

CHEMISTRY AND SPECTROSCOPY OF CHROMIUM IN ZEOLITES

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The diffuse reflectance spectra (DRS) and electron spin resonance spectra (ESR) of chromium containing zeolites prepared by ion exchange and impregnation (Y, Ga-Y, X and Mordenite) and hydrothermal synthesis (CrAPO-5 and Cr-silicalite) have been investigated before and after drying, after calcination, after CO-reduction and recalcination. In the Cr exchanged zeolites, Cr³⁺ is octahedrally coordinated before and after drying and almost quantitatively oxidized to Cr⁵⁺ and Cr⁶⁺ upon calcination at 550 °C. This Cr⁶⁺ is a chromate-like species with two lattice and two extra-lattice oxygens in the coordination sphere. The coordination and location of Cr⁵⁺ and the Cr-dispersion depends on the zeolite type and preparation method. A method of quantifying Cr⁶⁺ and Cr⁵⁺-ions was developed. The reducibility of Cr⁶⁺ and Cr⁵⁺ to Cr³⁺ and Cr²⁺ follows the order: Cr-Mordenite < Cr-Y (impregnated) < Cr-Y (ion exchange) < Cr-X < Cr-Ga-Y < Cr-Y (solid state exchange). Series of CrAPO-5 and Cr-silicalite molecular sieves were synthesized hydrothermally starting with different Cr-precursors and Cr- and template-contents. In the gels of CrAPO-5, Cr³⁺ and Cr⁶⁺ are present as respectively octahedral Cr(H₂O)₆³⁺ and dichromate, both in the liquid phase. In the as-synthesized CrAPO-5's and Cr-silicalites, only extra-lattice octahedral Cr³⁺ is present. Its redox chemistry is similar to that of the ion exchanged materials and Cr supported catalysts.

1. INTRODUCTION

Among the transition metal ions of the 3d series Cr takes a particular position because of its polymerization activity and its catalytic redox properties, especially useful in environmental catalysis [1,2]. A prerequisite for understanding the catalytic activity of Cr-containing zeolites is a thorough knowledge of the chemistry of these zeolites in dependence on the structure and chemical composition of the zeolite and on the method of incorporation of Cr. Diffuse reflectance spectroscopy (DRS) and electron paramagnetic resonance (EPR) are particularly useful techniques in this regard because they allow the identification of Cr⁶⁺, Cr⁵⁺, Cr³⁺ and Cr²⁺ [3]. This is presented in this paper with special emphasis on combined quantitative DRS and ESR.

2. EXPERIMENTAL SECTION

2.1. Sample preparation

Different Cr-exchanged zeolites were prepared using 3 methods (impregnation, solid state ion exchange and ion exchange) and 5 different zeolites. Na-X and Na-Y (Ventron), Na-Mordenite (Norton) and Na-Ga-Y (Exxon Research) were ion exchanged with a solution of

$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. Cr-impregnated Na-Y was prepared by the incipient wetness method with $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, using Na-Y from Ventron. The H-Y zeolite was made from the Na-Y and used for solid state ion exchange with $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$.

CrAPO-5 and Cr-silicalite were synthesised following a modified method of Flanigen *et al.* [4] and Klotz [5] respectively. Cr-silicalite samples were prepared by putting tetraethylorthosilicate (TEOS, Janssen Pharmaceutica) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or CrO_3 (UCB) in a glass flask kept under nitrogen, followed by adding a mixture of 40 wt% tetrapropyl ammonium hydroxide (TPAOH, Alfa, Na^+ -free). The obtained mixture was stirred for one hour, followed by gradually increasing the temperature. After 5 hours at 80 °C the solution was cooled down to room temperature and the volume was increased to 100 ml with bidistilled water. The synthesis mixture is then transferred to teflon lined autoclaves and dynamically synthesized at 170 °C for 3 days. After synthesis, the solid material was separated from the mother liquid by centrifugation and washed 5 times with distilled water. The obtained green product was dried at 60 °C. Two series of Cr-silicalite were prepared Cr(III) and Cr(VI) samples. The latter was made as described but CrO_3 was used. The synthesis conditions, notations and gel compositions of all these samples are summarized in table 1. The amounts of Cr in the samples were determined by atomic absorption spectrometry (AAS) after dissolution of known quantities of the samples in $\text{HF}/\text{H}_2\text{SO}_4$. Details of the preparation and the properties of the CrAPO-5 samples and Cr exchanged zeolites will be published elsewhere [6,7].

