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In situ UV–VIS diffuse reflectance spectroscopy–on-line activity measurements

Significance of Cr^{n+} species ($n = 2$, 3 and 6) in *n*-butane dehydrogenation catalyzed by supported chromium oxide catalysts

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The dehydrogenation of *n*-butane over supported chromium oxide catalysts has been investigated at 500 °C by *in situ* UV–VIS diffuse reflectance spectroscopy–on-line activity measurements as a function of the reaction time (0–60 min), the support composition ($SiO_2 : Al_2O_3$ ratio) and the Cr loading (0–8 wt.%). The catalytic reaction is characterized by an initial induction period, during which the supported chromium oxides are reduced to $Cr^{3+/2+}$, and CO/CO_2 and cracking products (C_1, C_2 and C_3) are formed. After this initial induction period, but-1-ene and but-2-ene are produced with a selectivity up to 90%. The catalytic activity increases with increasing Cr content and Al_2O_3 content of the support, and is maximum after 5–15 min on stream. A relation between the dehydrogenation activity and the amount of Cr^{3+} formed upon the reduction of Cr^{6+} has been established.

Introduction

Supported chromium oxide catalysts are crucial in chemical industries for the production of important commodity chemicals. Indeed, several large volume industrial processes rely on supported chromium oxides as a heterogeneous catalyst. Chromium-on-silica is the famous Philips polymerization catalyst, responsible for about one third of the world production of high density polyethylene (HDPE).[1,2] This system is still developing, and forms the basis of a new generation of supported mono-alkene polymerization catalysts, as an alternative to the recently commercialized metallocenes. Similarly, chromium-on-alumina is used as a light paraffin dehydrogenation catalyst employed in the Houdry CATOFIN and CATADIENE processes.[3,4] The Houdry CATOFIN process is responsible for approximately 50% of the catalytically derived world production of isobutane, for methyl *tert*-butyl ether (MTBE), and 50% of the catalytically generated propylene, mostly used for the production of polypropylene.

The industrial importance of supported chromium oxide catalysts has attracted a great deal of interest in industrial and academic research towards the elucidation of the molecular structure of chromium oxides and their relation with catalytic performances.[5–12] The state-of-the-art of these catalysts has been recently summarized in a review paper.[5] It has been shown that almost all previous characterization studies were conducted under controlled atmospheres, *i.e.*, hydrated, dehydrated and reduced conditions, and the data obtained could not be directly related to catalytic data. Therefore, in general, spectroscopic techniques have to be developed which allow measurements under conditions as close as possible to 'real' catalytic conditions. Thus, *in situ* spectroscopic studies, combined with on-line activity/selectivity measurements, are required to fully understand the catalytic action of supported metal oxide catalysts.

In this work, we have investigated supported chromium oxide catalysts in *n*-butane dehydrogenation reactions by using *in situ* UV–VIS diffuse reflectance spectroscopy. This allows us to probe Cr^{6+}, Cr^{3+} and Cr^{2+} in reaction conditions, while the reaction products (CO/CO_2, CH_4, C_2H_6, C_2H_4, C_3H_8, C_4H_{10}, …) can be monitored by on-line gas chromatography. The goal of this study is then to address the role of Cr^{n+} (with $n = 6$, 3 and 2) in alkane dehydrogenation reactions. The results will be discussed in relation to recent publications on the nature of the active dehydrogenation site.

Experimental

Catalyst preparation

Preparation of supports. SiO_2 was prepared by mixing H_2O at pH 2 (adding HCl) and tetraethyl orthosilicate (TEOS) (2/1, v/v) during 5 h at room temperature. The mixture was titrated under stirring to pH 6 with an NH_4OH solution at pH 9.5. After 16 h of gelation, the gel was dried at 130 °C for 72 h and calcined at 250 and 550 °C for 3 and 16 h, respectively. The so-obtained cake was crushed. $SiO_2 \cdot Al_2O_3$ with 20, 40 and 60 wt.% SiO_2 was prepared following a modified method of Chen *et al.*[13]. Appropriate amounts of TEOS and aluminium triisopropoxide were mixed in 128 ml of ethanol during 30 min at room temperature. After adding 35 ml of 1 M HCl, the hydrolysis started and the solution was mixed for 1 h. The gel was dried at 60 and 100 °C for 8 h, and calcined at 550 °C for 16 h. The samples of $SiO_2 \cdot Al_2O_3$ were then crushed. Al_2O_3 was prepared by drying an ethanol solution of aluminium triisopropoxide at 60 and 100 °C for 8 h. The dried solid was calcined further at 550 °C for 16 h. The supports are denoted as follows: SA-0 (Al_2O_3), SA-20 ($SiO_2 \cdot Al_2O_3$ with 20 wt.% SiO_2), SA-40 ($SiO_2 \cdot Al_2O_3$ with 40 wt.% SiO_2), SA-60 ($SiO_2 \cdot Al_2O_3$ with 60 wt.% SiO_2) and SA-100 (SiO_2).

