SPECTROSCOPIC CHARACTERIZATION OF SUPPORTED Cr and Cr,Ti CATALYSTS : INTERACTION WITH PROBE MOLECULES

Bert M. Weckhuysen[a], Israel E. Wachs[b] and Robert A. Schoonheydt[a]

[a] Centrum voor Oppervlaktechemie en Katalyse, K.U.Leuven, Kardinaal Mercierlaan 92, B-3001 Heverlee, Belgium

[b] Zettlemoyer Center for Surface Studies, Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015, USA

Cr and Cr,Ti supported catalysts, with different support composition were investigated by Diffuse Reflectance Spectroscopy (DRS) and Electron Spin Resonance (ESR). The interaction between a series of molecules (HCl, CH_2Cl_2, $CH_3CH_2CH_2OH$, CH_3CH_2OH, H_2O, CO, H_2, CH_2CH_2 and NH_3) and supported Cr was evaluated. Interaction with acids results in hydrolysis and reduction, while bases give only reduction of the supported Cr. With ethylene, CO and H_2, Cr^{2+} is the dominant species on silica, while on alumina Cr^{3+} is preferentially formed. The redox behavior of Cr is also dependent on the sequence of impregnation. Impregnation of Cr followed by impregnation with Ti retards the reduction of Cr, while the reverse order facilitates reduction. These results supports the idea of a support controlled redox behavior.

1.INTRODUCTION

Cr supported catalysts are known to be active in the polymerization of olefins [1,2]; hydrogenation and dehydrogenation reactions of respectively alkenes and alkanes [3], dehydrocyclisation reactions [3,4] and oxidation processes [5,6,7]. The catalysis is sensitive to minor changes in composition, preparation and treatment conditions [8]. For example, Ti is often incorporated in the silica support to control the molecular weight of the polyethylene polymer (lower average molecular weight and a broader molecular weight distribution) [9-12]. However, up to now the influence of these parameters on the properties of supported Cr are scarce. Diffuse Reflectance Spectroscopy (DRS) and Electron Spin Resonance (ESR) are excellent techniques in this regard because they allow the detection of Cr^{6+}, Cr^{5+}, Cr^{3+} and Cr^{2+}.

In previous studies [13-15], we have shown that the molecular structure and redox behavior of Cr is dependent on the support composition, i.e. the SiO_2-content. An increasing clustering of Cr is observed with increasing silica-content of the support, while a higher silica-content facilitates the reduction of Cr to Cr^{2+}. Thus, the dichromate:chromate ratio and

low Cr-loadings. For higher Cr loadings, chromium clusters are detected (polychromates, Cr_2O_7) even on an alumina support.

The purpose of this work is to use probe molecules in combination with DRS and ESR for studying the influence of the support composition (Si, Al) on the chemistry of supported Cr. Furthermore, the influence of Ti on the redox behavior of Cr is investigated.

2.EXPERIMENTAL SECTION

2.1. Sample preparation

The Cr catalysts were prepared by the incipient-wetness method with chromium(VI)oxide (CrO_3) (UCB) onto alumina and silica. The chromium loading was 0.2 wt%. Silica and alumina were prepared by the sol-gel method starting from respectively TEOS and $Al(iP)_3$ and H_2O, followed by titration. The obtained gels were dried, calcined and crushed. Details about the preparation method and the characteristics of the materials were published elsewhere [13,14] (TEOS = tetraethyl orthosilicate, $Al(iP)_3$ = aluminium triisopropoxide).

The Cr, Ti catalysts were prepared by impregnation with $Cr(NO_3)_3.9H_2O$ (Allied Chemical Co.) onto silica (Cab-O-Sil) followed by impregnation with $Ti(iP)_4$ (iP = isopropyl, Aldrich) (preparation method 1) or in the reverse order onto the same support (preparation method 2). Ti impregnation was done in a toluene solution under nitrogen to avoid decomposition of the air-sensitive precursor The Cr- and Ti-contents were respectively 0.5 and 1.5 wt%.

2.2. Pretreatment and Experimental Techniques

Pretreatments.

