Mobility of chromium in inorganic oxides

Spectroscopic fingerprinting of oxidation states and coordination environments

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The mobility of Cr^{n+} in inorganic oxides has been investigated by combined diffuse reflectance (DR)–EPR spectroscopies as a function of the Cr oxidation state, the type of inorganic oxide (silica, alumina and mordenite) and the environmental conditions (hydrated and dehydrated state). Cr^{n+} ions are mobile under hydrated and dehydrated conditions and Cr^{n+} preferentially migrates from silica to alumina and, to a lesser extent, to mordenite, although only a small amount of migration of Cr^{n+} is observed from alumina to mordenite and *vice versa*. The observed preference sequences are discussed in relation to the properties of the inorganic oxides.

Knowledge of the mobility of transition metal ions such as Cr^{n+} on the surface of inorganic oxides is important for the following reasons: (1) Cr^{n+} ions (with $n = 5$ and 6) are environmental and health hazards and (2) supported chromium oxides are industrially important catalysts *e.g.* for ethylene polymerization (Phillips catalyst) and alkane dehydrogenation (Houdry catalyst).[1-6] One generally assumes that CrO_4^{2-} and $Cr_2O_7^{2-}$ are mobile species under normal environmental conditions and that $Cr(H_2O)_6^{3+}$ is immobile. This is because the inorganic fraction of soils and natural waters is usually negatively charged and therefore adsorbs $Cr(H_2O)_6^{3+}$ and repels chromate and dichromate ions.[1,3]

In heterogeneous catalysts, Cr ions are anchored as chromate, dichromate or in the form of polychromate onto SiO_2 or Al_2O_3 surfaces, but can also be present as Cr_2O_3 particles. The relative amounts of each of these species depend on the Cr-loading, support and pretreatment.[4] Anchoring means that chemical bonds are formed between Cr and surface oxygens upon calcination above 300 °C.
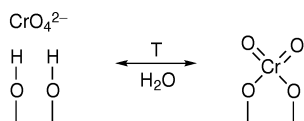
The questions are then (1) whether Cr^{n+} ions are mobile and to what extent and (2) which parameters govern the mobility of Cr^{n+} ions. *A priori*, the following factors will intervene: (1) the strength of the $Cr—O—M$ (M = Si, Al) bond and therefore the type of supporting oxide; (2) the presence of water molecules and (3) the Cr oxidation state.

When two oxides are in competition for Cr, the latter may selectively go to the oxide with which it has the strongest affinity. It is this competition that is studied and reported here. Spectroscopic fingerprints of Cr^{n+} are used to evaluate the preference of Cr^{n+} for oxides and its mobility. Silica, alumina and mordenite were chosen as inorganic oxides because we know, from our previous work, that different oxidation states and coordination environments of Cr on these supports can be distinguished from each other by DRS and EPR.[7-11] We will show that combined DRS–EPR is an excellent method to study preference sequences of transition metal ions in inorganic oxides.

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Experimental

Na-mordenite, from Norton, with a cation exchange capacity of 0.168 meq g^{-1} and an anhydrous unit cell composition of $Na_{0.5}Al_{0.5}Si_{47.5}O_{96}$ was put in its Na^+ form by two successive exchanges with 1 M NaCl solutions, washed Cl^--free and dried in air at room temperature overnight. SiO_2 (735 m² g^{-1}) and Al_2O_3 (365 m² g^{-1}) were home-made. Details about the preparation method and properties have been published elsewhere.[7,8] 2 g of these inorganic oxides were impregnated by the incipient wetness technique with an aqueous solution of CrO_3 (UCB, p.a.) so as to obtain a Cr-loading of 1 wt.%.

For the mobility measurements under hydrated conditions, 2 g of the Cr^{6+}-loaded inorganic oxide was physically mixed in a mortar with 2 g of an unloaded inorganic oxide. The mixtures were granulated and the size fraction 0.25–0.50 mm was loaded into a quartz flow cell with a Suprasil window for DRS and a side-arm for EPR measurements. EPR and DR spectra were taken of the sample before calcination, as a function of time, and after calcination. Calcination was performed at 550 °C for 15 h with an O_2 flow rate of 3600 ml h^{-1}.

