

The Union Carbide catalyst ($\text{Cp}_2\text{Cr} + \text{SiO}_2$), studied by solid-state NMR¹

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Abstract

The Union Carbide catalyst, that can be synthesized by reaction of chromocene (Cp_2Cr) with silica (SiO_2), allows the polymerization of olefins at low pressure and low temperature without any cocatalyst. Despite the interest in this heterogeneous catalyst, the nature of the active species is still unknown. In this contribution it is demonstrated that ^1H solid-state NMR serves as a powerful method for the investigation of the surface species. The spectra are evidence for the presence of one mononuclear and two dinuclear surface-attached complexes. The nature of these species is discussed on the basis of molecular model compounds and their NMR characteristics.

Keywords: Solid-state NMR spectroscopy; Union Carbide catalyst; Chromium; Chromocenes; Metallocenes

1. Introduction

The coordination polymerization of olefins such as ethylene or propylene is the most important industrial process with organometallic intermediates [1–4]. Among the various transition metal species that catalyze olefin polymerizations, the materials containing chromium are especially interesting. There are two classes of heterogeneous chromium catalyst: the Phillips catalyst [4] contains CrO_3 on SiO_2 and is activated by treatment with H_2 . In the early 1970s, Union Carbide (UC) developed a class of catalyst that can be generated by reaction of chromocene Cp_2Cr (1) with silica (Scheme 1) [5].

This UC catalyst displays high activity for ethylene polymerization at low pressure and low temperature. Its use requires no cocatalyst or any other activating treatment [6–10]. Furthermore, the system is very sensitive toward H_2 transfer to the polymer chain and allows the preparation of polyethylene with a specific polymer melt index. The UC catalyst can also be applied to other substituted or cyclic olefins or those with longer chains [11]. When the Cp ring is substituted by an allyl or aryl

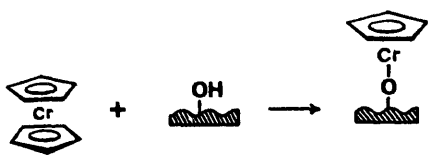
ligand, or the silica support by silica–alumina or alumina, the catalytic activity decreases [12,13]. Therefore, the Cp ligand assumes a special status that is also supported by the formation of methyl-substituted CpCr fragments during the ethylene polymerization with $\text{CrO}_3\text{-SiO}_2$ [14].

Despite the favorable characteristics of the UC catalyst, the structure of the active species is still unknown. All the analytical methods applied up to now are of an indirect nature. For example, the amount of cyclopentadiene released during the formation or heating of the UC catalyst was determined and correlated with catalytic activity [5,15]. An IR study of the UC catalyst after treatment with CO suggested dimeric species [16,17]; however, no molecular, catalytically active dinuclear chromium compounds are known at present. Among model compounds in solution [18–20], only some Cr(III) half-sandwiches are catalytically active for ethylene polymerization [21,22]. Even the oxidation state of the active species is still a matter of debate [5,6,21,22].

Nowadays, solid-state NMR spectroscopy [23,24] represents the most powerful analytical method for the characterization of heterogeneous and immobilized catalysts [25–28]. Since all chromium species relevant for the UC catalyst are paramagnetic, it has not yet been studied by NMR spectroscopy. However, great progress has been made with paramagnetic NMR on polycryst-

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¹ In honor of the late Professor H. Takaya.



Scheme 1. The formation of a catalytically active chromium surface species (UC catalyst) by reaction of chromocene with silica, as described in the literature.

talline compounds in the last decade [29,30]. Recently, we demonstrated that solid-state NMR spectra of paramagnetic chromocenes can be obtained easily within short measurement times [30].

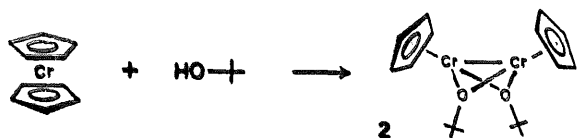
In this contribution we want to shed some light on the nature of the UC catalyst and demonstrate that especially ^1H magic angle spinning (MAS [23,24]) is extremely useful for the study of paramagnetic organometallic surface species.

2. Results and discussion

When chromocene is reacted with simple silanols such as Ph_3SiOH or $^t\text{BuMe}_2\text{SiOH}$ [31] or with $^t\text{BuOH}$ [20,31], or $2,6\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3\text{OH}$ [18], dinuclear Cr(II) compounds result that are analogous to the one shown in Scheme 2.