2.2. Pretreatment and Experimental Techniques

Pretreatments. After preparation and drying, the samples were granulated. The size fraction 0.25-0.4 mm was loaded in a quartz flow cell with suprasil window for DRS and a side arm for ESR. DRS and ESR spectra were taken of the samples as such and after drying at 75 °C overnight. Subsequently, the samples were calcined at 550 °C and reduced with CO at different temperatures during 30 min. DRS and ESR spectra were recorded on these calcined samples and after each reduction step. After reduction, the samples were recalcined in oxygen at 550 °C and DRS and ESR spectra were taken again.

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 reflectance 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. Some spectra were deconvoluted into Gaussian bands and the values of the KM function at the band maxima were used for quantitative DRS. ESR spectra were measured with a Bruker ESP 300E instrument in X band between 120 and 370 K. Absolute spin concentrations were determined by using $\text{Cu}(\text{acac})_2/\text{KCl}$ mixtures as standard (number of spins : 10^{16} - $10^{19}/\text{g}$). XRD diffractograms were taken with an automated Siemens diffractometer, equipped with a Kristalloflex K710 röntgengenerator and a position sensitive detector of Inel. AAS measurements were performed using an Instrumentation Laboratory Inc. apparatus with a nitrous oxide-acetylene flame. The light source was a hollow cathodelamp with a wavelength of 357.9 nm.

3. RESULTS AND DISCUSSION

3.1. Ion exchanged and impregnated Cr-zeolites

As an example we will discuss the DRS and ESR spectra of Cr/Na-Mordenite in detail (see

figures 1 and 2). In freshly prepared Cr-exchanged zeolites, Cr^{3+} is present as an octahedral ion in both the wet and dried samples. ESR shows an isotropic signal with a width of several hundred gauss and with a g -value around 1.98. A typical ESR spectrum is shown in figure 1A for Cr-Mordenite 0.23Cr/UC. The intensity of this signal follows the Curie-Weiss law. Drying has only a minor influence on the spectra.

Table 1. Conditions, notations and gel characteristics of Cr-silicalite samples.

Sample Name	Cr:Si ratio	pH	colour
Cr(III)0.0033	0.0033	11.6	light green
Cr(III)0.0096	0.0096	11.3	light green
Cr(III)0.0193	0.0193	10.9	green
Cr(III)0.0289	0.0289	10.5	green
Cr(VI)0.0033	0.0033	11.5	yellow-orange

After calcination, the colour of the samples is yellow. The ESR spectra of the calcined samples are characterized by a broad band of Cr^{3+} -clusters and an axially symmetric/rhombic signal of Cr^{5+} , the parameters of which are reported in table 2 (figure 1B). The intensity of the latter species follows the Curie-Weiss, whatever the treatment. As suggested by several authors, working on Cr-Y, Cr-X and Cr-Mordenite Cr^{5+} is a chromyl species. Our data allow to extend this interpretation to Cr-Ga-Y, Cr-silicalite and CrAPO-5. The intensity of the Cr^{5+} signal is maximized by reduction with CO between 300 and 400 °C, except for Cr-Na-Mordenite, for which it starts to disappear upon reduction above 150 °C.

A typical DRS spectrum is shown in figure 2a. The spectra are dominated by two absorption bands at 28,000 cm^{-1} and 38,000 cm^{-1} . These are $\text{O} \rightarrow \text{Cr}^{6+}$ charge transfer bands of metalochromates [3]. Some Cr^{3+} is also evidenced by a weak d-d band around 17,000 cm^{-1} . Upon reduction with CO the Cr^{3+} -band increases in intensity at the expense of the Cr^{6+} CT bands (figure 2b-e). When the chromate bands have completely disappeared, new bands become apparent around 33,000 cm^{-1} , 40,000 cm^{-1} and above 40,000 cm^{-1} , the latter being due to the zeolite matrix. Recalcination re-establishes the original chromate spectrum (figure 2f).

