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# Zeolite MCM-22 supported heterogeneous chromium catalyst for ethylene polymerization

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The chromium alkyl complex Cp $*$ Cr(py)$Me_2$ (Cp$*$ = $\eta^5$-pentamethylcyclopentadienyl, py = pyridine, Me = methyl) has been affixed to the surface of zeolite MCM-22 via methane elimination. The resulting composite material has been characterized by a variety of physical methods. The results are consistent with the presence of isolated organometallic fragments linked to the solid support by a covalent chromium–oxygen bond. Activation of this material with methylaluminoxane (MAO) yielded a highly active catalyst for the polymerization of ethylene. The polyethylene thus formed featured high molecular weights ($M_w \sim 4 \times 10^6$) and narrow molecular weight distributions ($M_w/M_n \sim 3.5$).

**KEY WORDS:** ethylene polymerization; chromium; zeolite; MCM-22.

## 1. Introduction

The structural characterization of heterogeneous catalysts remains a challenging problem, especially when the catalyst support is amorphous or features widely varying active site environments. This problem might be alleviated by the use of a structurally well-defined crystalline support material subject to selective functionalization with a homogeneous catalyst precursor. To test this notion, we have chosen the zeolite MCM-22, whose layered structure features regularly spaced silanol groups and a structurally characterized organometallic molecule belonging to a class of chromium alkyls known to catalyze the polymerization of ethylene [1]. Our goal was to prepare and characterize a heterogeneous “single site” catalyst.

The heterogenization of a homogeneous metallocene catalyst is a highly desirable objective [2]. Substantial improvement in polymerization activity often occurs when homogeneous species are deposited on supports [3]. Commercial chromium catalysts, *i.e.*, the Phillips catalyst (inorganic $Cr/SiO_2$) [4] and the Union Carbide catalyst ($Cp_2Cr/SiO_2$) [5] show that a support may in fact be required for the formation of active catalysts. However, the complexity of such heterogeneous catalysts makes them difficult to study; consequently, various aspects of their function are still not fully understood [6]. Basic issues such as the oxidation state of the active species as well as the mechanism of the polymerization reactions continue to be matter of considerable debate [2g,7,8]. Compounding the difficulty of the problem is the variety of the supports employed: silica [2], alumina [9], magnesium [9a] compounds, and in some cases zeolites [3] and MCM-41-type [10,11] materials have all been used as supports. It is clear that both the structure and composition of the support and the technique used for supporting the metallocene have crucial influence on the resulting catalytic properties.

Zeolite supports are particularly interesting because they can present well-defined external surface structures and allow control of composition (Si/Al ratio, acid sites, extraframework cations, *etc*.). We selected MCM-22 (MTW) as support for two reasons: first, MCM-22 grows as thin flat hexagonal crystals of a few unit cells in thickness, which allow the formation of large *external* surface areas available for anchoring the metal complex. Secondly, silanol groups in MCM-22 are isolated from each other, preventing the deactivation of catalyst sites by metal–metal interactions on the surface. Herein, we describe the preparation of a highly active homogeneous chromium catalyst and the covalent attachment of this Cr catalyst to the surface of MCM-22 zeolite supports of different Si/Al ratio. The influence of heterogenization on catalytic performance and on the final polymerization properties has been investigated.

The known chromium complex Cp $*$ Cr(py)$Me_2$ (**1**) was prepared according to scheme 1 [12]. The molecular structure of **1** has been determined by single-crystal X-ray diffraction; it features trivalent chromium in the pseudo-octahedral coordination environment of a three-legged piano stool as indicated in scheme 1. MCM-22 [13] supports with four different Si/Al ratios (Si/Al = 15, 30, 40 and $\infty$, denoted by **2**, **3**, **4** and **5** respectively) were chosen to gauge the influence of

