Ethylene polymerization over chromium complexes grafted onto MCM-41 materials

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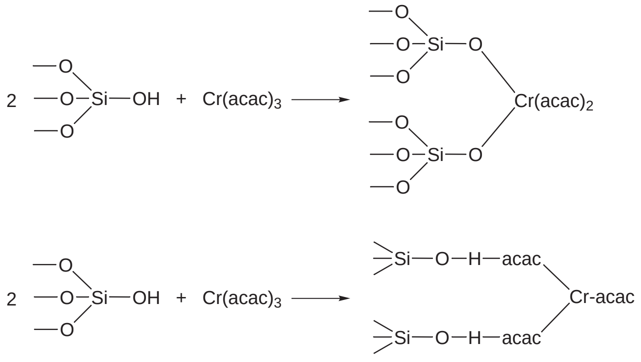
Chromium acetylacetonate [Cr(acac)$_3$] complexes have been grafted onto the surface of Al-MCM-41 materials and were characterised by combined DRS–EPR spectroscopies and TGA; these materials were found to be active for the polymerisation of ethylene.

The recent discovery of the M41S family of mesoporous crystalline solids with sharply distributed pore diameters in the range 2–10 nm has greatly increased the range of supports for preparing heterogeneous catalysts.[1] Among them, MCM-41 is the most studied. It possesses a hexagonally arranged array of uniform pores. Brönsted acidity may be generated in MCM-41 by isomorphous substitution of Al^{3+} for Si^{4+}.[2–4] Recently, transition metal complexes encapsulated in mesoporous molecular sieves have been shown to exhibit high catalytic activity in oxidation reactions. Examples are $[Mn(bipy)_2]^{2+}$ complexes in the oxidation of styrene[5a] and Schiff base complexes in the aerial oxidation of alkylaromatics.[5b] Supported chromium oxides, in particular Cr/SiO$_2$ and Cr/Ti/SiO$_2$, are industrially very important catalysts for the production of high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE).[6] Based on the pore size of the mesoporous solids, it was our view that the MCM-41 material should be an excellent support for grafting chromium complexes. Here, we report on the characterisation and catalytic activity of well defined Cr(acac)$_3$ complexes grafted onto MCM-41 materials. The goal of this study is two-fold: (1) to characterise chromium complexes grafted onto MCM-41 by spectroscopic methods and (2) to obtain novel and catalytically active materials for ethylene polymerisation.

Al-MCM-41 was prepared at 100 °C in a Teflon autoclave for 24 h.[7] The gel composition of the starting material was $1Al_2O_3:31SiO_2:2.2(HDTMABr)_2O:3.16(TEA)_2O:1.89 Na_2O:795H_2O$ (HDTMABr = hexadecyltrimethylammonium bromide, TEA = tetraethylammonium). This material after drying at 60 °C and calcination at 500 °C, was used for impregnation with a solution of Cr(acac)$_3$ in methanol under an N$_2$ atmosphere. The final product after calcination contained 1.5 wt% Cr and had a Si/Al ratio of 27.

The XRD patterns of calcined Al-MCM-41 and calcined Cr(acac)–Al-MCM-41 are identical to those previously reported for MCM-41 materials,[1–5] and confirm the hexagonal mesoporous structure. The *d*-spacings of Al-MCM-41 and Cr(acac)–Al-MCM-41 were 3.71 and 3.84 nm, respectively, while the surface area and pore volume of the Al-MCM-41 catalyst were 860 m^2 g^{-1} and 1.8 ml g^{-1}, respectively. TG analysis of the Cr(acac)–Al-MCM-41 catalyst showed two weight losses at 230 and 330 °C; *i.e.* acac ligands were removed in two stages. Thus, the supported Cr-complex is stable up to 200 °C in oxygen. In the first stage one ligand is removed as acetylacetone with the aid of the surface protons of MCM-41. In the second stage, the ligands which are not interacting with framework oxygens are removed by oxidation or pyrolysis. The amount of acac molecules per chromium atom was found to be 2.65, which suggests that there are two types of complexes present on the surface: one which has only two acac ligands, and a second with three acac ligands which has partial H-bonding with framework oxygen atoms (Scheme 1).



