

## Polymerization of Ethylene by Chromium Surface Compounds on Silica Gel<sup>1</sup>

In 1968 Krauss and Stach (1-3) stated that a coordinatively unsaturated chromium(II) surface compound is the active center of ethylene polymerization by the Phillips catalyst. They based this statement on evidence from determination of oxidation numbers and from the high polymerization activity even at room temperature of CO-reduced Phillips catalysts. In the last decade this surface complex has been investigated thoroughly by Krauss and co-workers (4-9) and others (10-14). Additional and more direct evidence for the above statement has, however, not emerged.

On the contrary, in 1975 Przhevalskaya, Shvets, and Kazansky (15) were able to show that also chromium(III) on silica gel could be an active polymerization center. Recently Naumann (16) proved convincingly that a coordinatively unsaturated chromium(III) surface complex on silica gel could be prepared which had as high a polymerization activity as that of chromium(II) samples. He oxidized chromium(II) on silica gel with H<sub>2</sub>O/O<sub>2</sub> and heated the samples to 800°C in an argon stream. Polymerization activity was measured by him thermometrically on 2 g samples with 0.3 to 1.1% chromium content. More recently Beck and Lunsford (17) showed that among samples prepared at low temperature (350 to 400°C) and with relatively low chromium concentration (0.4%) it was only a chromium(III) species that was active.

There are, however, several arguments that do not support the idea that the chromium(III) species of Beck and Lunsford

(17) can be the active center of the Phillips catalyst. The polymerization activity (0.56 g C<sub>2</sub>H<sub>4</sub>/mmol chromium (h<sup>-1</sup>, atm<sup>-1</sup>)) and the turnover number (0.03 C<sub>2</sub>H<sub>4</sub>/active site sec) are a thousand times lower than measured for the Phillips catalyst by Yermakov (18) (500 and 40, respectively). In addition the activation temperatures were rather low; the best catalysts are obtained using temperature pretreatment around 800°C (19).

We have recently shown that the chromium(II) surface compound contains a dinuclear surface complex and we have proposed the same for the chromium(III) surface compound (22, 23). We report here the results of polymerization activity measurements with these surface compounds using the same simple polymerization method (recording the pressure decrease of ethylene) as reported by Beck and Lunsford (17).

We used two catalysts with different chromium concentrations (0.247 and 0.089% after drying at 120°C), which were analyzed as described by Hierl and Krauss (20) by colorimetric determination of CrO<sub>4</sub><sup>2-</sup> after heating the sample with Na<sub>2</sub>CO<sub>3</sub> to 900°C. The silica gel ("Merck 7733") was impregnated with a CrO<sub>3</sub>/water solution and, after drying, was diluted with unimpregnated silica gel. This mixture was spread out in the polymerization reactor (an ordinary quartz tube) so that the thickness of the catalyst layer was less than 2 mm in order to diminish the heating due to polymerization. In spite of these precautions the catalyst temperature increased during polymerization due to the rapid reaction with ethylene caused by our highly active surface species. However, this temperature

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increase, directly related to the polymerization activity, did not destroy the difference between chromium(II) and chromium(III) catalysts during the polymerization (see below) and was therefore neglected. Contrary to Naumann's preparation of the chromium(III) catalyst we used vacuum heat treatment at 800°C.

As can be seen from Table 1 the best catalysts reached polymerization activities of 1000 g C<sub>2</sub>H<sub>4</sub>/mmol chromium (h<sup>-1</sup>, atm<sup>-1</sup>), which is in agreement with activity measurements for the Phillips catalyst (18). Although the high activity is shown by both chromium(II) and chromium(III), there is a clear difference between these two catalysts: the chromium(II) surface compound has a hundred times lower activity at room temperature. Using different amounts of catalyst or changing the chromium concentration did not destroy this difference (Table 1) and had only a minor influence on the magnitude of this effect.

Using samples with similar preparation conditions as used by Beck and Lunsford (17) our activity values are three times higher than theirs at room temperature, but

much lower at 100°C than those for the chromium(II) and chromium(III) high activity catalysts. As shown in Table 1 samples with a temperature pretreatment at 500°C had a similarly low activity to those investigated by Beck and Lunsford.

Our observations are clarified by Figs. 1 and 2. Figure 1 shows polymerization activity versus time curves for chromium(II) and chromium(III) catalysts (0.5 g, 0.247% Cr). Even though the initial temperature for the chromium(II) catalyst (curve 2) was 100°C the polymerization activity reached its maximum later than for the chromium(III) sample (curve 1), which had an initial temperature of 20°C. Curve 3 shows that, after the polymerization at 100°C on a chromium(II) catalyst has been interrupted after 30 s by evacuation of the ethylene, it will start again at room temperature after admission of ethylene (500 Torr). The activity curve reached the maximum as fast as for the chromium(III) sample.