The reduction of Cr^{6+} and Cr^{5+} can be followed quantitatively with respectively DRS and ESR. For DRS, the intensity of the 28,000 cm^{-1} band, obtained after deconvolution [3,7] is plotted vs Cr-content for each type of zeolite. The resulting lines (figure 3) are linear at low Cr content and can therefore only be used at small Cr-loadings. Figure 4 shows the amount of Cr^{6+} as function of pretreatment and preparation methods for different zeolites. If the relative decrease of Cr^{6+} for reduction between 200 °C and 600 °C is used as a reducibility criterion, the following sequence is obtained : Cr-Mordenite > Cr-Y (impregnated) > Cr-Y (ion exchange) > Cr-X > Cr-Ga-Y > Cr-Y (solid state ion exchange). Because of the weakness of the d-d transitions, quantification of Cr^{3+} and Cr^{2+} is impossible.

The amount of Cr^{5+} in ESR is obtained via double integration of the signals of table 2 and comparison with the intensities of the $\text{Cu}(\text{acac})_2/\text{KCl}$ standards. This is shown in figure 5. Cr^{5+} is easily reduced on Cr/Na-Mordenite, and can be maximized on the other zeolites by CO-reduction between 300 and 400 °C. If the disappearance of Cr^{5+} is used as a reducibility criterion, the following sequence is obtained : Cr-Mordenite > Cr-Y (impregnation) > Cr-Y (ion exchanged) > Cr-X \approx Cr-Ga-Y \approx Cr-Y (solid state ion exchange). This is close to the sequence obtained from the disappearance of Cr^{6+} . Recalcination re-establishes the original amount of Cr^{5+} .

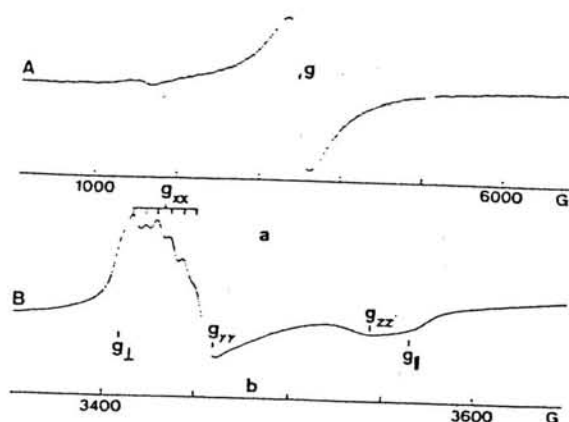


Figure 1. ESR spectra of Cr/Na-Mordenite : freshly prepared (A) and calcined (B) sample.

The differences in redox behavior can be explained with two parameters : (1) intrinsic zeolite properties and (2) dispersion/siting of Cr. It is known that the harder the support, the less susceptible the framework will be for electron fluctuations, necessary for reduction. Thus, the harder the zeolite, the more difficult CO-reduction. The hardness increases from Cr-Mordenite over Cr-Y and Cr-X to Cr-Ga-Y [11.12.13] and therefore our hypothesis is qualitatively valid. A second important factor is the siting of Cr, which determines the accessibility for CO. Our DRS results show less dispersion in Cr/Y (impregnation) than in Cr/Y (ion exchange) [7], resulting in a higher reducibility of the former zeolite. The low reducibility of Cr-Y (solid state ion exchange) can be explained by the residual acidity of this sample.

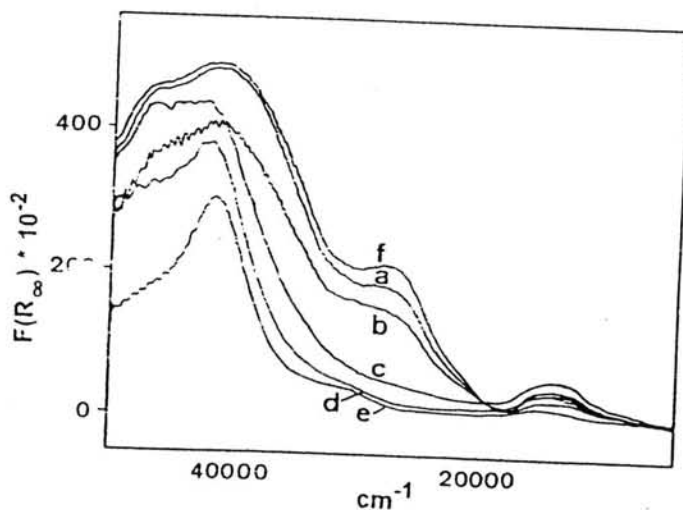
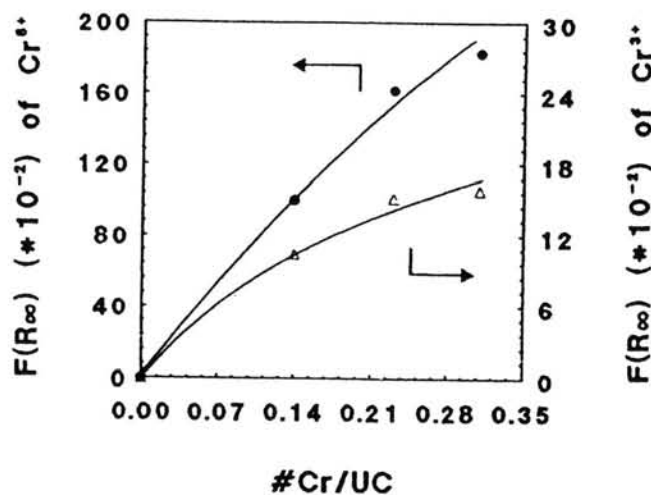