Scheme 1

The as-synthesized Cr(acac)$_n$–Al-MCM-41 (with n = 2 or 3) material has been characterised by combined DRS–EPR spectroscopies to study the coordination environment of Cr. Diffuse reflectance spectra are shown in Fig. 1. At room temperature, three absorption bands at 327, 389 and 562 nm are observed, which are typical for Cr^{3+}.[8] EPR reveals an intense signal with $g_{eff} \approx 4$, and zero field parameters D and $E \neq 0$ (Fig. 2). This is indicative for a strongly distorted Cr^{3+} complex.[9] During calcination in O$_2$, the intensity of the DRS band at 562 nm decreases with increasing calcination temperature. At 500 °C, two new DRS bands at 280 and 370 nm became apparent. These bands are charge transfer transitions of Cr^{6+}.[8] A fraction of Cr^{3+} could not be oxidised to $Cr^{6+/5+}$, which suggests that small clusters of Cr$_2$O$_3$ were formed on the catalyst surface. This has been confirmed by EPR spectroscopy. Indeed, the EPR spectra have a characteristic broad signal around g = 2 of clustered Cr^{3+} in pseudo-octahedral coordination.[9] In addition, small amounts of Cr^{5+} with $g_{\parallel}$ = 1.910 and $g_{\perp}$ = 1.978 have been detected.

Ethylene polymerization was carried out over calcined Cr(acac)$_n$–Al-MCM-41 in a quartz flow cell at 100 °C with 2 bar of pure ethylene. DRS and EPR spectra were recorded at regular time intervals in order to monitor the chromium

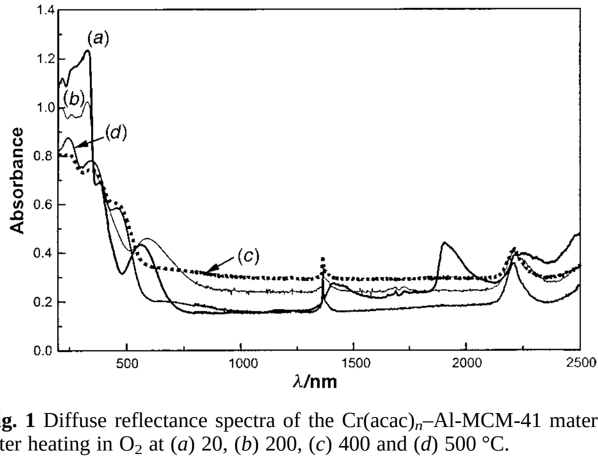


Fig. 1 Diffuse reflectance spectra of the Cr(acac)$_n$–Al-MCM-41 material after heating in O$_2$ at (*a*) 20, (*b*) 200, (*c*) 400 and (*d*) 500 °C.

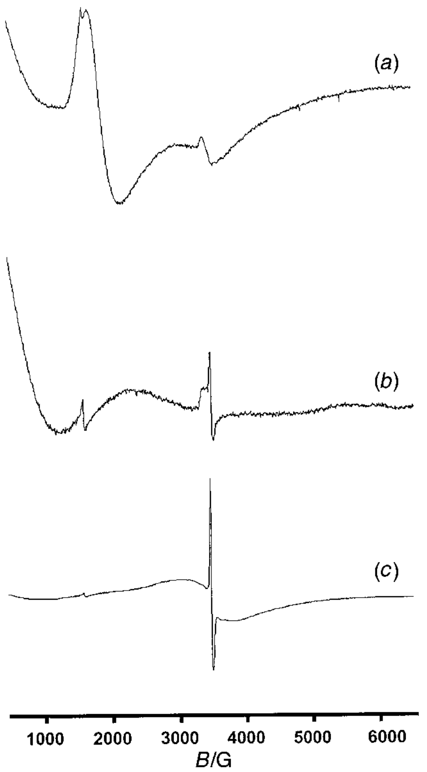


Fig. 2 Electron paramagnetic resonance spectra of Cr(acac)$_n$–Al-MCM-41 material after heating in O_2 at (*a*) 20, (*b*) 500 °C and (*c*) after 120 min reaction of ethylene at 100 °C.

