

# Dichloromethane as a Selective Modifying Agent To Create a Family of Highly Reactive Chromium Polymerization Sites\*\*

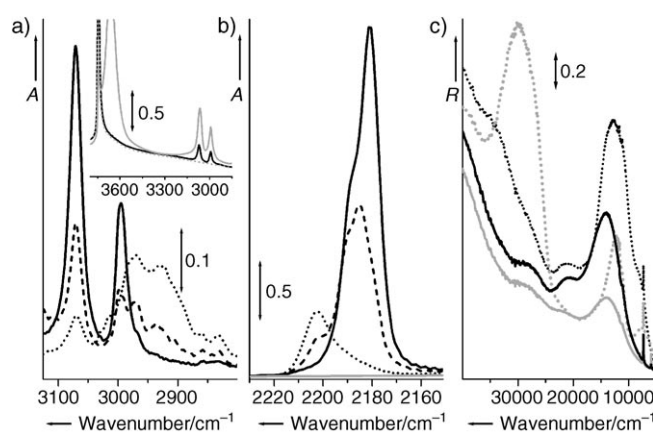
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The  $\text{Cr}^{\text{II}}/\text{SiO}_2$  Phillips catalyst,<sup>[1]</sup> although used in industrial plants since the 1960s, is still one of the most-debated systems with regard to both the molecular structure of the active sites and the related initiation mechanism, for which a unified picture is still missing.<sup>[2–5]</sup> The main reasons why these two strictly connected questions are not properly addressed are the high intrinsic heterogeneity of the  $\text{Cr}^{\text{II}}$  sites formed at the surface of amorphous silica and the high degree of Cr dilution (typically less than 1 wt % Cr). Furthermore, catalytically inactive  $\text{Cr}_2\text{O}_3$  clusters are formed at higher Cr loadings.<sup>[6]</sup> The presence of at least three families of  $\text{Cr}^{\text{II}}$  species that differ in their ability to coordinate ligand molecules and thus in their catalytic activity has been fully demonstrated, and preparative routes have been developed to minimize the formation of  $\text{Cr}_2\text{O}_3$  clusters.<sup>[3–7]</sup>

Attempts to reduce the complexity of the catalyst surface have been continuously made over the last decades. In this respect, the annealing method of McDaniel,<sup>[2]</sup> further developed by Groppo et al.,<sup>[4b]</sup> is a way to fine-tune the relative populations of  $\text{Cr}^{\text{II}}$  sites. By grafting Cr species on a flat  $\text{SiO}_2/\text{Si}(100)$  surface, van Kimmenade et al.<sup>[8]</sup> succeeded in obtaining better-defined Cr species. This approach is ideal for the application of specific surface-science methods such as X-ray photoelectron spectroscopy and atomic force microscopy. Recently, a method to completely remove the heterogeneity of the  $\text{Cr}^{\text{II}}/\text{SiO}_2$  system was reported.<sup>[9–11]</sup> By using the 1,3,5-tribenzylhexahydro-1,3,5-triazine (TAC) ligand as a surface-modifying agent, a single-site Cr species was made that results in the formation of polyethylene with a very low polydispersity index.

Herein we reveal that the much simpler  $\text{CH}_2\text{Cl}_2$  molecule acts as a surface-modifying agent for the  $\text{Cr}^{\text{II}}/\text{SiO}_2$  system. In this respect, it is important to recall the use of halocarbon promoters in the field of Ziegler–Natta-type polymerization catalysis,<sup>[12]</sup> although the true mechanism of promotion has not yet been fully reported. Indeed, results on, for example, vanadium-based catalysts suggest that the main role of the halogenated compounds may be due to their oxidizing character, as  $\text{V}^{\text{II}}$  species formed during the polymerization process are re-oxidized to  $\text{V}^{\text{III}}$ .<sup>[13,14]</sup> Herein we show that  $\text{CH}_2\text{Cl}_2$  has a dual function, that is, selectively enhancing the catalytic activity of a small fraction of Cr sites and poisoning the remainder. This novel approach represents a much simpler method to reduce the above-mentioned Cr heterogeneity and at the same time improves the catalytic performance of this industrially important catalyst system.