Figure 2. DRS spectra of Cr/Na-Mordenite 0.23 Cr/UC : calcination 550 °C (a); reduction 200 °C (b); reduction 300 °C (c); reduction 400 °C (d); reduction 600 °C (e) and recalcination 550 °C (f).

Table 2. Characteristics and Assignments of Cr^{5+} -species in calcined Cr-zeolites.

Cr-zeolite	ESR-parameters	Assignments
Cr/Na-Y (ion exchange)	$g_{\perp} = 1.98; g_{\parallel} = 1.92$ (A) $g_{\perp} = 1.99; g_{\parallel} = 1.95$ (B)	2 Cr^{5+} -species : A (supercage : site II); B (small cages : site I' or II') [9]
Cr/Na-Y (impregnation)	$g_{\perp} = 1.98; g_{\parallel} = 1.92$ (A) $g_{\perp} = 1.99; g_{\parallel} = 1.95$ (B)	2 Cr^{5+} -species
Cr/H-Y (solid state ion exchange)	$g_{\perp} = 1.99; g_{\parallel} = 1.93$ (A) $g_{\perp} = 1.98; g_{\parallel} = 1.94$ (B)	2 Cr^{5+} -species
Cr/Na-GaY	$g_{\perp} = 1.99; g_{\parallel} = 1.94$ (A) $g_{\perp} = 1.98; g_{\parallel} = 1.94$ (B)	2 Cr^{5+} -species
Cr/Na-Mordenite	$g_{\perp} = 1.995; g_{\parallel} = 1.92$ (C) $g_{xx} = 1.99; g_{yy} = 1.98; g_{zz} = 1.93$ ($A_{xx} = 7$ G) (D)	2 Cr^{5+} -species : C (junction) and D (main channel) [8]
Cr/Na-X	$g_{\perp} = 1.99; g_{\parallel} = 1.93$	1 Cr^{5+} -species [9]
Cr-silicalite	$g_{\perp} = 1.99; g_{\parallel} = 1.91$	1 Cr^{5+} -species
CrAPO-5	$g_{\perp} = 1.99; g_{\parallel} = 1.90$	1 Cr^{5+} -species

Figure 3. Calibration lines for Cr/Na-Mordenite : Cr^{3+} (Δ) and Cr^{6+} (\bullet).

3.2. Hydrothermally synthesized Cr-zeolites

Cr-silicalite molecular sieves were synthesized hydrothermally starting with different Cr-precursors and Cr-contents. The characteristics of the samples are summarized in table 1. All gels result in the formation of crystalline silicalite. This material has a green colour and is characterized by : (a) a broad ESR signal similar to that of Cr^{3+} in figure 1A and following the Curie-Weiss law and (b) three typical absorption bands of octahedral Cr^{3+} at 16,000, 22,700 and around 33,000 cm^{-1} . The spectrum of as-synthesized Cr(III)0.0033 is shown in

