

## Role of Silanol Groups in Formation of Supported Chromocene Catalysts

FREDERICK J. KAROL, CHISUNG WU, WALTER T. REICHLER,  
AND NORMA J. MARASCHIN

*Union Carbide Corporation, Research and Development Department, Chemicals and Plastics,  
Bound Brook, New Jersey 08805*

Received November 9, 1978; revised April 13, 1979

Deposition studies have established maximum values for the adsorption of chromocene on dehydroxylated silicas. The process of chemisorption of chromocene changes from reaction of predominantly two to one hydroxyl group as the temperature of silica increases from 100 to 800°C. Chromocene, deposited on Cab-O-Sil type silicas heated at 200 and 400°C, formed highly active catalysts for ethylene polymerization. Results from studies with this support are compatible with an active site model which involves reaction of chromocene with free, isolated silanol groups. Sterically hindered hydroxylic compounds such as triphenylsilanol and *t*-butanol react in solution with chromocene to form dimeric cyclopentadienyl chromium alkoxides. These chromium compounds do not show catalytic activity for ethylene polymerization under conditions typical for the  $(C_5H_5)_2Cr/SiO_2$  catalyst. Furthermore, deposition of these new chromium compounds on silica did not provide, in most cases, a route to catalytic activity. However, the addition of alkylsilanes to these supported chromium compounds did lead to active catalysts. The polymerization behavior of these catalysts resembles the supported chromocene catalyst. These overall results lend support to an active site model previously described.

### INTRODUCTION

In previous papers (1-4) we described the scope of ethylene polymerization with a supported chromocene catalyst and we determined some kinetic parameters for the polymerization process. Our studies also illustrated the effects of thermal aging of a chromocene catalyst and the influence of certain  $\pi$ -bonded ligands to chromocene on catalysis for ethylene polymerization. The present paper describes studies carried out with supported chromocene catalysts in an attempt to establish the role of silanol groups in the formation of active sites. We also describe studies which attempt to model, in solution, the formation of active chromocene sites.

### EXPERIMENTAL

#### *Materials*

The sensitivity of the chromocene catalyst to trace impurities such as oxygen and water requires high-purity raw materials and meticulous care in catalyst handling. All gases and solvents used for polymerization were dried using activated molecular sieves (Linde 5A) prior to use. Ethylene (99.8%) and *n*-hexane (85 vol% minimum) were obtained from Phillips. Hydrogen and nitrogen of a high-purity grade were obtained from Linde. Grade 56 and 952 silicas were purchased from Davison Chemical Company (Division of W. R. Grace and Co.). Cab-O-Sil silicas were purchased from Cabot Corporation.

Chromocene was conveniently prepared by the method previously described (1a). Purified chromocene was produced by removal of volatiles from toluene solutions, followed by one or two sublimations. This procedure provided dark red crystals, mp 172 to 173°C, lit. (5) mp 173°C. For ease in handling, solutions of chromocene in *n*-hexane, *n*-decane, and toluene were prepared. Aliquots for polymerization or catalyst study were conveniently removed by syringe.

Silicas were dried by fluidization in a stream of dry nitrogen for 18 h at various temperatures (1a). These silicas were transferred to 8-oz serum-capped bottles and stored in 1-qt jars maintained under a nitrogen atmosphere.

Supported chromocene catalysts for ethylene polymerization were prepared by depositing chromocene from *n*-hexane solution onto dehydroxylated silicas.

#### *Studies of Maximum Chromocene Adsorption on Silica*

Maximum adsorption of chromocene on silica was determined by slurring Grade 56 silica for 24 h with an excess of chromocene dissolved in decane or toluene. The silica, prior to adsorption studies, was heated at temperatures in the range of 100–800°C. The concentration of silica was 10 to 48 ml of solvent for 1 g of silica. The contents were mixed by a magnetic stirring bar and the supernatant solvent periodically analyzed for chromocene by visible spectroscopy ( $\lambda_{\max} = 453$  nm,  $\epsilon = 2.06 \times 10^2$  for decane;  $\lambda_{\max} = 456$  nm,  $\epsilon = 2.10 \times 10^2$  for toluene). The difference between the quantities initially added and measured after 24 h of contact with silica was assumed to be adsorbed on the silica. Although chromocene was allowed to react for 24 h with silica, the rate of deposition was very rapid during the first hour and nearly the maximum amount of chromocene was deposited during this first hour.

