Identification of Cr oxidation state active in ethylene polymerization on Cr/SiO_2 at room temperature

P.A. Zielinski [1], J.A. Szymura [2] and I.G. Dalla Lana

Department of Chemical Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6

Received 27 September 1991; accepted 24 February 1992

High temperature treatment under vacuum or in a pure N_2 atmosphere can be used instead of a reduction step to activate Cr/SiO_2 catalysts used for ethylene polymerization. After this procedure, the Cr species active over a range of temperature has been identified as Cr(III) using CO adsorption (IR triplet bands at 2228, 2214, and 2202 cm^{-1}) and an ethylene polymerization activation energy of 12.1 kcal/mol. The Cr(III) species has also been shown to be present after activation using CO reduction, the more commonly used procedure. Cr(II) sites are always present when activation involves reduction with CO and become increasingly active as the temperature rises above room temperature.

Keywords: Ethylene polymerization; silica-supported chromium catalyst; IR; CO adsorption; oxidation states of active Cr sites

1. Introduction

Silica-supported chromium used to catalyze the polymerization of ethylene (Phillips-type catalysts) is usually activated by high temperature oxidation followed by reduction using ethylene (industrial conditions) or CO (common laboratory procedure). The oxidation state of the resulting active Cr sites has remained contentious since the development of these catalysts in the early 1950's [1]. The dispute centers about the role of the Cr(II) and Cr(III) oxidation states on the catalyst surface. Rebenstorff [2,3] suggested that both of these oxidation states are involved as active polymerization sites. This view was corroborated by Lunsford et al. [4–6] in experiments using catalysts prepared from Cr(II) and Cr(III) salts. Nonetheless, despite extensive efforts, the activity of Cr(III) species at industrial polymerization conditions is not clear [7].

While examining this problem [8], a correlation between the adsorption of the probe molecule, CO, and catalyst activity at room temperature (RT) after

[1] Technical University of Lodz, Lodz, Poland.
[2] Technical and Agricultural University, Bydgoszcz, Poland.

different pretreatments was not evident. On the other hand, the beneficial role of high temperature (HT) treatment in activating such catalysts was noted. The HT treatment resulted in sufficiently active catalysts that a new method of activating Cr/SiO_2 was developed: one which eliminated the reduction step since HT treatment was sufficient [8,9]. The verification of the effectiveness of these HT-activated catalysts for ethylene polymerization and the determination of the nature of the active sites created were the objectives of the research reported herein.

