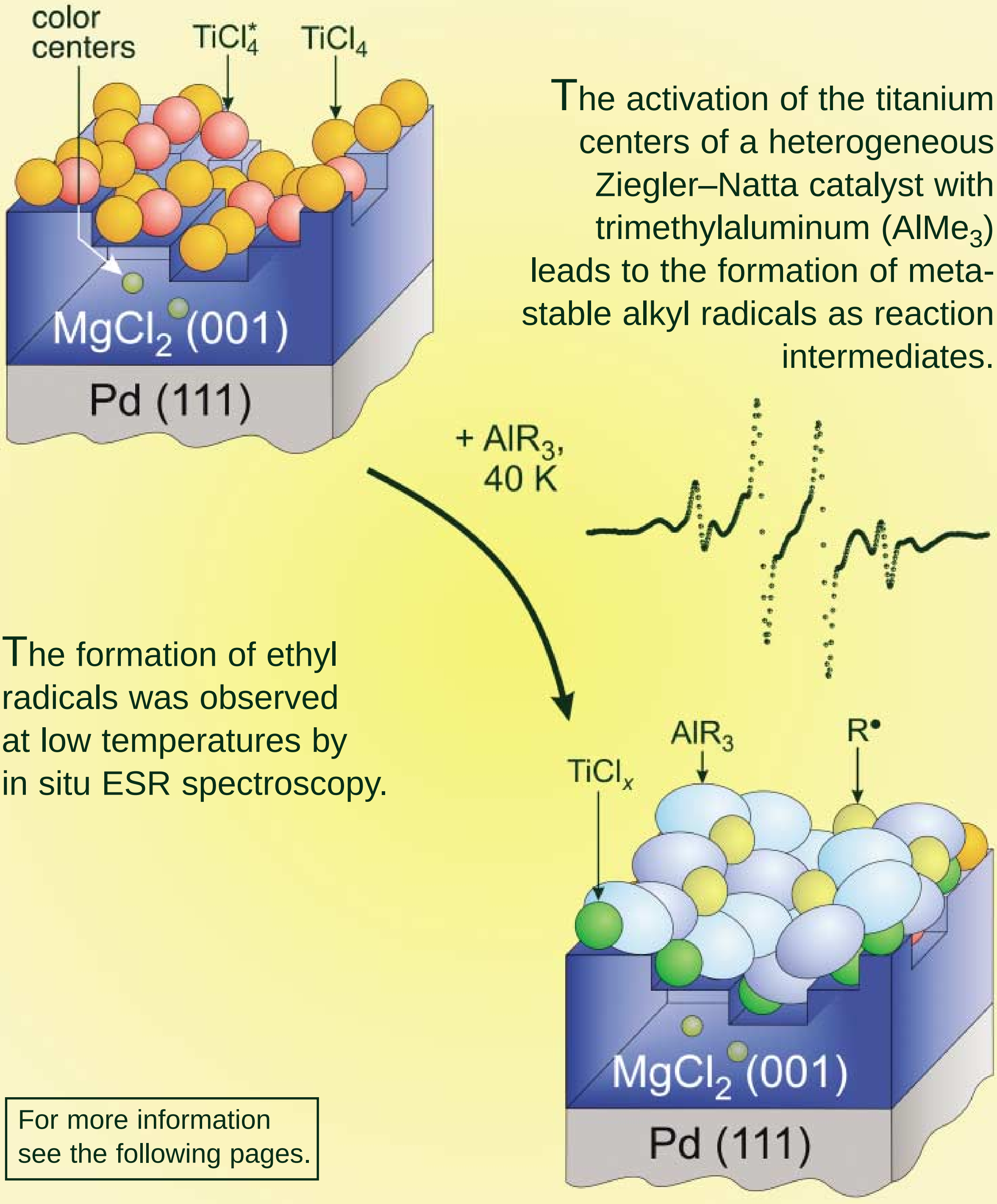

The activation of the titanium centers of a heterogeneous Ziegler–Natta catalyst with trimethylaluminum ($AlMe_3$) leads to the formation of metastable alkyl radicals as reaction intermediates.

The formation of ethyl radicals was observed at low temperatures by in situ ESR spectroscopy.

