

# Nonequilibrium Plasma Activation of Supported Cr(III) Phillips Catalyst Precursors

V. J. Ruddick and J. P. S. Badyal\*

Department of Chemistry, Science Laboratories, Durham University, Durham DH1 3LE, England, UK

Received: September 27, 1996; In Final Form: August 27, 1997<sup>®</sup>

The ethylene polymerization activities of low-temperature plasma-activated  $\text{CrO}_x/\text{SiO}_2$  catalysts prepared from two different types of precursor are compared. Chromium(III) acetate wet impregnated onto high surface area silica is found to yield polyethylene, while chromium(III) acetylacetonate dry blended with silica does not. This is despite both precursors exhibiting good catalytic activity following conventional thermal activation.

## Introduction

Most supported catalyst systems conventionally require a high-temperature activation procedure. In the case of the Phillips  $\text{CrO}_x/\text{SiO}_2$  ethylene polymerization catalyst, this comprises heating a silica-supported chromium precursor to 1073 K for several hours in a dry air or oxygen atmosphere.<sup>1</sup> Such thermal activation methods tend to be energy intensive and can lead to sintering or segregation of the active catalytic component.<sup>2</sup>

Low-temperature activation of heterogeneous catalysts can be achieved by using nonequilibrium (nonlocal thermodynamic equilibrium) plasmas. Such a "cold" plasma can be considered as a partially ionized gas consisting of ions, electrons, neutrals, and electromagnetic radiation, where the electron temperature ( $T_e$ ) is much greater than the gas temperature ( $T_g$ ). Typically,  $T_e/T_g$  is of the order 10–100.<sup>3</sup> Therefore, although the bulk gas temperature is near ambient, the electrons possess sufficient energy to cause the rupture of molecular bonds, thus enabling conventional high-temperature thermally driven reactions to proceed at low temperatures. For instance, the problems related to high-temperature segregation within zeolitic Fischer–Tropsch catalysts can be overcome by the use of oxygen or argon plasma treatments, which leads to enhanced catalytic activities compared to their thermally activated counterparts.<sup>4</sup> Similar improvements have also been found for hydrogenation catalysts<sup>5,6</sup> and alkene disproportionation catalysts.<sup>7</sup>

It has previously been reported that air plasma activation of silica–alumina-supported chromium(VI) oxide precursors can yield a high-activity ethylene polymerization catalyst.<sup>8</sup> However, current safety legislation prohibits any human contact with carcinogenic chromium(VI) species during the production of polyethylene using the Phillips catalyst. Therefore, in the present study, we investigate the nonisothermal plasma oxidation of two different types of silica-supported chromium(III) catalyst precursors using *in situ* mass spectrometry. These comprise chromium(III) acetate wet impregnated onto silica and chromium(III) acetylacetonate dry blended with the support. Previous thermal activation studies have shown that both of these precursor materials give rise to an active ethylene polymerization catalyst via the same intermediate species.<sup>9</sup> Here, we seek to establish whether low-temperature plasma treatment prohibits the intermixing of the dry blended chromium(III) acetylacetonate/silica system.

## Experimental Section

High surface area silica (Crosfield Limited, surface area =  $323 \text{ m}^2 \text{ g}^{-1}$ , pore volume =  $1.81 \text{ cm}^3 \text{ g}^{-1}$ ) served as a reference

sample. The  $\text{CrO}_x/\text{SiO}_2$  catalyst precursors (Crosfield Limited) were prepared by either impregnating silica with an aqueous solution of basic chromium(III) acetate and then drying or, alternatively, dry blending chromium(III) acetylacetonate with high surface area silica. In both cases, the activated catalyst contained 1 wt % chromium loading.