Figure 2 shows polymerization activity curves of catalysts with lower chromium concentration (1 g, 0.089% Cr). It now takes longer to reach the maximum poly-

TABLE 1

Maximum Ethylene Polymerization Activity of Chromium(II) and Chromium(III) Surface Compounds (g C<sub>2</sub>H<sub>4</sub>/mmol Chromium (h<sup>-1</sup>, atm<sup>-1</sup>))

Catalyst pretreatment	Amount of catalyst		
	1 g 0.247% Cr 4 g Silica gel	0.5 g 0.247% Cr 4.5 g Silica gel	1 g 0.089% Cr 4 g Silica gel
850°C/Vac/15 min	10 (20°C, 12)	10 (20°C, 26)	
800°C/O <sub>2</sub> /15 min		130 (80°C, 200)	
380°C/CO/10 min	970 (100°C, 408)	590 (100°C, 320)	1060 (100°C, 920)
Chromium(II)		1450 (120°C, 360)	
As chromium(II) + 20°C/H <sub>2</sub> O/O <sub>2</sub>	1110 (20°C, 240)	980 (20°C, 200)	570 (20°C, 580)
800°C/Vac/15 min		900 (100°C, 260)	
Chromium(III)			
500°C/O <sub>2</sub> /15 min		2 (20°C, 8)	
500°C/CO/15 min		8 (100°C, 30)	
350°C/Vac/60 min		2 (20°C, 8)	(Ref. (17): 0.56 (20°C),
400°C/CO/10 min		5 (100°C, 30)	(0.3 g 0.42% Cr)

Note. Initial ethylene pressure: 500 Torr. In brackets: initial temperature and polymerized ethylene (mol) per chromium (mol) after 10 min.

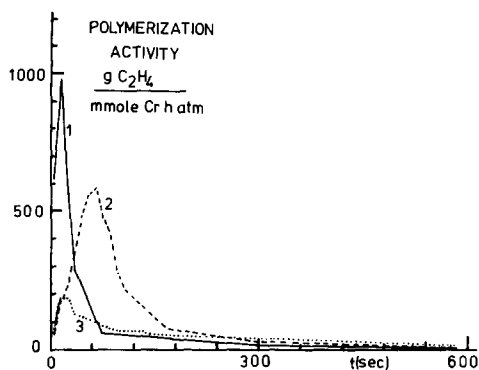


FIG. 1. Polymerization activity versus time for catalysts with chromium concentration of 0.247% (0.5 g). Curve 1 is a chromium(III) and curve 2 a chromium(II) catalyst at room temperature/100°C, respectively. Curve 3 shows the polymerization activity of an interrupted chromium(II) polymerization after readmission of ethylene (see text).

merization activity and the catalyst is active for a longer period of time. The latter effect may be explained by the possibility that with lower chromium concentration every polymerization site has a larger volume to fill with polymer. The overall amount of polyethylene produced is possibly limited by the pore volume of the silica gel. As can be seen from Table 1, the amount of ethylene polymerized per mole chromium after 10 min is increasing by

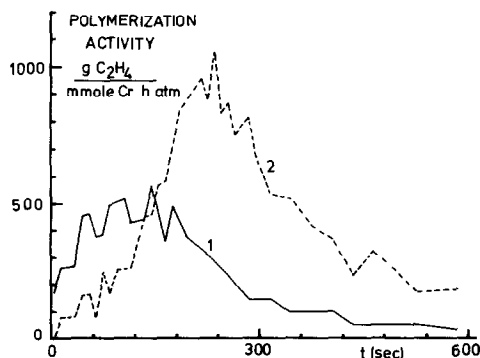


FIG. 2. Polymerization activity versus time for catalysts with low chromium concentration of 0.089% (1 g). Curve 1 shows again the chromium(III) and curve 2 the chromium(II) catalyst at room temperature/100°C, respectively.

nearly the same factor as that by which the chromium concentration is decreased. That chromium(III) catalysts polymerize less ethylene (after 10 min at 100°C, Table 1) and that the polymerization activity maximum is reached faster for these catalysts than for the chromium(II) ones is taken as evidence that the chromium(III) catalyst has generally fewer active sites than the chromium(II) one.

