

# Mobility of chromium in inorganic oxides

## Spectroscopic fingerprinting of oxidation states and coordination environments

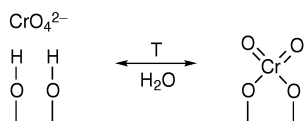
Bert M. Weckhuysen,\*† Bart Schoofs and Robert A. Schoonheydt

Centrum voor Oppervlaktechemie en Katalyse, Departement Interfasechemie, K. U. Leuven, Kardinaal Mercierlaan 92, 3001 Heverlee (Leuven), Belgium

The mobility of  $\text{Cr}^{n+}$  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).  $\text{Cr}^{n+}$  ions are mobile under hydrated and dehydrated conditions and  $\text{Cr}^{n+}$  preferentially migrates from silica to alumina and, to a lesser extent, to mordenite, although only a small amount of migration of  $\text{Cr}^{n+}$  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  $\text{Cr}^{n+}$  on the surface of inorganic oxides is important for the following reasons: (1)  $\text{Cr}^{n+}$  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).<sup>1–6</sup> One generally assumes that  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  are mobile species under normal environmental conditions and that  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  is immobile. This is because the inorganic fraction of soils and natural waters is usually negatively charged and therefore adsorbs  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  and repels chromate and dichromate ions.<sup>1,3</sup>

In heterogeneous catalysts, Cr ions are anchored as chromate, dichromate or in the form of polychromate onto  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  surfaces, but can also be present as  $\text{Cr}_2\text{O}_3$  particles. The relative amounts of each of these species depend on the Cr-loading, support and pretreatment.<sup>4</sup> Anchoring means that chemical bonds are formed between Cr and surface oxygens upon calcination above 300 °C.



The questions are then (1) whether  $\text{Cr}^{n+}$  ions are mobile and to what extent and (2) which parameters govern the mobility of  $\text{Cr}^{n+}$  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  $\text{Cr}^{n+}$  are used to evaluate the preference of  $\text{Cr}^{n+}$  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.<sup>7–11</sup> We will show that combined DRS–EPR is an excellent method to study preference sequences of transition metal ions in inorganic oxides.

## Experimental

Na-mordenite, from Norton, with a cation exchange capacity of 0.168 meq  $\text{g}^{-1}$  and an anhydrous unit cell composition of  $\text{Na}_{0.5}\text{Al}_{0.5}\text{Si}_{47.5}\text{O}_{96}$  was put in its  $\text{Na}^+$  form by two successive exchanges with 1 M NaCl solutions, washed  $\text{Cl}^-$ -free and dried in air at room temperature overnight.  $\text{SiO}_2$  (735  $\text{m}^2 \text{g}^{-1}$ ) and  $\text{Al}_2\text{O}_3$  (365  $\text{m}^2 \text{g}^{-1}$ ) were home-made. Details about the preparation method and properties have been published elsewhere.<sup>7,8</sup> 2 g of these inorganic oxides were impregnated by the incipient wetness technique with an aqueous solution of  $\text{CrO}_3$  (UCB, p.a.) so as to obtain a Cr-loading of 1 wt. %.

For the mobility measurements under hydrated conditions, 2 g of the  $\text{Cr}^{6+}$ -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  $\text{O}_2$  flow rate of 3600  $\text{ml h}^{-1}$ .

For the mobility measurements under dehydrated conditions, equal amounts of a  $\text{Cr}^{6+}$ -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  $\mu\text{W}$  with a double rectangular  $\text{TE}_{104}$  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.<sup>7,8</sup>