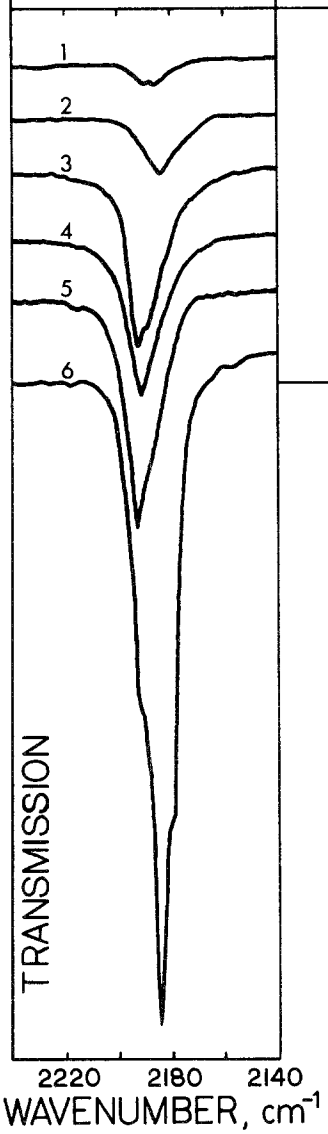
2. Experimental details

2.1. MATERIALS AND PROCEDURES

The supported 0.5 wt% Cr on silica catalyst was prepared by impregnating Cab-O-Sil support (Cabot Corporation, USA) with an aqueous solution of CrO_3 (Fisher Scientific, Certified A.C.S.), followed by drying at 105°C and calcination at 550°C for 16 h. To prepare catalysts for IR transmission measurements, the catalyst powder was compressed (280 MPa) into thin wafers (≈ 12 mg/cm^2). The IR studies employed a modified Kiselev-type IR transmission cell in which the activation procedures were also done. The new activation procedure (B) involves heating in dry oxygen at 800°C for 1 h followed by evacuation to nearly 10^{-5} Pa (UHV) for 16 h at the same temperature prior to being cooled to the desired polymerization temperature. In contrast, the customary laboratory procedure (A) required CO reduction at 350°C for 1 h after the oxidation. Additional modifications to activation procedures were tested as indicated in fig. 1.

To measure the initial activity for ethylene polymerization, the reaction was carried out in an IR cell ($p = 2$ kPa, C_2H_4) at temperatures from RT to 100°C for about 25 s under closed conditions. The course of the reaction was monitored by noting the changes in the ethylene pressure as a function of time. For better reproducibility, runs involving activation–polymerization cycles were repeated on the same catalyst wafer until the initial activity stabilized (usually within 3 to 5 cycles). Activation at the start and after each cycle required linear heating in oxygen (15 kPa) from the reaction temperature to 500°C over 0.5 h, evacuation at this temperature for 2 h, continued heating in oxygen linearly to 800°C and then at constant temperature for 0.5 h, and final evacuation at 800°C for 2 h. This procedure for "cleaning" the catalyst surface was followed by activation using either procedure A or B.

The IR spectra were recorded using either a Perkin-Elmer model 580B spectrophotometer or a Nicolet model 740 FTIR spectrometer. The P-E instrument was used for the earlier experiments in which the adsorption spectra of CO were compared to the initial catalytic activity after various pretreatments.



CO SPECTRUM (p= 1.33 kPa, RT)	ACTIVITY [gC2H4/min gCAT]	PRETREATMENT t[h], T[°C]		
		OXIDATION	REDUCTION	UHV
1	4.0	1, 750	-	3, 750
2	0.5	1, 750	0.2, 500, H_2	0.5, 500
3	9.5	1, 750	0.2, 500, H_2	11, 850
4	18.1	1, 750	1, 750, CO	10, 750
5	18.7	1, 750	-	20, 850
6	0.3	1, 750	2, 400, CO	0.3, 400

Fig. 1. Comparison of catalytic activity with catalyst activation treatment based upon IR spectra for CO adsorption.

The FTIR spectra were averaged over 1600 scans to obtain a smooth spectrum. Individual scans were recorded with 4 cm^{-1} resolution. The difference spectra shown in figs. 2 and 4 were obtained by subtracting the spectra for active catalyst before CO admission from the spectra taken after CO adsorption.

2.2. POLYMERIZATION IN A SLURRY MICROREACTOR

To increase the polymer yields (g polymer/g catalyst) from the small values obtained in the IR cell (< 1) to larger values (an attempt to approach the rather large values obtained industrially) and to check whether the new activation procedure B was effective at different process conditions a slurry microreactor was used [8]. Ethylene (near atm pressure) flowed continuously without recycle through 50 ml of liquid *n*-hexane in which about 0.5 g of catalyst was suspended. The microreactor was designed to enable the catalyst to be calcined and activated in place.

3. Results and discussion

The spectra of fig. 1 were taken in the hope that absorbances of adsorbed CO (at RT and low ethylene pressures) could be correlated with the initial activities of catalysts prepared using various activation procedures. These data were procured early in these investigations using the P-E 580B instrument and the final procedures, A and B, described above differ somewhat from those used to obtain the curves of fig. 1. Curves 1 to 6 in fig. 1 were measured sequentially on the same catalyst wafer but using different activation procedures. No correlation resulted between the extent of CO adsorption (band intensities) and the corresponding catalytic activities. Even small adsorption occurs with relatively high activity and the reverse is also observed. The HT-UHV treatment shows a beneficial effect on activity (cf. curves 1 and 5).

