

EPR and UV–visible spectroscopic studies of alumina-supported chromium oxide catalysts

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Abstract

The oxidation state, the mobility and the molecular structure of chromium species present on $\text{CrO}_x\text{-Al}_2\text{O}_3$ catalysts have been studied by combined diffuse reflectance spectroscopy, EPR and reduction–extraction by ethane 1,2 diol. CrO_4^{2-} species exist on the alumina surface in the form of loosely-interacting species on hydrated surface (species A) and in the form of strongly bonded species on dehydrated Al_2O_3 surface (species B). The CrO_4^{2-} species show high mobility and are probably responsible for the formation of CrO_x clusters. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Supported chromium oxide catalysts have been widely used for the polymerization of ethylene [1,2] and dehydrogenation of light alkanes [3,4]. Earlier works in this laboratory, showed that chromia–alumina catalysts prepared in aerogel form by the autoclave method [5], is active and selective for the nitrooxidation of olefins [6], paraffins [7] and aromatics [8–11]. The interesting feature of alumina-supported chromium oxide catalysts was their high selectivity towards the formation of nitrile aromatic compounds either by nitrooxidation or by amoxidation of the corresponding aromatic

molecules. A variety of methods have been employed to increase the initial dispersion of chromium oxide on alumina surface: impregnation of Al_2O_3 carrier [12], co-hydrolysis of Al and Cr organic compounds under supercritical conditions [8,9] forming aerogels, co-precipitation of alumina and chromium salts with ammonia in aqueous solutions forming xerogels [8], sol–gel method [13,14]. Fundamental studies have provided evidence for a strong dependence of the oxidation state, and aggregation state of chromium species on the catalytic behavior of the mixed oxides. Several techniques have been used to discriminate among the various chromium species present on the carrier surface. Raman spectroscopy, UV–visible (Vis) diffuse reflectance and electron paramagnetic resonance have revealed interesting information on the

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molecular structures of surface chromium oxide species and on the oxidation state of the chromium ions. Chromium species on Al_2O_3 surface exist in the forms of mono, di and polychromate entities, the mobility of these species depending on the bond strength with Al_2O_3 surface. Chromium species are generally in the form of oxo compounds, the oxidation state of Cr strongly depending not only on the activation conditions but also on the chemical interaction with the carrier. Co-polymerization of chromium acetylacetonate and aluminium sec-butoxide through the sol–gel technique has been adopted to prepare $\text{CrO}_x\text{--Al}_2\text{O}_3$ catalysts. The present work is an attempt to determine how similar are the molecular structures of the surface chromium oxide species with those previously observed on the classical $\text{CrO}_x\text{--Al}_2\text{O}_3$ prepared by impregnation, or by adsorption of Cr(V)-1,2 ethylene diol complex on the support to ensure a higher dispersion of chromium species [15]. By combining diffuse UV–Vis spectroscopy with EPR along with the systematic study of $\text{CrO}_x\text{--Al}_2\text{O}_3$ before and after extraction with ethane 1,2 diol [16,17], we expect to determine the molecular structures and the oxidation states of chromium species present on the alumina surface. Although in general, the relative amount of polychromate species relative to monochromate increases with chromium loading [18,19] on samples, obtained by impregnation of the carrier, one could expect that on those samples obtained by the sol–gel technique allowing a better dispersion of chromium, the relative amount of monochromate and/or dichromate species would be high even at high chromium loading.

2. Experimental

2.1. Catalyst preparation

Appropriate amounts of chromium acetylacetonate and aluminum sec-butoxide were, respectively, dissolved in 100 cm^3 of methanol and 75 cm^3 of sec-butanol. The two solutions were

mixed and vigorously stirred. To this new solution, a small amount of water was added to start the hydrolysis of the chromium and aluminum compounds. The hydroxide forms polymerized with the subsequent formation of a gel. The gel was introduced in an autoclave and dried, within the hypercritical conditions of methanol. The solid formed was calcined at 410°C in air during 24 h in order to remove the organic residues and to convert the hydroxide form into the oxide form. Low temperature calcination was selected to avoid possible migration of Cr ions into the Al_2O_3 framework. Also the 410°C treatment temperature used in the preparation was chosen to correspond to the conditions used in the nitrooxidation and amoxidation reactions. The calcined samples are kept at ambient atmosphere.

