
3% $\text{TiO}_2/\text{SiO}_2$	—	39.8	49.0	1.6	1.7	1.9
1% $\text{CrO}_3/3\% \text{TiO}_2/\text{SiO}_2$	$7.5 \times 10^{-2}$	66.7	13.8	1.5	4.6	13.4
2% $\text{CrO}_3/3\% \text{TiO}_2/\text{SiO}_2$	$4.7 \times 10^{-2}$	68.8	10.9	2.2	7.3	10.8
3% $\text{CrO}_3/3\% \text{TiO}_2/\text{SiO}_2$	$3.1 \times 10^{-2}$	64.5	17.8	1.5	6.1	10.1
3% $\text{SiO}_2/\text{TiO}_2$	—	—	—	—	100	—
1% $\text{CrO}_3/3\% \text{SiO}_2/\text{TiO}_2$	$9.5 \times 10^{-2}$	82.5	3.5	1.8	4.5	7.8
1% $\text{CrO}_3/(\text{TiO}_2\text{-SiO}_2)$	$6.1 \times 10^{-2}$	70.8	9.9	—	6.7	11.5

<sup>a</sup> TOF, turnover frequency.

species on  $\text{SiO}_2$  or 3%  $\text{TiO}_2/\text{SiO}_2$  supports. The  $\text{TiO}_2$  support primarily yields DME owing to the presence of Lewis acid sites on this surface and the absence of redox sites is reflected in the lack of FM/DME production. Introduction of silica onto titania, 3%  $\text{SiO}_2/\text{TiO}_2$ , results in 100% selectivity towards DME, which reflects the increased surface acidity of this system. The increase in DME selectivity and the complex suppression of  $\text{CO}_x$  formation from the pure titania support strongly suggest that silica is present as a surface overlayer on the titania support in the 3%  $\text{SiO}_2/\text{TiO}_2$  sample. Deposition of surface chromium oxide species onto either  $\text{TiO}_2$  or 3%  $\text{SiO}_2/\text{TiO}_2$  increases the selectivity towards FM production. Unfortunately, the selectivity patterns of all of the supported-chromia catalysts are very similar and it is difficult to make any further conclusions based on selectivity.

Previous methanol oxidation studies over supported chromia catalysts have shown that the turnover frequency (TOF) is strongly dependent on the specific oxide support.<sup>6</sup> However, as shown in Table 4, the TOFs for methanol oxidation over  $\text{Cr}/\text{SiO}_2$  and  $\text{Cr}/\text{TiO}_2$  are very similar and almost indistinguishable. 1%  $\text{CrO}_3/3\% \text{SiO}_2/\text{TiO}_2$  shows a slight decrease in TOF relative to 1%  $\text{CrO}_3/\text{TiO}_2$ , but this may just be due to experimental error. The deposition of chromia on the 3%  $\text{TiO}_2/\text{SiO}_2$  support results in a reduced methanol oxidation TOF. This is most probably due to the reduced redox activity of oxides supported on the surface of 3%  $\text{TiO}_2/\text{SiO}_2$  as was previously observed for the  $\text{V}_2\text{O}_5/\text{TiO}_2/\text{SiO}_2$  catalyst system,<sup>28</sup> but experimental error cannot be ruled out entirely. Chromia deposited on the  $\text{TiO}_2\text{-SiO}_2$  physical mixture also exhibited a somewhat lower methanol oxidation TOF which may be due to experimental error. In summary, the TOFs for methanol oxidation over the various  $\text{TiO}_2/\text{SiO}_2$ -supported chromium oxide catalysts are very similar and it is rather difficult to draw definite conclusions on the location of the surface Cr oxide species based on this chemical probe reaction. The methanol oxidation data do, however, show that the TOFs are not dependent on the specific structure of the surface chromium oxide species (monochromates *vs.* polychromates).

## Discussion

The characterization results of the supports showed that the deposited  $\text{TiO}_2$  on  $\text{SiO}_2$  was present as a surface titania overlayer. No detailed structural characterization studies (*e.g.* EXAFS/XANES, <sup>29</sup>Si solid-state NMR) have been performed on the surface titania and silica phases in the presence of chromium oxide or under reaction conditions to determine if there are additional structural changes. However, the surface phases were stable in the presence of surface chromium oxide species, since crystalline  $\text{TiO}_2$  phases were completely absent under ambient conditions as well as in the methanol oxidation reaction.