For more information see the following pages.

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Direct Observation of Radicals in the Activation of Ziegler–Natta Catalysts**

Thomas Risse,* Jörg Schmidt, Heiko Hamann, and Hans-Joachim Freund

Dedicated to Professor Georg Hohlneicher
on the occasion of his 65th birthday

Since the discovery of low-pressure ethene polymerization by Karl Ziegler and Giulio Natta in 1953 and 1954, several generations of catalysts have been developed which exceed the activity and selectivity of the original catalysts by several orders of magnitude.[1, 2] The literature on this topic is huge and is still growing as a result of the development of new generations of catalysts, such as metallocene-/methylaluminoxane-based catalysts. The third generation of catalysts, the basis for the model system used in this study, represents a supported catalyst that was developed in 1975. A detailed understanding of the reaction mechanism, however, lags behind these developments. This occurresnce has arisen because of the fact that direct characterization of the catalyst is still a challenge; most of the characterization has been done indirectly by analysis of the polymer products. First attempts to characterize the surfaces of model Ziegler–Natta catalyst systems have been published during recent years by Somorjai and his group.[3, 4] Ab initio calculations on the structural as well as dynamic aspects of the reaction also gave some insight on the mechanism of the reaction.[5, 6] In the present study we have used a model system consisting of an epitaxially grown $MgCl_2$ film onto which $TiCl_4$ was anchored as the active component. The anchoring process has been studied by electron spectroscopy[7] and, recently in our group, by ESR spectroscopy, we have shown that surface defects in the $MgCl_2$ film are crucial in this process.[8] The key step, however, is the so-called activation of the system by adding a co-catalyst, namely an alkyl aluminum compound (trimethylaluminum (TMA), triethylaluminum (TEA)). In this process it is believed that Ti ions assume a lower oxidation state and when TMA is used radicals ($R^\bullet$) are created according to Equation (1), whereas the activation with TEA takes place through a disproportionation reaction.[9–12] So far, however, no convincing direct experimental evidence has been presented for the formation of such alkyl radicals during the activation of the catalyst. Herein we prove for the first time, by ESR spectroscopy, the formation of alkyl radicals.

$$TiCl_4 + AlR_3 \rightarrow RTiCl_3 + AlClR_2 \rightarrow TiCl_3 + R^\bullet + AlClR_2 \ (R = CH_3) \quad (1)$$

Before we discuss the main issue of this communication, namely the observation of radicals created in the catalyst activation process, we briefly summarize the structure and morphology of the pre-activated catalyst. As shown schematically in Figure 1a, a Pd(111) substrate is covered by a $MgCl_2$ film in a (001) orientation which grows in a layer by layer mode.[13] The surface is terminated by chloride ions and the film has a thickness of between 6–12 layers of $MgCl_2$, as shown by LEED (Low Energy Electron Diffraction) and Auger spectroscopy. CO adsorption/desorption investigations proved that the film was free of pin holes. In line with the work of Magni and Somorjai, we find that it is necessary to produce defects in the film to bind the $TiCl_4$ precursor.[3] We have created defects by various routes, such as by using kinetically controlled growth conditions as well as electron and ion bombardment. A certain class of defects, namely so-called color centers were identified by ESR spectroscopy. When, for example, $TiCl_4$ was anchored to a film grown under non-equilibrium conditions, 40% of the ESR signal arising from the color center could be quenched by the adsorption of $TiCl_4$. This result proves the importance of defects, in this