For the mobility measurements under dehydrated conditions, equal amounts of a Cr^{6+}-loaded inorganic oxide and an unloaded inorganic oxide were calcined at 550 °C for 15 h in a specially designed quartz cell. This cell, with a Suprasil window for DRS measurements, has two cups in which the two powders were calcined separately. A transfer-arm between the two cups enables the mixing of the dehydrated powders, after calcination, without atmospheric exposure. The mixture was then further calcined at 550 °C and DR spectra were taken after 10 h.

EPR spectra were taken on a Bruker ESP 300E instrument in X-band at a microwave power of 200 μW with a double rectangular TE_{104} mode cavity between 120 and 300 K. DR spectra were taken on a Varian Cary 5 UV–VIS–NIR spectrophotometer at room temperature. The spectra were recorded against a halon white reflectance standard in the range 2500–200 nm and treated with a commercial software package Grams/386 of Galactic Industries Inc. as described elsewhere.[7,8]

Results

Spectroscopic fingerprints of Cr^{n+} on inorganic surfaces

Silica, alumina and mordenite were chosen as inorganic oxides because previous work has shown that, on these supports,

Cr^{n+} ions exist in different oxidation states and coordination environments, which can be distinguished by a combination of DR and EPR spectroscopies.[7–11] The reference DR and EPR spectra are given in Fig. 1 and 2, respectively. The DR spectra of hydrated Cr^{6+} are characterized by charge-transfer transitions of the type O → Cr^{6+} (d^0).[7,8] The DR spectra of Cr/Al$_2$O$_3$ and Cr/mordenite have two charge-transfer transitions around 270 and 370 nm, characteristic for chromate. For Cr/SiO$_2$ these bands are slightly shifted to shorter wavelengths and a third band appears at 450 nm. This is indicative of the presence of dichromate and polychromate species. DR spectra of both Cr/mordenite and Cr/SiO$_2$ have a weak broad band in the region 550–800 nm. This is a d–d transition of Cr^{3+}.[12]

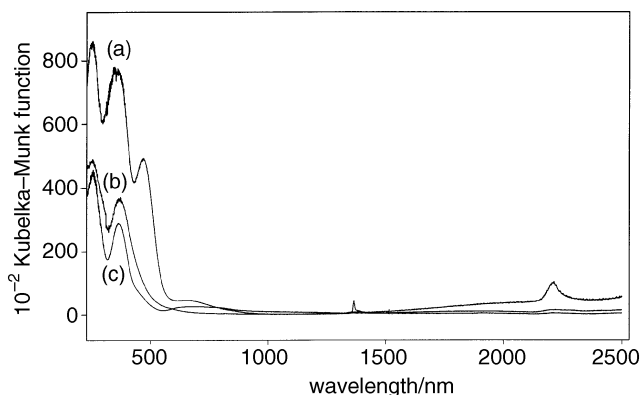**Fig. 1** DR reference spectra of Cr supported on inorganic oxides after calcination at 550 °C: (a) 1 wt.% Cr/SiO$_2$; (b) 1 wt.% Cr/Al$_2$O$_3$ and (c) 1 wt.% Cr/mordenite