The molecular structures of the surface chromium oxide species on the various oxide supports under ambient hydrated conditions were elucidated. At low Cr oxide loadings, the surface of the oxide support determines the pH of the aqueous solution near the surface and thus the equilibria:  $\text{chromate} \rightleftharpoons \text{dichromate} \rightleftharpoons \text{trichromate} \rightleftharpoons$ . The lower the pH at the point of zero charge (PZC) of the support, the higher the  $\text{H}^+$  concentration and the more these reactions are driven to the right. Therefore, more polymeric Cr oxide species exist on the surface. The net surface pHs at the PZC of the  $\text{TiO}_2$  and  $\text{SiO}_2$  supports are about 6.4 and 3.9. Consequently, the hydrated surface chromium oxide species on  $\text{TiO}_2$  are primarily present as monochromates

because of the higher pH of the thin aqueous film, and are primarily present as polychromates on  $\text{SiO}_2$  because of the lower pH of the thin aqueous film. The silica-titania-supported  $\text{CrO}_3$  catalysts possess a behaviour dependent on their exact composition. On 1%  $\text{CrO}_3/3\% \text{TiO}_2/\text{SiO}_2$ , the amount of polychromate is lower, while on  $\text{CrO}_3/3\% \text{SiO}_2/\text{TiO}_2$  and  $\text{CrO}_3/(\text{TiO}_2\text{-SiO}_2)$  almost the same behaviour is observed as on  $\text{CrO}_3/\text{TiO}_3$ . These observations can be explained by (1) an increase/decrease of pH at the ZPC by the addition of  $\text{TiO}_x/\text{SiO}_x$  onto the support and (2) the preference of Cr for the  $\text{TiO}_2/\text{TiO}_x$  surface. The latter can be understood in terms of the positively charged surface of  $\text{TiO}_x/\text{TiO}_2$ , which reacts more easily with the negative chromium oxide species ( $\text{CrO}_4^{2-}/\text{CrO}_2\text{O}_7^{2-}$ ).

The molecular structures of the dehydrated surface chromate species are different from those of their hydrated counterparts. Primarily, surface monochromate species are present on  $\text{SiO}_2$  and polychromate species are present on  $\text{TiO}_2$ . Impregnation of chromium oxide on a physical mixture of  $\text{SiO}_2$  and  $\text{TiO}_2$  supports, possessing equal surface areas of the two supports, revealed the Raman characteristics of the dehydrated surface polychromates which suggests that surface chromium oxide species may have a preference for  $\text{TiO}_2$  over  $\text{SiO}_2$ . This preference for the  $\text{TiO}_2$  support was confirmed by heating a physical mixture of  $\text{TiO}_2$  and 3%  $\text{CrO}_3/\text{SiO}_2$  which revealed that the surface chromate species migrated from the silica support to the titania support after calcination at 500°C for 2 h. Additional information was obtained by DRS of a mixture of alumina and silica and by  $\text{Cr}^{5+}$  EPR. The migration of Cr species from the  $\text{SiO}_2$  support to the  $\text{TiO}_2$  support reflects the weak interaction of metal oxides with the silica surface and is related to the low reactivity of surface silanols on  $\text{SiO}_2$ . Furthermore,  $\text{Cr}^{5+}$  ions coordinate preferentially with the  $\text{TiO}_x/\text{TiO}_2$  phase.

The dehydrated surface chromium oxide species on the 3%  $\text{SiO}_2/\text{TiO}_2$  support exhibited comparable Raman signals of monochromate as on  $\text{Cr}/\text{SiO}_2$ . This suggests that surface monochromate species were primarily formed on the silica overlayer on the  $\text{TiO}_2$  support and is consistent with the conclusion that the  $\text{TiO}_2$  support is extensively covered with a surface silica overlayer. The exposed titania patches must have possessed very small dimensions since the length of the polychromates appears to be shorter than found from the pure  $\text{TiO}_2$  support (ratio of the intensities of the 800–900 and 1000  $\text{cm}^{-1}$  chromate Raman bands).

Surface monochromate and polychromates were primarily formed on the 3%  $\text{TiO}_2/\text{SiO}_2$  supports which possess an orange colour and an additional DRS band around 22000  $\text{cm}^{-1}$ . The corresponding  $\text{CrO}_3/\text{SiO}_2$  did not exhibit this additional band and the orange colour. Therefore, the polychromates are associated with the surface titania sites. These observations are reflected in the chromate:polychromate ratios on  $\text{TiO}_x/\text{SiO}_2$  and  $\text{SiO}_2$ , respectively, showing a higher amount of polychromate on  $\text{TiO}_x/\text{SiO}_2$  than on  $\text{SiO}_2$ . The preference of polychromates for the surface titania on a silica support is not surprising since titania prefers to coordinate polychromates. The atomic ratio of Cr:Ti for the 3%  $\text{CrO}_3/3\% \text{TiO}_2/\text{SiO}_2$  catalyst, the maximum amount of surface Cr and Ti oxides that can be dispersed as a two-dimensional overlayer on this silica support, corresponds to *ca.* 0.9. This suggests that on average one surface Cr atom can associate with one surface Ti atom. The preferential interaction between the surface chromate and surface titania site is consistent with the low affinity of the silica support for oxides and the high affinity of the titania support. However, there is no direct spectroscopic evidence for the coordination of surface monochromate to the surface titania species since (1) RS monitors only the  $\text{Cr}=\text{O}$  and  $\text{Cr}-\text{O}-\text{Cr}$  bonds

rather than the Cr—O support bonds and, unfortunately, the surface chromate Raman bands are not support specific and (2) DRS takes into account only the first coordination sphere around Cr (*i.e.* the oxygens).