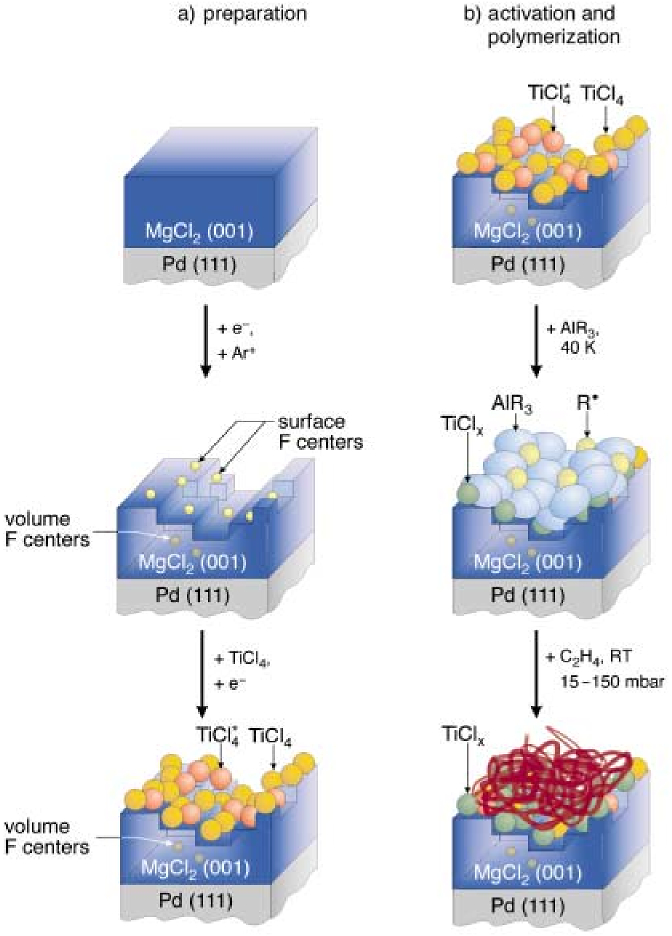

Figure 1. Preparation of the model catalyst. a) Top: preparation of a well-ordered defect-free $MgCl_2$ film. Center: defect creation by different techniques; color centers are symbolized by yellow spheres. Bottom: anchoring of $TiCl_4$; $TiCl_4^*$ (red) denotes $TiCl_4$ moieties adsorbed to color centers of the substrate. b) Top: see bottom of part a. Center: adsorption of AlR_3 on the surface at 40 K; alkyl radicals are symbolized by yellow spheres. Bottom: catalyst after polymerization of ethene. $TiCl_x$ (green) symbolizes reduced and perhaps active catalytic sites for polymerization.

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particular case color centers, for the adsorption of $TiCl_4$ on the surface. Since ESR is not an inherently surface-sensitive technique, the result suggests that only part of the color centers really reside at the surface of the $MgCl_2$ film.

There is evidence in the literature that Ti^{4+} ions are reduced to either Ti^{3+} or Ti^{2+} ions in the process of anchoring $TiCl_4$ to the $MgCl_2(001)$ surface. X-ray photoelectron spectroscopy indicates that besides Ti^{4+}, Ti^{2+} is formed exclusively in the model systems.[7, 14, 15] Our ESR results show that Ti^{3+} centers are formed by electron bombardment, but neither the presence nor the intensity of the Ti^{3+} signal could be correlated with the reactivity of the system towards ethene polymerization. Figure 1a summarizes the various steps described above.

We have activated the $TiCl_4/MgCl_2$ system with either TMA or TEA by gas-phase deposition of the components onto the surface at 40 K. The FT-IR spectra of the resulting adsorbate are typical for a condensed film or for matrix-isolated TMA and TEA species, including dimers.

Figure 2 shows ESR spectra after reaction of the TMA with the $TiCl_4/MgCl_2$ system. A typical low coverage of $TiCl_4$ leads to the spectra shown in the upper trace. Increasing the amount of $TiCl_4$ on the surface by a factor of three increases the intensity of the ESR spectrum by a factor of 1.7, as shown in spectrum b. This correlation between the amount of deposited titanium and the intensity of the ESR signal can be understood by means of an islandlike growth mode of the $TiCl_4$ on the surface. The spectrum is free of any signal arising from Ti^{3+} ions. This result is in accordance with the literature reports that mainly Ti^{2+} species are formed as a result of the reduction with alkyl aluminum compounds.[14, 15] Although it might be thought that methyl radicals are the most likely products in the reduction of a mixed titanium-methyl-chlorine species, a comparison of the spectrum of a methyl radical taken from the literature (see Figure 2d[16]) with the line shape of the observed spectra clearly reveals distinct differences, thus proving the species formed are not methyl radicals. Whereas the ESR spectrum of a methyl radical is a quartet of lines, the observed spectra show additional multiplet structures around the four dominating lines, which indicates there are further interactions of the unpaired electron relative to those for a methyl radical. By comparison of the line shape to the spectra obtained for other alkyl radicals the present spectrum can be attributed to ethyl radicals. Figure 2c shows for comparison the ESR spectrum of ethyl radicals generated in an ethyl chloride matrix by photolysis.[17] The line shape of the ESR spectrum of the ethyl radicals can be understood as follows: The unpaired electron on the methylene group couples through a superhyperfine interaction to the three protons of the methyl group, which are magnetically equivalent at this temperature as a result of a fast rotation along the C–C bond, and thus gives rise to a quartet of lines. The two protons of the methylene group, however, give rise to an anisotropic superhyperfine interaction as the adsorption of the molecule on the surface hinders the rotation of the molecule in the laboratory framework defined by the magnetic field. A good description of the observed line shape, as already shown by Shiga et al.,[16] can be obtained by assuming the anisotropic interaction to be axially symmetric.

