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

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The Cr^{II}/SiO_2 Phillips catalyst,[1] 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.[2–5] The main reasons why these two strictly connected questions are not properly addressed are the high intrinsic heterogeneity of the Cr^{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 Cr_2O_3 clusters are formed at higher Cr loadings.[6] The presence of at least three families of Cr^{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 Cr_2O_3 clusters.[3–7]

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,[2] further developed by Groppo et al.,[4b] is a way to fine-tune the relative populations of Cr^{II} sites. By grafting Cr species on a flat SiO_2/Si(100) surface, van Kimmenade et al.[8] 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 Cr^{II}/SiO_2 system was reported.[9–11] 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 CH_2Cl_2 molecule acts as a surface-modifying agent for the Cr^{II}/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,[12] 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 V^{II} species formed during the polymerization process are re-oxidized to V^{III}.[13,14] Herein we show that CH_2Cl_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 CH_2Cl_2 is brought into contact with Cr^{II}/SiO_2 under different conditions, as probed by IR and diffuse-reflectance (DR) UV/Vis/NIR spectroscopy. When dosed at room temperature, CH_2Cl_2 interacts with both the silica support and the Cr^{II} sites. Interaction with silanol groups is
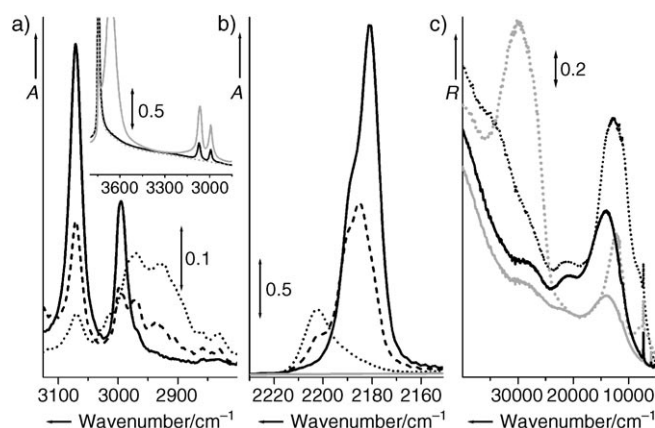
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Figure 1. Effect of interaction of the Cr^{II}/SiO_2 system (1.0 wt% Cr) with CH_2Cl_2, as detected with FTIR (a, C—H stretching region, extended to the O—H stretching region in the inset) and UV/Vis/NIR spectroscopy (c). b) FTIR spectra in the C—O stretching region of CO adsorbed at room temperature ($p_{CO} = 40$ Torr) on the Cr^{II}/SiO_2 system subjected to the same treatments reported in parts (a) and (c). Line code: Cr^{II}/SiO_2 system before (gray dotted line) and after (gray full line) contact with CH_2Cl_2 (150 Torr) and subsequent evacuation at room temperature (full black line); effect of heating for 15 min under 150 Torr of CH_2Cl_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).

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

Direct interaction with Cr^{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 cm^{-1} disappear, while new d–d bands occur at 12900 and 21300 cm^{-1}. In addition, the charge-transfer band at 30100 cm^{-1}, typical of highly coordinatively unsaturated Cr^{II} sites, is eroded. This behavior is typical when a strong ligand is dosed onto Cr^{II} sites.[4] CH$_2$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, Cr$^{II}\cdots$(CH$_2$Cl$_2$)$_n$ adducts are irreversibly formed (see left-hand side of Scheme 1), as shown by the ν_{asym} and ν_{sym} modes remaining after evacuation at room temperature, the former now shifted to 3071 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 CH$_2$Cl$_2$ physisorption process observed at room temperature turns into dissociative chemisorption on heating the system. Solymosi and Rasko[15] have already investigated the interaction of CH$_2$Cl$_2$ with a bare silica support. They showed that, on heating, the bands related with the SiOH$\cdots$(CH$_2$Cl$_2$)$_m$ complexes disappear, as a result of molecular desorption of CH$_2$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.
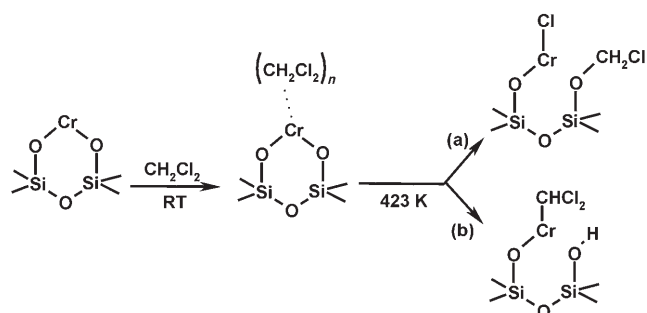
Figure 1 shows the effects of heating the Cr^{II}/SiO$_2$ system in the presence of a high CH$_2$Cl$_2$ pressure from 373 (dashed line) to 423 K (dotted black line) followed by evacuation at the same temperature. The bands due to ν_{asym} and ν_{sym} modes of the physisorbed Cr$^{II}\cdots$(CH$_2$Cl$_2$)$_n$ 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 cm^{-1}. The demonstration that at least a fraction of these new 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 cm^{-1}, a red shift and intensity increase of the band now located around 12800 cm^{-1}, as well as the formation of a shoulder at about 8400 cm^{-1}. These observations point to strong changes in the coordination environment of the Cr sites on heating the system in CH$_2$Cl$_2$.