The Cr-catalysts were dried at 50 °C for 8 h and granulated. The size fraction of 0.16-0.40 mm was loaded in a quartz flow cell with Suprasil window for DRS and a side arm for ESR. The samples were subsequently dried at 90 °C during 16 h followed by calcination at 550 °C during 6 h in an oxygen stream. DRS spectra were recorded on these calcined samples. The samples were then contacted during 30 min. with a N_2-stream saturated with hydrochloric acid, ethanol, propanol, water, ammonia at room temperature and with carbon monoxide, hydrogen, dichloromethane at 400 °C and ethylene at 100 °C. After each treatment, DRS spectra were taken.

The Cr, Ti-catalysts were pretreated in the same way and DRS and ESR spectra were taken of the calcined samples. The samples were then reduced with CO at 400 °C during 30 min.. After reduction ESR and DRS spectra were recorded. An oxygen flow of 3600 ml/h and a N_2/probe molecule flow of 1800 ml/h were used for all the treatments.

Experimental Techniques.

DRS spectra were taken with a Varian Cary 5 UV-Vis-NIR spectrophotometer at room temperature. The spectra were recorded against a halon white standard in the range 2200 - 200 nm. 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. ESR spectra were measured with a Bruker ESP300E instrument in the

spins : 10^{16} - 10^{19}/g) after double integration of the recorded spectra.

3.RESULTS AND DISCUSSION

3.1. Interaction of probe molecules with supported Cr

Dependent on the pretreatment and probe molecule, three oxidation states of Cr can be detected on the surface of the amorphous supports by DRS. Cr^{6+} can be either chromate or polychromate and is detected by its charge transfer bands $O \rightarrow Cr^{6+}$ (d^0). Chromates have two strong bands at 27,000 - 30,000 and 36,000 - 40,000 cm^{-1}, while dichromates (polychromates) possess an additional band at around 22,000 cm^{-1}. Cr^{3+} (d^3) and Cr^{2+} (d^4) possess typical d-d absorption bands : Octahedral Cr^{3+}, 15,000 - 18,000 cm^{-1} ($^4A_{2g} \rightarrow {}^4T_{2g}$), 22,000 - 25,000 ($^4A_{2g} \rightarrow {}^4T_{1g}(F)$) and 30,000 - 36,000 ($^4A_{2g} \rightarrow {}^4T_{1g}(P)$); (pseudo) octahedral Cr^{2+}, 12,500 cm^{-1} ($^5E_g \rightarrow {}^5T_{2g}$) and (pseudo) tetrahedral Cr^{2+}, 7,500 - 10,000 cm^{-1} ($^5T_2 \rightarrow {}^5E$) [13,14,16].

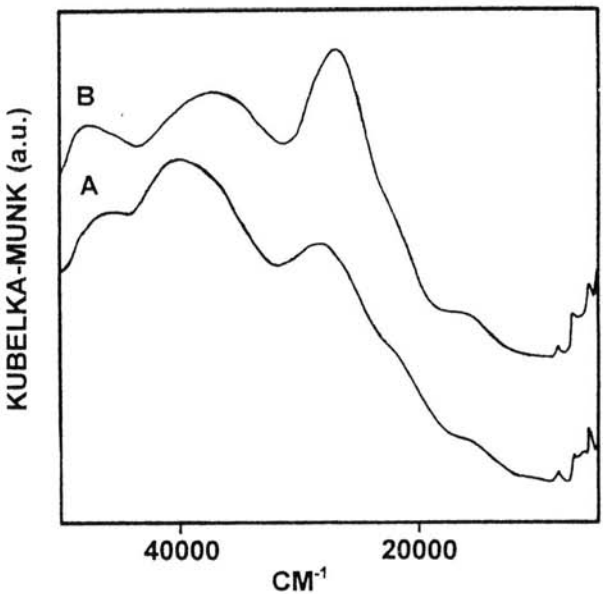

Figure 1. DRS spectra of supported Cr/SiO_2 (A) and Cr/Al_2O_3 (B) after interaction with propanol at room temperature.

are respectively yellow and light orange. The spectrum of Cr/Al_2O_3 is dominated by two bands at 27,500 and 41,000 cm^{-1}, typical for chromate. For Cr/SiO_2, four bands at 15,500, 22,000, 30,500 and 40,500 cm^{-1} and a shoulder at 27,000 cm^{-1} are visible. They are due to the presence of chromate, dichromate and traces Cr^{3+}. After interaction with different probe molecule (H_2O, CH_3CH_2OH, $CH_3CH_2CH_2OH$, HCl, CO, H_2, CH_2CH_2 and CH_2Cl_2) the colour of the samples and the related DRS spectra are drastically changed. The colour and observed Cr-species are summarized in table 1.