#### *Preparation of Cyclopentadienyl Chromium Alkoxides (6)*

*Reaction of triphenylsilanol with chromocene.* In a 100-ml round bottom flask fitted with nitrogen inlet and outlet tubes were charged 1.82 g (0.01 mole) of chromocene, 2.76 g (0.01 mole) of triphenylsilanol, and 15 ml of toluene under nitrogen. The reaction mixture was refluxed for 5 h during which time a dark purple solution was obtained. Evaporation of toluene gave a dark purple solid which could not be sublimed at 200°C/0.2 mm. This dark purple solid dissolved readily in hexane ( $\lambda_{\max} = 545$  nm).

*Reaction of *t*-butanol with chromocene.* To a toluene solution of chromocene (0.027 mole in 20 ml of solvent) was added 0.033 mole of dry *t*-butanol and the mixture refluxed for 4 h. The volatiles were then removed under vacuum. The residue was sublimed (110°C/0.001 mm Hg) to yield dark red crystals—4.08 g, 79% yield, mp 117 to 119°C. Crystallization from pentane (three times at –70°C) yielded dark red crystals, mp 120 to 121°C. Molecular weight measurements gave MW = 365, 370 (dimer), determined in freezing benzene at 0.5%.

*Anal.* Calcd for  $C_9H_{14}OCr$ : C, 56.84; H, 7.37; Cr, 27.35. Found: C, 55.65; H, 7.36; Cr, 27.50.

*Reaction of 2,6-ditertiarybutyl phenol with chromocene.* To a toluene (20 ml) solution of chromocene (0.012 mole) was added 0.013 mole of 2,6-ditertiarybutyl phenol and the contents refluxed for 18 h. The brown solution was pumped dry. The resulting solids were sublimed to 60°/0.1 mm Hg. This procedure separated unreacted phenol and chromocene from the residual, beautiful blue crystals. The residue was crystallized from hexane to yield 0.338 g of blue crystals, mp 247 to 250° w. dec.

*Anal.* Calcd for  $C_{19}H_{26}OCr$ : C, 70.81;

H, 8.07; Cr, 16.15. Found: C, 71.05; H, 8.21; Cr, 17.0.

*Polymerization Studies with Cyclopentadienyl Chromium Alkoxides (6).*

The supported cyclopentadienyl chromium alkoxides were prepared in a manner previously described for the supported chromocene catalyst. Sieve-dried (Linde 5A) *n*-hexane (100 ml) was added to an 8-oz serum-capped bottle and purged with argon for 30 min. Dehydroxylated silica (0.4 g) was added to the hexane through a small hole in the cap. A second serum cap was fitted over the first to prevent contamination by air and water. After purging the contents in the bottle for 15 min, a solution of the cyclopentadienyl chromium alkoxide in toluene was added by syringe. The contents were rapidly agitated by a magnetic stirring bar for 30 min during which time complete deposition usually took place. The alkylsilanes were added by syringe as dilute solutions in *n*-hexane. All polymerizations were carried out in a 1-liter chrome-plated, stainless steel autoclave, equipped with pressure gauge, appropriate argon and ethylene inlets and outlets, and a propeller stirring blade for agitation. The details of the polymerization procedure have been described in a previous paper (1a).

## RESULTS

### *Chromocene Chemisorption on Silica*

Deposition of chromocene on silica liberates cyclopentadiene which suggests that there is a chemical reaction with surface silanol (hydroxyl) groups on silica. Previous data showed that more cyclopentadiene was evolved when chromocene was deposited on supports that had minimal thermal treatment (1a). Cyclopentadiene evolution ranged from 43 to 86% (theoretical) using silicas heated at 800°C and unheated silicas, respectively. Other workers (7, 8) using allyl-transition metal compounds have reported a similar release of an

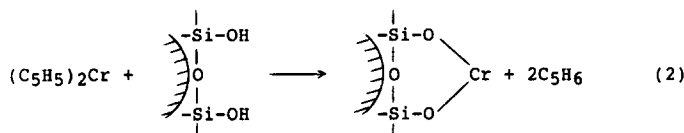
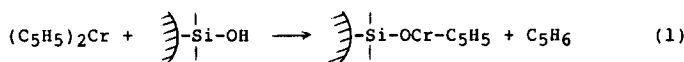
organic ligand on reaction with surface hydroxyl groups of silica. Likewise the number of allyl ligands released as propylene from Zr ( $\pi$ -C<sub>3</sub>H<sub>5</sub>)<sub>4</sub> was higher for silica heated to 100°C than for 800°C silica (8).