The interaction of CO with activated catalyst at RT has been used to characterize the oxidation states of surface Cr sites. Fig. 2 shows the absorption spectra recorded using the FTIR spectrometer when CO (1.3 kPa) adsorbed on catalysts activated by procedures A and B. Three relatively weak bands at 2228, 2214, and 2202 cm^{-1} are distinguishable on catalyst activated using procedure B. Rebenstorf [10] has associated the 2200 cm^{-1} band with Cr(III) sites based on studies of CO adsorption on Cr(III)/silica catalyst at $-145°C$. Closer examination of his spectra reveals a small shoulder around 2214 cm^{-1}. On the basis of these two bands, it seems evident that Cr(III) must be present in catalyst B (activated by HT-UHV treatment). The weakest 2228 cm^{-1} band may also relate to Cr(III). Furthermore, the absence of the large band between 2200 and 2170 cm^{-1}, indicative of Cr(II) [11], suggests that only Cr(III) is present and therefore responsible for the activity of catalyst B.

According to Ghiotti et al. [11], activation by procedure A should produce about 98% Cr(II) sites with the balance attributed to inactive Cr_2O_3. However, spectrum A of fig. 2 clearly shows the presence of two of the three bands comprising the triplet associated with the Cr(III) species. The large broad band between 2200 and 2170 cm^{-1} of spectrum A represents a combination of at least

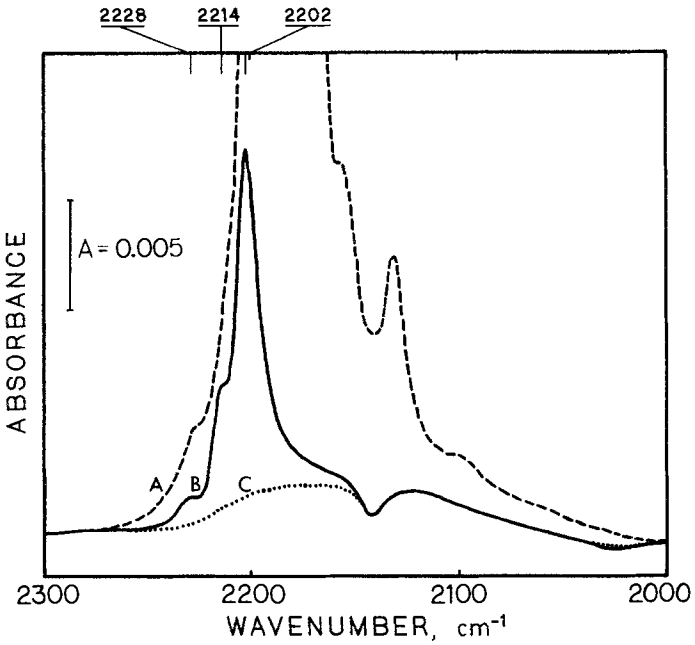


Fig. 2. FTIR spectra of CO (1.33 kPa) adsorbed on catalyst wafer activated via procedure A or B. Curve C represents background CO spectrum of IR cell (with or without oxidized wafer).

three forms of Cr(II) sites [11]. Relative to spectrum B, the Cr(III) bands of spectrum A have shifted 3.5 cm^{-1}, towards lower wave numbers. This shift may be the result of the changing degree of interaction between CO and the various oxidation states of Cr atoms, (II), (III) and (IV), available on the surface and whose distribution on the surface changes with extent of their reduction. The coexistence of the Cr(II) and Cr(III) surface species after CO reduction at 350°C has been suggested by Myers and Lunsford [4], based on activation energy measurements.