Upon hydration of the Cr-catalysts, the colours are yellow for Cr/Al_2O_3 and yellow-orange for Cr/SiO_2. The spectrum of Cr/Al_2O_3 consists of two bands at 26,900 and 36,500 cm^{-1}, while the spectrum of Cr/SiO_2 is dominated by bands at 22,500, 28,400 and 37,100 cm^{-1}. The shift of the absorption at 38,000 cm^{-1} with respect to the same band after calcination (around 40,000 cm^{-1}) is due to the transformation of an anchored Cr-species to a non-anchored Cr. Thus, the interaction of supported Cr with water vapour at room temperature results in a hydrolysis of the X-O-Cr bondings (with X = Si or Al). The molecular structure of the non-anchored Cr depends on the iso-electric point (IEP) of the support : on alumina (IEP = 7-8) only chromate is observed, while on silica (IEP = 1 - 2) dichromate is the dominant species [14,15].

Table 1. Summary of the colour and DRS observable Cr-species on supported Cr-catalysts after interaction with small probe molecules.

Cr catalyst →	Cr/SiO_2		Cr/Al_2O_3	
Probe molecule ↓	Colour	Cr-species	Colour	Cr-species
water	yellow-orange	dichromate, chromate	yellow	chromate
ethanol	yellow-green	Cr^{6+}, Cr^{3+}	yellow-green	Cr^{6+}, Cr^{3+}
propanol	yellow-green	Cr^{6+}, Cr^{3+}	yellow-green	Cr^{6+}, Cr^{3+}
hydrochloric acid	orange-red	Cr^{6+} (Cr^{3+})	deep orange	Cr^{6+} (Cr^{3+})
dichloro-methane	green	Cr_2O_3	green	Cr_2O_3
carbon monoxide	blue	Cr^{2+} (Cr^{3+})	blue-green	Cr^{3+} (Cr^{2+})
hydrogen	blue	Cr^{2+} (Cr^{3+})	green-blue	Cr^{3+} (Cr^{2+})
ethylene	blue	Cr^{2+} (Cr^{3+})	blue	Cr^{3+} (Cr^{2+})
ammonia	yellow-green	Cr^{6+}, Cr^{3+}	green-yellow	Cr^{6+}, Cr^{3+}

can hydrolyse the X-O-Cr bondings at room temperature resulting in the formation of non-anchored Cr on silica and alumina, with typical spectral features of respectively dichromate and chromate. However, this non-anchored Cr^{6+} oxidizes alcohols and consequently Cr^{6+} isreduced to the green Cr^{3+}. This is evidenced by a decrease in intensity of the $O \rightarrow Cr^{6+}$ CT-bands and the formation of an additional band around 16,000 cm^{-1}. Increasing of the contact time results in an almost complete reduction of Cr^{6+} to Cr^{3+}.

By addition of hydrochloric acid vapour onto calcined Cr/SiO_2 and Cr/Al_2O_3, the colour is drastically changed to respectively orange-red and deep orange. On alumina three intense bands are observed at 24,300; 33,700 and 41,000 cm^{-1} and one shoulder around 19,000 cm^{-1}. Treated Cr/SiO_2 is dominated by three intense bands at 26,800; 33,700 and 40,300 cm^{-1}, one weak band at 14,500 cm^{-1} and one shoulder at 19,500 cm^{-1}. These spectral features suggest the formation of traces of Cr^{3+} and polymeric Cr^{6+}.

