Activation of CO by surface carbide on Fe(110) *

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Surface carbide was found to be present along with surface oxide on Fe(110) by first oxidation at 573 K and subsequent treatment with CO at 673 K on the basis of EELS and Auger studies. Adsorption of CO on this surface carbide on Fe(110) at 135 K gives rise to an energy loss peak at 1560 cm^{-1} which does not appear on an oxidized surface of Fe(110) under identical conditions and is much different from that obtained on a clean Fe(110) surface at room temperature (1967 cm^{-1}). This activation of CO by a surface carbide on Fe(110) is believed to be relevant to the catalytic behavior of an iron catalyst in the Fischer–Tropsch synthesis.

Keywords: CO activation; surface carbide; iron catalyst

1. Introduction

Iron catalysts have been widely employed in the Fischer–Tropsch synthesis. It is generally agreed that iron carbides, both surface and bulk, are formed during the reaction and have an important effect on the catalytic behavior of the iron catalysts. However, the catalytic role of the iron carbide is still controversial and not well understood [1–3]. Bulk iron carbide has been shown to be relatively

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inactive in the hydrogenation of CO compared to the surface carbon [4,5], and most attention has been reasonably directed to the behavior of the surface carbon called appropriately the surface carbide [6].

Strong evidence has been presented that surface carbide is an active intermediate on the surface of iron [6] and nickel [7] catalyst in the Fischer–Tropsch synthesis. It has also been found that the surface of an iron catalyst at steady state during the Fischer–Tropsch synthesis is mostly covered by surface carbide [5]. It has further been suggested that direct hydrogenation of such surface carbide occurs on a relatively small number of special sites [4], and deactivation of the catalyst is due to the formation of inactive carbon on the surface blocking the active sites [8].

The chemical nature of the surface carbon on iron has been studied by surface science techniques and the inactive species of surface carbon was identified as the graphitic carbon [9,10]. But no adsorption of CO on a surface carbide of iron has been reported in the literature to our knowledge. This work was undertaken to study the adsorption behavior of CO on a single crystal of Fe(110) as the model iron catalyst on which surface carbide is present. It is hoped that some light may be shed on the possible role of surface carbide as the site of CO activation in addition to its role of an active intermediate in the Fischer–Tropsch synthesis.

2. Experimental

The experiment was performed in a stainless steel UHV system (Leybold-Heraeus) with a base pressure of 5×10^{-9} Pa and equipped with an ELS-22 high resolution electron energy loss spectrometer as well as a four grid LEED-Auger optics (Varian).

Before it was installed in the UHV system, the high purity Fe(110) sample was mechanically polished to an optical finish with 0.05 μm Al_2O_3 powder. A procedure described in the literature [11] was adopted to remove the various impurities present in the Fe(110) sample. The cleanliness of the sample surface was verified by the exhibition of a sharp p(1 × 1) LEED pattern, a clean energy loss spectrum and the Auger surface compositional analysis shown in fig. 1. Temperatures were measured with chromel–alumel thermocouple spotwelded to the side of the single crystal. The crystal temperature can be varied from 135 to 1000 K by liquid nitrogen cooling and resistive heating.

Throughout the experiments, CO and oxygen with a purity better than 99.98% were used. All experiments were carried out after the UHV system was baked at 473 K for 16 h. The LEED, AES, EELS and HREELS measurements for the clean and adsorbed surface were made in separate runs.

3. Results

3.1. THE OXIDATION OF THE Fe(110) SURFACE

The clean iron surface is characterized by three Auger peaks at 598, 651 and 707 eV as well as a low energy Auger peak at 47 eV respectively, as shown in fig. 1 in good agreement with the data given in the literature [12]. According to Leygraf and Ekelund [13], the low energy peak at 47 eV corresponds to a transition of $M_{II,III}M_{IV,V}M_{IV,V}$ and decreases its intensity with the adsorption of oxygen, then vanishes when the surface coverage of oxygen is roughly unity. As the 47 eV peak vanishes, two peaks at 44 and 52 eV appear and are related to the concentration of Fe^{2+} and Fe^{3+} respectively. On careful examination of the iron Auger spectrum, it may be seen that there is a small peak at 591 eV as shown in fig. 1 and ref. [12]. But such a peak cannot be observed for the case of α-Fe_2O_3 and Fe_3O_4 [14], so this peak originates solely from the Fe^0 species.