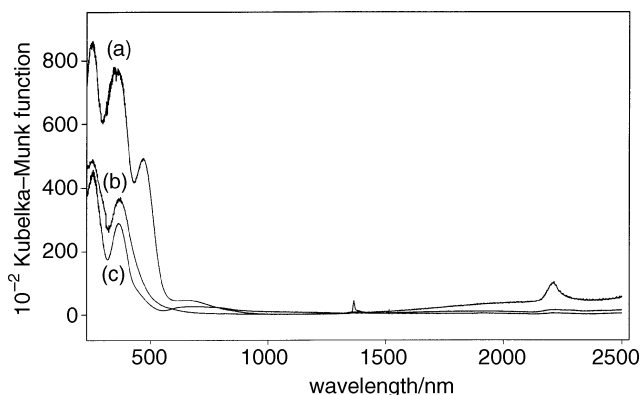
## Results

### Spectroscopic fingerprints of $\text{Cr}^{n+}$ on inorganic surfaces

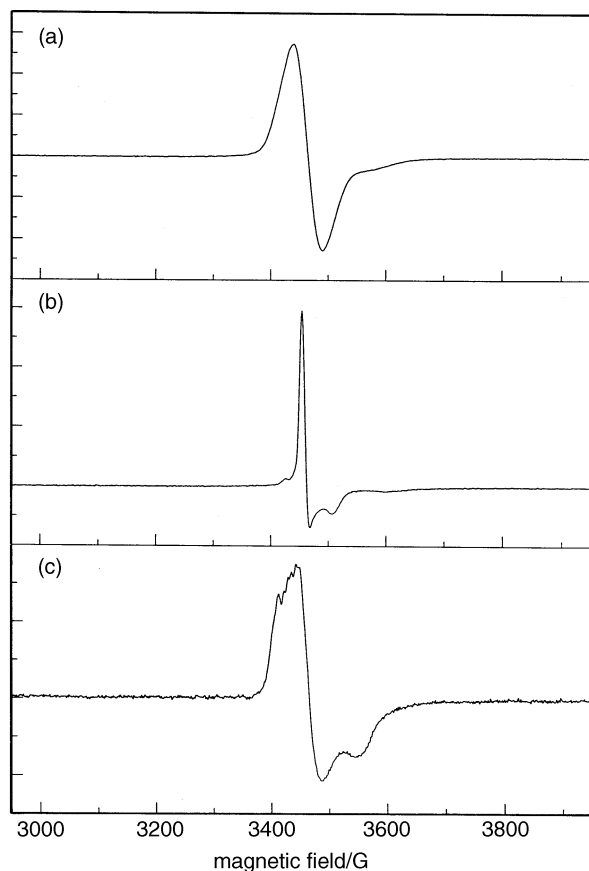
Silica, alumina and mordenite were chosen as inorganic oxides because previous work has shown that, on these supports,

† E-mail: Bert.Weckhuysen@agr.kuleuven.ac.be

$\text{Cr}^{n+}$  ions exist in different oxidation states and coordination environments, which can be distinguished by a combination of DR and EPR spectroscopies.<sup>7–11</sup> The reference DR and EPR spectra are given in Fig. 1 and 2, respectively. The DR spectra of hydrated  $\text{Cr}^{6+}$  are characterized by charge-transfer transitions of the type  $\text{O} \rightarrow \text{Cr}^{6+} (\text{d}^0)$ .<sup>7,8</sup> The DR spectra of  $\text{Cr}/\text{Al}_2\text{O}_3$  and  $\text{Cr}/\text{mordenite}$  have two charge-transfer transitions around 270 and 370 nm, characteristic for chromate. For  $\text{Cr}/\text{SiO}_2$  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  $\text{Cr}/\text{mordenite}$  and  $\text{Cr}/\text{SiO}_2$  have a weak broad band in the region 550–800 nm. This is a d–d transition of  $\text{Cr}^{3+}$ .<sup>12</sup>