2.2. Characterization of the catalyst

The specific surface area was determined from the adsorption isotherms of N_2 at 77 K using ASAP 2000 apparatus from Micrometrics. The crystallinity of the supported chromium oxide, was analyzed by X-ray diffraction (XRD), using a Phillips PW 1050/70 diffractometer and the copper K_α ($\lambda = 1.54051\text{ \AA}$). Analysis by UV–Vis was performed under ambient conditions, on a Perkin Elmer Lambda 9 spectrometer operating in the diffuse reflectance mode and using BaSO_4 as the reference. Measurements on solid were obtained by pressing the powder into pellet form in a special cell possessing spectrasil windows. EPR measurements were made on a Varian E101 spectrometer operating in the X-mode and 100 kHz field modulation. The apparatus was equipped with a dual cavity, the DPPH being the reference for g value determination. All spectra were recorded at 25°C and -196°C .

3. Results and discussion

The solids $\text{CrO}_x\text{--Al}_2\text{O}_3$ ($\%$, t , $^\circ\text{C}$) were referenced by the percentage of chromium ($\%\text{Cr}$)

and the temperature of calcination (t , °C). Thus, $\text{CrO}_x\text{-Al}_2\text{O}_3(10,410)$ corresponds to 10% chromium content and 410°C calcination temperature. The XRD spectrum indicated that the sample was amorphous. The BET surface area was $420 \text{ m}^2/\text{g}$.

3.1. Oxidation state of chromium ions in calcined $\text{CrO}_x\text{-Al}_2\text{O}_3(10,410)$ after rehydration in air

(a) Diffuse reflectance spectroscopy. Fig. 1a shows the spectrum recorded in the 200–1000 nm range. Two intense bands are observed at 270 and 370 nm. These bands are generally assigned [20–24] to $\text{O}^{2-} \rightarrow \text{Cr}^{6+}$ charge transfer transitions for chromate species. The band at 270 nm (I_1) was attributed to the charge transfer transition ${}^1A_1 \rightarrow {}^1T_2$ ($1t_1 \rightarrow 7t_2$ and $6t_2 \rightarrow 2e$) and the band at 370 nm (I_2) to ${}^1A_1 \rightarrow {}^1T_2$ ($1t_1 \rightarrow 2e$) transition. Fig. 1a shows also that along with these two intense bands, a shoulder

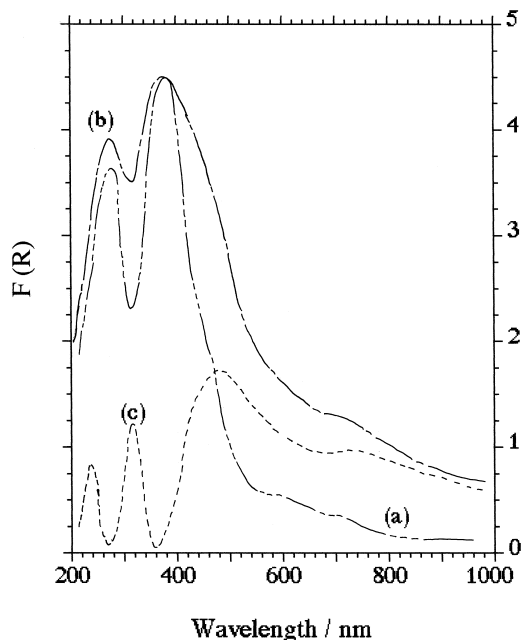


Fig. 1. Reflectance spectrum of $\text{CrO}_x\text{-Al}_2\text{O}_3$: (a) hydrated sample, (b) after thermal treatment at 410°C, and (c) difference spectrum (b-a).

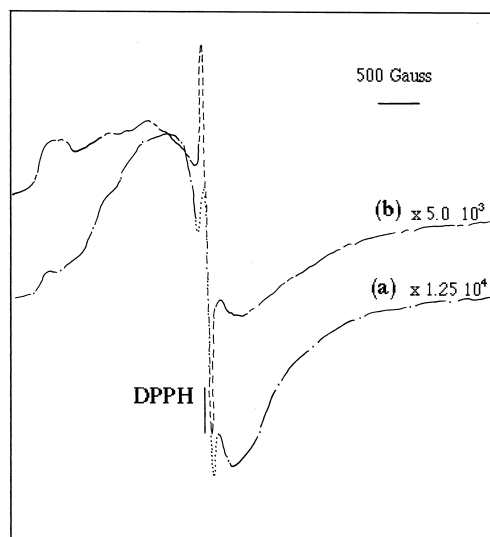


Fig. 2. EPR spectrum of hydrated $\text{CrO}_x\text{-Al}_2\text{O}_3$: (a) at room temperature, and (b) at liquid nitrogen.