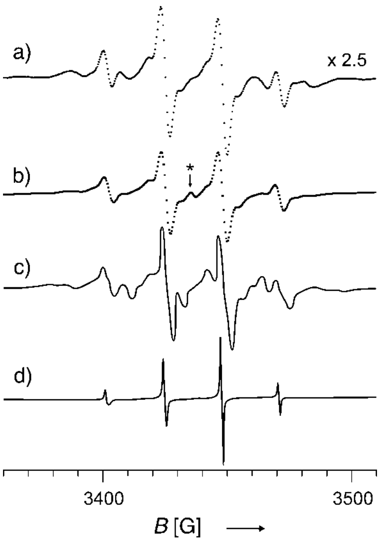

Figure 2. ESR spectra of alkyl radicals taken under various conditions: a) after $AlMe_3$ is adsorbed at 40 K on a model catalyst with a small Ti content; the spectrum is enlarged by a factor of 2.5 with respect to b); b) after $AlMe_3$ is adsorbed at 40 K on a model catalyst with three times the Ti content of a), the signal denoted with * is from a background signal; c) ethyl radicals in an ethyl chloride matrix at 77 K;[17] d) methyl radicals on a silica surface at 77 K.[16]

There are two key questions that have to be answered:

1. Have the radicals been created at the interface between TMA and $TiCl_4/MgCl_2$ or in the TMA activating materials?
2. How can it be rationalized that C_2H_5 and not CH_3 radicals have been created?

The first question can be answered by studying the amount of radicals formed as a function of the amount of $TiCl_4$ at the interface and also as a function of the TMA exposed to the surface. As stated above, the ESR intensity increases as a function of $TiCl_4$ at low concentrations of $TiCl_4$. Most importantly, no radical signal can be observed in the ESR spectrum in the absence of $TiCl_4$. Increasing the amount of TMA on the surface results in a saturation of the radical signal. Further evidence for a surface reaction is provided by the observation that the line width of the signal is larger when there is a large amount of titanium on the surface. If it is assumed that radical production occurs at the $TiCl_4/AlR_3$ interface, an increase in the number of radicals should also increase the concentration of the radicals close to the interface–these radicals can cause line broadening as a result of dipolar coupling. These observations are compatible with a radical-creation process happening at the interface between TMA and $TiCl_4/MgCl_2$, where an alkylation of the $TiCl_4$ by ligand exchange is supposed to happen. The homolytic bond cleavage that follows this ligand exchange will result in the primary generation of a methyl radical. The size and high mobility, even at low temperature, in the solid state means there are several possibilities for consecutive reactions of this radical.[18] The most likely reaction that yields ethyl radicals is given in Equation (2). Even though such a reaction has not been investigated so far, it can be crudely estimated that it should be possible from an energetic point of view. The intensity of the ESR signal of the ethyl radicals is attenuated irreversibly above 50 K and decreases below the detection limit above 80 K. This observation can be explained by assuming that the ethyl radicals diffuse and recombine at these temperatures, as has been observed for methyl radicals above 45 K[19] and NO_2 radicals on an oxide surface above 75 K.[20] After heating the surface to elevated temperatures at which TMA desorbs from the surface, carbon is found on the surface; this arises as a result of successful alkylation of the $TiCl_4$. It is, however, important to note that new C_2H_5 radicals can be created after removing the reacted $TiCl_x$ moieties from the surface, for example, by soft argon sputtering, and redosing with TMA.