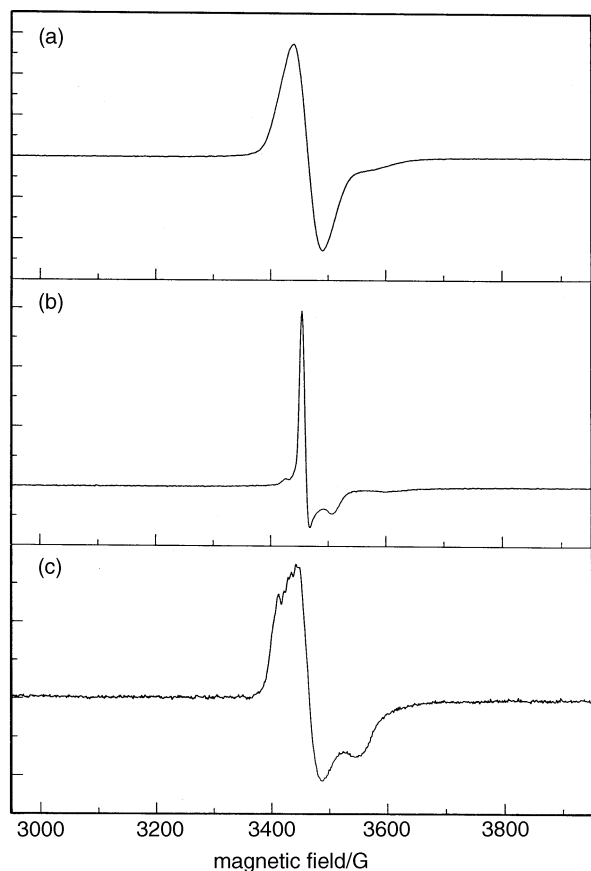**Fig. 2** EPR reference spectra of Cr supported on inorganic oxides after calcination at 550 °C: (a) 1 wt.% Cr/Al$_2$O$_3$; (b) 1 wt.% Cr/SiO$_2$ and (c) 1 wt.% Cr/mordenite (measured at 120 K after flushing in He)

The EPR spectra are typical for Cr^{5+} (d^1) in various coordination environments.[1] Cr^{5+} on alumina possesses an axially symmetric EPR signal with broad lines centred at $g_{\parallel}$ = 1.910 and $g_{\perp}$ = 1.978, whereas, on silica, this signal is rhombic with sharp lines centred at g_{xx} = 1.978, g_{yy} = 1.969 and g_{zz} = 1.895. Cr^{5+} in mordenite has a special EPR signal, which is the combination of two spectra: one rhombic with ^{27}Al superhyperfine splitting (g_{xx} = 1.98; g_{yy} = 1.99; g_{zz} = 1.93 and A_{xx} = 7 G) and another, rhombic without superhyperfine splitting (g_{xx} = 2.00; g_{yy} = 1.98 and g_{zz} = 1.92).[11] On the basis of these spectroscopic differences, one can distinguish Cr on different inorganic oxides and study its preference for inorganic oxides.

Mobility and preference of Cr^{n+} in hydrated conditions

In an initial experiment, Cr^{6+}-impregnated silica was mixed with an equal amount of alumina and DR spectra of the mixture were measured as a function of time. The DR spectra are shown in Fig. 3. At time 0, the DR spectrum is silica-like. With time, the two main charge-transfer bands shift to longer wavelength and the shoulder at 450 nm decreases in intensity. The final DR spectrum, 2 h after mixing, is clearly alumina-like. Thus, hydrated Cr^{6+} readily migrates from silica to alumina.

In another experiment, air-dry Cr^{6+}-impregnated silica was mixed with an equal amount of hydrated and unloaded silica, alumina or mordenite and the obtained mixtures were calcined at 550 °C immediately after mixing. After calcination, the presence of Cr^{n+} was evaluated by DRS (Cr^{6+} and Cr^{3+}) and EPR (Cr^{5+}) and the spectra obtained are shown in Fig. 4 and 5. The DR and EPR spectra of 1 wt.% Cr/SiO$_2$–Al$_2$O$_3$ after calcination are Cr/Al$_2$O$_3$ spectra. Thus, both chromate and Cr^{5+} species are found on Al$_2$O$_3$. The shoulder at 450 nm may be indicative of some residual Cr^{6+} on silica. Additionally, the weak d–d band of Cr^{3+} around 550 nm has disappeared, showing that Cr^{3+} has also been oxidized and migrated to alumina. For the 1 wt.% Cr/SiO$_2$–mordenite mixtures both the DR and EPR spectra are 'mixed' spectra. Both Cr^{6+} and Cr^{5+} are distributed over SiO$_2$ and mordenite and a clear indication for preference cannot be given. The Cr^{3+} band of the mixture is broader than that of Cr^{3+}/SiO$_2$, which is indicative of migration of Cr^{3+} to mordenite without oxidation to Cr^{6+}.