Reaction of dichloromethane and oxygen at 400 °C over Cr-catalysts results in a degradation to hydrochloric acid and CO/CO_2 [17,18,19]. During reaction the color of the catalyst turns from yellow/orange to green. The spectra on silica and alumina are almost the same and consists of three bands at 15,100; 23,300 and around 30,000 cm^{-1}, typical for

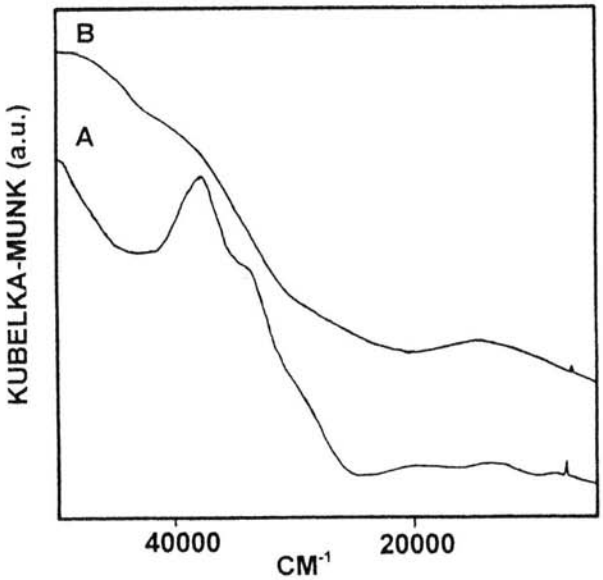

Figure 2. DRS spectra of Cr/SiO_2 (A) and Cr/Al_2O_3 (B) after interaction at 400 °C with CO.

free Cr^{6+} at 400 °C readily tranforms to Cr_2O_3, which cannot be reoxidized to Cr^{6+} by oxygen.

The DRS spectra of supported Cr catalysts after interaction with CO and H_2 are shown in respectively figure 2 and 3. Interaction at 400 °C results in a total removal of the CT bands of Cr^{6+} with the formation of d-d bands in the visible region, typically for reduced Cr (Cr^{3+} and/or Cr^{2+}). Blue Cr-silica catalysts are formed, while Cr/Al_2O_3 turns to blue-green and green-blue with respectively CO and H_2. On silica, mainly octahedral Cr^{2+} was formed with hydrogen, while with CO both tetrahedral and octahedral Cr^{2+} is present. On alumina, mainly Cr^{3+} is formed but traces of octahedral Cr^{2+} are detected after reduction with H_2.
Thus, after reduction with CO and H_2 mainly Cr^{3+} is formed on alumina, while on silica Cr^{2+} is the dominant species.

Reduction with ethylene at 100 °C gives blue catalysts. On alumina the spectrum is dominated by bands at 17,200; 24,900 and 38,600 with a shoulder at 12,800 cm^{-1}, while on silica the spectrum consists of bands at 16,400; 33,800 and a weak band at 10,000 cm^{-1}. In any case, the amount of Cr^{2+} is higher on silica than on alumina. The better catalytic performances of Cr/SiO_2 for ethylene polymerization [8] can be explained by the higher amount of Cr^{2+} on the silica surface.

The DRS spectra of ammonia treated supported Cr catalysts are totally different from

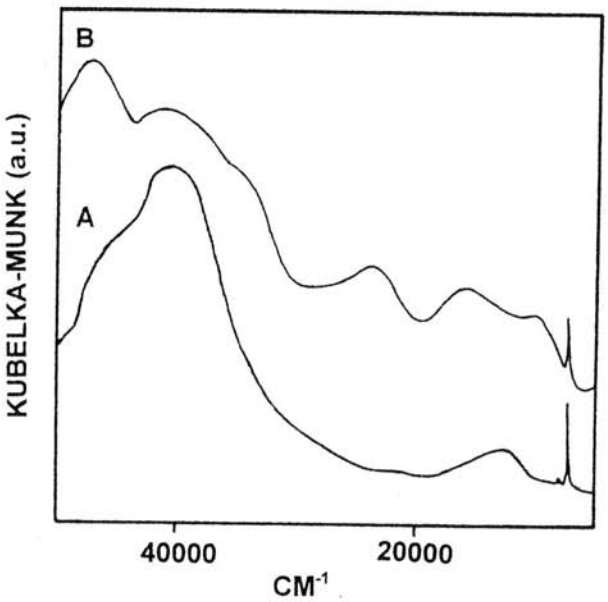

Figure 3. DRS spectra of Cr/SiO_2 (A) and Cr/Al_2O_3 (B) after interaction at 400 °C with H_2.