It is instructive to review briefly the chemistry of silica drying and dehydroxylation (9-11). Prior to heating at high temperatures, the silica surface is covered with silanol groups on which molecular water may be adsorbed. Thermal treatment at 200°C may remove all physically bound water, but hardly affects surface silanol groups. At elevated temperatures progressive elimination of water takes place between neighboring silanols. The surface chemistry of these heat-treated, amorphous silicas indicates that silanol and siloxane groups are present on the silica surface. With an increase in the dehydroxylation temperature of silica the fractional population of isolated silanol groups is increased (12). Many different techniques have been described for determining the concentration of hydroxyl groups on silica (11). From knowledge of the chemical reaction of chromocene and the hydroxyl content of heat-treated silicas, it was possible to compare experimental and calculated values for the maximum chemisorption of chromocene on dehydroxylated silicas. Maximum values for adsorption of chromocene on Davison Grade 56 silica (13), heated at temperatures between 100 and 800°C, were experimentally determined (Fig. 1). These deposition studies were carried out using an excess of chromocene in decane or toluene.

Published data (11) on the change in hydroxyl content of silica as a function of dehydroxylation temperature permit a calculation for maximum chemisorption of chromocene on silica (Fig. 1). In these calculations the surface area (285 m<sup>2</sup>/g) of Davison silica was assumed to remain constant for temperatures up to 800°C. For reaction of all hydroxyl groups as single units (Eq. (1)) the maximum value

for chemisorption should be equal to the hydroxyl content. If all surface hydroxyl groups react in pairs with chromocene

(Eq. (2)), the maximum value for chemisorption should equal one-half the hydroxyl content of silica.



Deposition studies of chromocene from toluene solution at 25°C showed 6.3 g  $(C_5H_5)_2Cr/100$  g silica deposited on Grade 56 silica heated at 800°C. At a deposition temperature of 55°C, 9.8 g of  $(C_5H_5)_2Cr/100$  g silica deposited on Grade 56. Calculation shows a value near 9% should be measured if chemisorption occurred exclusively by monosubstitution (Eq. 1). The close agreement between experimental and

calculated values suggest that only chemisorption of chromocene from toluene solution occurs on silica dehydroxylated at 800°C. It should be noted that previous studies showed that thermal aging of the chromocene catalyst at 55°C did not alter catalytic activity or lead to decomposition of the catalyst (3). When *n*-decane was substituted for toluene under identical conditions, about 16 g  $(C_5H_5)_2Cr/100$  g silica deposited on Grade 56 silica. Addition of toluene to this slurry in decane led to a decrease in adsorption to 11 g  $(C_5H_5)_2Cr/100$  g silica. Since the process of chemisorption is believed to be irreversible under the experimental conditions, extraction of chromocene from the surface should only remove the physically-adsorbed materials. These results suggest physical adsorption in addition to chemisorption can occur on deposition of excess chromocene from decane.

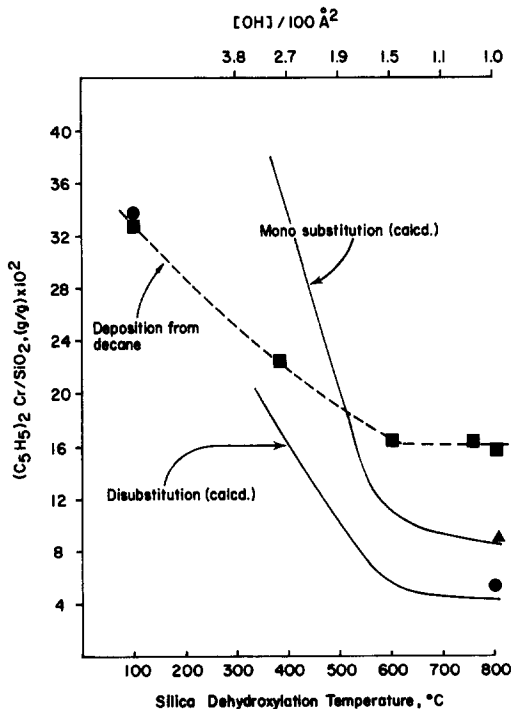


FIG. 1. Effect of silica (Grade 56) dehydroxylation temperature on maximum adsorption of chromocene: (●), from toluene at 25°C; (▲), from toluene at 55°C; (■), from decane at 25°C.