The Auger peaks in the two regions concerned, namely those around 47 and 598 eV respectively, for the Fe(110) sample before and after the adsorption of oxygen are shown in fig. 2. Before the adsorption of oxygen, the Auger peaks of a clean iron surface were observed as those in fig. 1 and are shown in fig. 2a. Upon an exposure to oxygen of about 300 L under a pressure of 5×10^{-6} Pa at 573 K, significant changes in the shape of the Auger peaks took place, as shown in fig. 2b. The 47 eV peak vanishes completely, and the characteristic doublet appears at 44 and 52 eV instead. Meanwhile the 591 eV peak due to Fe^0 also vanishes completely. This means the surface of the Fe(110) under examination is covered by a layer of iron oxide.

The composition of the Fe(110) surface upon exposure to oxygen of 300 L at 573 K was also examined by EELS. Lee and Montano [15] made a detailed

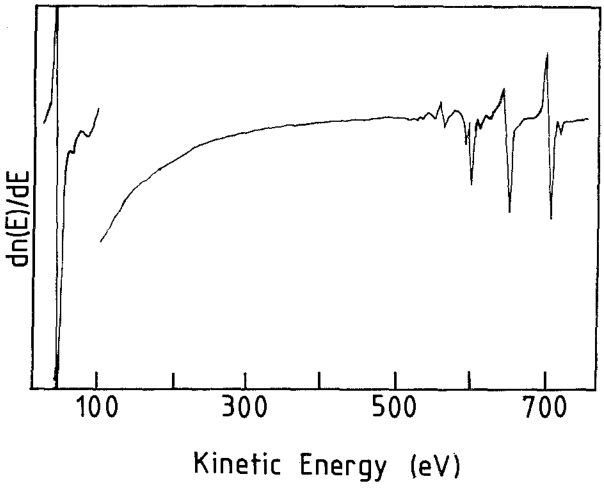

Fig. 1. Auger spectrum of the clean Fe(110) surface.

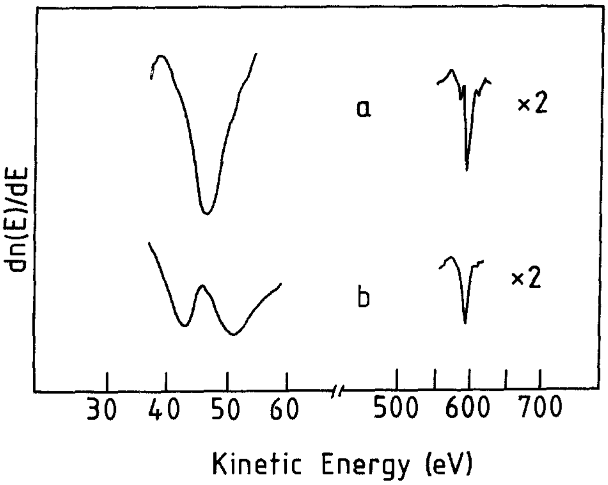

Fig. 2. Auger spectra for (a) clean Fe(110) surface, (b) oxidized surface of Fe(110).

EELS study of the chemisorption of oxygen on iron, iron oxide and iron carbide. With the primary electron energy of 150 eV, the energy loss peaks for α-Fe_2O_3 are found to be at 3.9, 6.8, 12.6, 19.7 and 23.0 eV respectively. While those for Fe_3O_4 are at 4.2, 6.8, 12.7, 19.5 and 23.4 eV respectively. The primary electron energy we used was also 150 eV, and we obtained peaks at 4.0, 6.7, 12.0, 16.8, 19.4 and 22.4 eV respectively as shown in fig. 3a. The formation of an oxide layer on the surface of the Fe(110) sample is thus indicated.

3.2. THE FORMATION OF IRON CARBIDE

To the oxidized surface of Fe(110), where oxides α-Fe_2O_3 and Fe_3O_4 are formed, CO at a temperature of 673 K was introduced through an iron capillary and the CO backfilling of the chamber was at a pressure of 1×10^{-4} Pa. The electron energy loss spectrum for the resulted Fe(110) is shown in fig. 3b. Energy loss peaks at 4.1, 5.0, 6.9, 8.0, 11.7, 12.8, 18.4, 20.2 and 23.0 eV respectively are obtained. While those peaks ascribed to the original oxide, e.g. 6.9 and 17.0 eV peaks due to the volume plasmon of the oxides diminished significantly, new peaks appear at 8.0 and 12.8 eV which are attributed to the interband transition of iron carbide [15]. It can thus be seen that on the oxidized surface of Fe(110), iron oxide and iron carbide coexist as the result of a reaction of the oxidized surface with CO at 673 K.