at about 470 nm and two additional weak bands at about 600 and 720 nm are present. The band at 600 nm is usually assigned to a $d \leftrightarrow d$ transition of Cr^{3+} ions [22,25] in a strongly distorted octahedral crystal field: the transition ${}^4A_{2g} \rightarrow {}^4T_{2g}$ being invoked. These Cr^{3+} ions are present in a cluster of chromium oxide (β phase), which was not detected by XRD since the sample was amorphous. It has also been suggested that the band at 600 nm could be due to the presence of Cr^{6+} and Cr^{3+} ions, which interact through $d \leftrightarrow d$ electron exchange [26,27]. The shoulder at 470 nm and the weak $d \leftrightarrow d$ transition at 600–700 nm are indicative of chromate and dichromate species [21,25,28]. However it appears difficult, since $\text{Cr}^{4+}(3d^2)$ and $\text{Cr}^{5+}(3d^1)$ in octahedral symmetry, produce $d \leftrightarrow d$ transitions at almost identical values to propose univocal identification of the existing chromium species.

(b) EPR study. Fig. 2a shows the EPR spectrum for the $\text{CrO}_x\text{-Al}_2\text{O}_3(10,410)$ sample. The spectrum recorded at room temperature shows a weak isotropic resonance at ($g = 1.97$) with a line width of 65 G and a relatively broad resonance of 800 G width, centered at ($g = 1.95$). The former signal [29] was assigned to Cr^{5+}

ions (γ phase) and the latter signal [29] at ($g = 1.95$) to Cr^{3+} in Cr_2O_3 crystallites (β phase). In addition to these signals, weak peaks at higher g values (4.3–2.5) are observed and ascribed [29] to isolated Cr^{3+} ions experiencing low symmetry crystal field (δ phase). One can suggest that these ions correspond to Cr^{3+} ions, which have migrated in the alumina lattice and were incorporated in the framework. Fig. 2b represents the change in the EPR line intensity when the temperature of the measurement was lowered down to -196°C . Quantitative measurements show that the signal intensity of Cr^{3+} (δ phase) and Cr^{5+} (γ phase) followed the Curie law, the magnetic susceptibility being proportional to the reciprocal value of the absolute temperature. The line width of the Cr^{5+} species (65 G) did not vary significantly with the temperature. In contrast, the line width of the signal attributed to Cr^{3+} in β phase increased to 1200 G as the measurement temperature decreased to -196°C as expected for chromium ions in β phase. This β phase is assigned to Cr_2O_3 clusters [30]. The line width dependence of the β signal with the temperature, confirms that Cr(III) clusters are responsible for the broad EPR signal at ($g = 1.95$). The line width depends on the dipolar interaction between Cr(III) ions, which broadens the line and on spin coupling exchange which narrows the line. At low temperature, spin coupling exchange, is substantially decreased resulting in a subsequent line broadening.

(c) Reaction with ethane 1,2 diol. It has been shown that the reaction of supported chromium oxide with ethane 1,2 diol results in the formation of the bis-ethane 1,2 dioatochromate (V) anion, which can be detected by EPR. The formation of these anions is due to the reduction of Cr^{6+} ions, present on the surface, to form a Cr(V) anion complex with the ethane 1,2 diol [31]. Such reaction and the identification by EPR of a well resolved nine line hyperfine structure attributed to the interaction of the unpaired electron with eight equivalent protons from two coordinated ethane 1,2 diol molecules

represents a very sensitive test to reveal the existence of Cr^{6+} ions [16,17,30].

The sample of $\text{CrO}_x\text{-Al}_2\text{O}_3(10,410)$ rehydrated in air, was contacted with a solution of ethane 1,2 diol, incubated during 5 min at 80°C , filtered and then dried at 80°C . UV–Vis reflectance spectroscopy and EPR techniques were applied to identify the oxidation state of the chromium species, present on the ethane 1,2 diol treated sample and in the mother ethane 1,2 diol solution.