Analogous experiments were carried out with Cr/alumina and Cr/mordenite, where the DR and EPR spectra of Cr^{6+}/alumina, mixed with alumina, silica or mordenite, show that Cr^{5+} and Cr^{6+} ions are always present on alumina, independent of the mixed oxide. Similar results were obtained with
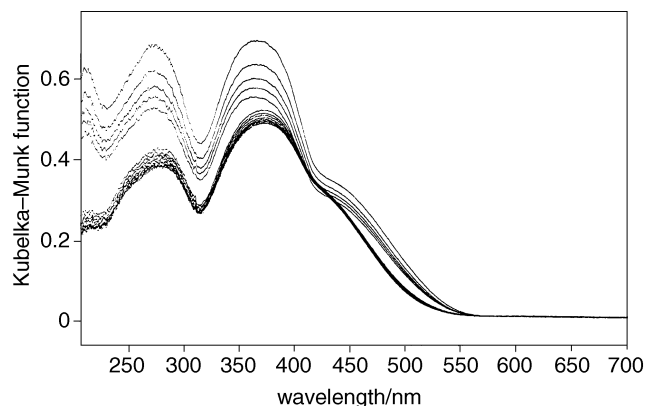

Fig. 3 DR spectra of 1 wt.% Cr/SiO$_2$ mixed with Al$_2$O$_3$ under hydrated conditions as a function of time. (The initial material is characterized by the DR spectrum with the highest Kubelka–Munk values at *ca.* 270, 370 and 450 nm. The Kubelka–Munk values at *ca.* 270, 370 and 450 nm gradually decrease with increasing time.)
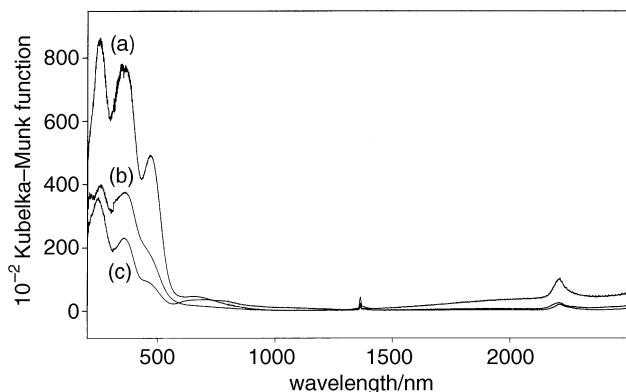
Fig. 4 DR spectra of 1 wt.% Cr/SiO_2 mixed and calcined at 550 °C with (a) SiO_2, (b) Al_2O_3 and (c) mordenite

Fig. 6 DR spectra of (a) a mixture of calcined 1 wt.% Cr/SiO_2 and calcined Al_2O_3 after heating at 550 °C for 10 h and (b) a mixture of calcined 1 wt.% Cr/SiO_2 and calcined mordenite after heating at 550 °C for 10 h

Cr^{6+}-impregnated mordenite, mixed with mordenite, silica or alumina, and in all cases DR and EPR spectra typical of Cr^{n+}-mordenite were measured. Thus, Cr^{n+} preferentially migrates from silica to alumina and, to a lesser extent, to mordenite, but little migration of Cr^{n+} from alumina or mordenite to the other oxides is observed.

Mobility and preference of Cr^{n+} in dehydrated conditions

When a calcined Cr catalyst was mechanically mixed with a calcined support with complete exclusion of air (10^{-5} Pa), and the mixture was heated at 550 °C for 10 h, it was observed that no migration of Cr^{n+} from Cr/alumina to silica and mordenite occurred. The same observation was made for Cr^{n+}/mordenite.