More specifically, the spectrum contains absorption maxima of both Cr^{II} and Cr^{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 12000–15000 cm^{-1} range indicate the presence of at least two close absorption maxima, assigned to Cr^{II} ($^5B_1\rightarrow$ $^5T_{2g}$) and Cr^{III} ($^4A_{2g}\rightarrow^4T_{2g}$). The occurrence of the d–d transition assigned to Cr^{III}O$_6$ (16600 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 Cr^{II} to Cr^{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.[16] After interaction with CH$_2$Cl$_2$ and subsequent evacuation at room temperature (full line) we observe an intense band at 2180 cm^{-1} with a pronounced shoulder around 2190 cm^{-1}. These bands differ from the well-known room-temperature triplet (components at 2191, 2183, and 2178 cm^{-1}, curve b in the inset of Figure 2),[4] and reflect the presence of adsorbed CH$_2$Cl$_2$ in the proximity of the Cr^{II} sites. Heating and outgassing the sample at 373 K (dashed line) has two effects: 1) restoration of the classical room-temperature triplet for a fraction of sites, which indicates that the perturbing CH$_2$Cl$_2$ molecules have been desorbed, and 2) the appearance of a new component with an anomalously high $\tilde{\nu}_{CO}$ value of 2204 cm^{-1}, which shows that a new Cr species has been created. This becomes the unique species on heating and outgassing at 423 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 CH$_2$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 Cr^{II} site, which is structurally in line with the theoretical model developed by Espelid and Borve (i.e., the pseudotetrahedral mononuclear Cr^{II} B site).[5a] The

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

experimentally observed d–d transitions at 7600 and 12300 cm^{-1} (see the Supporting Information) are in accordance with those calculated for this model.[5d] This surface Cr^{II} species will first physisorb CH$_2$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.[4] 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
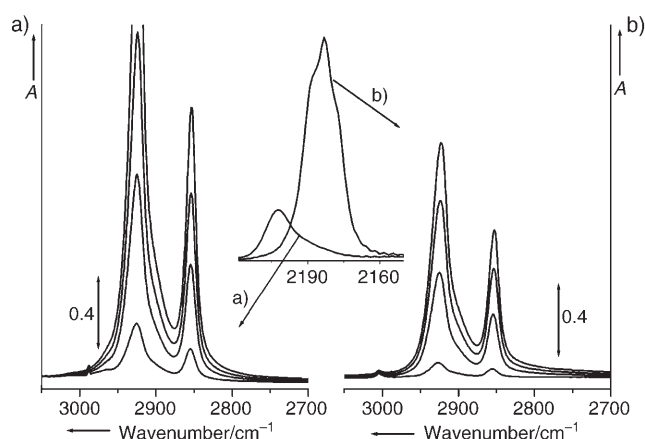

Figure 2. a) Time-resolved FTIR spectra in the CH$_2$ stretching region of ethylene polymerization reaction conducted at room temperature on 1.0 wt% Cr^{II}/SiO$_2$ modified with CH$_2$Cl$_2$ at 423 K. b) The same experiment performed on the same system activated in a standard way. Initial $p_{C_2H_4}=10$ 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 Cr^{II} sites in both cases. A = absorbance (in absorbance units).

of the two IR bands due to the CH$_2$ stretching modes.[4] Clearly, the CH$_2$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 C$_2$H$_4$,[16] 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).[17]

Furthermore, the vibrational properties of the polymer growing on the CH$_2$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 cm^{-1} versus 2925 and 2855 cm^{-1}) and for the full width at half-maximum (15 versus 20 cm^{-1} for the low-frequency band). These spectroscopic findings, together with the pronounced decrease in CO adsorption (Figure 1b), suggest that on the CH$_2$Cl$_2$-modified system longer and more ordered chains are formed more rapidly on fewer sites[4b] in comparison with the standard system. This reflects the higher homogeneity of the active sites remaining after interaction with CH$_2$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 $\tilde{v}_{CO}$ value (2204 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 σ-donor character of the Cr−CO bond, which causes a blue shift in $\tilde{v}_{CO}$.[18] This demonstrates that insertion of a Cl ligand from CH$_2$Cl$_2$ into the Cr coordination sphere is not a peculiarity of the TAC-modified Cr/SiO$_2$ system,[10,11] but occurs also in the much simpler Cr/SiO$_2$ system.

Dissociative chemisorption of CH$_2$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 Cr^{III}OCl unit. Such an oxidation process has some similarity with that observed for V-based Ziegler–Natta polymerization catalysts when activated with halocarbon compounds.[13,14] Inactive sites are also generated by the side products of the decomposition of CH$_2$Cl$_2$ on the silica surface (H$_2$O and HCl),[15] 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 Cr^{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).[19] 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 Cr^{II} species, which must be transformed from precursors into active species by ethylene.[20]

In summary, a highly active Cr polymerization site can be created by dissociative chemisorption of CH$_2$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 feature will be optimization of the experimental procedure (e.g., time, pressure, temperature of CH$_2$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.[17] As a side remark, our study indicates that one should be aware of the potential other roles CH$_2$Cl$_2$ may play in catalysis. This is

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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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