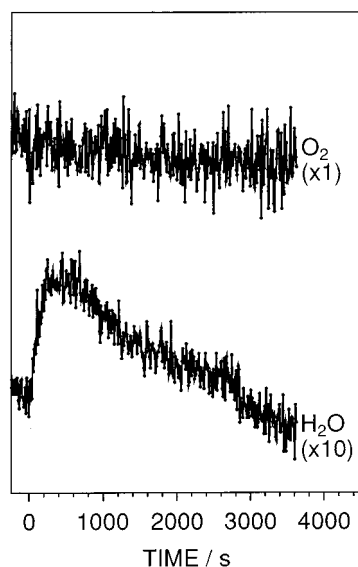
Plasma activation experiments were carried out in a capacitively coupled 13.56 MHz Bio-Rad E2000 plasma asher, which had been fitted with a rotating powder holder. Rotation of the reaction vessel was controlled by a  $33 \text{ dm}^3 \text{ h}^{-1}$  Edwards E2M2 Fomblin rotary pump via a liquid air cold trap to yield a base pressure of  $2 \times 10^{-2} \text{ mbar}$ . Prior to each experiment, the reaction vessel was scrubbed with detergent, rinsed with acetone, oven-dried, and then cleaned *in situ* using a 40 W air plasma at 0.2 mbar pressure. (This corresponds to a plasma power density,<sup>10</sup>  $P/p$ , of  $200 \text{ W mbar}^{-1}$ .) A 0.5 g sample of catalyst precursor was then loaded into the reactor and evacuated down to base pressure. Next, oxygen gas (BOC, 99.5% purity, dried by passing through a  $\text{P}_2\text{O}_5$  drying column and then a 3A molecular sieve at a flow rate of  $1.5 \text{ dm}^3 \text{ h}^{-1}$ ) was introduced into the plasma chamber at a pressure of 0.9 mbar via a fine needle valve. The oxygen glow discharge was then ignited at 40 W (plasma power density,  $P/p = 44.4 \text{ W mbar}^{-1}$ ) while rotating the vessel containing the catalyst powder. Reaction was allowed to proceed for approximately 45 min, after which time the oxygen flow was switched off and the reactor evacuated to its original base pressure.

The plasma reactor outlet was connected via a heated capillary tube to a Vacuum Generators SX200 quadrupole mass spectrometer; this was multiplexed to a PC computer, thus enabling the composition of gases within the reactor to be monitored in real time. For each set of experiments, the whole background mass spectrum was recorded as a function of time, thereby allowing all desorbing species to be identified. Each experiment was subsequently repeated using fresh material, but on this occasion, actual reaction profiles were obtained by tuning into the previously identified mass fragments. The fragmentation patterns for carbon monoxide and carbon dioxide were also measured independently using the respective gases and normalized using the appropriate ion gauge sensitivity factors.<sup>11,12</sup> Any contribution from  $\text{CO}_2$  toward the  $m/e$  28 profile was taken into consideration.

Ethylene polymerization activity was tested by reducing the plasma-oxidized  $\text{CrO}_x/\text{silica}$  catalysts at 623 K with a 15 min exposure of carbon monoxide (BOC, 99.9% purity, dried in the same way as for oxygen, at a flow rate of  $1.5 \text{ dm}^3 \text{ h}^{-1}$ ), followed by cooling to 383 K and exposing to a 50:50 mixture of argon: ethylene (Scott Speciality Gases, 99.8%, dried over  $\text{P}_2\text{O}_5$  and

\* To whom correspondence should be addressed.

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, October 15, 1997.



**Figure 1.** Change in mass signal intensity during oxygen plasma treatment of silica.

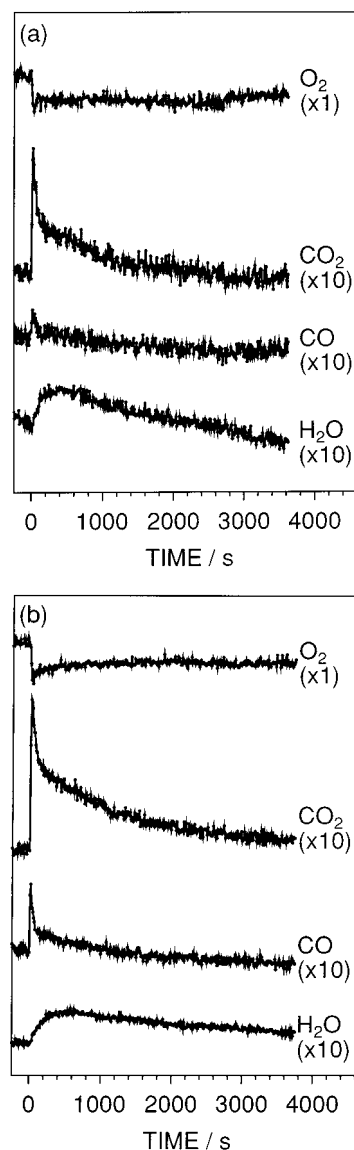
then 3A molecular sieve (Aldrich) columns). The resultant material was mixed with KBr and pressed into a disk to allow characterization by Fourier transform infrared spectroscopy using an FTIR Mattson Polaris instrument. Typically, 100 scans were acquired at a resolution of  $4\text{ cm}^{-1}$ .