Additional adsorption studies were carried out with Grade 56 silica dehydroxylated below 800°C. Results from these studies showed that the value for maximum adsorption of chromocene increased with a decrease in silica dehydroxylation. With silica dried at 100°C, nearly the same quantity of chromocene deposited from *n*-decane and toluene solution (Fig. 1).

#### Activity Studies With Cab-O-Sil Supports

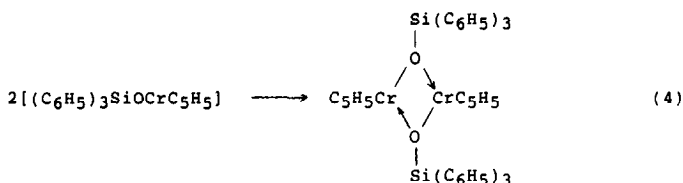
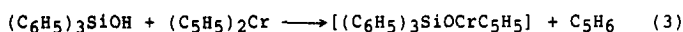
Active chromocene catalysts for ethylene polymerization can be prepared by deposit-

ing chromocene on Cab-O-Sil silicas (14) heated at temperatures as low as 200°C. These supported catalysts exhibit higher activity than catalysts prepared on porous Davison Grade 952 and 56 silicas (13) (Fig. 2). This improvement in activity appears to correlate with the higher concentration of free silanol to hydrogen-bonded silanol groups present on the Cab-O-Sil surface. Published results (15) of an infrared study with different silicas have shown that water was eliminated from hydrogen-bonded silanol groups, and the ratio of free silanol groups to hydrogen-bonded silanol groups increased with an increase in dehydroxylation temperature of the silicas. In all cases, catalyst activity increased with an increase in the dehydroxylation temperature of silica from 200 to 800°C. Specifications (Table 1) characterizing the different silicas show pore diameter and particle size are distinctly different for Cabot and Davison silicas. In general, polyethylenes of a smaller particle size are produced with chromocene catalyst on a Cab-O-Sil support. This smaller particle size probably originates from the very small particle size of Cab-O-Sil supported catalysts.

### Studies with Model Compounds

Triphenylsilanol was allowed to react with chromocene at ambient temperature in toluene or tetrahydrofuran at molar ratios of 1:1 and 3:1 (Table 2). The reaction was slow, taking about 2 h to complete. In each case, approximately one equivalent of cyclopentadiene was generated, one equivalent of triphenylsilanol was consumed, and one purple species ( $\epsilon_{545} = 2.7 \times 10^3$ ) was produced. These data are consistent with a mechanism involving monosubstitution of chromocene by triphenylsilanol.

Disubstitution of chromocene by triphenylsilanol most likely does not occur due to the steric bulk of the triphenylsiloxy group. Thermal aging of the reaction mixture at 90 to 100°C did not provide a route to disubstitution. Since the monosubstituted product is coordinatively unsaturated, it would be expected to rapidly dimerize to the complex illustrated in Eq. (4). The monosubstituted derivative from chromocene and triphenylsilanol can be isolated from hexane as a crystalline solid.



Several attempts to use this dimeric complex in solution to catalyze the polymerization of ethylene were unsuccessful. The purple species deposited readily on dehydroxylated silica with release of some cyclopentadiene, but the supported material was not catalytically active for ethylene polymerization. Hydrolysis of the supported chromium compound liberated the

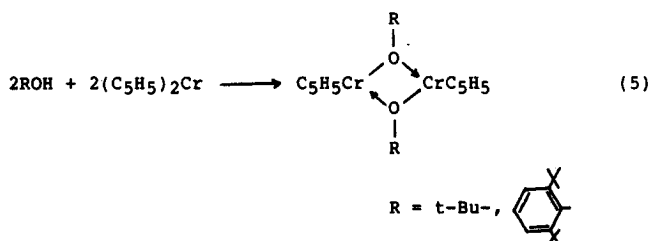
TABLE 1  
Specifications for Different Silica Types

	Cab-O-Sil		Davison	
	EH5	H5	952	56
Surface area (m <sup>2</sup> /g)	390	325	350	285
Avg. pore diameter (Å)	0	0	200	168
Avg. particle size (μ)	0.007	0.007	76	69
Bulk density (lb/ft <sup>3</sup> )	2.3 (max)	2.3 (max)	25	24

remaining cyclopentadienyl ligands as cyclopentadiene. Catalytic activity was achieved by the addition of butylsilane to the supported triphenylsiloxy cyclopentadienyl chromium compound. This catalyst

behaved much like a supported chromocene catalyst.