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



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

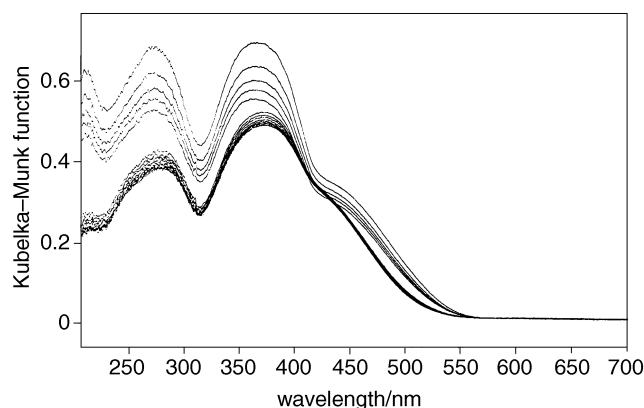
The EPR spectra are typical for  $\text{Cr}^{5+} (\text{d}^1)$  in various coordination environments.<sup>1</sup>  $\text{Cr}^{5+}$  on alumina possesses an axially symmetric EPR signal with broad lines centred at  $g_{\parallel} = 1.910$  and  $g_{\perp} = 1.978$ , whereas, on silica, this signal is rhombic with sharp lines centred at  $g_{xx} = 1.978$ ,  $g_{yy} = 1.969$  and  $g_{zz} = 1.895$ .  $\text{Cr}^{5+}$  in mordenite has a special EPR signal, which is the combination of two spectra: one rhombic with  $^{27}\text{Al}$  superhyperfine splitting ( $g_{xx} = 1.98$ ;  $g_{yy} = 1.99$ ;  $g_{zz} = 1.93$  and  $A_{xx} = 7 \text{ G}$ ) and another, rhombic without superhyperfine splitting ( $g_{xx} = 2.00$ ;  $g_{yy} = 1.98$  and  $g_{zz} = 1.92$ ).<sup>11</sup> 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 $\text{Cr}^{n+}$ in hydrated conditions

In an initial experiment,  $\text{Cr}^{6+}$ -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  $\text{Cr}^{6+}$  readily migrates from silica to alumina.

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

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



**Fig. 3** DR spectra of 1 wt.%  $\text{Cr}/\text{SiO}_2$  mixed with  $\text{Al}_2\text{O}_3$  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.)

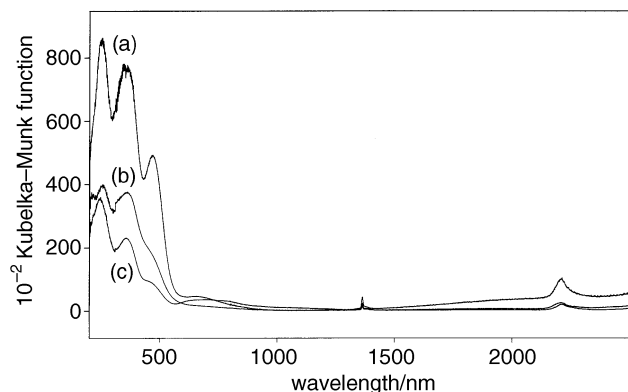


Fig. 4 DR spectra of 1 wt.% Cr/SiO<sub>2</sub> mixed and calcined at 550 °C with (a) SiO<sub>2</sub>, (b) Al<sub>2</sub>O<sub>3</sub> and (c) mordenite

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

#### Mobility and preference of Cr<sup>n+</sup> in dehydrated conditions

When a calcined Cr catalyst was mechanically mixed with a calcined support with complete exclusion of air (10<sup>-5</sup> Pa), and the mixture was heated at 550 °C for 10 h, it was observed that no migration of Cr<sup>n+</sup> from Cr/alumina to silica and mordenite occurred. The same observation was made for Cr<sup>n+</sup>/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<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> mixture a Cr<sup>6+</sup>/Al<sub>2</sub>O<sub>3</sub> DR spectrum is obtained. The transfer of Cr<sup>n+</sup> 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<sup>3+</sup> at 600–800 nm. For the calcined mixture of Cr/SiO<sub>2</sub>-mordenite, there is no residual Cr<sup>3+</sup>, and a pro-