Fig. 3 presents the second derivatives of the spectral curves (fig. 2) for catalysts A and B. This plot provides a more sensitive indicator of the presence and position of the various absorption bands. For reference, the original spectral curve of B is also shown. Both 2228 (weak) and 2214 cm^{-1} bands are apparent on both catalysts but the 2202 cm^{-1} band of catalyst A is concealed by the broad dominant Cr(II) band. The manipulation of the data of fig. 2 to enable plotting the second derivatives resulted in a somewhat larger shift in the 2202 cm^{-1} band, as seen in fig. 3. This is likely error associated with the large overlap from the 2200 to 2170 cm^{-1} band. A comparison between the integrated absorbances of the 2228 cm^{-1} band on curves A and B of fig. 2 showed these to be nearly equal and between the near-identical shapes of curves A″ and B″ in this region of fig. 3 suggest that both procedures A and B have yielded comparable quantities of Cr(III) species. Additionally, the catalytic activities for ethylene

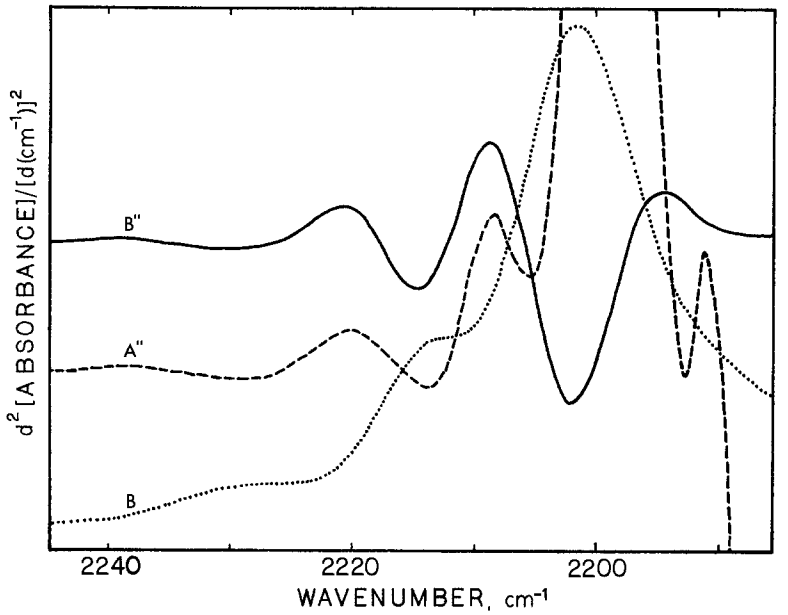


Fig. 3. Second derivatives, A″ and B″, of CO spectra presented in fig. 2. Curve A″ has been shifted to the left by 3.5 cm^{-1} to improve comparison. Spectrum B from fig. 2 is also shown for reference purpose.

polymerization using catalysts A and B (at RT) were nearly identical, 10.0 and 10.7, respectively. From this evidence, one may surmise that Cr(III) sites present in both catalysts A and B are active in ethylene polymerization but only Cr(III) sites are present on the catalyst activated using HT-UHV treatment. At room temperature, only the Cr(III) sites appear to be active.

Fig. 4 shows an attempt to track the changes in populations of Cr(II) and Cr(III) being formed during prolonged reduction at low CO pressure and room temperature (RT). Curve I shows that freshly activated catalyst B has (III) sites and (VI) sites are also present implicitly, but curve V shows that the catalyst has become depleted of (II) and (III) sites after 20 h even though Cr(II) sites were initially being formed! Presumably, the involved (II) and (III) sites have somehow been oxidized completely to non-adsorbing Cr(VI) sites. During this process, those Cr(III) sites which are initially present and which adsorb CO at RT seem to be less easily reduced than the non-adsorbing Cr(VI) sites. The explanation for the deactivation process must lie in the residual amounts within or very slow leak-rates into the IR cell of impurity gases, e.g., oxygen (air) which preferentially oxidizes the reduced Cr sites and water vapor which is known to deactivate such catalysts. These minute amounts of such gases, being almost immeasureable in the IR cell and yet exhibiting deactivating influence, suggest that the populations of Cr(II) and Cr(III) sites comprise a very small fraction of the total Cr atoms present on the silica support. The easier formation and lower