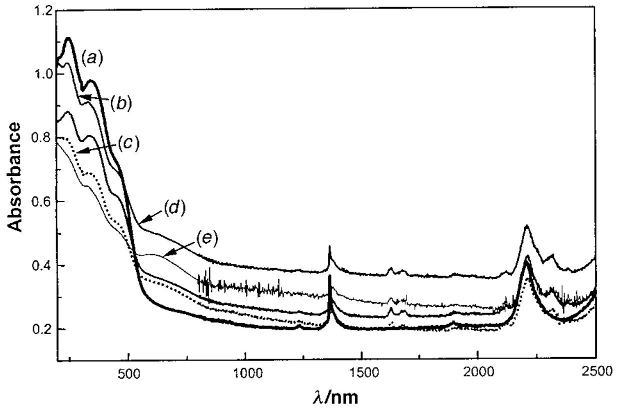


Fig. 3 Diffuse reflectance spectra of the Cr(acac)$_n$–Al-MCM-41 exposed to ethylene at 100 °C as a function of the reaction time: (*a*) 10, (*b*) 15, (*c*) 30, (*d*) 45 and (*e*) 120 min.

oxidation state during the reaction. $Cr^{6+/5+}$ is readily reducible upon interaction with ethylene, and the corresponding DRS spectra are shown in Fig. 3. After 2 h of reaction, a broad and ill defined absorption band is observed with maximum around 600 nm. This maximum is indicative for the formation of Cr^{3+}.[8] This observation has been confirmed by EPR spectroscopy. Indeed, the corresponding EPR spectrum [Fig. 2(*c*)] is dominated by a broad $g = 2$ signal, due to Cr^{3+}, and a sharp axial signal typical for Cr^{5+}.[9] In addition, new features in the NIR region of the DRS spectra were observed (Fig. 3). To further investigate this behaviour, a detailed FTIR study was performed for the catalytic materials exposed to ethylene. A band at *ca.* 1476 cm^{-1} was observed, due to the CH_2 bending mode of polyethylene.[10]

Ethylene polymerisation over Cr(acac)$_n$–Al-MCM-41 materials was then further studied at 100 °C for 2 h in a catalytic reactor, in which the ethylene consumption is reflected by a pressure decrease in the reactor system. Typical results are shown in Fig. 4. It is clear that, depending on the initial ethylene pressure, high polymerization rates between 50 and 500 mg ethylene (g catalyst)$^{-1}$ min^{-1} were obtained. After reaction the catalyst was dispersed in the polyethylene formed during reaction, and the formation of polyethylene was confirmed *via* FTIR spectroscopy.

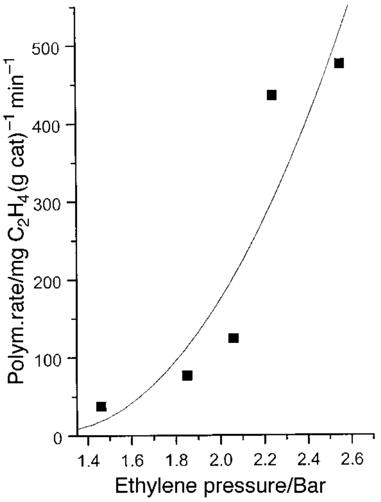


Fig. 4 Polymerization rate over Cr(acac)$_n$–Al-MCM-41 catalyst as a function of the initial ethylene pressure at 100 °C.

Summarising, the present study demonstrates that $Cr(acac)_3$ complexes can be grafted onto Al-MCM-41 materials. It results in a novel catalytic system, which is able to polymerise ethylene at relatively low pressures. Further research has to be directed towards the influence of the pore diameter of MCM-41 on the polymer characteristics.

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