Similar dimeric derivatives can be prepared from chromocene and *t*-butanol or 2,6-di-*t*-butylphenol (Eq. (5)).



These unsupported model compounds did not show activity for ethylene polymerization. In addition, the silica-supported model compound from *t*-butanol did not provide catalytic activity. The addition of alkylsilanes provided supported catalysts which showed significant activity in ethylene polymerization (Table 3). These catalysts, like the catalyst derived from

supported triphenylsiloxy cyclopentadienyl chromium, behaved like a supported chromocene catalyst.

## DISCUSSION

An essential step in the generation of active sites with supported chromocene catalysts involves reaction of chromocene with surface silanol groups on dehydroxylated silica. The extent of this reaction should depend on the reactivity and availability of these silanol groups. The pK<sub>a</sub> values of surface silanol groups fall in the range of 4 to 7, depending upon the method of measurement (16). A relationship exists between the mean concentration of silanol groups, the number of isolated silanol groups, and the temperature of thermal dehydroxylation. The close agreement between the published value for the silanol concentration on silica dehydroxylated at 800°C (1[OH]/100 Å<sup>2</sup>), and the measured value for the amount of chromocene deposited from toluene solution at 55°C, is compatible with a model involving monosubstitution of chromocene (Eq. (1), Fig. 1). These results are consistent with measurements which show that only isolated silanol groups are present on silica heated at 800°C (17).

A much larger amount of chromocene deposited on 800°C silica from decane

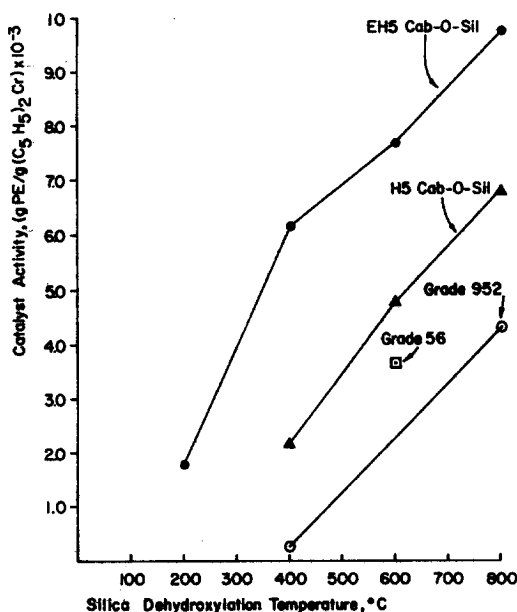


FIG. 2. Effect of silica dehydroxylation temperature for different silicas on catalyst activity. Conditions: 20 psi H<sub>2</sub>, 180 psig ethylene pressure, and 30-min reaction time at 85°C.

TABLE 2  
Stoichiometry of Reaction of Chromocene with Triphenylsilanol<sup>a</sup>

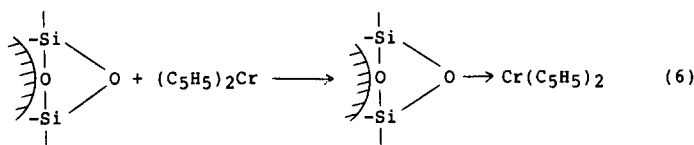
$\phi_3\text{SiOH}/$ $(\text{C}_5\text{H}_5)_2\text{Cr}$ , molar ratio	Reaction conditions	Time (h)	$\text{C}_5\text{H}_6$ yield <sup>b</sup> (%)
1	Room temperature	69	52
1	Room temperature	118	56
1	952 Silica (300°C) added to 118-h solution	3	76
1	952 Silica (800°C) added to 118-h solution	3	65
1	952 Silica (800°C) plus water added to 118-h solution	0.5	97
3	Room temperature	70	56
3	Room temperature	119	56
3	119-h Solution heated to 90°C	5	53

<sup>a</sup> Other conditions: 0.5 mmole  $(\text{C}_5\text{H}_5)_2\text{Cr}$ , 0.5 or 1.5 mmole  $\phi_3\text{SiOH}$ , and 0.25 g silica in 35 ml toluene. Silica surface  $[\text{OH}] = 0.5$  mmole/0.25 g silica heated at 370°C and 0.13 mmole/0.25 g silica heated at 800°C.