While the X-ray structure of the *t*-butoxy-bridged chromium half-sandwich **2** has been determined [20], no NMR data of this paramagnetic compound have been obtained. However, ^1H and ^{13}C NMR spectra of dinuclear Cr(II) species can be obtained easily in solution as well as in the solid state [31]: the δ values of the polycrystalline samples are similar to the NMR data obtained in solution [31]. For example, the ^1H MAS spectrum is displayed in Fig. 1. Both, methyl and cyclopentadienyl proton signals at 3.2 and 36.9 ppm, are well-resolved. The signals of the alkoxy or siloxy groups of the dinuclear complexes are mostly within the diamagnetic region of the ^{13}C and ^1H NMR spectra. However, the $\delta(^1\text{H})$ values of the Cp rings lie within the narrow range of 36 to 46 ppm, which proves to be characteristic for this class of compound [31].

As in the case of chromocenes [30], the use of 4 mm rotors and spinning speeds higher than 10 kHz are mandatory for the reduction of residual line widths and spinning sidebands, owing to large chemical shift



Scheme 2. Reaction of Cp_2Cr (**1**) with $^t\text{BuOH}$ [20,31], one example of the general reactivity **1** displays toward alcohols and silanols.

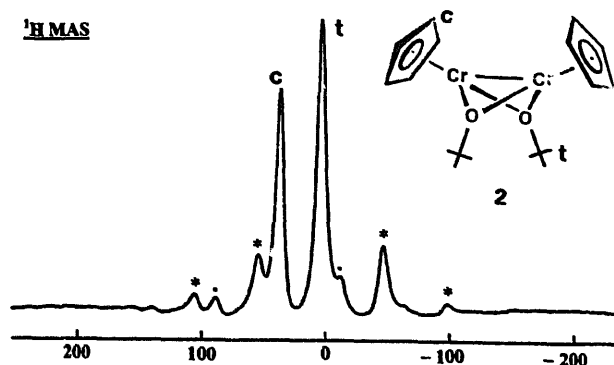


Fig. 1. 300.1 MHz ^1H MAS spectrum of polycrystalline **2**. Rotational frequency: 15 kHz. The asterisks denote rotational sidebands of the methyl protons, the dots those of the ring proton resonance.

anisotropies. However, there are differences in the temperature dependence of the chemical shifts of chromocenes and dinuclear species such as **2**. For chromocenes the $\delta(^1\text{H})$ and $\delta(^{13}\text{C})$ decrease with increasing temperature [30]. In contrast to this, the dinuclear species display only minute changes of δ with temperature. This is due to antiferromagnetic coupling of the unpaired electrons of both chromium centers in dinuclear species and can, for example, also be seen in the NMR spectra of dinuclear Cr(III) complexes [32–34]. Therefore, mononuclear chromium species can easily be distinguished from dinuclear complexes. Even without external heating of the sample this distinction can be made, because the rotor heats up substantially at higher spinning speeds due to friction at the rotor walls [30]. Hence, a change of δ with the rotational frequency is indicative of a mononuclear paramagnetic species.

A typical ^1H MAS spectrum of the material after reaction of **1** with SiO_2 [35] is displayed in Fig. 2.

The otherwise, from an analytical point of view, disadvantageous large chemical shifts of paramagnetic

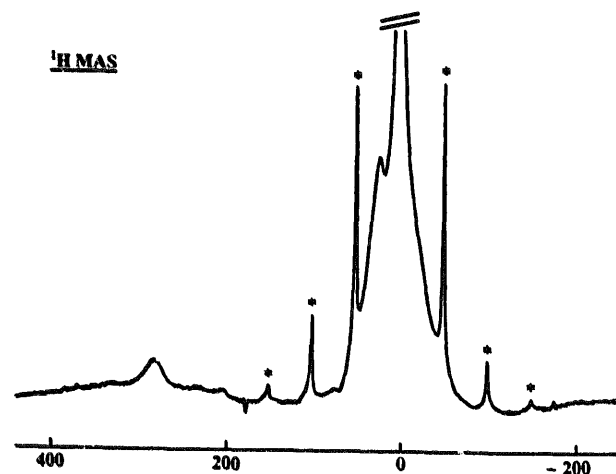


Fig. 2. 300.1 MHz ^1H MAS spectrum of the UC catalyst. Asterisks denote rotational sidebands of the ^1H signal of the silica support. Rotational frequency: 15 kHz.

compounds are favorable in this case, since signals of surface-attached chromium species are outside of the diamagnetic region with the large silanol and water proton signals of the silica support. Besides the latter, two other signals are clearly visible in the spectrum of Fig. 2: one resonance at 282 and another at 25 ppm. While the signal at 282 ppm is shifted towards higher field with increasing temperature, the 25 ppm resonance remains practically unchanged. For example, when the rotational frequency is lowered to 10 kHz, the low field signal is shifted to 295 ppm, while no significant change of δ takes place for the 25 ppm resonance. When the amount of Cp_2Cr deposited on silica is increased from 105 to 183 mg g^{-1} of SiO_2 , the intensity of the signal at 282 ppm decreases and a new resonance at 148 ppm shows up in the ^1H MAS spectrum. The chemical shift of this latter signal does not change with temperature, which is again indicative of antiferromagnetic coupling and therewith a dinuclear species. When oxygen is admitted to the UC catalyst, paramagnetically shifted NMR signals can no longer be detected.