3.1.1. Study of the solid

Fig. 3 shows the UV–Vis reflectance spectrum of the ethane 1,2 diol extracted sample. Two intense bands at 435 and 600 nm are observed. They correspond to the $d \leftrightarrow d$ transition of Cr^{3+} ions in octahedral crystal field. Two additional bands at 250 and 340 nm are also present. By comparing Figs. 1 and 3, it is concluded that the charge transfer bands I_1 and I_2 existing on the untreated sample have considerably decreased. The decrease is due to the reaction of ethane 1,2 diol with Cr^{6+} ions initially present, and their extraction into the solution. The second observation which can be made, is that subsequently to the extraction of Cr^{6+}

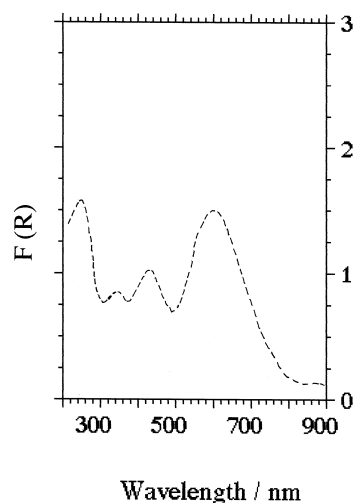


Fig. 3. UV–Vis reflectance spectrum of ethane 1,2 diol extracted sample.

ions by ethane 1,2 diol, Cr^{6+} ions initially present are reduced to the Cr^{3+} oxidation state as evidenced by the reflectance bands at 600 and 435 nm. These conclusions are further supported by the EPR study of ethane 1,2 diol extracted sample. Fig. 4a and b represent the EPR spectra of the sample at room temperature and at -196°C . By comparison with Fig. 2, one may conclude, that the signal due to Cr^{5+} (γ phase) has disappeared and simultaneously, an intense and broad signal at ($g = 1.98$) has appeared, this signal being attributed to Cr^{3+} in Cr_2O_3 clusters. As expected, the line width of this signal, increased from 550 to 1000 G as the measurement temperature decreased from 25°C to -196°C . Treatment with ethane 1,2 diol removes completely the γ signal, attributed to isolated Cr(V) . It is concluded that isolated CrO_4^- species formed with ethane 1,2 diol soluble Cr(V) complexes. $\text{CrO}_x\text{-Al}_2\text{O}_3$ prepared by sol-gel procedure presents on its surface, even for Cr contents up to 10%, isolated chromate $[(-\text{O})_2\text{Cr(=O)}_2]^{2-}$ and Cr(V) chromyl $[\text{O}_3\text{Cr=O}]$ which are washed out by ethane 1,2 diol. It has been shown that Cr(VI) on silica was readily reduced to Cr(III) by ethanol at low temperature [32].

On the basis of the foregoing, the surface of oxidized $\text{CrO}_x\text{-Al}_2\text{O}_3(10,410)$ can be described by isolated Cr^{6+} ions, easily extracted and reduced to Cr^{5+} by reaction with ethane 1,2 diol and Cr_2O_3 in the form of small crystallites

supported on Al_2O_3 and exhibiting ferromagnetic properties. In addition to these chromium species, one can suggest that chromium oxide oligomers, which as $(\text{Cr-O-Cr-O-Cr})_x$ may also be present on the Al_2O_3 surface, where the oxidation state of Cr ions are Cr^{3+} and Cr^{6+} . These Cr ions would experience electron interaction or electron exchange through the Cr-O bond, to produce Cr(V) species. The suggestion that Cr(V) ions revealed by the EPR signal at ($g = 1.97$) exist either in isolated chromyl(V) and dichromyl(V) species $[(-\text{O})_3\text{Cr=O}]$, and in chromium oligomers $(\text{Cr}^{6+}\text{-O}^{2-}\text{-Cr}^{3+}\text{-O}^{2-}\text{-Cr}^{6+})_x$ is supported by the temperature dependence of the Cr(V) EPR signal intensity with the temperature. Before ethane 1,2 diol reaction, the signal at 1.97 due to Cr(V) followed the Curie-Weiss law indicating that Cr(V) ions were magnetically isolated. Following ethane 1,2 diol reaction, these isolated Cr(V) species were removed and Cr(VI) clusters reduced into Cr_2O_3 . Heat treatment in air at 410°C partially oxidized these chromium clusters, $(\text{Cr}^{6+}\text{-O}^{2-}\text{-Cr}^{3+}\text{-O}^{2-}\text{-Cr}^{6+})$ species being formed. EPR spectrum of the sample extracted and reoxidized at 410°C showed signal at (1.97). In contrast with the previous signal, the latter signal did not follow the Curie-Weiss law. It behaves like a ferro or antiferromagnetic substance, the magnetic susceptibility decreasing as the temperature decreased. Cr(V) ions were found in $(\text{Cr}^{6+}\text{-O}^{2-}\text{-Cr}^{3+}\text{-O}^{2-}\text{-Cr}^{6+})_x$ clusters.