Preparation of catalysts. The supported chromium oxide catalysts were prepared by the incipient-wetness method with chromium(VI) oxide (CrO_3). The catalysts were dried at 50 °C for 8 h and granulated. The size fraction between 0.2 and 0.5 mm was used for *in situ* DRS measurements. The following catalysts were prepared: 0.2 wt.% Cr/SA-0, 0.2 wt.% Cr/SA-20, 0.2 wt.% Cr/SA-40, 0.2 wt.% Cr/SA-60, 0.2 wt.% Cr/SA-100, 1.0 wt.% Cr/SA-0, 2.0 wt.% Cr/SA-0, 4.0 wt.% Cr/SA-0 and 8.0 wt.% Cr/SA-0.

In situ on-line GC analysis during diffuse reflectance spectroscopy

In situ diffuse reflectance spectra were taken on a Varian Cary 5 UV–VIS–NIR spectrophotometer equipped with a specially designed Praying Mantis diffuse reflection attachment (DRA) of Harrick. A schematic drawing and the technical details of this cell are given in recent papers.[14,15] The white reflectance standard $BaSO_4$ (Kodak) was used to take a baseline at 25 °C in the Praying Mantis cell. The thickness of the catalyst bed was 3 mm, and the amount of the catalyst used was *ca.* 40–65 mg. The catalyst was first treated in oxygen in the *in situ* cell at 550 °C for 1 h, and then cooled in He to 500 °C. The catalyst was then subjected to an 18% *n*-butane stream in He (50 ml min^{-1}) at 1 atm. The measured *in situ* DRS spectra were processed with Grams/386 (Galactic Industries Corp). On-line gas chromatography analysis was done with an HP 5830 GC instrument equipped with an FID detector, six-way valve inlet system, and a packed column filled with *n*-octane/porasil-C (100–120 mesh, Durapack, Applied Science Laboratories). The thermodynamically expected conversion at 500 °C will be *ca.* 20%. However, as will be shown below, the conversions obtained in the *in situ* cell are much lower. Indeed, the best catalyst employed in this study has a conversion below 10%. Thus, the *in situ* DRS cell cannot be considered as an ideal fixed bed reactor, and gas by-pass and eventually an inhomogeneous temperature profile have to be invoked to explain the lower conversions.

Results

Catalytic performance

The dehydrogenation of *n*-butane over supported chromium oxide catalysts has been investigated at 500 °C in the *in situ* cell as a function of the support composition, the Cr loading, and the reaction time. As an example, we will discuss the catalytic performance of the 0.2 wt.% Cr/SA-0 catalyst in detail (Fig. 1). Other Cr catalysts had a similar activity and selectivity pattern, although their exact conversions/selectivities were different. It is also important to notice that the catalytic activity of the empty *in situ* cell at 500 °C was below 0.10%, while the selectivities towards but-1-ene and but-2-ene were *ca.* 50%.

Fig. 1A shows that the catalytic activity of the 0.2 wt.% Cr/SA-0 catalyst reached a maximum after 6 min on-stream, and decreased with increasing reaction time. In addition, the selectivity pattern of the reaction was quite complex (Fig. 1B).