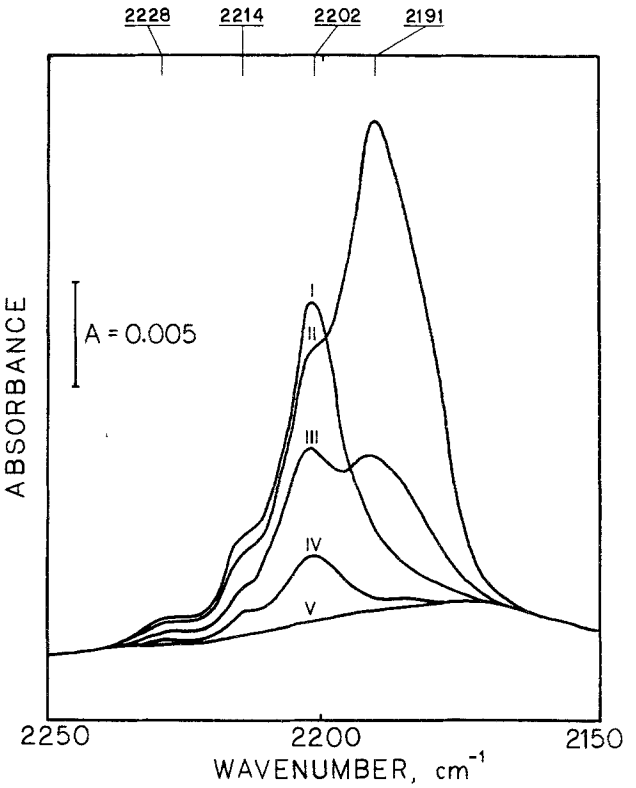


Fig. 4. Changes in FTIR spectra of CO (1.33 kPa) adsorbed on catalyst wafer (activated according to procedure B) as a function of time. Curves I–V denote contact times of 0, 4, 8, 12 and 20 h, respectively.

reducibility (greater resistance) of Cr(III) may account for its presence in small quantities observed after activation by procedure A. These observations suggest that extreme care is necessary to eliminate undesireable gases from contact with these catalysts, especially when conducting experiments of many hours duration.

Additional kinetics evidence indicative of the type of Cr oxidation states present after activation procedure B was obtained. Activation energies of 11 kcal/mol for Cr(III) species [6] and 18 kcal/mol for Cr(II) species [5] have been reported. The initial rates of polymerization of ethylene were measured over the range, RT to 100°C, and fitted to a first order rate function. Fig. 5 shows an Arrhenius plot of the resulting rate constants versus temperature. The linear portion of the plot gives an activation energy of 12.1 ± 0.5 kcal/mol, confirming that Cr(III) species are present. The upper limit of 60°C to the linear Arrhenius plot also conforms to that reported [4,5] for Cr(III) species. In contrast, an upper limit of 75°C has been reported for Cr(II) species [5].

The effectiveness of this new activation procedure was tested by larger-scale polymerization in the slurry microreactor at RT. The HT-UHV treatment was