The results obtained from the Auger study of this oxidized surface of Fe(110) treated with CO are shown in fig. 4. In the low energy region, the peak at 47 eV is not observed. Instead, the 44 and 52 eV doublet takes its place, suggesting the presence of iron oxide. In the high energy region, the shape of the Auger

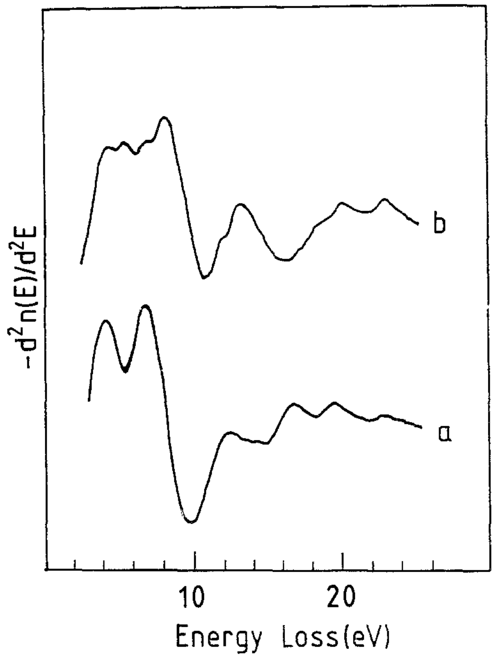

Fig. 3. EEL spectra for (a) oxidized surface of Fe(110), (b) oxidized surface of Fe(110) treated with CO at 673 K.

spectrum is not the same as that of pure carbon [12], but resembles that of a metal carbide [10,16]. Thus a surface on which iron oxide and iron carbide coexist is also suggested for this sample by the Auger study.

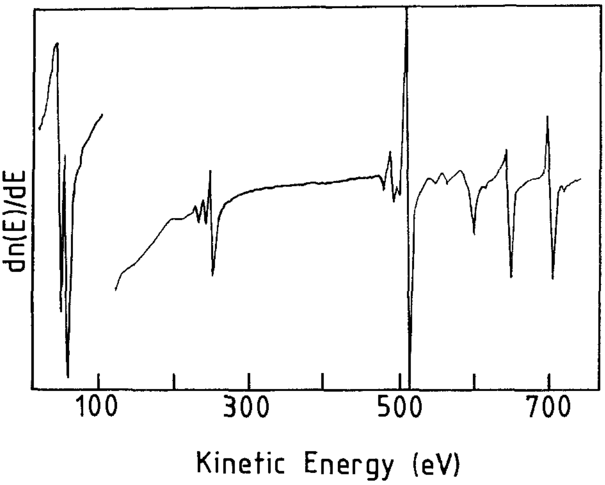

Fig. 4. Auger spectrum of the oxidized surface of Fe(110) treated with CO at 673 K.

3.3. THE CO CHEMISORPTION

In order to study the CO adsorption on the surface of Fe(110) on which iron oxide and iron carbide coexist, it is necessary to examine the CO adsorption on clean Fe(110) and its oxidized surface first. Many studies on the adsorption of CO on single crystals of iron including Fe(110) have been made. For instance, Erley [17] observed a shift of vibrational frequency of adsorbed CO on Fe(110) at 120 K from 1895 to 1985 cm^{-1} when the CO exposure was increased from 0.05 to 15 L. The HREELS spectra for the Fe(110) studied in this work are shown in fig. 5.

From the energy loss spectrum of fig. 5a it may be seen that the Fe(110) surface under investigation is clean as found by the Auger analysis presented earlier. It is seen that a single loss peak for the molecularly adsorbed CO was observed at 1967 cm^{-1}. In addition there are energy loss peaks at 363 and 476 cm^{-1} respectively, which may be attributed to the vibration of Fe–C and Fe–O respectively [17–19].