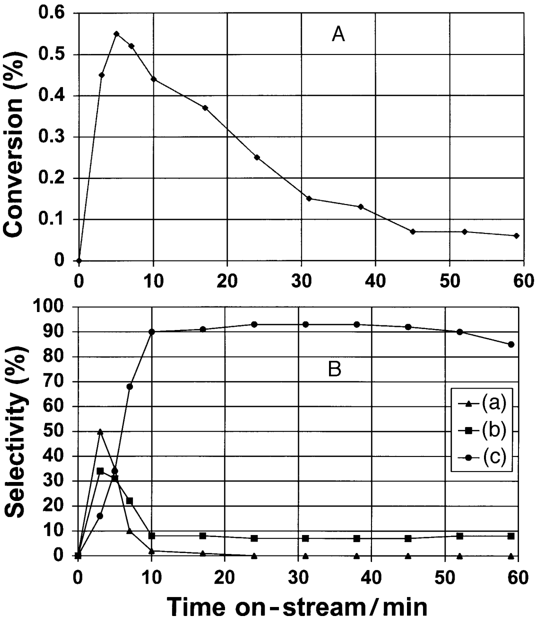

Fig. 1 A, Conversion (%) *vs.* time on-stream (min) for *n*-butane dehydrogenation at 500 °C over a 0.2 wt.% Cr/SA-0 catalyst in the *in situ* UV–VIS DRS cell. B, Selectivity (%) *vs.* time on-stream (min) for *n*-butane dehydrogenation at 500 °C over a 0.2 wt.% Cr/SA-0 catalyst in the *in situ* UV–VIS DRS cell: (a) CO/CO_2; (b) cracking products (C_1, C_2 and C_3) and (c) but-1-ene and but-2-ene.

The catalytic reaction is characterized by an initial induction period, during which CO/CO_2 and some cracking products are formed. The maximum selectivity towards these products was reached after 3 min on-stream, and was *ca.* 50 and 35% for CO/CO_2 and the cracking products, respectively. The cracking products formed were CH_4, C_2H_4, C_2H_6, C_3H_8 and C_3H_{10}. The selectivity towards these products was highest (*ca.* 50%) for 0.2 wt.% Cr/SA-40 and Cr/SA-60 catalysts. This must be due to the acidity of the silica–alumina supports. After this initial induction period, but-1-ene and but-2-ene were produced selectively. The selectivity towards alkenes reached a maximum of *ca.* 90% after 10 min, and decreased slightly with increasing time on-stream.

Fig. 2 compares the catalytic activity of 0.2 wt.% Cr catalysts as a function of the support composition ($SiO_2 : Al_2O_3$ ratio). The dehydrogenation activities were measured after 10 min on-stream. It is clear that the catalytic activity decreased from 0.44% for a Cr/SA-0 catalyst, through 0.35% for a Cr/SA-40 to 0.18% for a Cr/SA-100 catalyst. Thus, the dehydrogenation activity decreased with increasing SiO_2 content of the support. The dependency of the dehydrogenation activity on Cr loading is illustrated in Fig. 3 for Cr/Al_2O_3 catalysts. It is shown that the conversion towards alkenes increased almost linear with increasing Cr loading.

Significance of Cr^{n+} (with $n = 6$, 3 and 2) in *n*-butane dehydrogenation

In situ UV–VIS diffuse reflectance spectra were monitored between 300 and 800 nm as a function of time on-stream for

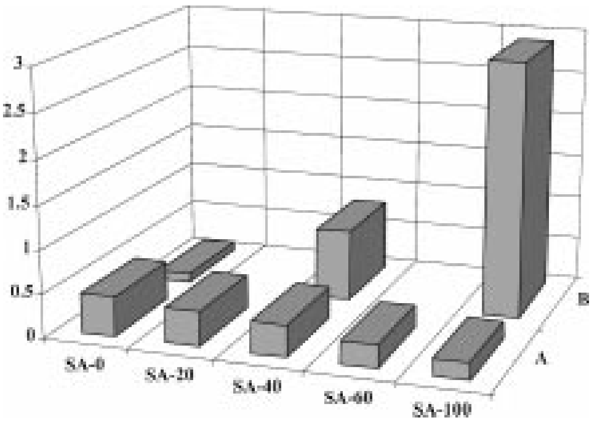

Fig. 2 A, Conversion (%) and, B, $Cr^{2+} : Cr^{3+}$ ratio as a function of the support composition for *n*-butane dehydrogenation at 500 °C over 0.2 wt.% Cr catalysts. The $Cr^{2+} : Cr^{3+}$ ratio was derived from previous CO reduction experiments.[5,17] The DRS spectra obtained after CO reduction of the supported Cr catalysts at 600 °C for 30 min were deconvoluted in a set of Gaussian bands typically for Cr^{3+} and Cr^{2+}. The ratio of the absorption maxima was used to determine the $Cr^{2+} : Cr^{3+}$ ratio.