<sup>b</sup> Determined by gas chromatography.

than from toluene. This observation probably illustrates the greater solvation of chromocene by toluene and suggests that adsorption of chromocene on silica from

decane can occur, not only by reaction with surface silanol groups, but also by interaction with certain siloxane groups (Eq. (6)). This reaction



with siloxane groups probably occurs after reaction of chromocene with some silanol groups. Our previous studies, at lower concentrations of chromocene in decane, showed cyclopentadiene is released on deposition of chromocene from decane (1). The increase in the quantity of chromocene deposited on silica dehydroxylated at temperatures below 800°C reflects the reaction of chromocene with a higher concentration of active silanol groups. The concentration of surface silanol groups decreases from about  $4.8[\text{OH}]/100 \text{ \AA}^2$  in the fully-saturated state to about  $1[\text{OH}]/100 \text{ \AA}^2$  for silica heated at 800°C. The similarity in the maximum quantity of chromocene deposited from decane or

toluene on silica dried at 100°C suggests that reaction takes place with only silanol groups and/or water.

The polymerization results with Cab-O-Sil as a support for chromocene illustrate the important role of isolated, silanol groups as reactants in formation of highly active catalysts. Various silica samples, subjected to similar conditions of heating, have different relative infrared intensities for the free and hydrogen-bonded silanol bands (15a). The intensities of these infrared bands depend on the origin of the sample, and the temperature and time of evacuation of the sample. Silica gels, like Grade 56, are precipitated from aqueous solution and have a far greater surface hydration with

a higher proportion of hydrogen-bonded hydroxyls than silica powder such as Cab-O-Sil. Cab-O-Sil is prepared by flame hydrolysis of silicon tetrachloride (14). The high proportion of free hydroxyl groups found on this silica probably arises from the extreme temperature (900°C) employed during manufacture. The surface groups on these nonporous silica powders are on the outside of the curved particle.

The chemically anchored, disubstituted chromium species (Eq. (2)) prepared on silicas dried at low temperatures is believed to be inactive or only weakly active in ethylene polymerization. On these low-temperature silicas excessive amounts of hydroxyl groups are present which can coordinate or react with the disubstituted chromium species and thereby block the ethylene polymerization reaction. The disubstituted chromium species, when prepared under conditions in which hydroxyl groups are absent, probably remains coordinately unsaturated and can be highly active in ethylene polymerization. Unsaturated chromium of this type has been postulated to be the source of the active species in the  $\text{CrO}_2/\text{SiO}_2$  (Phillips) catalyst (17-19). With the Phillips catalyst high temperatures ( $\geq 600^\circ\text{C}$ ) are used in catalyst activation to reach high polymerization activity.

Studies in solution with cyclopentadienyl chromium alkoxide compounds ( $\text{ROCrCp}$ ) illustrate a basic dilemma in attempting to model a heterogeneous reaction with compounds in solution. Interaction of

potential catalytic sites in solution can result in reactions which remove available positions necessary for catalytic activity. Sterically hindered hydroxylic compounds such as triphenylsilanol and *t*-butanol react in solution with chromocene to form dimeric cyclopentadienyl chromium alkoxides. These compounds probably do not show catalytic activity for ethylene polymerization because available coordination sites are satisfied in dimer formation. Silanol supports such as silica are unique because they do react with chromocene and prevent formation of dimeric compounds by anchoring the chromium compound on the support. This anchoring process prevents mutual interaction of the supported chromium compounds.

Deposition and polymerization studies with cyclopentadienyl chromium alkoxides suggest a reaction sequence of the type shown by Eqs. (7) and (8). Deposition on silica occurs with release of the corresponding alcohol, which remains, in most cases, complexed to the chromium center. Addition of an alkylsilane destroys this complex and generates an active catalytic center which exhibits polymerization characteristics which are similar to a supported chromocene catalyst. This same site can be generated by reaction of chromocene with silica. In this case, addition of *t*-butanol to the supported chromocene catalyst destroys catalytic activity and leads to a modified site containing *t*-butanol complexed to the chromium center.