For the oxidized surface, loss peaks of 403, 660 and 903 cm^{-1} are observed (fig. 6). The peak at 406 cm^{-1} is attributed to the Fe–O bulk phonon vibration [19]. While the 660 cm^{-1} peak was assigned by Onari et al. [20] as the phonon vibrational peak of α-Fe_2O_3. The 910 cm^{-1} peak was suggested to correlate with the formation of iron oxide [19]. But no energy loss peaks of adsorbed CO in the expected range of 1200–2000 cm^{-1} were observed when this sample was exposed to 50 L of CO in the temperature range of 135 K to room temperature.

When the oxidized surface of Fe(110) was treated with CO at 673 K, and after the formation of a surface on which iron oxide and iron carbide coexist has been

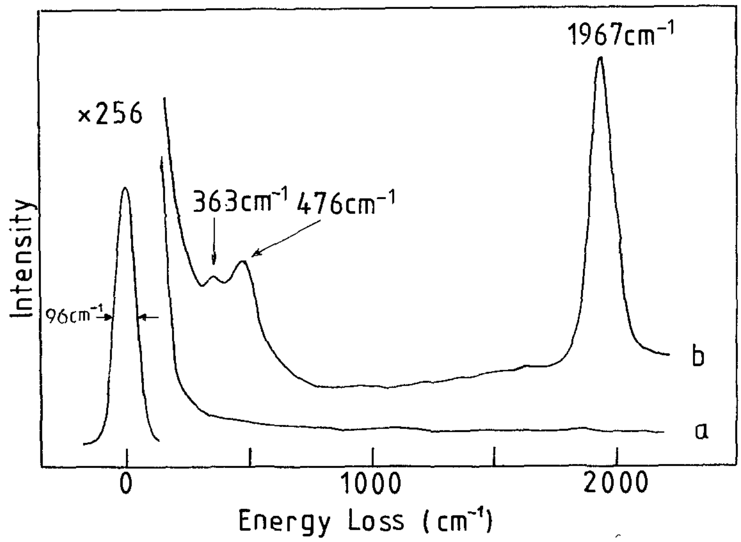

Fig. 5. HREEL spectra for (a) clean Fe(110), (b) Fe(110) after saturation exposure to CO at 300 K.

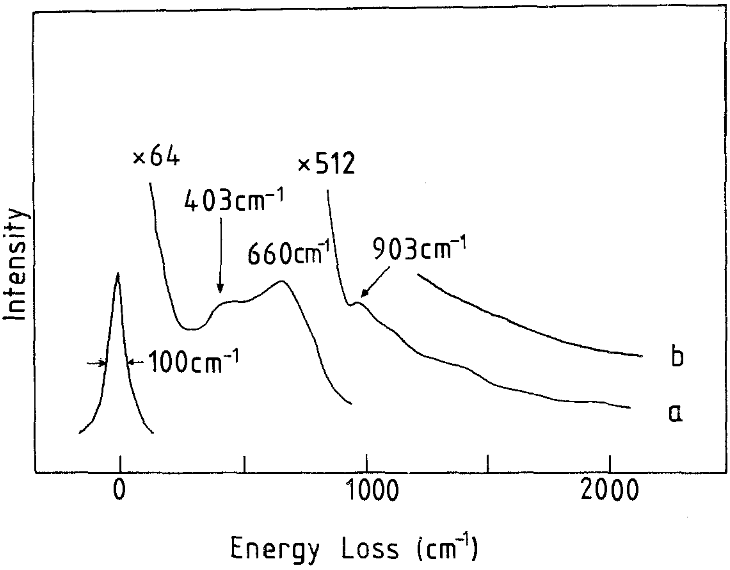

Fig. 6. HREEL spectra for (a) oxidized surface of Fe(110), (b) oxidized Fe(110) surface after saturation exposure to CO at temperatures from 135 K to room temperature.

established, this surface was again exposed to about 50 L of CO at 135 K. The resulted HREEL spectrum is shown in fig. 7. In addition to a combined peak of Fe–O and Fe–C phonon vibrations in the low wave number region as described earlier, there is a CO stretching frequency at 1560 cm^{-1}, which is significantly