absorption bands at 14,900; 17,700; 28,100 and 38,300 cm^{-1} are observed. For Cr/SiO_2, bands are resolved at 14,900; 18,300; 27,000 and 36,900 cm^{-1}. The two latter bands are typical $O \rightarrow Cr^{6+}$ bands, while the two former absorptions are the first allowed d-d transitions of surface Cr^{3+}-complexes. The high value of 17,700 and 18,300 cm^{-1} for the first transition suggests the presence of at least one NH_3 molecule in the coordination sphere around Cr.

In summary, the interaction between a series of molecules with increasing basicity ($HCl < CH_2Cl_2 < CH_3CH_2CH_2OH \approx CH_3CH_2OH < H_2O < CO \approx H_2 \approx CH_2CH_2 < NH_3$) and Cr supported silica and alumina was spectroscopically evaluated. Two phenomena can occur : (1) hydrolysis of the Cr-O-Support bonding and (2) reduction of Cr^{6+} to a lower oxidation state. It is concluded that interaction with (weak) acids results in hydrolysis and reduction, while (weak) bases give only reduction. Reduction of Cr with ethylene, CO and H_2 goes mainly to Cr^{3+} on Cr/alumina, while on Cr/silica a mixture of Cr^{2+} and Cr^{3+} is formed. Interaction with ethanol and propanol gives reduction of non-anchored Cr^{6+} to Cr^{3+} and consequently an oxidation of the alcohols.

The observation that silica facilitates reduction, while on alumina reduction of Cr is more difficult, supports the idea of a support controlled redox behavior. Thus, the supports take actively part in the redox chemistry of Cr. This can be explained with the hardness-softness concepts, first introduced by Pearson : the higher the Al-content of the support, the harder the support, the less polarizable or susceptible for electron fluctuations, the more difficult reduction [13,14].

3.2. Influence of Ti on the interaction of CO as probe molecule with supported Cr

After calcination the supported Cr, Ti catalysts are orange, independently of the preparation method. The related ESR spectra show an axially symmetric signal with $g_\perp$ = 1.96 and $g_\parallel$ = 1.92, which is due to isolated Cr^{5+} (γ-signal) [8]. With DRS, the typical $O \rightarrow Cr^{6+}$ CT bands are detected. After reduction with CO at 400 °C, the colour turns to blue-green and green for respectively the first and second preparation method. The obtained DRS and ESR spectra are dependent on the preparation method. In ESR, a weak Cr^{5+} signal is observed on a broad isotropic signal with g around 2 (β-signal, due to clustered Cr^{3+} [8]). Quantitative ESR show that more than 98 % of the Cr^{5+}-species is reduced away for the Cr, Ti supported catalyst prepared by the first method, while for the other catalyst this amounts to 80 %. With DRS, octahedral and tetrahedral Cr^{2+} are observed on the catalyst surface prepared by the first method, while Cr^{3+} is the dominant species for the catalyst prepared by the second method.

In summary, the redox behavior of Cr on amorphous supports is dependent on the order of impregnation of Ti and Cr. When Cr is impregnated before Ti, the reduction of Cr is more difficult (more Cr^{3+} and Cr^{5+}), while the reverse order facilitates the reduction of Cr (more Cr^{2+}). This can be explained by a covering Cr by TiO_x, resulting in a redardation of the reduction.

Diffuse Reflectance Spectroscopy (DRS) and Electron Spin Resonance (ESR) are valuable spectroscopic techniques for the evaluation of the interaction of probe molecules with supported Cr and Cr, Ti catalysts. Two phenomena can take place upon interaction of supported Cr^{6+} with various probe molecules : (1) hydrolysis of the support-Cr bond and (2) reduction of supported Cr. The latter process is influenced by the support composition, the presence of additional elements (Ti, Al) and the sequence of impregnation. The supports take actively part in the redox chemistry of Cr and therefore one can suggest a support controlled redox behavior.

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