From these results, some fundamental conclusions can already be drawn: (a) ^1H MAS is a powerful tool for studying paramagnetic surface-attached organometallic species; (b) at least three different chromium species, containing still one or more Cp rings, play a role on the surface of the UC catalyst; (c) there must be at least one mononuclear chromium compound (282 ppm) and two dinuclear surface-attached complexes (148 and 25 ppm).

On the basis of the chemical shifts, the nature of the surface species can tentatively be discussed. The signal at 282 ppm lies well in the range where the ring protons of chromocenes are found [30,36] and, therefore, one choice is to ascribe it to adsorbed chromocene. An excess of adsorbed chromocene has, for example, been studied by Zecchina and coworkers [9,10]; this was deemed responsible for the decreasing activity of the UC catalyst with increasing Cp_2Cr loading, due to clogging of the silica pores and the catalytic centers. Support for this comes, for example, from the mass spectra of the UC catalyst: a peak of 1 is always shown, even at room temperature where decomposition of dinuclear chromium species should not yet take place. However, mass spectroscopy might be oversensitive with respect to the very volatile 1. The temperature dependence of the $\delta(^1\text{H})$ of the 282 ppm signal matches that of Cp_2Cr [30] very well. Here too, for example, a 5 kHz decrease in the rotational frequency leads to a shift of about 13 ppm to lower field. However, the chemical shift value of 282 ppm is about 25 ppm smaller than that of polycrystalline 1 [30]. Of course, this difference might be due to the adsorption and interactions of 1 with the silica surface. However, the intensity of the resonance at 282 ppm should increase along with the loading if it were due to adsorbed chromocene, which is

not the case. Alternatively, one might attribute the resonance at 282 ppm to a surface-attached chromium half-sandwich species, formed by reaction with acidic protons of the silica surface in analogy with Ref. [32]. For example, the chemical shift of the Cp protons of $\text{CpCrI}_2 \cdot \text{THF}$ is 270 ppm, while the δ values for Cr(III) half-sandwich compounds vary within a wide range of about 230 to 320 ppm, depending on the ligands [32]. No model compounds, directly comparable with the expected surface species is available at present. Since equilibria between mono- and dinuclear Cr(III) complexes are known [32], it is tempting to suggest that on reacting silica with an increasing amount of Cp_2Cr , first surface-bound half-sandwich complexes are formed. This reaction proceeds until the surface coverage is sufficiently dense as to allow further reaction to dinuclear CpCr(III) species. Indeed, the chemical shift of 148 ppm corresponds very well, for example, to the $\delta(^1\text{H})$ value of the dinuclear Cr(III) compound *cis*- $[\text{CpCrCl}_2]_2$ with 154.8 ppm [34]. This suggestion is supported by the long-known decrease of the catalytic activity with increasing loading of silica with 1. While some Cr(III) half-sandwich complexes are active catalysts for ethylene polymerization even in solution [21], no catalytically active dinuclear chromium complexes are known at present. In addition to this, rigorously dried silica with isolated silanol groups produces the most active catalysts [7,13,18]. This might be due to the effective spatial separation of the catalytically active half-sandwich species on the silica surface.

Comparing the 25 ppm resonance of the UC catalyst with the ^1H NMR chemical shift range of the Cp proton signals of dinuclear Cr(II) complexes [31] (see above), one might suggest a dinuclear surface-attached Cr(II) species. However, the latter cannot be expected to be catalytically active according to Ref. [18].

Finally, it should be mentioned that the nature of the surface species cannot be deduced from the color of the UC catalyst, since all the relevant mono- and dinuclear Cr(II) and Cr(III) compounds are dark violet to black.

To sum up, we have shown for the UC catalyst, that ^1H MAS spectroscopy can fruitfully be applied to the study of surface-bound organometallic paramagnetic compounds. While the detailed structures, as well as the oxidation states must remain the subject of further studies, the number of relevant surface species of the UC catalyst has been enlarged and their mono- or dinuclear character could be determined unequivocally.

Acknowledgements

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