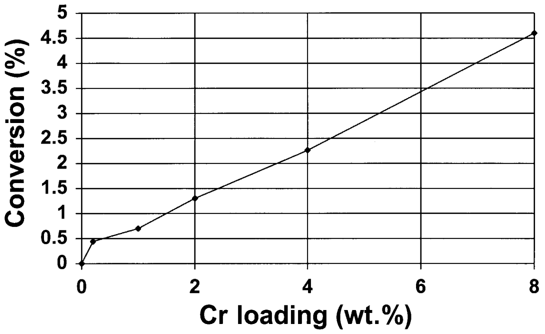

Fig. 3 Conversion (%) *vs.* Cr loading (wt.%) for *n*-butane dehydrogenation at 500 °C over Cr/SA-0 catalysts

each supported chromium oxide catalyst treated in *n*-butane at 500 °C. The scan time was 1 min, and 60 different spectra were recorded during 60 min. An example of a set of *in situ* diffuse reflectance spectra is given in Fig. 4 for the 0.2 wt.% Cr/SA-0 catalyst. Fig. 4 shows a gradual decrease of the absorption maximum at *ca.* 360 nm with increasing reaction time at the expense of a new weak band with an absorption maximum at *ca.* 590 nm. Fig. 4 also shows the presence of an isobestic point at *ca.* 490 nm, suggesting the presence of two different Cr species. The first absorption band is typical for the presence of Cr^{6+}, whereas the broad absorption band at 590 nm is indicative for the presence of Cr^{3+}.[5,16,17] In the case of Cr/SA-100 catalysts, the absorption maximum of reduced Cr is at *ca.* 625 nm, which is typical for the formation of Cr^{2+}, although some Cr^{3+} may contribute to the spectra as well. Indeed, the absorption maximum at 590 nm shifts to higher energy with decreasing Al_2O_3 content of the support, which is indicative of an increase of the $Cr^{2+} : Cr^{3+}$ ratio with decreasing Al_2O_3 content of the support. Thus, the differences in Cr speciation are related to the support composition, *i.e.*, mainly Cr^{3+} on Al_2O_3, a mixture of Cr^{3+} and Cr^{2+} on $SiO_2 \cdot Al_2O_3$ and, mainly Cr^{2+} on SiO_2.[5,17]

By monitoring the intensity of the absorption bands at *ca.* 590–625 nm and 360 nm as a function of time on-stream, one can measure the amount of Cr^{6+} and $Cr^{3+/2+}$ during catalytic action, according to eqn. (1):[15]

$$I_{KM}(Cr^{n+}) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} = kC(Cr^{n+}) \qquad (1)$$

with $I_{KM}(Cr^{n+})$, the Kubelka–Munk intensity; R_∞, the diffuse reflectance of the Cr catalyst; K and S, the absorption and scattering coefficients; k, a proportionality coefficient and $C(Cr^{n+})$, the amount of Cr^{n+}. However, it is important to notice here that previous work[5,17] has shown that eqn. (1) is only valid for low loaded Cr catalysts and, as a consequence, the $I_{KM}(Cr^{n+})$ values will deviate from linearity at higher Cr loadings. As an example, the intensity profiles of the 360 and 590 nm band for the 0.2 wt.% Cr/SA-0 catalyst treated in *n*-butane are given in Fig. 5, and similar plots were obtained for other Cr catalysts. This figure shows a gradual decrease of the intensity of the 360 nm band with increasing time on-stream. It is also clear that almost all Cr^{6+} was reduced to Cr^{3+} after 10 min on-stream. Indeed, the amount of Cr^{3+} formed upon the reduction of Cr^{6+} gradually increased with reaction time, and reached a maximum after 10–20 min on-stream. It is also important to notice that there was still a small increase in the absorption intensities with reaction time after the reduction of surface Cr^{6+} took place. This is most probably due to the formation of coke on the catalyst surface, which is responsible for the deactivation of the catalyst.

By comparing the amount of Cr^{3+} formed (upon the reduction of Cr^{6+}) in Cr/SA-0 catalysts differing in their Cr content, we noticed that the amount of Cr^{3+} increased almost linearly with increasing Cr loading up to 2 wt.% Cr (Fig. 6). The deviation from linearity at higher Cr loadings must be due to the inherent limitations of the Kubelka–Munk theory [eqn. (1)].[15]

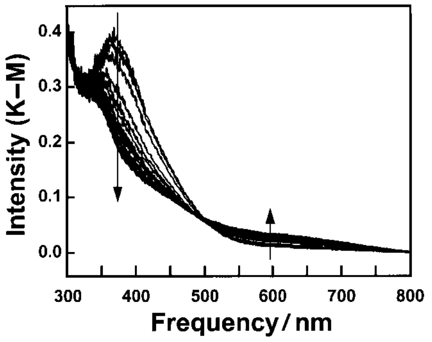

Fig. 4 *In situ* UV–VIS diffuse reflectance spectra of a 0.2 wt.% Cr/SA-0 catalyst treated at 500 °C in 18% *n*-butane in N_2 as a function of time on-stream