## Results

Room-temperature oxygen glow discharge treatment of the silica control samples resulted in a gradual loss of water from the surface with no observable change in the oxygen signal (mass 32), Figure 1.

Plasma oxidation of chromium(III) acetate/silica and chromium(III) acetylacetonate dry blended with silica was accompanied by a color change from pale blue or maroon, respectively, to bright orange. This is similar in appearance to what is observed during the thermal activation of these  $\text{CrO}_x/\text{silica}$  catalyst precursors.<sup>9</sup> For both types of chromium(III) precursor, a sharp rise in CO and  $\text{CO}_2$  evolution coincided with the onset of plasma ignition; this was followed by a gradual drop in signal intensity with treatment time, Figure 2. Oxygen consumption mirrored this trend. (This behavior was absent for just the silica support material.) Water loss displayed a broad peak, which was similar in appearance to that observed previously during oxygen plasma treatment of silica. No other products were observed (e.g.,  $\text{H}_2$ ,  $\text{CH}_4$ , etc.). The respective peak areas for the various gases detected by mass spectrometry are summarized in Table 1.

The plasma-oxidized  $\text{CrO}_x/\text{SiO}_2$  catalysts were then heated to 623 K (no loss of gaseous products was detected by mass spectrometry) and reduced using CO gas; this was followed by cooling to 383 K and exposure to a 50:50 argon:ethylene gas mixture. In the case of the chromium(III) acetate wet impregnated onto silica precursor, the formation of white granules was observed. These were identified by FTIR analysis as being polyethylene.<sup>13</sup> C—H stretches at  $2920$  and  $2850\text{ cm}^{-1}$ , methylene bending mode at  $1469\text{ cm}^{-1}$ , and methylene rocking mode at  $719\text{ cm}^{-1}$  (all remaining peaks were assigned to the silica support<sup>14</sup>), Figure 3. The catalyst activity of plasma-activated chromium(III) acetate supported on silica was comparable to that found following thermal calcination in terms of the amount of polymer produced. No polymer formation was detected for the starting material based on the dry blended physical mixture of chromium(III) acetylacetonate with silica.



**Figure 2.** Change in mass signal intensity during oxygen plasma treatment of (a) chromium(III) acetate wet impregnated onto silica and (b) chromium(III) acetylacetonate dry blended with silica.

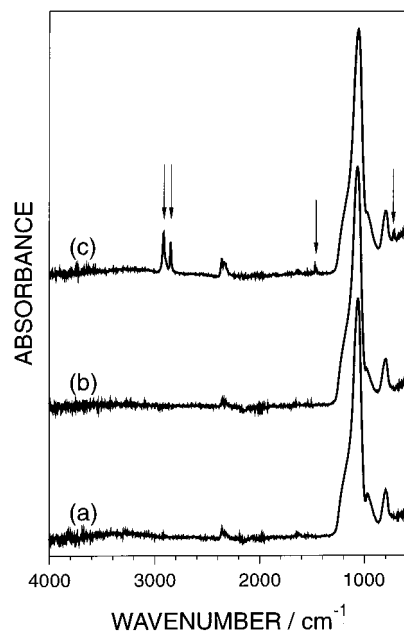
**TABLE 1: Summary of CO and  $\text{CO}_2$  Peak Areas Produced during the Plasma Oxidation of Catalyst Precursors (arbitrary units  $\pm 5\%$ )**

molecule	Cr(III) acetate/silica	Cr(III) acetylacetonate/silica	silica
CO	1.6	5.3	0
$\text{CO}_2$	24.3	87.4	0
$\text{H}_2\text{O}^a$	22.4	41.3	11.7

<sup>a</sup> Uncorrected for sensitivity factor

## Discussion

The excitation of a gas into the plasma state can greatly enhance its chemical reactivity. Application of an electric field causes free electrons to gain energy, which is subsequently lost via electron—neutral or electron—ion collisions.<sup>15</sup> A wide variety of reactants are generated by these processes, including neutral ground-state (e.g., O,  $\text{O}_2$ , and  $\text{O}_3$ ) and metastable (e.g.,  $\text{O}_2(a^1\Delta_g)$ ) species and positively charged (e.g.,  $\text{O}^+$ ,  $\text{O}_2^+$ ,  $\text{O}_3^+$ ,  $\text{O}_4^+$ ) and negatively charged ( $\text{O}^-$ ,  $\text{O}_2^-$ ,  $\text{O}_3^-$ ,  $\text{O}_4^-$ ) ions, alongside electrons and electromagnetic radiation.<sup>3,16,17</sup> The most abundant neutral species is ground-state  $\text{O}_2$ , while atomic oxygen is the predominant reactive constituent.<sup>16</sup>