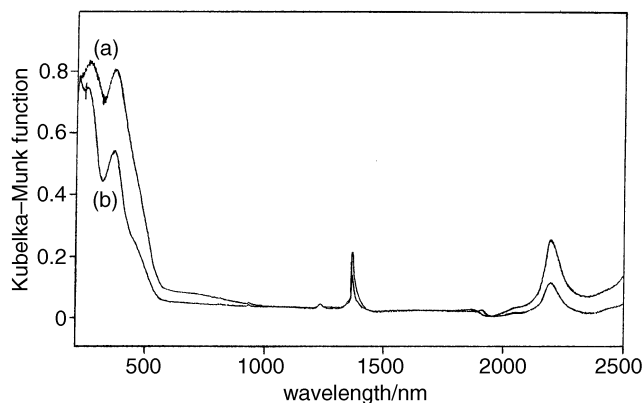


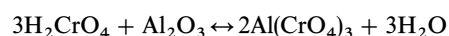
Fig. 6 DR spectra of (a) a mixture of calcined 1 wt.% Cr/SiO<sub>2</sub> and calcined Al<sub>2</sub>O<sub>3</sub> after heating at 550 °C for 10 h and (b) a mixture of calcined 1 wt.% Cr/SiO<sub>2</sub> and calcined mordenite after heating at 550 °C for 10 h

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<sup>6+</sup> from silica to mordenite in the absence of water. Thus, the sequence of preference seems to be: alumina > mordenite > silica.

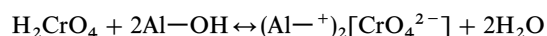
#### Discussion

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<sup>n+</sup> can be used to study preferences when different inorganic oxides are in competition for Cr<sup>n+</sup> ions. What is needed for such a spectroscopic study are clearly distinguishable spectra with well established interpretation. Cr<sup>6+</sup> (chromate, dichromate, . . .), Cr<sup>5+</sup> and Cr<sup>3+</sup> 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<sup>n+</sup>, 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.<sup>7</sup> 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.<sup>13</sup> Finally, by *in situ* DR spectroscopy it has been possible to follow the kinetics of the reduction of Cr<sup>6+</sup> and to propose a kinetic model.<sup>14</sup>

On the hydrated surfaces, CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> are present in the adsorbed water phase. This allows a fast and easy migration which is indeed observed. For all binary mixtures, Cr<sup>6+</sup> prefers the alumina surface, where it is adsorbed as a chromate anion. There are two reasons for this preference: (1) electrostatic attraction between CrO<sub>4</sub><sup>2-</sup> and positively charged sites at the alumina surface (Al—OH<sub>2</sub><sup>+</sup>); (2) an acid–base reaction between chromic acid and alumina. The bulk reaction is:



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



The silica surface is much more acidic,<sup>15,16</sup> and thus chromate and dichromate are present in the adsorbed aqueous phase

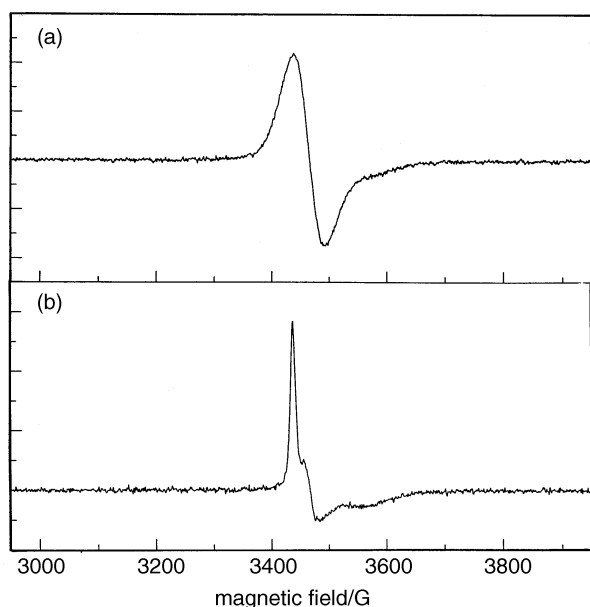
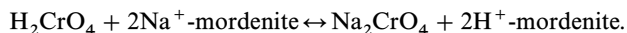