The situation is different for calcined Cr/silica mixed with calcined alumina or calcined mordenite, as shown in Fig. 6. For the calcined Cr/SiO_2–Al_2O_3 mixture a Cr^{6+}/Al_2O_3 DR spectrum is obtained. The transfer of Cr^{n+} from silica to alumina is incomplete as indicated by a weak band of dichromate/polychromate at 450 nm and a weak d–d band of Cr^{3+} at 600–800 nm. For the calcined mixture of Cr/SiO_2–mordenite, there is no residual Cr^{3+}, and a pro-

nounced shoulder at 450 nm is evident in the DR spectrum of Fig. 6. As this shoulder is absent for calcined Cr/mordenite (Fig. 1) it is indicative of incomplete migration of Cr^{6+} from silica to mordenite in the absence of water. Thus, the sequence of preference seems to be: alumina > mordenite > silica.

Discussion

With the series of mobility experiments described here it is not possible to give a detailed quantitative speciation of Cr or to describe the kinetics of its mobility, but it is possible to show that spectroscopic signatures of Cr^{n+} can be used to study preferences when different inorganic oxides are in competition for Cr^{n+} ions. What is needed for such a spectroscopic study are clearly distinguishable spectra with well established interpretation. Cr^{6+} (chromate, dichromate, . . .), Cr^{5+} and Cr^{3+} are favourable cases in that respect. The next steps, the quantitative interpretation and a study of the kinetics of the migration of transition metal ions, in our case Cr^{n+}, over hydrated and calcined oxide surfaces, are major challenges in heterogeneous catalysis. In principle, the tools are now available to perform such studies. At low Cr loadings, a quantitative analysis of DR spectra is possible.[7] If a sufficiently large dataset of spectra can be generated, statistical data analysis is possible, giving the number of components involved and the evolution of their intensity or concentration.[13] Finally, by *in situ* DR spectroscopy it has been possible to follow the kinetics of the reduction of Cr^{6+} and to propose a kinetic model.[14]

On the hydrated surfaces, CrO_4^{2-} and $Cr_2O_7^{2-}$ are present in the adsorbed water phase. This allows a fast and easy migration which is indeed observed. For all binary mixtures, Cr^{6+} prefers the alumina surface, where it is adsorbed as a chromate anion. There are two reasons for this preference: (1) electrostatic attraction between CrO_4^{2-} and positively charged sites at the alumina surface ($Al—OH_2^+$); (2) an acid–base reaction between chromic acid and alumina. The bulk reaction is:

$$3H_2CrO_4 + Al_2O_3 \leftrightarrow 2Al(CrO_4)_3 + 3H_2O$$

but it only occurs at the surface, where it can be represented as an acid–base reaction:

