

CH₂Cl₂ as a selective modifying agent to create a new family of highly reactive Cr polymerization sites

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Introduction

The Cr^{II}/SiO₂ Phillips catalyst is still one of the most debated systems, concerning both the active sites and the related initiation mechanism, for which a unifying picture is still missing [1]. 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 Cr dilution. The second point is related to the formation of catalytically inactive Cr₂O₃ clusters at higher Cr loadings. As for the first point, the presence of at least three families of Cr^{II} species, differing in their ability to coordinate ligand molecules and thus in their catalytic activity, has been fully demonstrated. Attempts to reduce the complexity of the catalyst surface have been continuously made over the last decades. In this work, we report for the first time that CH₂Cl₂ acts as a surface-modifying agent, having the dual function to selectively enhance the catalytic activity of a small fraction of Cr sites, while poisoning the remaining ones [2].

Results and Discussion

Figure 1 shows the physicochemical processes taking place when CH₂Cl₂ has been brought into contact with Cr^{II}/SiO₂ as probed by IR and UV-Vis-NIR spectroscopies. When dosed at room temperature (RT), CH₂Cl₂ interacts with both the silica support and Cr^{II} sites. Interaction with silanols is testified by the strong perturbation of the 3745 cm⁻¹ band of the system in vacuo that red shifts to 3660 cm⁻¹. 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. Direct interaction with Cr^{II} sites is evidenced by the modification observed in the UV-Vis-NIR spectra, showing a dramatic perturbation of the electronic structure of 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. CH₂Cl₂ molecules hydrogen-bonded to the silica surface are easily removed by RT evacuation. Conversely, Cr^{II}...-(CH₂Cl₂)_n adducts are irreversibly formed, as shown by the ν_{asym} and ν_{sym} modes remaining after evacuation at RT, the former now shifted to 3071 cm⁻¹. This finding is confirmed by the corresponding UV-Vis-NIR spectrum as the starting situation cannot be recovered. In order to assess the polymerization properties of the modified catalyst we have the ethylene polymerization reaction with time-dependent IR. The growth of the polyethylene chains is evidenced by the progressive increase of the two IR bands due to the CH₂ stretching modes. It was found that for the CH₂Cl₂-modified catalyst, although containing much less Cr sites able to coordinate CO and thus C₂H₄, a much higher polymerization activity was found. This means that the turnover frequency of the new sites must be much higher than that of the standard ones.

These spectroscopic findings indicate that on the CH₂Cl₂-modified system longer and more ordered chains on fewer and faster sites are formed, in comparison with the standard system. This reflects the higher homogeneity of the active sites remaining after interaction with CH₂Cl₂.

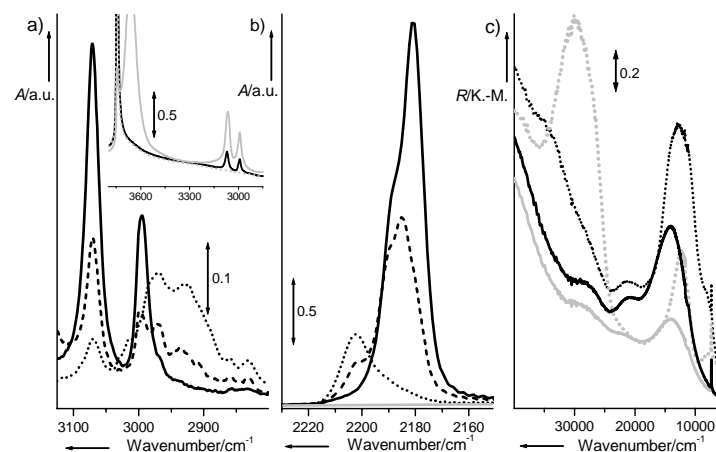


Figure 1. Effect of interaction of 1 wt% Cr^{II}/SiO₂ with CH₂Cl₂ as detected with FTIR (part a: C-H stretching region, extended to the O-H one in the inset) and UV-Vis DRS (part c). Part b: FTIR spectra, in the C-O stretching region, of CO adsorbed at RT on the Cr^{II}/SiO₂ system subjected to the same treatments reported in parts a,c. The line code is as follows: Cr^{II}/SiO₂ before (grey dotted line) and after (grey full line) contact with CH₂Cl₂ and subsequent evacuation at RT (full black line); effect of heating for 15 min in CH₂Cl₂ and subsequent evacuation at 373 K (dashed line) and at 423 K (dotted line), respectively.

Significance

A highly active Cr polymerization site can be created by the dissociative chemisorption of CH₂Cl₂ leading to a species that does not need the first initiation step by ethylene. This work will stimulate the appearance of a new class of highly active polymerization catalysts. As a side remark, our study indicates that one should be aware of the potential other roles CH₂Cl₂ may play in catalysis. This is particularly relevant, as chlorinated hydrocarbons have found widespread use as solvent in a variety of reactions.

References

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