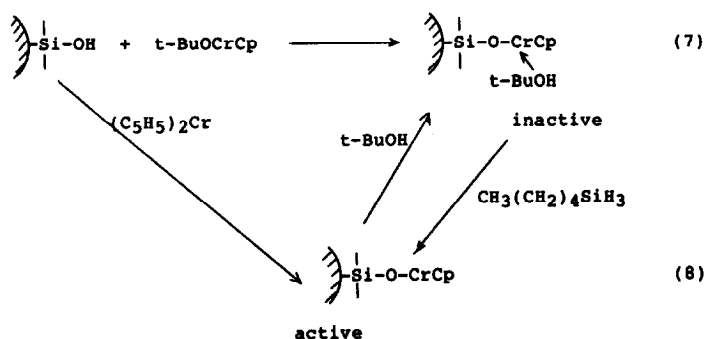
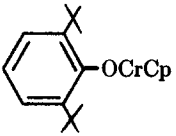




TABLE 3  
Ethylene Polymerization Studies with Supported Cyclopentadienyl Chromium Alkoxides<sup>a</sup>

Chromium compound		Silane compound		Polymer yield (g)
Type	mmole	Type	mmole	
<i>t</i> -BuOCrCp	0.21	—	—	0
<i>t</i> -BuOCrCp	0.11	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> SiH <sub>3</sub>	0.50	176
φ <sub>3</sub> SiOCrCp	0.53	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> SiH <sub>3</sub>	7.7	138
	0.11	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> SiH <sub>3</sub>	0.44	52
Cp <sub>2</sub> Cr	0.11	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> SiH <sub>3</sub>	0.50	192
Cp <sub>2</sub> Cr <sup>b</sup>	0.11	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> SiH <sub>3</sub>	0.92	167
Cp <sub>2</sub> Cr	0.11	—	—	115

<sup>a</sup> Other conditions: Chromium compounds deposited on 0.4 g of Grade 56 silica dehydrated at 600°C; polymerization run for 1 h at 89°C at an H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> pressure ratio of 0.05–0.13 and ethylene pressure of 200 psi.

<sup>b</sup> 0.12 mmole *t*-butanol added to supported Cp<sub>2</sub>Cr prior to addition of silane.

## REFERENCES

- (a) Karol, F. J., Karapinka, G. L., Wu, C., Dow, A. W., Johnson, R. N., and Carrick, W. L., *J. Polym. Sci. Part A1* **10**, 2621 (1972); (b) Karapinka, G. L., *United States Patent* 3,709,855 (1973).
- Karol, F. J., Brown, G. L., and Davison, J. M., *J. Polym. Sci. Part A1* **11**, 413 (1973).
- Karol, F. J., and Wu, C., *J. Polym. Sci. Part A1* **12**, 1549 (1974).
- Karol, F. J., and Johnson, R. N., *J. Polym. Sci. Part A1* **13**, 1607 (1975).
- Wilkinson, G., *J. Amer. Chem. Soc.* **76**, 209 (1954).
- Karol, F. J., Wu, C., Reichle, W. T., and Maraschin, N. J., *U. S. Patent* 4,115,425 (1978).
- Ballard, D. G. H., *Advan. Catal.* **23**, 263 (1973).
- Yernakov, Y. I., *Catal. Rev. Sci. Eng.* **13** (1), 7 (1976).
- Kisilev, A. V., "Infrared Spectra of Surface Compounds." Wiley, New York, 1975.
- Boehm, H. P., *Advan. Catal.* **16**, 179 (1966).
- Little, L. H., "Infrared Spectra of Adsorbed Species." p. 275. Academic Press, New York, 1966.
- Wagner, B. E., Helbert, J. N., and Poindexter, E. H., *Surface Sci.* **67**, 251 (1977).
- Davison Technical Bulletin, "Davison Silica Gel in Catalysis." L-401-466. Davison Chemical Division of W. R. Grace and Co., Baltimore, Maryland 21203.
- Cabot Technical Bulletin, "Cab-O-Sil." C-10. Cabot Corporation, Boston, Massachusetts 02110.
- (a) McDonald, R. S., *J. Phys. Chem.* **62**, 1168 (1958); (b) Reference (11), p. 251.
- Benesi, H. A., and Winkvist, B. H. C., *Advan. Catal.* **27**, 98 (1978).
- Krauss, H. L., and Stach, H., *Inorg. Nucl. Chem. Lett.* **4**, 393 (1968).
- Krauss, H. L., and Stach, H., *Z. Anorg. Allg. Chem.* **366**, 280 (1969).
- Baker, L. M., and Carrick, W. L., *J. Org. Chem.* **33**, 616 (1968).