figure 6a. The spectra of Cr-silicalites with higher Cr-content are identical. Replacing the Cr^{3+} -salt by CrO_3 in the synthesis mixture results also in the formation of a green material ($\text{Cr(VI)}0.0033$) with an XRD diffractogram, DRS and ESR spectra identical to those of the $\text{Cr(III)}0.0033$ sample. Therefore, Cr^{6+} is reduced to Cr^{3+} during synthesis. Upon calcination, Cr^{5+} and Cr^{6+} are formed at the expense of Cr^{3+} . The characteristics of the Cr^{5+} -species are summarized in table 2. A typical spectrum of calcined Cr-silicalite is shown in figure 6b. The spectrum is characterized by two bands at 28,300 and at 40,000 cm^{-1} with a shoulder at 22,500 cm^{-1} , all due to Cr^{6+} [3]. CO-reduction at 350 °C results in an almost complete disappearance of the Cr^{6+} -bands and new bands in the d-d region are formed at around 12,000 and 7,500 cm^{-1} , as shown in figure 6c. These bands are due to respectively pseudo-octahedral and pseudo-tetrahedral Cr^{2+} [3], while the band of octahedral Cr^{3+} is reduced in intensity and shifted to lower energy values (around 14,500 cm^{-1}). Recalcination restores the spectrum as given in figure 6b.

The same behavior is found for CrAPO-5 molecular sieves [6]. In the as-synthesized Cr-zeolites, Cr^{3+} is octahedrally coordinated, whatever synthesis time, temperature, Cr-source, loading and template content. ESR spectra of as-synthesized CrAPO-5 show a broad isotropic signal with $g = 1.98$, which is due to hexa-aquo Cr^{3+} . The DRS spectra show the three typical bands of this complex. Even vacuo pretreatments cannot transform this octahedral Cr to a tetrahedral one. Furthermore, in the gels of CrAPO-5, Cr^{3+} is present as an octahedral aquo-complex, which can easily be washed off. Oxidation results in the formation of Cr^{6+} and Cr^{5+} , which are reduced to Cr^{3+} and Cr^{2+} by CO. Recalcination re-establishes the Cr^{6+} situation.

Our results about Cr-silicalite and CrAPO-5 molecular sieves show that Cr^{3+} has no tendency to change to the tetrahedral coordination, necessary for isomorphous substitution in molecular sieves. A strong argument in favor of this can be found in the Crystal Field Stabilization Energy (CFSE) of octahedral (224.5 kJ/mol) versus tetrahedral Cr^{3+} (66.9 kJ/mol) [14]. This suggests that a d^3 ion, like Cr^{3+} , has a too strong preference for the octahedral relative to the tetrahedral coordination to be forced in tetrahedral coordination under synthesis conditions [15]. Furthermore, the redox behavior of Cr in AlPO-5 and silicalite is similar to that of ion-exchanged zeolites and Cr supported catalysts [3].

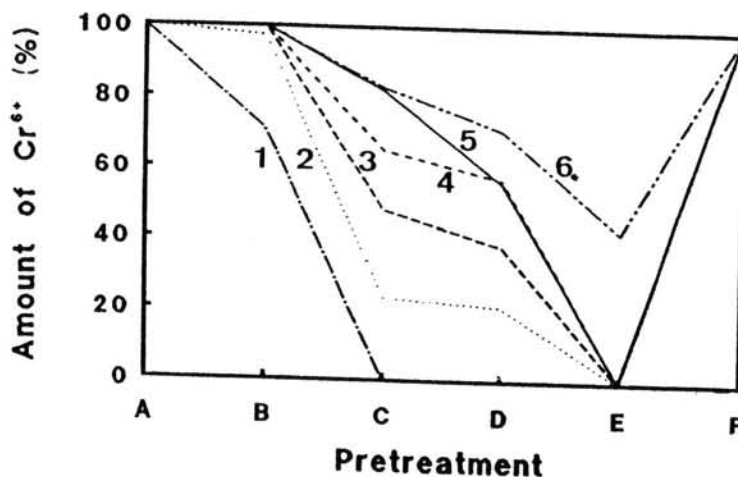


Figure 4. Amount of Cr^{6+} as function of zeolite (1, Cr/Na-Mordenite; 2, Cr/Na-Y impregnation; 3, Cr/Na-Y ion exchanged; 4, Cr/Na-X; 5, Cr/Na-GaY and 6, Cr/H-Y solid state ion exchange) and pretreatment (A, calcination 550 °C; B, reduction 200 °C; C, reduction 300 °C; D, reduction 400 °C; E, reduction 600 °C and F, recalcination 550 °C).