Figure 1 shows the physicochemical processes taking place when  $\text{CH}_2\text{Cl}_2$  is brought into contact with  $\text{Cr}^{\text{II}}/\text{SiO}_2$  under different conditions, as probed by IR and diffuse-reflectance (DR) UV/Vis/NIR spectroscopy. When dosed at room temperature,  $\text{CH}_2\text{Cl}_2$  interacts with both the silica support and the  $\text{Cr}^{\text{II}}$  sites. Interaction with silanol groups is



**Figure 1.** Effect of interaction of the  $\text{Cr}^{\text{II}}/\text{SiO}_2$  system (1.0 wt % Cr) with  $\text{CH}_2\text{Cl}_2$ , as detected with FTIR (a, C–H stretching region, extended to the O–H stretching region in the inset) and UV/Vis/NIR spectroscopy (c). b) FTIR spectra in the C–O stretching region of CO adsorbed at room temperature ( $p_{\text{CO}} = 40$  Torr) on the  $\text{Cr}^{\text{II}}/\text{SiO}_2$  system subjected to the same treatments reported in parts (a) and (c). Line code:  $\text{Cr}^{\text{II}}/\text{SiO}_2$  system before (gray dotted line) and after (gray full line) contact with  $\text{CH}_2\text{Cl}_2$  (150 Torr) and subsequent evacuation at room temperature (full black line); effect of heating for 15 min under 150 Torr of  $\text{CH}_2\text{Cl}_2$  and subsequent evacuation at 373 K (dashed line) and at 423 K (dotted line), respectively. A = absorbance (in absorbance units); R = diffuse reflectance (in Kubelka–Munk units).

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testified by the strong perturbation of the  $3745\text{-cm}^{-1}$  band of the system in vacuo, which is red-shifted to  $3660\text{-cm}^{-1}$  (compare the dotted and full gray lines in the inset of Figure 1a). In addition, two bands, due to the asymmetric ( $\nu_{\text{asym}}$ ) and symmetric ( $\nu_{\text{sym}}$ ) modes of the adsorbed molecule, appear at  $3065$  and  $2992\text{-cm}^{-1}$ , respectively.<sup>[15]</sup>

Direct interaction with  $\text{Cr}^{\text{II}}$  sites is evidenced by the modification observed in the UV/Vis/NIR spectra (compare the dotted and full gray lines in Figure 1c), which indicates dramatic perturbation of the electronic structure of the Cr sites. More specifically, the two d–d bands at  $7600$  and  $12300\text{-cm}^{-1}$  disappear, while new d–d bands occur at  $12900$  and  $21300\text{-cm}^{-1}$ . In addition, the charge-transfer band at  $30100\text{-cm}^{-1}$ , typical of highly coordinatively unsaturated  $\text{Cr}^{\text{II}}$  sites, is eroded. This behavior is typical when a strong ligand is dosed onto  $\text{Cr}^{\text{II}}$  sites.<sup>[4]</sup>  $\text{CH}_2\text{Cl}_2$  molecules hydrogen-bonded to the silica surface are easily removed by room-temperature evacuation (see full black line in the inset of Figure 1a). Conversely,  $\text{Cr}^{\text{II}}\cdots(\text{CH}_2\text{Cl}_2)_n$  adducts are irreversibly formed (see left-hand side of Scheme 1), as shown by the  $\nu_{\text{asym}}$  and  $\nu_{\text{sym}}$  modes remaining after evacuation at room temperature, the former now shifted to  $3071\text{-cm}^{-1}$ . This finding is confirmed by the corresponding UV/Vis/NIR spectrum (full black line in Figure 1c), as the starting situation cannot be recovered.

The  $\text{CH}_2\text{Cl}_2$  physisorption process observed at room temperature turns into dissociative chemisorption on heating the system. Solymosi and Rasko<sup>[15]</sup> have already investigated the interaction of  $\text{CH}_2\text{Cl}_2$  with a bare silica support. They showed that, on heating, the bands related with the  $\text{SiOH}\cdots(\text{CH}_2\text{Cl}_2)_m$  complexes disappear, as a result of molecular desorption of  $\text{CH}_2\text{Cl}_2$  (detected by mass spectrometry). In addition, the elimination of a small quantity of HCl has also been claimed, which may lead to the formation of a partially chlorinated silica surface. Our results demonstrate that the dissociative phenomenon is not restricted to the support alone, but also influences the coordination environment of the Cr sites.