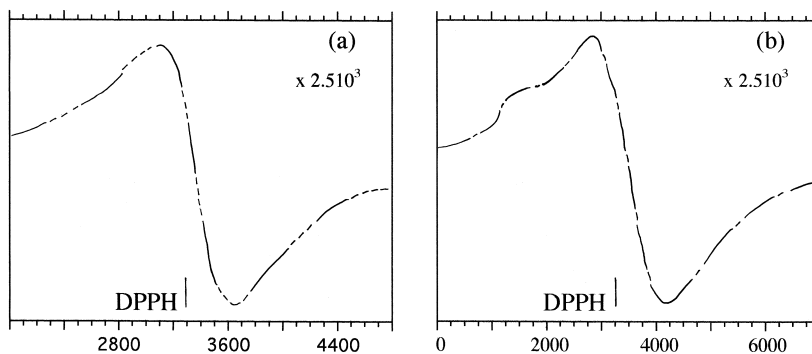


Fig. 4. EPR spectrum of ethane 1,2 diol extracted sample. (a) At room temperature, and (b) at liquid nitrogen.

3.1.2. Study of the liquid phase

The solution of ethane 1,2 diol which has been contacted with $\text{CrO}_x\text{-Al}_2\text{O}_3(10,410)$ and then filtered was analyzed by EPR and by UV–Vis spectroscopy. Fig. 5 shows the EPR spectrum of solution at room temperature. The measured g -value of the paramagnetic species is found to be (1.98). The EPR spectrum shows a well-resolved, hyperfine structure with nine hyperfine lines and a hyperfine splitting of 6.4 G. This spectrum is identical to that previously, identified to the bis-ethane 1,2 dioatochromate (V) complex anion with the unpaired electron of Cr^{5+} interacting with eight equivalent protons of two ethane 1,2 diol ligands [16,17], no complex was formed with Cr^{3+} [17]. These results confirm that Cr^{6+} indeed exists on the 410°C oxidized $\text{CrO}_x\text{-Al}_2\text{O}_3$ sample and that, at least, part of these Cr^{6+} ions can be as expected, reduced to Cr^{5+} by ethane 1,2 diol and extracted through solubilization by complexation with ethane 1,2 diol. Fig. 6a shows the transmission UV–Vis spectrum of the ethane 1,2 diol solution after $\text{CrO}_x\text{-Al}_2\text{O}_3$ extraction. A

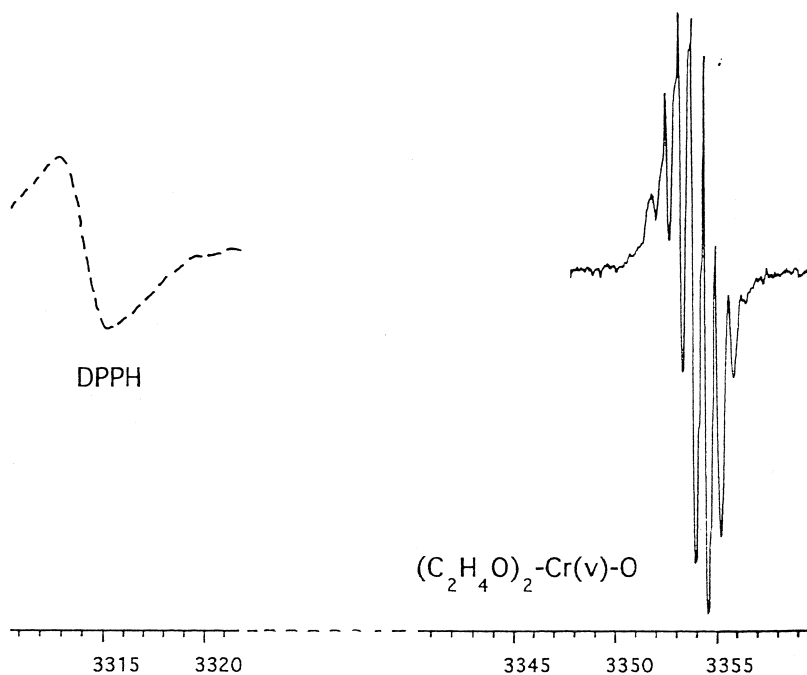


Fig. 5. EPR spectrum of ethane 1,2 diol solution, at room temperature.