$$CH_3^{\bullet} + Al(CH_3)_3 \rightarrow H_3C{-}CH_2^{\bullet} + AlH(CH_3)_2 \qquad (2)$$

An interesting observation is made if TEA is used instead of TMA. Even though the catalyst can be activated with TEA in a similar way as for TMA, ethyl radicals have never been observed. This is in line with a disproportionation reaction proposed in the literature [Eqs. (3) and (4)].

$$TiCl_4 + AlEt_3 \rightarrow TiCl_3Et + AlClEt_2 \qquad (3)$$

$$2\,TiCl_3Et \rightarrow 2\,TiCl_3 + C_2H_4 + C_2H_6 \qquad (4)$$

The observation of ethyl radicals in the preceding experiment suggests that these radicals are stable at 40 K, hence the formation of ethyl radicals would undoubtedly lead to an ESR signal. The absence of an ESR spectrum therefore strongly suggests a reaction route which does not involve radicals. This is in accordance with a disproportionation reaction proposed from indirect evidence.[9–12] The activation is summarized schematically in Figure 1 b. To the best of our knowledge this is the first clear experimental proof for the formation of free radicals in the activation process generated at the interface of a heterogeneous $TiCl_4/AlR_3$ system.

The model catalyst prepared in this manner does polymerize ethene with high efficiency. The kinetics of polyethylene film growth was followed by in situ FT-IR spectroscopy, and the results, which will be described in detail elsewhere,[8] are as follows: The polyethylene film created on the surface is partially crystalline with a chain length considerably larger than 20 units. The chains are in a *trans* configuration but do contain some *gauche* defects. The morphology of the $MgCl_2$ substrate has a strong influence on the growth kinetics of the polymer film: If the substrate is rough the polyethylene film grows in such a way that the ethene can access the reactive interface for comparitively long periods of time, which leads to thick, but rough polymer films. A smooth film, on the other hand, terminates the film thickness very quickly because the polyethylene spreads across the surface and blocks further ethene reaching the reactive interface from the gas phase.

In conclusion, we have prepared an active model Ziegler–Natta catalyst and were able to demonstrate, for the first time, the production of free radicals created at the catalyst interface by in situ ESR spectroscopy, while controlling the preparation of the catalyst by surface science techniques. The model catalyst polymerizes ethene and the morphology of the catalyst controls the reaction kinetics of the created *trans*-polyethylene film.

Experimental Section

The experiments have been performed in an ultrahigh vacuum (UHV, base pressure: 10^{-10} mbar) apparatus which is described in detail elsewhere.[8, 21] The apparatus combines ESR with FT-IR spectroscopy and other standard UHV characterization facilities. The Pd(111) single crystal serves as a substrate and is cleaned by sputter/anneal cycles. $MgCl_2$ was evaporated from a Knudsen cell in a preparation chamber integrated into the apparatus. During evaporation the Pd(111) single crystal was heated to 700 K and treated with $MgCl_2$ vapor for 30–60 min. The temperature of the Knudsen cell was typically 810 K. After this initial evaporation, the Pd(111) substrate was cooled to 610 K and then exposed to $MgCl_2$ vapor for several hours (typically 4–5 h). During this procedure we observed an increase in the background pressure up to 10^{-8} mbar as a result of hydrogen evanescence from the $MgCl_2$ used. The pressure was brought back to the base pressure range by prolonged pumping. Both sides of the Pd(111) crystal have been prepared in this way to increase the sensitivity of the ESR measurements.

For various steps in the preparation of the model catalyst the $MgCl_2$ films, whose order and composition was controlled by LEED and Auger spectroscopy, could be bombarded with electrons or ions.

The $TiCl_4$, alkyl aluminum compounds, as well as the ethene were dosed to the surface in the preparation chamber. Details of the preparation and characterization procedures will be published elsewhere.[8]

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