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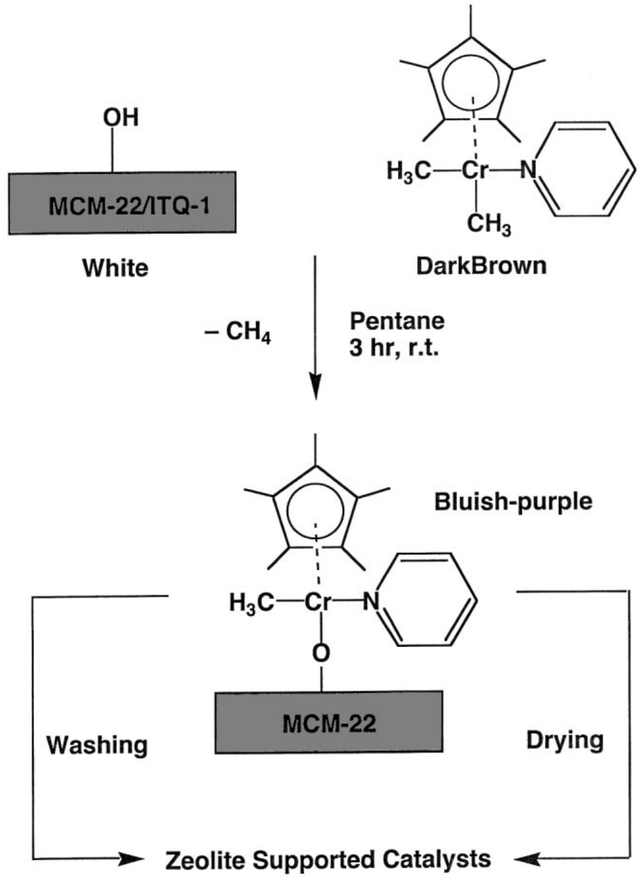
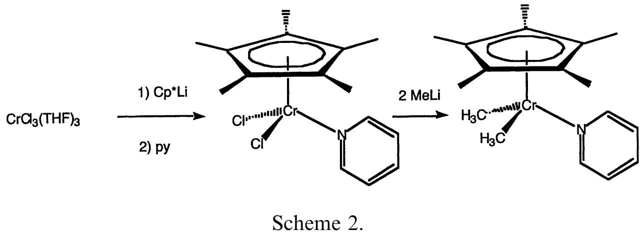


Scheme 1.

framework aluminum on the catalytic polymerization processes. The corresponding chromium-containing zeolite-supported catalysts are denoted by **2***, **3***, **4*** and **5*** contain 1.4, 2.7, 2.0 and 1.00 wt% of chromium, respectively. They were prepared by reacting 1 mmol (0.296 g) of **1** per gram of the respective support in pentane at room temperature (scheme 2).

Powder XRD patterns of the supported catalysts were nearly identical to that of the pure support, except for the expected reduction in peak intensity [14]. Nitrogen adsorption/desorption isotherm measurements showed that some of the micropores of the support have been occluded by the chromium complex (or by-products thereof), and consequently the adsorption capacity of the support is reduced after grafting [14]. The liberation of only one of the methyl groups of **1** during the grafting reaction was confirmed by a Toepler pump experiment, wherein 1.00(5) equivalent of $CH_4$ gas per chromium atom on the surface was collected from the reaction. In a similar vein, GC analysis of the remaining reaction solution showed the absence of free pyridine, suggesting that the Lewis base is still coordinated to the surface-bound chromium. The FTIR spectra of **2***, **3***, **4*** and **5*** showed that the reaction of the Cr complex with the zeolite was accompanied by a sharp decrease in intensity of the absorption band around 3745 $cm^{-1}$ (the stretching vibration of the SiO–H bond) and by the appearance of bands around 2915, 2860 and 1460 $cm^{-1}$ assigned to $\nu_{asym}$CH, $\nu_{sym}$CH and $\delta$CH respectively. Powder EPR spectra of **1** and **2***– **5*** exhibited two signals: a strong signal around 3.9 and a weaker one around 1.97. These signals arise due to the presence of large and nonuniform distortions of octahedral $Cr^{3+}$ surface states [15]. The line width of the strong signal for the anchored catalysts (**2***–**5***) was about 5 times narrower than that of the precursor **1**. This observation indicates that the $Cr^{3+}$ species in the supported catalysts are highly dispersed and isolated. This is consistent with $Cr^{3+}$ species sitting on the surface of the support as isolated species. The diffuse reflectance UV/Vis spectrum of **1** exhibited a band at 700 nm assignable to the d–d transition of octahedral Cr ion [16]; this band was blue-shifted to around 650 nm for all the supported catalysts. These observations indicate that we have succeeded in anchoring the precursor **1** on the surface of MCM-22 crystals as isolated and stable species.