**Figure 3.** FTIR spectra of (a) the silica support material, (b) following exposure of plasma activated chromium(III) acetylacetonate dry blended with silica to ethylene, and (c) following exposure of plasma-activated chromium(III) acetate/silica to ethylene.

Water loss from the silica support surface must be initiated via interaction with one of the reactive constituents of the oxygen glow discharge. The absence of a dip in the oxygen profile during oxygen plasma treatment of just the silica support material rules out the involvement of any oxygen-containing species, thereby leaving electrons and UV/VUV radiation as contenders. The negative charge associated with the plasma sheath region adjacent to a particle surface means that incident electrons will be retarded as they approach the silica surface; hence, there is minimal electron bombardment. Therefore, UV/VUV radiation must be responsible for the elimination of water from the silica support surface. This deduction is consistent with previous UV/VUV exposure studies which have shown that silanol groups undergo a condensation reaction in the presence of water to form siloxane bonds along with the concomitant loss of water from the surface.<sup>18–21</sup>

The mass spectrometry peak profiles of the gaseous products evolved during plasma oxidation of the supported chromium(III) catalyst precursors can be explained in terms of the various types of electrical discharge–substrate interactions which can potentially occur during treatment. CO and CO<sub>2</sub> formation coincides with ignition of the glow discharge and rapid consumption of oxygen; therefore, this corresponds to straightforward oxidation by excited oxygen species (probably atomic oxygen) in the presence of UV/VUV irradiation.<sup>22</sup> The intensity of oxidized carbon moieties diminishes with reaction time. It is found that approximately 3.6 times more carbon species are evolved from the Cr(III) acetylacetonate/silica precursor compared to the Cr(III) acetate/silica precursor (Table 1). This may be rationalized by taking into consideration that in Cr(CH<sub>3</sub>-COCHCOCH<sub>3</sub>)<sub>3</sub> there are 15 carbon atoms for every chromium atom, whereas in chromium(III) acetate (Cr<sub>3</sub>(OH)<sub>2</sub>(CH<sub>3</sub>COO)<sub>7</sub>) there are only 4.7 carbon atoms per chromium atom, thereby yielding an overall theoretical ratio of 3.2 (which makes the experimentally measured value of 3.6 seem reasonable). The water profile does not follow the behavior seen for CO and CO<sub>2</sub>; instead, a broad peak of similar appearance to that observed during oxygen plasma treatment of just the silica support material is measured. This difference can be attributed to the water byproduct of oxidative decomposition being initially

**TABLE 2: Relative Amounts of Oxidized Carbon Species Produced during Plasma and Thermal Oxidation Procedures (±2%)**

activation procedure	CO <sub>2</sub> /(CO + CO <sub>2</sub> ) × 100	
	Cr(III) acetate/silica	Cr(acac) <sub>3</sub> /silica
thermal <sup>9</sup>	84.6	84.3
plasma	93.8	94.3

adsorbed onto the silica support, since the plasma oxidation reaction is proceeding at ambient temperatures. Furthermore, it should be noted that the plasma oxidation procedure employed in the present study requires approximately 0.1% of the total energy input and takes ~3% of the time required for the corresponding thermal activation procedure.<sup>9</sup> Also, low-temperature glow discharge treatment gives rise to a faster rate of oxidation (as measured by the greater proportion of CO<sub>2</sub> loss, Table 2). All of these observations are consistent with an oxygen plasma being a more reactive medium compared to conventional thermal oxidation.<sup>9</sup> Finally, since the evolution of CO<sub>2</sub> and CO returns to zero during plasma activation, it can be concluded that carbon is totally removed from the catalyst surface.

The lack of any ethylene polymerization following plasma activation and CO reduction of the dry blended chromium(III) acetylacetonate/silica precursor system can be taken as being indicative of the absence of migration of chromium species onto the silica support, whereas in the case of thermal calcination, it has been previously shown that chromium centers become mobile during treatment leading to the formation of an active ethylene polymerization catalyst.<sup>9</sup> Such thermally activated reaction pathways are not viable during nonisothermal plasma oxidation.