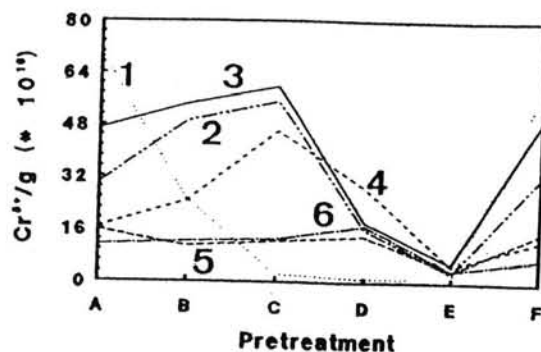


Figure 5. Amount of Cr^{5+} as function of zeolite (1, Cr/Na-Mordenite; 2, Cr/Na-Y impregnation; 3, Cr/Na-Y ion exchanged; 4, Cr/Na-X; 5, Cr/Na-GaY and 6, Cr/H-Y solid state ion exchanged) and pretreatment (A, calcination 550 °C; B, reduction 200 °C; C, reduction 300 °C; D, reduction 400 °C; E, reduction 600 °C and F, recalcination 550 °C).

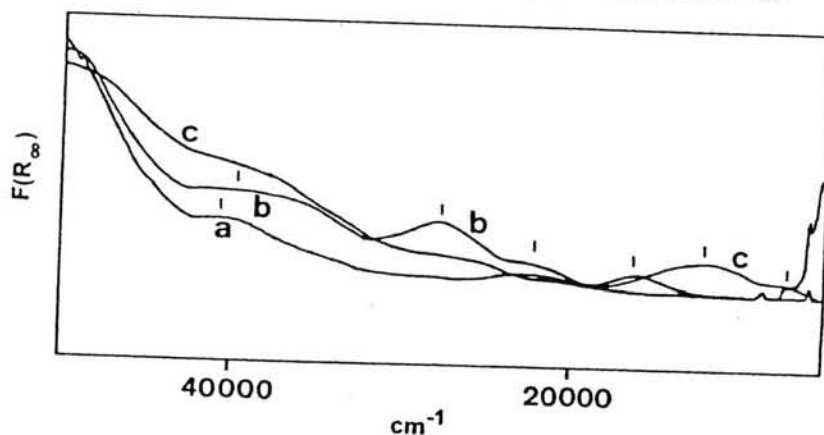


Figure 6. DRS spectra of Cr-silicalite : as-synthesised (A); calcined at 550 °C (B) and reduced at 350 °C with CO (C).

All these results are in accordance with those of Cornaro *et al.* [16], those of Nakamura and co-workers [17] and those of Rajic *et al.* [18]. Cornaro *et al.* have shown by IR that the predominant part of Cr^{3+} in silicalite is present in cationic positions and no Cr is inserted in the framework. Furthermore, calcination of Cr-silicalite results in the formation of chromate/dichromate, which can easily be washed off from the crystalline material, suggesting a weak interaction between silicalite and Cr [17]. This Cr is not incorporated in the silicalite skeleton, because Cr^{6+} can also be extracted from calcined Cr-exchanged zeolites [9]. Recently, Rajic *et al.* have shown that Cr^{3+} cannot be incorporated in SAPO-34 and is present as an octahedral species [18].

4. CONCLUSIONS

The chemistry of Cr^{n+} in zeolites is the same whatever the zeolite structure and the type

of immobilization. Freshly prepared Cr exchanged zeolites and as-synthesised CrAPO-5 and Cr-silicalite molecular sieves contain octahedral Cr^{3+} , both before and after drying. Upon calcination, Cr^{5+} and Cr^{6+} are formed which, upon reduction with CO transform to Cr^{3+} and Cr^{2+} . Recalcination restores the initial Cr^{6+} state. The DRS and ESR spectra of Cr containing zeolites allow a quantitative determination of Cr^{6+} and Cr^{5+} . The redox behavior of Cr is dependent on the intrinsic zeolite properties, Cr-dispersion and preparation method. The chemistry of Cr in AlPO-5 and silicalite is similar to that of ion-exchanged zeolites and Cr supported catalysts.

ACKNOWLEDGMENTS

B.M.W. acknowledges the Belgian National Fund for Scientific Research (N.F.W.O.) for a grant as research assistant. The authors thank Hans Spooren for technical assistance; Piet Grobet and Hilde Geerts for MAS-NMR measurements of the zeolites; Jan Uytterhoeven for the use of the Spectra Calc program; Herman Bosmans and Lut Ooms for chemical analyses; Hans Verduyn for the supply of the Ga-Y zeolite and Wilfried Mortier for fruitful discussions. The work was financially supported by the Fonds voor Kollektief Fundamenteel Onderzoek (FKFO) under grant N° 2.0050.93.

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