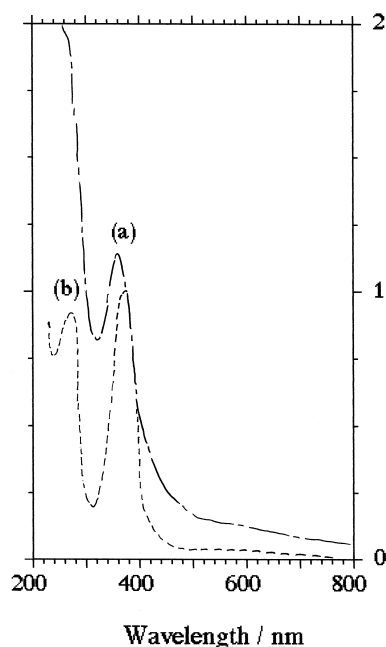


Fig. 6. UV–Vis transmittance spectrum of ethane 1,2 diol solution after $\text{CrO}_x\text{-Al}_2\text{O}_3$ extraction. (a) Before NaOH addition, and (b) after NaOH addition.

narrow and intense band at 360 nm along with a relatively broad and low intensity band at 600

nm were observed. It is obvious that at least one of these two bands should be attributed to the Cr^{5+} in the bis-ethane 1,2 dioatochromate (V) anion, identified by EPR. In order to discriminate which of the two UV–Vis bands shown in Fig. 6a is due to the Cr (V) complex, a small amount of NaOH (0.1M) was added to the chromium ethane 1,2 diol solutions. It has been mentioned in the literature [33] that upon addition of a dilute solution of NaOH, Cr^{5+} ions are spontaneously converted to Cr^{6+} and Cr^{3+} ions following a dismutation reaction.



Fig. 6b shows the UV–Vis spectrum of the previous solution in which, NaOH solution has been added. One observes that the band at 600 nm is almost unchanged while apparently the band at 360 nm is replaced by UV–Vis bands at 370 and 270 nm attributed to the I_2 and I_1 charge transfer bands in Cr^{6+} species formed by Cr^{5+} dismutation. Hence, one can conclude that the UV–Vis band at 360 nm is due to Cr^{5+} in the bis-ethane 1,2 dioatochromate anion, formed by reduction of Cr^{6+} present in $\text{CrO}_x\text{-Al}_2\text{O}_3(10,410)$.

3.2. Oxidation state of $\text{CrO}_x\text{-Al}_2\text{O}_3(10,410)$ sample after dehydration at 410°C

The $\text{CrO}_x\text{-Al}_2\text{O}_3$ sample was again calcined in air at 410°C . This sample was studied by diffuse reflectance spectroscopy and by EPR.

(a) UV–Vis Study. Fig. 1b shows the reflectance spectrum. This spectrum contains the previous charge transfer bands I_1 and I_2 at 270 and 370 nm whose width are much larger than those in Fig. 1a. In addition, the band intensity at 720 nm has increased. Fig. 1c resulting from the difference of spectrum Fig. 1b and a indicates the presence of an intense band at 480 nm and two charge transfer bands at 240 and 320 nm.

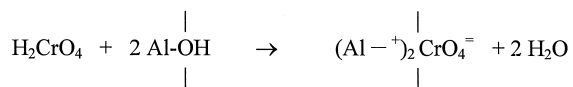
(b) EPR study. Upon heating the sample at 410°C , the EPR spectrum of Cr^{5+} ions (γ

species) was found approximately three times more intense than that of the hydrated sample. This γ signal obeyed the Curie–Weiss law when the temperature of the measurement decreased from room temperature to liquid nitrogen temperature, while the line width remained unchanged. By contrast, the EPR signal of the Cr^{3+} (β phase and δ phase) was unchanged following dehydration, indicating that these species are indeed bulk species.