## Conclusions

Plasma oxidation of silica-supported chromium(III) metal-organic catalyst precursors results in the instantaneous breakdown of the organic ligands into CO and CO<sub>2</sub> along with the concomitant adsorption of water onto the support surface. Subsequent UV/VUV radiation from within the electrical discharge leads to the gradual desorption of water from the silica surface. Nonequilibrium glow discharge oxidation proceeds at near-ambient temperatures in a matter of minutes and is approximately a factor of 1000 times more efficient in terms of energy consumption. Chromium(III) acetate wet impregnated onto silica gives rise to an active ethylene polymerization catalyst, whereas a physical dry mixture of chromium(III) acetylacetonate with silica does not. This difference can be attributed to the lack of dispersion of the oxidized chromium species across the silica support surface during low-temperature plasma oxidation of the latter.

**Acknowledgment.** We thank Crosfield Limited for provision of samples.

## References and Notes

- (1) McDaniel, M. P. *Adv. Catal.* **1985**, *33*, 47.
- (2) Dadashova, E. A.; Yagodovskaya, T. V.; Beilin, L. A.; Shpiro, E. S.; Lunin, V. V. *Kinet. Catal.* **1991**, *32*, 1350.
- (3) Bell, A. T. In *Techniques and Applications of Plasma Chemistry*; Hollahan, J. R., Bell, A. T., Eds.; Wiley: New York, 1974.
- (4) Dadashova, E. A.; Yagodovskaya, T. V.; Shpiro, E. S.; Beilin, L. A.; Lunin, V. V.; Kiselev, V. V. *Kinet. Catal.* **1993**, *34*, 670.
- (5) Nogier, J. P.; Bonardet, J. L.; Fraissard, J. P. *Stud. Surf. Sci. Catal.* **1983**, *17*, 233.
- (6) Tiep, V. L.; Thoang, H. S.; Bureau-Tardy, M.; Djega-Mariadassou, G.; Che, M. *Tap Chi Hoa Hoc* **1985**, *23*, 1.
- (7) Blecha, J.; Dudáš, J.; Lodes, A.; Derco, J. J. *Catal.* **1989**, *116*, 285.

- (8) Horvath, B. U.S. Pat. 3,485,771 (filed Dec 1966, issued Dec 1969).
- (9) Ruddick, V. J.; Dyer, P. W.; Bell, G.; Gibson, V. C.; Badyal, J. P. *S. J. Phys. Chem.* **1996**, *100*, 11062.
- (10) Yasuda, H. *Plasma Polymerization*; Academic: London, 1985; p 304.
- (11) Barteau, M. A.; Bowker, M.; Madix, R. J. *Surf. Sci.* **1980**, *94*, 303.
- (12) Ko, E. I.; Benziger, J. B.; Madix, R. J. *J. Catal.* **1980**, *62*, 264.
- (13) Koenig, J. L. *Chemical Microstructure of Polymer Chains*; Wiley: New York, 1980; p 199.
- (14) Guiton, T. A.; Pantano, C. G. *Colloids Surf., A* **1993**, *74*, 33.
- (15) Friedel, P.; Gourier, S. *J. Phys. Chem. Solids* **1983**, *44*, 353.
- (16) Ichikawa, Y.; Wu, R. L. C.; Kaneda, T. *J. Appl. Phys.* **1990**, *67*, 108.
- (17) Shibata, M.; Nakano, N.; Makabe, T. *J. Appl. Phys.* **1995**, *77*, 6181.
- (18) Debauche, C.; Licoppe, C.; Flicstein, J.; Dulac, O.; Devine, R. A. B. *Appl. Phys. Lett.* **1992**, *61*, 306.
- (19) Fominski, V. Y.; Markeev, A. M.; Naumenko, O. I.; Nevolin, V. N.; Alyokhin, A. P.; Vyukov, L. A. *Appl. Surf. Sci.* **1994**, *78*, 437.
- (20) Van de Leest, R. E. *Appl. Surf. Sci.* **1995**, *86*, 278.
- (21) Parada, E. G.; González, P.; Serra, J.; León, B.; Pérez-Amor, M.; Flicstein, J.; Devine, R. A. B. *Appl. Surf. Sci.* **1995**, *86*, 294.
- (22) Hopkins J.; Wheale S. H.; Badyal J. P. S. *J. Phys. Chem* **1996**, *100*, 14062.