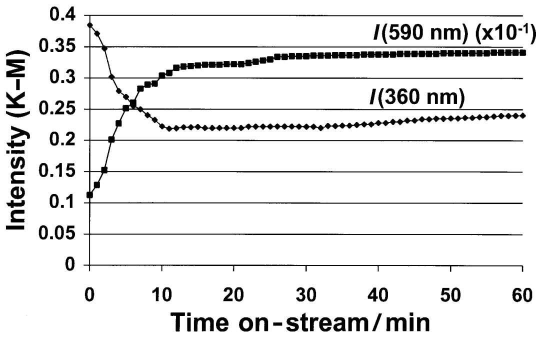

Fig. 5 Intensity profiles of the absorption maxima at 360 and 590 nm for a 0.2 wt.% Cr/SA-0 catalyst treated at 500 °C in 18% *n*-butane in N_2 as a function of time on-stream

Discussion

The goal of this work was to address the role of Cr^{6+}, Cr^{3+} and Cr^{2+} in alkane dehydrogenation reactions by using *in situ* on-line GC analysis during UV–VIS DRS spectroscopy. First of all, it is important to stress that, although the conversions obtained in the *in situ* cell are always low, substantial differences in catalytic performance were obtained between the different Cr catalysts. This suggests that this method will be useful for characterizing other supported metal oxide catalysts in catalytic action. Furthermore, our experiments clearly show that Cr^{6+} was instantly reduced to $Cr^{3+/2+}$ after exposing the catalyst to a stream of *n*-butane. Thus, the initially low selectivity towards alkenes must be explained by the cracking and oxidation properties of high-valence chromium species. After 5–10 min on-stream, all Cr^{6+} was reduced to $Cr^{3+/2+}$, and the catalytic activity reached a maximum. The selectivity towards but-1-ene and but-2-ene, on the other hand, was *ca.* 90%, and similar values are obtained for Cr/Al_2O_3 catalysts in industrial practice.[3,4]

Another comment concerns the oxidation state of the active Cr species for alkane dehydrogenation, which has been the subject of debate and controversy for many years in the literature.[3] According to several authors the active species is Cr^{3+}, while other authors propose both Cr^{2+} and Cr^{3+}, or solely Cr^{2+} as the active dehydrogenation site.[6–12] The almost linear relationship between the catalytic activity and the amount of Cr^{3+} formed upon Cr^{6+} reduction, as measured by *in situ* DRS spectroscopy, indicates that Cr^{3+} is the active species for *n*-butane dehydrogenation (Fig. 6). Further evidence comes from Fig. 2, which shows the relationship between the $Cr^{2+} : Cr^{3+}$ ratio on the catalyst surface (as determined by DRS after CO reduction at 600 °C[5,17]) and the

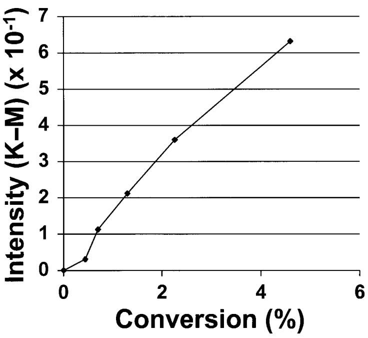

Fig. 6 Amount of Cr^{3+} formed upon Cr^{6+} reduction *vs.* conversion (%) for Cr/SA-0 catalysts differing in their Cr content

catalytic activity. It is clear that the catalytic activity increases with decreasing $Cr^{2+}:Cr^{3+}$ ratio. However, it is also clear that our experiments do not allow us to rule out the possible activity of Cr^{2+} sites. Indeed, an alternative explanation could be that Cr^{3+} species are more active than Cr^{2+} species. In addition, the d–d absorption band is always very broad, and different $Cr^{2+/3+}$ species may be involved in catalysis.