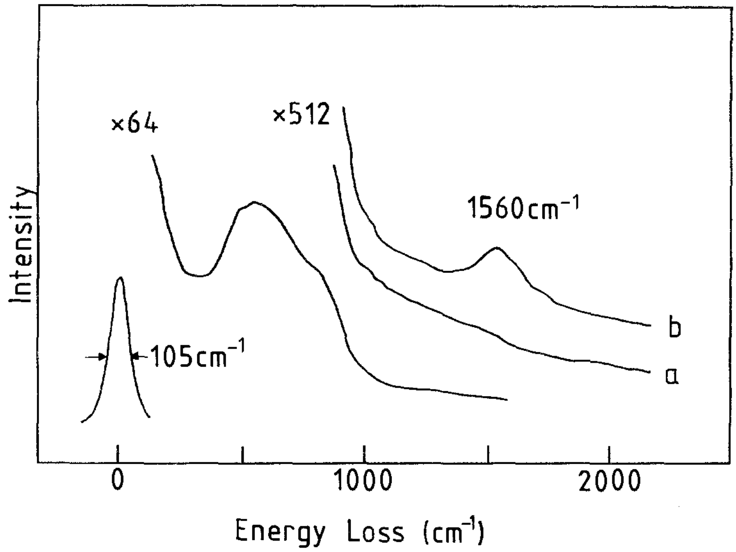

Fig. 7. HREEL spectra for (a) Fe(110) surface on which iron oxide and iron carbide coexist, (b) after saturation exposure to CO for the sample in (a) at 135 K.

lower than the 1967 cm^{-1} of the vibrational frequency of CO adsorbed on a clean Fe(110) at room temperature.

4. Discussion

The surface chemistry of the iron catalyst used in the Fischer–Tropsch synthesis has attracted the attention of many investigators. Particular attention has been paid to the carbon deposited on the iron surface in the form of a surface carbide as the result of dissociation of CO. Some workers have advanced the idea that surface carbide is the reaction intermediate in the hydrogenation of CO on nickel and iron catalysts [6,7]. Others have proposed the same idea by surface science studies [9,10], and surface carbide has been differentiated from the graphitic carbon on iron surface which is found to be inactive in the reaction. Still others, based on the kinetic measurements of the Fischer–Tropsch synthesis on iron catalyst, drew the conclusion that surface carbide is intimately involved in the reaction, and in effect it is implied that the surface carbide plays the role of an active site [4,5]. However, no direct experimental evidence of the activation of CO by surface carbide as an active site on an iron catalyst has been reported to our knowledge. This work is presented with the hope that some insight may be gained into this possible role of the surface carbide by studying a model iron catalyst of Fe(110).

An oxidized surface of Fe(110) was first produced. From fig. 2b, it is seen that the 47 eV peak in the low energy Auger spectrum characteristic of metallic iron vanishes with the appearance of a 44 and 52 eV doublet characteristic of iron oxide instead. Meanwhile, the 591 eV peak of the iron Auger spectrum also vanishes with the treatment of oxygen at 573 K. Thus we are dealing with an oxidized surface of Fe(110) covered by a layer of iron oxide exceeding the escape depth of the Auger electrons. On this oxidized surface, it is seen from fig. 6b that no adsorption of CO was detected by HREELS in the usual range of 1200–2000 cm^{-1}.

Upon treatment of this oxidized surface with CO at 673 K, a surface on which iron oxide and iron carbide coexist is produced as evidenced by fig. 3b. This is seen from the characteristic loss peaks of iron oxide at 4, 6.8 and 17 eV that still remain but are greatly reduced in intensity with the concomitant appearance of new loss peaks at 5.1, 8 and 12.8 eV characteristic of iron carbide, not the graphitic carbon [15]. This interpretation is further supported by the Auger spectrum shown in fig. 4. The shape of the carbon Auger spectrum around 250 eV is similar to that of the carbidic carbon on Ni [16] as well as the surface carbide on Fe(110) [10] reported in the literature. The simultaneous presence of an oxide is also obvious from the inspection of fig. 4.

It was on this Fe(110) surface composed of both iron oxide and iron carbide that a stretching frequency of 1560 cm^{-1} of the adsorbed CO at 135 K was found as shown in fig. 7. This frequency is distinctively different from the 1967 cm^{-1} of the CO adsorbed on a clean surface of Fe(110) at room temperature as shown in fig. 5. The latter is consistent with the adsorption of CO terminally bound to the metal surface [21]. As we have shown that iron oxide does not adsorb CO at temperatures from 135 K to room temperature, then the stretching frequency of the adsorbed CO observed on a Fe(110) surface on which iron oxide and iron carbide coexist can only come from the CO adsorbed on the surface carbide on Fe(110). And this frequency is significantly lower than that of CO adsorbed on clean Fe(110). Thus, CO is activated by the surface carbide of iron.