Fig. 5 EPR spectra of 1 wt.% Cr/SiO<sub>2</sub> mixed and calcined at 550 °C with (a) Al<sub>2</sub>O<sub>3</sub> and (b) mordenite (measured at 120 K after flushing in He)

and the acid–base reaction is much less important. Finally, in the presence of Na<sup>+</sup>-mordenite, Na<sup>+</sup> ions are exchanged for protons to form the acidic zeolites and an adsorbed Na<sub>2</sub>CrO<sub>4</sub> phase:



The reaction is driven to the right and Na<sup>+</sup>-mordenite takes an intermediate position in the preference scale of CrO<sub>4</sub><sup>2-</sup>.

When the hydrated mixed oxides are calcined, the same preference scale is observed, because CrO<sub>4</sub><sup>2-</sup> redistribution has occurred in the adsorbed water phase before calcination. In the calcined oxides, Cr<sup>6+</sup> 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.<sup>15,16</sup> In the case of Cr/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>, it is the absorption band of (poly)dichromate which decreases in intensity upon mixing with Al<sub>2</sub>O<sub>3</sub>. In the case of Cr/SiO<sub>2</sub>-mordenite, the mobility also involves migration of Cr<sup>3+</sup> 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<sub>2</sub>O<sub>3</sub> 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<sup>n+</sup> in silica, alumina and mordenite. Cr<sup>n+</sup> ions are mobile and selectively migrate from one inorganic oxide to another when two different oxides are brought in contact. Cr<sup>n+</sup> 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<sup>n+</sup> 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.

B.M.W. acknowledges the Fonds voor Wetenschappelijk Onderzoek-Vlaanderen for a postdoctoral fellowship. This work was financially supported by the Geconcerteerde Onderzoeksakcie (GOA) of the Flemish Government and by the Fonds voor Kollektief Fundamenteel Onderzoek (FKFO) under grant no. 2.0050.93.

## References

- 1 W. Stumm, *Aquatic Surface Chemistry, Chemical Processes at the Particle–Water Interface*, Wiley, New York, 1981.
- 2 W. Gerhartz, *Ullmann's Encyclopedia of Industrial Chemistry*, VCH Verlagsgesellschaft, Weinheim, 1986.
- 3 F. C. Richard and A. C. M. Bourg, *Water Res.*, 1991, **25**, 807.
- 4 B. M. Weckhuysen, I. E. Wachs and R. A. Schoonheydt, *Chem. Rev.*, 1996, **96**, 3327.
- 5 M. P. McDaniel, *Adv. Catal.*, 1985, **33**, 47.
- 6 H. Knozinger and E. Taglauer, *Catalysis*, 1993, **10**, 1.
- 7 B. M. Weckhuysen, L. M. De Ridder and R. A. Schoonheydt, *J. Phys. Chem.*, 1993, **97**, 4756.
- 8 B. M. Weckhuysen, A. A. Verberckmoes, A. L. Buttiens and R. A. Schoonheydt, *J. Phys. Chem.*, 1994, **98**, 579.
- 9 B. M. Weckhuysen, L. M. De Ridder, P. J. Grobet and R. A. Schoonheydt, *J. Phys. Chem.*, 1995, **99**, 320.
- 10 B. M. Weckhuysen, H. J. Spooen and R. A. Schoonheydt, *Zeolites*, 1994, **14**, 450.
- 11 B. M. Weckhuysen, R. A. Schoonheydt, F. E. Mabbs and D. Collison, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 2431.
- 12 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 2nd edn., 1984.
- 13 B. M. Weckhuysen, A. A. Verberckmoes, A. R. De Baets and R. A. Schoonheydt, *J. Catal.*, 1997, **166**, 160.
- 14 A. Bensalem, B. M. Weckhuysen and R. A. Schoonheydt, *J. Phys. Chem.*, 1997, **101**, 2824.
- 15 G. A. Parks, *Chem. Rev.*, 1965, **65**, 177.
- 16 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, New York, 1984.

Paper 7/00046D; Received 2nd January, 1997