$$H_2CrO_4 + 2Al—OH \leftrightarrow (Al—^+)_2[CrO_4^{2-}] + 2H_2O$$

The silica surface is much more acidic,[15,16] and thus chromate and dichromate are present in the adsorbed aqueous phase
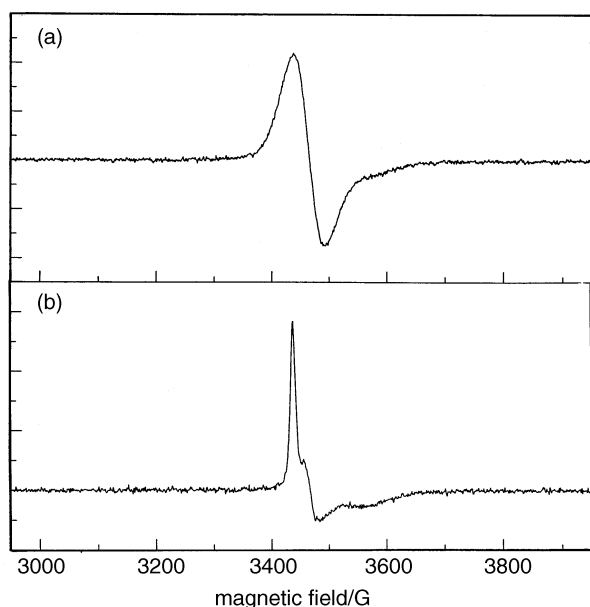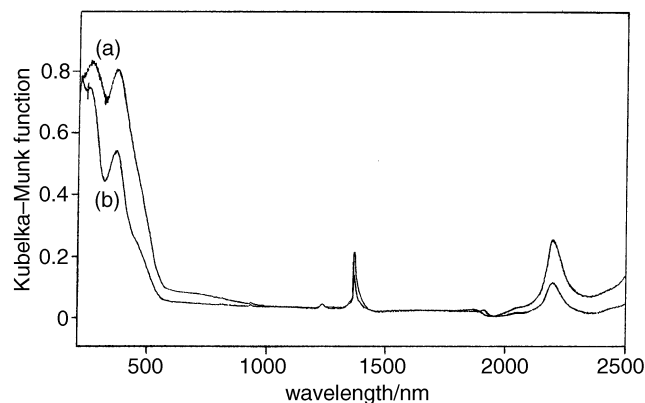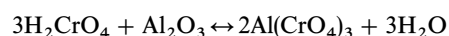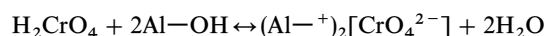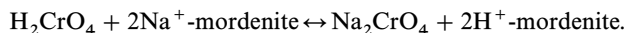

Fig. 5 EPR spectra of 1 wt.% Cr/SiO_2 mixed and calcined at 550 °C with (a) Al_2O_3 and (b) mordenite (measured at 120 K after flushing in He)

and the acid–base reaction is much less important. Finally, in the presence of Na^+-mordenite, Na^+ ions are exchanged for protons to form the acidic zeolites and an adsorbed Na_2CrO_4 phase:

$$H_2CrO_4 + 2Na^+\text{-mordenite} \leftrightarrow Na_2CrO_4 + 2H^+\text{-mordenite}.$$

The reaction is driven to the right and Na^+-mordenite takes an intermediate position in the preference scale of CrO_4^{2-}.

When the hydrated mixed oxides are calcined, the same preference scale is observed, because CrO_4^{2-} redistribution has occurred in the adsorbed water phase before calcination. In the calcined oxides, Cr^{6+} is anchored as chromate or dichromate and mobility is expected to be strongly reduced since it involves breaking and formation of bonds. A mechanism cannot be proposed, but the preference is always for alumina, because of its basic character.[15,16] In the case of $Cr/SiO_2–Al_2O_3$, it is the absorption band of (poly)dichromate which decreases in intensity upon mixing with Al_2O_3. In the case of Cr/SiO_2–mordenite, the mobility also involves migration of Cr^{3+} towards mordenite, because of the ion-exchange properties of the latter. The migration of anchored transition metal ions over calcined oxide surfaces has major consequences for the lifetime of heterogeneous catalysts in industrial plants (*e.g.* Houdry Cr/Al_2O_3 catalysts) and only a little is known about it. The problem may need closer attention, now that tools are available to study this phenomenon.

Conclusions

We have shown that combined DR–EPR spectroscopies provide an excellent method to study mobility and preference sequences of Cr^{n+} in silica, alumina and mordenite. Cr^{n+} ions are mobile and selectively migrate from one inorganic oxide to another when two different oxides are brought in contact. Cr^{n+} preferentially migrates from silica to alumina and to a lesser extent to mordenite, while little migration is observed from alumina to mordenite and *vice versa*. In all cases, the strong preference of Cr^{n+} ions for alumina is evident. The use of spectroscopic fingerprints to study preference sequences in inorganic oxides is, in principle, also applicable to other transition metal ions.

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