Scheme 2.

Table 1 lists the results of catalytic ethylene polymerization using **1**, **2***, **3***, **4*** and **5***. The ethylene polymerization shows a clear difference in catalytic behavior before and after heterogenization. Interestingly, the activity for the aluminum-containing zeolite-supported catalysts are higher than the one of the siliceous support (table 1) and the activity trend observed is in the order **2*** > **3*** > **4*** > **5*** > **1** (on a per chromium atom basis). We have reason to believe that this order is an indirect effect, due to changes in the crystal morphology, dimensions and surface structure that affect the anchoring of the chromium complexes. The high activity of MCM-22-supported catalysts maybe due to the blocking of bimolecular deactivation pathways in the liquid phase or between chromocene and MAO in zeolite-supported catalysts [17]. The catalyst with minimum Cr loading (**2***) was the most active among the zeolite-supported catalysts. The data in table 1 also show that the activity of **1** increased considerably when Al/Cr ratio was increased from 20 to 50 (by adding additional MAO). However, this effect was not observed with the supported catalyst where maximum activity was essentially achieved even at Al/Cr ratio 20. A control reaction carried out under the same conditions using MAO and the support (without Cr) did not show any activity. Polyethylene produced by catalysts **1**, **3*** and **5*** were examined by SEM, and they showed different polyethylene morphology—presumably due to the influence of the support [18]. The

Table 1
Catalytic activity of homogeneous and heterogenized catalysts for the polymerization of ethylene

| Catalyst sample | Si/Al ratio of support | Amount of catalyst[a] (total), (mg) | Cr loading (wt%) | Al/Cr ratio (from MAO) | Activity, Kg $(g_{Cr}h\ bar)^{-1}$ |
|---|---|---|---|---|---|
| **1** | – | 6 | – | 50 | 0.579 |
| **1** | – | 6 | – | 20 | 0.240 |
| **2*** | 15 | 71 | 1.4 | 50 | 1.621 |
| **2*** | 15 | 71 | 1.4 | 20 | 1.590 |
| **3*** | 30 | 38 | 2.67 | 20 | 1.308 |
|  | 40 | 51 | 1.97 | 20 | 1.204 |
| **5*** | ∞ | 100 | 1.00 | 20 | 1.071 |

*Note*: Polymerization conditions: solvent = toluene (50 g), reaction time = 0.5 h, co-catalyst = MAO (methylaluminoxane), ethylene pressure = 13.6 bar (200 psi), initial temperature = 18 to 20 °C.

[a] The total amount of catalyst added was selected such that a total of 19 to 20 $\mu$mol of Cr are present in the sample.

melting temperatures, $T_m$ (139–141 °C), and molecular weights, $M_w$ (3 885 000–4 005 000 g mol$^{-1}$), for the polymers produced by the supported catalysts were slightly higher than the polyethylene produced by homogeneous catalyst **1** ($T_m = 132.7\,°C$ and $M_w = 3\,661\,000\,g\ mol^{-1}$). Okuda *et al.* reported similar behavior when titanium was supported on a modified silica surface [2c]. $M_w/M_n$ ratios for the supported catalysts were around 3.5, whereas for the homogeneous system the corresponding value was 2.8. The similar molecular weight distributions for the homogeneous and heterogeneous catalysts indicate that the active sites on the surface are rather uniform; the supported catalysts show the characteristics of single-site catalysts. The observed melting temperatures $T_m$ of the polyethylene were high (133–141 °C) and indicated the formation of linear high-density polyethylene [19]. The $^{13}C$ NMR spectra of the polyethylene samples obtained from all catalysts show that all samples are highly linear with no branching. A full account of our efforts to anchor homogeneous chromium catalyst onto the surface of zeolite MCM-22 will be given later.

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