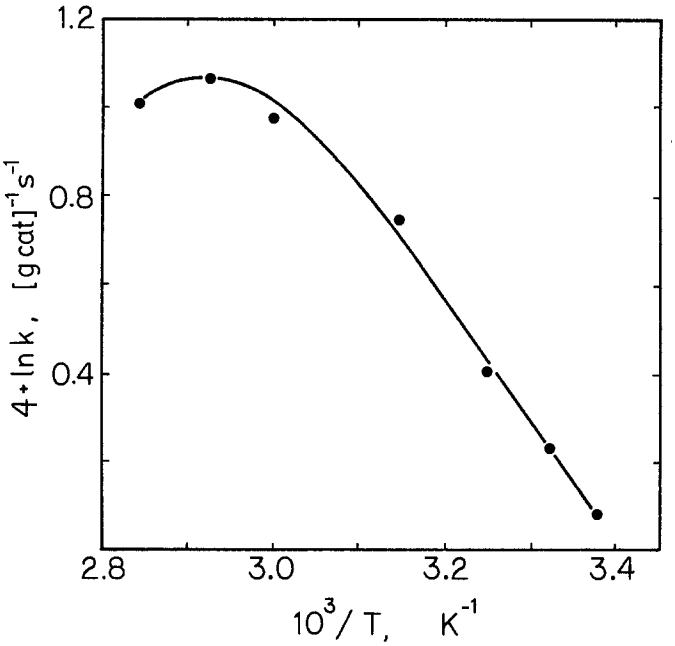


Fig. 5. Arrhenius plot of first order kinetics rate constant, obtained from reaction rates measured 5 s after ethylene admission to IR cell.

replaced by continuous purging with high purity N_2 during the HT heating. Subsequent polymerization resulted in yields of up to 3 g polymer/g catalyst being easily obtained. Because both the IR cell and the slurry microreactor, two quite different reactors, formed polymer with this catalyst B, HT activation in the absence of oxygen must be the real cause of the Cr(VI) to Cr(III) transformation. Other factors such as the presence of traces of impurities (such as organic vapors in the UHV system) are not involved.

4. Conclusions

Prolonged heating of oxidized Cr/Silica catalysts under high vacuum (or impurity-free N_2) converts a small portion of the Cr(VI) surface species into Cr(III), which appears to be the Cr component active in catalyzing the polymerization of ethylene at room temperature.

The Cr(III) active species was characterized by adsorption of CO (triplet IR bands at 2228, 2214, and 2202 cm^{-1}) and by measurement of the activation energy (12.1 kcal/mol). Only the Cr(III) species could be observed on the catalyst B, activated by HT-UHV treatment, whereas both Cr(II) and Cr(III) appear on catalyst A, activated by CO reduction. Catalyst B contains large amounts of inactive Cr, presumably Cr(VI), and much smaller amounts of

reduced Cr species. Exposure of this catalyst to CO at RT results in the reduction of some of this Cr(VI) to Cr(II), Cr(III) being more resistant to such reduction. Because of its higher activation energy, Cr(II), relatively inactive at room temperature, becomes increasingly active with increasing temperature accounting for the activity of catalyst A.

The commonly used procedure of activating by reduction with CO results mainly in the conversion of Cr(VI) to Cr(II), inactive for ethylene polymerization at RT. However, a small amount of Cr(III), comparable to that observed on catalyst B, we also found. This suggests that certain support sites favor stabilization of the surface Cr(III) species.

Acknowledgement

Financial support for this work from NOVACOR Ltd. and from the Natural Science and Engineering Research Council of Canada is gratefully acknowledged.

References

[1] M.P. McDaniel, *The State of Cr on the Phillips Polymerization Catalyst*, 11th Midland Macromolecular Meeting, August 17–21, 1981, Midland, MI, USA.
[2] B. Rebenstorf and R. Larsson, J. Catal. 84 (1983) 240.
[3] B. Rebenstorf, Z. anorg. allg. Chem. 513 (1984) 103.
[4] D.L. Myers and J.H. Lunsford, J. Catal. 92 (1985) 260.
[5] D.L. Myers and J.H. Lunsford, J. Catal. 99 (1986) 140.
[6] J.H. Lunsford, S.-L. Fu and D.L. Myers, J. Catal. 111 (1988) 231.
[7] M.P. McDaniel, Adv. Catal. 33 (1985) 47.
[8] P. Zielinski, J. Szymura and I.G. Dalla Lana, *An Alternative Means for the Activation of Cr/SiO_2 Polyethylene Polymerization Catalyst*, The 65th Annual Colloid and Surface Science Symposium, Norman, Oklahoma, June 17–19, 1991.
[9] W.K. Jozwiak and I.G. Dalla Lana, submitted for publication.
[10] B. Rebenstorf, Z. anorg. allg. Chem. 571 (1989) 148.
[11] G. Ghiotti, E. Garrone and A. Zecchina, J. Mol. Catal. 46 (1988) 61.