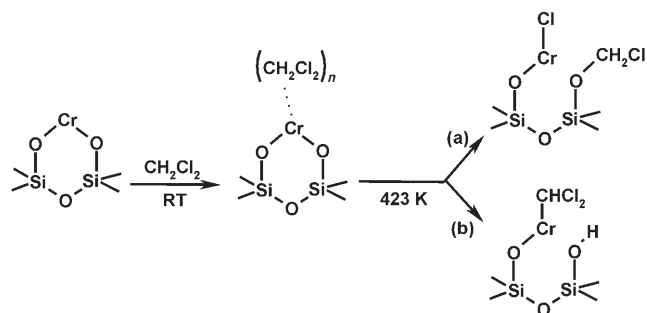
Figure 1 shows the effects of heating the  $\text{Cr}^{\text{II}}/\text{SiO}_2$  system in the presence of a high  $\text{CH}_2\text{Cl}_2$  pressure from  $373$  (dashed line) to  $423\text{ K}$  (dotted black line) followed by evacuation at the same temperature. The bands due to  $\nu_{\text{asym}}$  and  $\nu_{\text{sym}}$  modes of the physisorbed  $\text{Cr}^{\text{II}}\cdots(\text{CH}_2\text{Cl}_2)_n$  complexes gradually decrease with increasing temperature (Figure 1a), accompanied by the appearance of a broad absorption in the O–H stretching region (not shown) due to reactions occurring at the silica surface and by the growth of new ill-resolved components at frequencies below  $3000\text{-cm}^{-1}$ . The demonstration that at least a fraction of these new  $\text{CH}_2$ -containing species are related to the Cr sites comes from the UV/Vis/NIR data (black dotted line in Figure 1c). More specifically, we observe the formation of a band at  $23000\text{-cm}^{-1}$ , a red shift and intensity increase of the band now located around  $12800\text{-cm}^{-1}$ , as well as the formation of a shoulder at about  $8400\text{-cm}^{-1}$ . These observations point to strong changes in the coordination environment of the Cr sites on heating the system in  $\text{CH}_2\text{Cl}_2$ .

More specifically, the spectrum contains absorption maxima of both  $\text{Cr}^{\text{II}}$  and  $\text{Cr}^{\text{III}}$  species (see discussion in the Supporting Information, as well as Figure S1 and Table S1).

The asymmetric shape and the width of the absorption band in the  $12000\text{--}15000\text{-cm}^{-1}$  range indicate the presence of at least two close absorption maxima, assigned to  $\text{Cr}^{\text{II}}$  ( ${}^5\text{B}_1 \rightarrow {}^5\text{T}_{2g}$ ) and  $\text{Cr}^{\text{III}}$  ( ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ ). The occurrence of the d–d transition assigned to  $\text{Cr}^{\text{III}}\text{O}_6$  ( $16600\text{-cm}^{-1}$ ) at lower wavenumbers suggests the presence of at least one chloride ligand in the coordination sphere of chromium. Complementary extended X-ray absorption fine-structure (EXAFS) analysis supports these findings and shows the possible presence of some chloride ligands (Figure S3 and Table S2). Moreover, Cr K-edge X-ray absorption near-edge structure (XANES) analysis (Figure S2) clearly indicates partial oxidation of  $\text{Cr}^{\text{II}}$  to  $\text{Cr}^{\text{III}}$ .

To gain deeper insight into the modified Cr sites, we probed their coordinative unsaturation with CO at the different stages discussed above (Figure 1b). The ability of this method to probe polymerization-active Cr sites was demonstrated recently.<sup>[16]</sup> After interaction with  $\text{CH}_2\text{Cl}_2$  and subsequent evacuation at room temperature (full line) we observe an intense band at  $2180\text{-cm}^{-1}$  with a pronounced shoulder around  $2190\text{-cm}^{-1}$ . These bands differ from the well-known room-temperature triplet (components at  $2191$ ,  $2183$ , and  $2178\text{-cm}^{-1}$ , curve b in the inset of Figure 2),<sup>[4]</sup> and reflect the presence of adsorbed  $\text{CH}_2\text{Cl}_2$  in the proximity of the  $\text{Cr}^{\text{II}}$  sites. Heating and outgassing the sample at  $373\text{ K}$  (dashed line) has two effects: 1) restoration of the classical room-temperature triplet for a fraction of sites, which indicates that the perturbing  $\text{CH}_2\text{Cl}_2$  molecules have been desorbed, and 2) the appearance of a new component with an anomalously high  $\tilde{\nu}_{\text{CO}}$  value of  $2204\text{-cm}^{-1}$ , which shows that a new Cr species has been created. This becomes the unique species on heating and outgassing at  $423\text{ K}$  (dotted line). During this experiment, pronounced reduction of the integrated intensity of the carbonyl bands is observed, that is, most of the Cr sites are no longer available for CO. In other words, IR spectroscopy with CO as probe molecule and UV/Vis/NIR data show that thermal treatment in  $\text{CH}_2\text{Cl}_2$  creates some new Cr sites at the surface, characterized by different spectroscopic features, while poisoning most of the remaining sites.