For the corresponding  $\text{VO}_x/\text{TiO}_2/\text{SiO}_2$  system, the surface vanadia Raman band is support specific,  $1038\text{ cm}^{-1}$  for silica and  $1027\text{--}1031\text{ cm}^{-1}$  for titania, and it is clear that surface vanadate coordinates to the surface titania sites on  $\text{SiO}_2$  since the resulting Raman band appears at  $1029\text{ cm}^{-1}$ . Thus, analogous to the corresponding surface vanadia system, the surface chromium oxide species most probably associates with isolated surface titania sites on the silica surface. The present studies cannot discriminate between the possible coordinations of this surface species: a surface chromium oxide species coordinated to two isolated surface titania sites, as suggested by Pullukat *et al.*,<sup>24</sup> a surface chromium oxide species bridging an isolated surface titania site and an adjacent surface silica site or a combination of both. The corresponding  $\text{V}_2\text{O}_5/\text{TiO}_2/\text{SiO}_2$  system suggested that the surface vanadate species was bridging the surface titania and monochromate sites because the tetrahedral  $\text{O}=\text{V}(\text{—O—})_3$  structure required three ligands to be anchored. By analogy to the corresponding vanadia system, the bridging structure is probably more likely to be the preferred coordination for the chromium oxide system and is consistent with the Cr:Ti ratio of 0.9. Additional molecular insights into the coordination of this species on surface  $\text{TiO}_2/\text{SiO}_2$  supports can possibly be obtained from high-resolution *in situ* EXAFS studies which may be able to obtain detailed information about the second coordination shell, but the analysis of such data is very difficult to interpret.

The methanol oxidation reactivity probe was also not able to discriminate clearly between the various locations of the surface chromium oxide species on the oxide supports because of the very similar reactivity properties of Cr species on all of the Ti and Si sites. The corresponding reactivity studies with the  $\text{V}_2\text{O}_5/\text{TiO}_2/\text{SiO}_2$  system were much more informative since the TOF varies by  $10^3$  as a function of the specific oxide support. For the vanadia system, the TOFs were  $10^{-3}$  and  $1\text{ s}^{-1}$  for the  $\text{SiO}_2$  and  $\text{TiO}_2$  supports, respectively, and  $10^{-1}\text{ s}^{-1}$  for the  $\text{V}_2\text{O}_5/\text{TiO}_2/\text{SiO}_2$  system where only surface titania was present. The reactivity results from the vanadia system clearly show that: (a) surface vanadia species are preferentially associated with surface titania sites on  $\text{SiO}_2$  because of the two orders of magnitude increase in TOF for vanadia/titania/silica over vanadia/silica and (b) coordination of surface vanadia to the surface titania sites on silica results in a TOF that is one order of magnitude less than that for vanadia on pure  $\text{TiO}_2$ . The lower reactivity of vanadia coordinated to surface titania sites on  $\text{SiO}_2$  also appears to be reflected in the somewhat lower methanol oxidation TOFs for the  $\text{CrO}_3/\text{TiO}_2/\text{SiO}_2$  catalysts in the present studies, since these catalysts exhibited the lowest TOFs. Therefore, the methanol oxidation results appear to be consistent with the surface chromium oxide species which are coordinated to the surface titania sites on  $\text{SiO}_2$ , but finding a more sensitive reaction probe for surface chromate coordination sites should be an important objective of future investigations.

### Conclusions

Combined DRS and RS structures demonstrate that the supported chromium oxide phase is almost exclusively present as a surface  $\text{Cr}^{6+}$  overlayer, although traces of  $\text{Cr}^{3+}$  and  $\text{Cr}^{5+}$  have also been detected. Different  $\text{Cr}^{6+}$  molecular structures can be present, depending on the pretreatment and support

composition. Under hydrated conditions, the molecular structures of the surface chromate (monochromates *vs.* polychromates) are dependent on the net pH at the PZC of the thin aqueous film: mainly, monochromate on titania-rich samples and polychromate on silica-rich samples. Under dehydrated conditions, the molecular structures are dependent on the specific support and its composition. Monochromates predominate on  $\text{SiO}_2$  and on the surface silica overlayer on  $\text{TiO}_2$ . Both polychromates and chromates are present on the surface titania overlayer on  $\text{SiO}_2$ , while surface polychromates are primarily present on  $\text{TiO}_2$  as well as the  $\text{TiO}_2$  and  $\text{SiO}_2$  physical mixtures. The physical mixtures mainly possess polychromates because  $\text{Cr}^{6+}$  preferentially migrated and coordinated to the titania phase. The surface chromate species also appear to coordinate preferentially to the surface titania sites present in the surface titania overlayer on  $\text{SiO}_2$ . The DRS and EPR results also show that Cr probably migrates to and coordinates with surface  $\text{TiO}_x$  or with the  $\text{TiO}_2$  support. The methanol oxidation probe reaction could not readily discriminate between the different surface chromate coordination sites because of the very similar reactivity and selectivity patterns of all the different surface sites present in the supported chromium oxide catalysts. The reactivity patterns, however, were consistent with the coordination of  $\text{Cr}^{6+}$  to surface titania sites on  $\text{SiO}_2$ .

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