(c) Reaction with ethane 1,2 diol. The sample was subjected to ethane 1,2 diol reaction and UV–Vis analysis along with EPR measurement, similar to those described above. Again, one observed that Cr^{5+} ions have disappeared, as well as the charge transfer bands of Cr^{6+} ions. However, it is important to point out that, although the EPR signal of bis-ethane 1,2 dioatochromate (V) complex is still detectable in the solution, its concentration is very low, as compared to the results obtained on the hydrated sample.

4. Conclusion

The results presented above and the proposed interpretations allow us reasonably to conclude that the surface of $\text{CrO}_x\text{-Al}_2\text{O}_3$ calcined and dehydrated at 410°C is formed by chromate species CrO_4^- anchored on the surface of Al_2O_3 :



following the surface reaction [24]. We do not exclude the possible existence of dichromate Cr_2O_7^- . These chromium species Cr^{6+} (CrO_4^-) are isolated and atomically dispersed on the alumina surface. In addition to these chromium species, bulk CrO_3 and Cr_2O_3 crystals are present, Cr_2O_3 showing anti or ferromagnetic properties. To explain the presence of Cr^{5+} ions, it is assumed that in the bulk CrO_x particles,

($\text{Cr}^{6+}-\text{O}^{2-}-\text{Cr}^{3+}-\text{O}^{2-}-\text{Cr}^{6+}$) species are present, Cr^{6+} and Cr^{3+} within these species experiencing electron transfer ($\text{Cr}^{6+}-\text{O}^{2-}-\text{Cr}^{3+}-\text{O}^{2-}-\text{Cr}^{6+}$) \Leftrightarrow ($\text{Cr}^{5+}-\text{O}^{2-}-\text{Cr}^{5+}-\text{O}^{2-}-\text{Cr}^{5+}$). In addition, we also concluded that part of the anchored isolated chromium species were in the form of Cr(V) chromyl species such as $[(-\text{O})_3\text{Cr}=\text{O}]$. Upon reaction of the chromium species with ethane 1,2 diol, there is very little reduction and extraction of the Cr^{6+} ions in the form of the bis-ethane 1,2 dioatochromate (V) complex probably because the isolated surface chromate CrO_4^- species are strongly bonded to the surface of alumina. It has been recognized that, upon impregnation of the alumina surface with the solution of H_2CrO_4 , acid–base reaction occurs [21–25,34,35]. These anchored chromate species are responsible for the charge transfer band at 260–250 nm, which is shifted by about 10–20 nm from the value measured on nearly free CrO_4^- chromate ions at 270 nm. This shift reflects the strong interaction existing between CrO_4^- ions and the alumina surface [23,24,34,35]. This strong interaction renders difficult, if not impossible, the extraction of CrO_4^- by ethane 1,2 diol. Upon rehydration of the solid, an OH, H_2O monolayer is formed on the alumina surface. The hydrated surface of Al_2O_3 becomes less reactive towards CrO_4^- ions and the strong interaction between CrO_4^- and Al_2O_3 surface is suppressed. CrO_4^- ions behave now like unperturbed free chromate species, charge transfer bands are observed at 270 nm as expected. Furthermore, there is no restriction for these Cr^{6+} species to be reduced by ethane 1,2 diol and extracted following complexation with the reducing organic solvent. The Cr(V) complex is thus recovered in the ethane 1,2 diol solution, as demonstrated by the EPR results.

In conclusion, we have shown by the combined studies of alumina supported chromium oxide by UV–Vis and EPR spectroscopies and by the use of ethane 1,2 diol to reduce and to extract chromium species, that several chromium species are present at the alumina surface, among them CrO_4^- bound to the surface of Al_2O_3 ; the

extent of bonding being strongly dependent on the surface hydration. Bulk chromium oxides are responsible for the presence of ($\text{Cr}^{5+}-\text{O}^{2-}-\text{Cr}^{5+}-\text{O}^{2-}-\text{Cr}^{5+}$) clusters. Cr_2O_3 particle gives rise to the ferromagnetic properties revealed by EPR. Furthermore the sol–gel preparation technique employed in this work, allowed to maintain relatively high dispersion of chromium species at high chromium content. Two decades ago, Derouane et al. [15] have shown that chromium species highly dispersed on oxide carriers were obtained by the adsorption of Cr(V)-1,2 ethane diol complex.

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