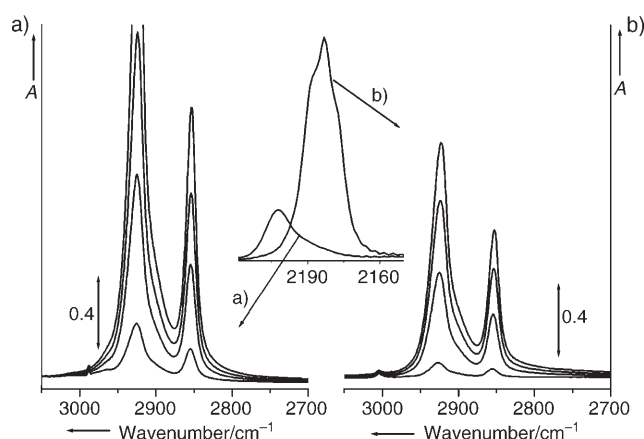
Many reactions can occur under these conditions, both on silica and at the Cr sites. For the latter, we tentatively propose the reactions shown on the right-hand side of Scheme 1. The starting point is a reduced  $\text{Cr}^{\text{II}}$  site, which is structurally in line with the theoretical model developed by Espelid and Borve (i.e., the pseudotetrahedral mononuclear  $\text{Cr}^{\text{II}}$  B site).<sup>[5a]</sup> The



**Scheme 1.** Proposed reaction scheme for the reaction of  $\text{CH}_2\text{Cl}_2$  with  $\text{Cr}^{\text{II}}/\text{SiO}_2$ .

experimentally observed d–d transitions at 7600 and 12300  $\text{cm}^{-1}$  (see the Supporting Information) are in accordance with those calculated for this model.<sup>[5d]</sup> This surface  $\text{Cr}^{\text{II}}$  species will first physisorb  $\text{CH}_2\text{Cl}_2$ ; this intermediate will react further via two distinct pathways. Reaction (a) leads to the formation of poisoned Cr sites, while we believe (see below) that reaction (b) results in the formation of highly reactive Cr sites. We stress here that the experimental conditions to create this situation are extremely critical in terms of both activation temperature and contact time (see the Supporting Information). When the treatment is too mild (lower temperatures or shorter contact times) one ends up with the classical Cr sites, besides a very small fraction of new Cr sites (see dashed line in Figure 1b). Conversely, treatment that is too severe will lead to complete catalyst deactivation, as suggested by the absence of CO adsorption (not reported).

To assess the polymerization properties of the modified catalyst we monitored ethylene polymerization in situ with time-dependent IR spectroscopy, the ability of which to determine the polymerization activity has been demonstrated in the past.<sup>[4]</sup> Figure 2 compares these data (Figure 2a) with those obtained for the same catalyst activated in the standard manner (Figure 2b). In both cases the growth of the polyethylene chains is evidenced by the progressive increase



**Figure 2.** a) Time-resolved FTIR spectra in the  $\text{CH}_2$  stretching region of ethylene polymerization reaction conducted at room temperature on 1.0 wt%  $\text{Cr}^{\text{II}}/\text{SiO}_2$  modified with  $\text{CH}_2\text{Cl}_2$  at 423 K. b) The same experiment performed on the same system activated in a standard way. Initial  $p_{\text{C}_2\text{H}_4} = 10$  mbar. In both parts, each spectrum was collected every 40 s. Inset: IR spectra of adsorbed CO prior to polymerization were used to probe the coordinative unsaturation of the  $\text{Cr}^{\text{II}}$  sites in both cases. A = absorbance (in absorbance units).

of the two IR bands due to the  $\text{CH}_2$  stretching modes.<sup>[4]</sup> Clearly, the  $\text{CH}_2\text{Cl}_2$ -modified catalyst, although it contains far fewer Cr sites able to coordinate CO (compare the spectra in the inset of Figure 2) and thus  $\text{C}_2\text{H}_4$ ,<sup>[16]</sup> has a much higher polymerization activity. Thus, the turnover frequency of the new sites must be much higher than that of the standard sites (by about one order of magnitude).<sup>[17]</sup>