Two possible modes of the CO adsorbed on the surface carbide of iron are envisioned. One is the formation of a ketenylidene ligand of CCO like the one in the organometallic compounds $[M_3(CO)_9(\mu_3\text{-}CCO)]^{2-}$ (M = Fe, Ru, Os) as reported by Shriver and co-workers [22,23]. The other is the one proposed by Sachtler et al. [24] in which C and O of the adsorbed CO are both bonded to a promoter ion. The latter mode appears more probable, with the carbidic carbon replacing the promoter ion.

The surface carbide which is known to be invariably present on the iron Fischer–Tropsch catalysts thus may play a dual role in the synthesis. One is the well-known reaction intermediate to produce methane and perhaps higher hydrocarbons as well, the other is the active site for the activation of CO as revealed by the experimental result reported herein. This suggestion may be helpful in better understanding of some of the not well understood experimental findings in the literature such as why the initial rate of hydrogenation of CO is always slow and the activity curve lies above the extent of carbide formation of the iron catalyst during the early stage of the Fischer–Tropsch synthesis [4].

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References

[1] D.J. Dwyer and G.A. Somorjai, J. Catal. 52 (1978) 291.
[2] J.A. Amelse, J.B. Butt and L.H. Schwartz, J. Phys. Chem. 82 (1978) 558.
[3] G.B. Raupp and W.N. Delgass, J. Catal. 58 (1979) 348.
[4] G.B. Raupp and W.N. Delgass, J. Catal. 58 (1979) 361.
[5] H. Matsumoto and C.O. Bennett, J. Catal. 53 (1978) 331.
[6] M. Araki and V. Ponec, J. Catal. 44 (1976) 439.
[7] P. Biloen, J.N. Helle and W.M.H. Sachtler, J. Catal. 58 (1979) 74.

[8] J.W. Niemantsverdriet, A.M. van der Kraan, W.L. van Dijk and H.S. van der Baan, J. Phys. Chem. 84 (1980) 3363.
[9] H.J. Krebs, H.P. Bonzel and G. Gafner, Surf. Sci. 88 (1979) 269.
[10] H.P. Bonzel and H.J. Krebs, Surf. Sci. 91 (1980) 499.
[11] G. Brodén, G. Gafner and H.P. Bonzel, Appl. Phys. 13 (1977) 37.
[12] E.L. Davis, N.C. Donald, P.W. Palmberg, G.E. Riach and R.E. Weber, *Handbook of Auger Electron Spectroscopy*, 2nd Ed. (Physical Electronics, Eden Prairie, 1976).
[13] C. Leygraf and S. Ekelund, Surf. Sci. 40 (1973) 609.
[14] Y. Chen, Z. Lin, S. Wu, S. Qi and X. Wu, Acta Phys. Sin. 36 (1987) 1371.
[15] Y.C. Lee and P.A. Montano, Surf. Sci. 149 (1985) 471.
[16] J.P. Coad and J.C. Rivière, Surf. Sci. 25 (1971) 609.
[17] W. Erley, J. Vacuum Sci. Technol. 18 (1981) 472.
[18] H. Ibach and D.L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic Press, New York, 1982).
[19] W. Erley and H. Ibach, Solid State Commun. 37 (1981) 937.
[20] S. Onari, T. Arai and K. Kondo, Phys. Rev. B16 (1979) 1717.
[21] N. Sheppard and T.T. Nguyen, in: *Advances in Infrared and Raman Spectroscopy*, Vol. 5, eds. R.J.H. Clark and H.E. Hester (Heyden, London, 1978) p. 67.
[22] J.W. Kolis, E.M. Holt, M.A. Drezdzon, K.H. Whitmore and D.F. Shriver, J. Am. Chem. Soc. 104 (1982) 6134.
[23] M.J. Sailor and D.F. Shriver, Organometallics 4 (1985) 1476.
[24] W.M.H. Sachtler, D.F. Shriver, W.B. Hollenberg and A.F. Long, J. Catal. 92 (1985) 429.