The above observations prove that both chromium(II) and chromium(III) dinuclear surface complexes (22, 23) are highly active polymerization centers and might be considered as catalytic centers of the Phillips catalyst. If ethylene itself is used as the reduction agent (instead of CO) one can only obtain an active catalyst if the reduction temperature is lower than 300°C. At higher temperatures the ethylene is totally oxidized (to CO<sub>2</sub> and H<sub>2</sub>O) and produces possibly a surface compound similar to that investigated by Beck and Lunsford (activity at 20°C: 15, at 100°C: 30 g C<sub>2</sub>H<sub>4</sub>/mmol Cr (h<sup>-1</sup>, atm<sup>-1</sup>)).

At lower temperatures than 300°C, ethylene is most probably converted to formaldehyde, a reaction that was first described by Baker and Carrick (21). Such a reaction would be similar to the reduction with CO (oxidized to CO<sub>2</sub>) and should therefore involve a similar surface complex, i.e., the chromium(II) dinuclear surface complex.

Naumann's observation that chromium(II) and chromium(III) surface compounds have similar polymerization activities (16) has, however, to be explained. The samples used in that case had a chromium content of 0.3 to 1.1% and 2 g of catalyst were used. It is known (4) that all chromium(II) samples contain some 2 to 10% chromium(III). This chromium(III) can start polymerization at 20°C (see above) and the polymerization heat of this reaction may produce an avalanche effect that raises the temperature high enough for the chromium(II) catalyst to polymerize with high activity. In low concentration samples (and diluted ones) the polymerization heat pro-

duced is not sufficient for this avalanche effect. In the case of samples pretreated at only 500°C two additional oxygen ligands (from surface silanol groups coordinated to chromium(II) (9)) have to be pushed away. The energy required for this process results in a much lower temperature increase during the polymerization on such catalysts (16).

## REFERENCES

1. Krauss, H. L., and Stach, H., *Inorg. Nucl. Chem. Lett.* **4**, 393 (1968).
2. Krauss, H. L., and Stach, H., *Z. Anorg. Allg. Chem.* **366**, 34 (1969).
3. Krauss, H. L., and Stach, H., *Z. Anorg. Allg. Chem.* **366**, 280 (1969).
4. Krauss, H. L., Rebenstorf, B., and Westphal, U., *Z. Anorg. Allg. Chem.* **414**, 97 (1975).
5. Krauss, H. L., and Hierl, G., *React. Kinet. Catal. Lett.* **2**, 47 (1975).
6. Krauss, H. L., and Naumann, D., *Z. Anorg. Allg. Chem.* **430**, 23 (1977).
7. Krauss, H. L., and Westphal, U., *Z. Naturforsch.* **33b**, 1278 (1978).
8. Krauss, H. L., and Hums, E., *Z. Naturforsch.* **34b**, 1628 (1979).
9. Krauss, H. L., and Naumann, D., *Z. Anorg. Allg. Chem.* **446**, 23 (1978).
10. Zecchina, A., Garrone, E., Ghiotti, G., Morterra, C., and Borello, E., *J. Phys. Chem.* **79**, 966 (1975).
11. Zecchina, A., Garrone, E., Ghiotti, G., and Coluccia, S., *J. Phys. Chem.* **79**, 972 (1975).
12. Zecchina, A., Garrone, E., Morterra, C., and Coluccia, S., *J. Phys. Chem.* **79**, 978 (1975).
13. Garrone, E., Ghiotti, G., Coluccia, S., and Zecchina, A., *J. Phys. Chem.* **79**, 984 (1975).
14. Ghiotti, G., Garrone, E., Coluccia, S., Morterra, C., and Zecchina, A., *J. C. S. Chem. Commun.* (1979), 1032.
15. Przhevalskaya, L. K., Shvets, V. A., and Kazansky, V. B., *J. Catal.* **39**, 383 (1975).
16. Naumann, D., thesis, Freie Universität Berlin, West Berlin, 1979.
17. Beck, D. D., and Lunsford, J. H., *J. Catal.* **68**, 121 (1981).
18. Zakharov, V. A., and Yermakov, Yu. I., *Catal. Rev.-Sci. Eng.* **19**, 67 (1979).
19. Hogan, J. P., *J. Poly. Sci.* **8**, 2637 (1970).
20. Hierl, G., and Krauss, H. L., *Z. Anorg. Allg. Chem.* **401**, 263 (1973).
21. Baker, L. M., and Carrick, W. L., *J. Org. Chem.* **33**, 616 (1968).
22. Rebenstorf, B., and Larsson, R., *J. Mol. Catal.* **11**, 247 (1981).
23. Rebenstorf, B., and Larsson, R., *Z. Anorg. Allg. Chem.* **478**, 119 (1981).

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