Furthermore, the vibrational properties of the polymer growing on the  $\text{CH}_2\text{Cl}_2$ -modified system are different to those of the polymer obtained on the standard catalyst. This holds

both for the frequency (2922 and 2853  $\text{cm}^{-1}$  versus 2925 and 2855  $\text{cm}^{-1}$ ) and for the full width at half-maximum (15 versus 20  $\text{cm}^{-1}$  for the low-frequency band). These spectroscopic findings, together with the pronounced decrease in CO adsorption (Figure 1b), suggest that on the  $\text{CH}_2\text{Cl}_2$ -modified system longer and more ordered chains are formed more rapidly on fewer sites<sup>[4b]</sup> in comparison with the standard system. This reflects the higher homogeneity of the active sites remaining after interaction with  $\text{CH}_2\text{Cl}_2$ . In other words, site narrowing has been performed by the surface-modifying agent.

One can speculate on the molecular structure of the new highly active polymerization Cr sites. In our opinion, the anomalously high  $\tilde{\nu}_{\text{CO}}$  value (2204  $\text{cm}^{-1}$ ) characterizing these sites can be explained only on the basis of the presence of a strong charge acceptor, like Cl, in the close surroundings of Cr, which has indeed been detected by X-ray absorption spectroscopy (see the Supporting Information). The depletion of electron density around Cr results in increased  $\sigma$ -donor character of the Cr–CO bond, which causes a blue shift in  $\tilde{\nu}_{\text{CO}}$ .<sup>[18]</sup> This demonstrates that insertion of a Cl ligand from  $\text{CH}_2\text{Cl}_2$  into the Cr coordination sphere is not a peculiarity of the TAC-modified  $\text{Cr}/\text{SiO}_2$  system,<sup>[10,11]</sup> but occurs also in the much simpler  $\text{Cr}/\text{SiO}_2$  system.

Dissociative chemisorption of  $\text{CH}_2\text{Cl}_2$  may lead to at least two situations (right-hand part of Scheme 1). Species resulting from reaction (a), certainly more abundant as favored on purely electrostatic grounds, are probably inactive. Based on the X-ray absorption spectroscopy data (see the Supporting Information) one anticipates that the oxidation state of this species is III and the nearby oxygen atom most probably forms a bond with the surface  $\text{Cr}^{\text{III}}\text{OCl}$  unit. Such an oxidation process has some similarity with that observed for V-based Ziegler–Natta polymerization catalysts when activated with halocarbon compounds.<sup>[13,14]</sup> Inactive sites are also generated by the side products of the decomposition of  $\text{CH}_2\text{Cl}_2$  on the silica surface ( $\text{H}_2\text{O}$  and  $\text{HCl}$ ),<sup>[15]</sup> and this explains the pronounced decrease in Cr sites able to coordinate CO (inset of Figure 2). Conversely, reaction (b) leads to the formation of a  $\text{Cr}^{\text{II}}$  species which has close resemblance to the structure of the active sites for Ziegler–Natta-type systems (i.e., a metal site with a metal–carbon bond and an available coordination vacancy).<sup>[19]</sup> These species themselves can be considered as active sites for ethylene polymerization. This explains the faster reaction of the new sites with respect to the standard  $\text{Cr}^{\text{II}}$  species, which must be transformed from precursors into active species by ethylene.<sup>[20]</sup>

In summary, a highly active Cr polymerization site can be created by dissociative chemisorption of  $\text{CH}_2\text{Cl}_2$  to give a species that does not need initiation by ethylene. This work will stimulate the appearance of a new class of highly active polymerization catalysts. The challenge in the near future will be optimization of the experimental procedure (e.g., time, pressure, temperature of  $\text{CH}_2\text{Cl}_2$  contact) to maximize the fraction of sites (b) in Scheme 1. This means that the order of magnitude that we have gained here in the activity per active site could be gained for the overall catalyst.<sup>[17]</sup> As a side remark, our study indicates that one should be aware of the potential other roles  $\text{CH}_2\text{Cl}_2$  may play in catalysis. This is

particularly relevant, as chlorinated hydrocarbons have found widespread use as solvents in a variety of reactions, a fact that makes this work of impact in the field of homogeneous catalysis as well.

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