Further evidence for the significance of Cr^{3+} species (formed upon Cr^{6+} reduction) in alkane dehydrogenation reactions can be found in the literature.[6,10,12] Masson *et al.*[12] and Hakuli *et al.*[6] found that high-valence chromium species were the precursors of the active Cr^{3+} sites of the catalyst because (1) the amount of Cr^{6+} decreased in parallel with the initial activity, and (2) Cr^{3+} was the only species detected by XPS measurements in a reduced Cr/Al_2O_3 catalyst. In addition, De Rossi *et al.*[10] found that the dehydrogenation activity of Cr/Al_2O_3 and Cr/ZrO_2 catalysts was due to coordinatively unsaturated Cr^{3+} sites. In view of this work, it is important to underline that our analysis (1) is not able to give a more detailed picture of the coordination geometry and polymerization degree of the active Cr^{3+} site, and (2) does not exclude the possibility that the active Cr^{3+} species could also arise from reduction of Cr^{5+}. Indeed, De Rossi *et al.*[10] have concluded from EPR measurements that Cr^{5+}-species are the precursors of the active Cr^{3+} species, and *in situ* EPR measurements are under way in our laboratory to substantiate this point.

Conclusions

The following conclusions can be made.

(1) *In situ* on-line GC analysis during UV–VIS DRS spectroscopy is a useful technique for studying supported metal oxide catalysts in catalytic action.

(2) The dehydrogenation activity of supported chromium oxide catalysts increased with increasing Cr content, and Al_2O_3 content of the support, and a maximal conversion was reached after 5–15 min on-stream. The selectivity towards but-1-ene and but-2-ene was *ca.* 90%, and deactivation of the catalysts was due to coke formation.

(3) The initial reduction of Cr^{6+} after exposing the catalyst to *n*-butane was responsible for the formation of CO/CO_2 and cracking products (C_1, C_2 and C_3).

(4) The dehydrogenation activity was proportional to the amount of Cr^{3+} formed upon Cr^{6+} reduction. Although the dehydrogenation activity of Cr^{2+} species cannot be ruled out, it seems that Cr^{3+} was more active than Cr^{2+}.

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References

1 B. M. Weckhuysen and R. A. Schoonheydt, *Catal. Today*, in press, and references therein.
2 M. P. McDaniel, *Adv. Catal.*, 1985, **33**, 47, and references therein.
3 B. M. Weckhuysen and R. A. Schoonheydt, *Catal. Today*, 1998 in press, and references therein.
4 F. Buonomo, D. Sanfilippo and F. Trifiro, in *Handbook of Heterogeneous Catalysis*, ed. G. Ertl, H. Knözinger, J. Weitkamp, Wiley–VCH, Weinheim, 1997, p. 2140, and references therein.
5 B. M. Weckhuysen, I. E. Wachs and R. A. Schoonheydt, *Chem. Rev.*, 1996, **96**, 3327, and references therein.
6 A. Hakuli, A. Kytokivi, A. O. Krause and T. Suntola, *J. Catal.*, 1996, **161**, 393.
7 F. Cavani, M. Koutyrev, F. Trifiro, A. Bartolini, D. Ghisletti, R. Iezzi, A. Santucci and G. Del Piero, *J. Catal.*, 1996, **158**, 236.
8 H. J. Lugo and J. H. Lunsford, *J. Catal.*, 1985, **91**, 155.
9 A. Kytokovi, J. P. Jacobs, A. Hakuli, J. Merilainen and H. H. Brongersma, *J. Catal.*, 1996, **162**, 190.
10 S. De Rossi, G. Ferraris, S. Fremiotti, E. Garrone, G. Ghiotti, M. C. Campa and V. Indovina, *J. Catal.*, 1994, **148**, 36; S. De Rossi, G. Ferraris, S. Fremiotti, V. Indovina and A. Cimino, *Appl. Catal.*, 1993, **106**, 125.
11 B. M. Weckhuysen and I. E. Wachs, *J. Phys. Chem.*, 1996, **100**, 14 437; B. M. Weckhuysen and I. E. Wachs, *J. Phys. Chem. B*, 1997, **101**, 2793.
12 J. Masson, J. M. Bonnier, P. H. Duvigneaud and B. Delmon, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 1471.
13 K. C. Chen, T. Tsuchiya and J. D. Mackenzie, *J. Non-Cryst. Solids*, 1986, **81**, 227.
14 A. Bensalem, B. M. Weckhuysen and R. A. Schoonheydt, *J. Phys. Chem. B*, 1997, **101**, 2824.
15 B. M. Weckhuysen and R. A. Schoonheydt, *Catal. Today*, submitted.
16 B. M. Weckhuysen, A. A. Verberckmoes, A. R. De Baets and R. A. Schoonheydt, *J. Catal.*, 1997, **166**, 160.
17 B. M. Weckhuysen, L. M. De Ridder and R. A. Schoonheydt, *J. Phys. Chem.*, 1993, **97**, 4756.

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