

**Chromium supported onto swelled Al-MCM-41 materials: a promising catalysts
family for ethylene polymerization**

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Abstract

Swelled MCM-41 and Al-MCM-41 materials with large pore size and pore volume were synthesized and used as supports to prepare novel chromium catalysts for ethylene polymerization. Aluminium incorporation favoured chromium anchorage onto MCM-41 surface. Attachment of Cr species resulted from H-bonding of quasi π -electron system of the acetylacetonate ligands with hydroxyls groups or with electron acceptor centres like Al^{3+} .

Chromium supported onto swelled Al-MCM-41 showed higher ethylene polymerization activity than conventional Cr/SiO₂ catalysts tested in the same conditions. Properties of both obtained polymers were similar, indicating the formation of linear high-density polyethylene.

Keywords: Mesoporous, MCM-41, chromium, ethylene, polymerization.

1. Introduction.

In the early 1950's J.P. Hogan and R. L. Banks discovered that chromium oxide supported on silica and other carriers would polymerize olefins to high polymers [1]. Since then, this catalytic system has showed an important development, and nowadays Phillips-type catalysts are responsible for the commercial production of more than one third of all polyethylene sold worldwide [2]. In fact, many types of chromium-based catalysts are used in the Phillips polymerization process. The reason for this catalyst variety comes from the wide variations in the properties of the polymer depending upon its molecular structure [3].

Thus, the activity of these polymerization catalysts is very sensitive towards the support textural properties and particularly with its porosity [4]. The recently discovered M41S family of mesoporous solids are amorphous materials having a uniform pore size distribution [5].

Typical MCM-41 pores (20 Å) can be enlarged up to 90 Å by solubilization of a swelling agent, like 1,3,5-trimethylbenzene (TMB), in the surfactant micelles[6]. Ethylene polymerization over chromium supported onto conventional MCM-41, has been previously reported [7, 8], but activity values were lower than those obtained using conventional Cr/SiO₂ catalysts. However, chromium catalysts supported onto swelled Al-MCM-41 materials prepared in our laboratory, were even more active in ethylene polymerization than a conventional Cr/SiO₂ catalysts. This paper presents the preparation method, the characterization and polymerization results of these promising catalysts.

2. Experimental

MCM-41 supports were synthesized according to the hydrothermal procedure described by Lin et al.[9] but using 1,3,5-trimethylbenzene as swelling micelle agent[9]. The

composition of the synthesis gel was 1CTAB : 6.7SiO₂ : (0-0.11-0.056-0.037)Al₂O₃ : 10DMA : 13TMB : 800H₂O (CTAB= cetyltrimethylammonium bromide, DMA = dimethylamine).

These materials, after drying and calcination at 550 °C, were outgassed under vacuum conditions overnight and grafted with a solution of Cr(acac)₃ in toluene (0.05 grams of Cr per gram of solid) for 24 hours under reflux. Next, solids were recovered by filtration and intensively washed with toluene. Finally, grafted materials were calcined with air on a fluidized bed reactor at 600°C.

Textural properties of mesoporous materials were determined by means of nitrogen adsorption-desorption isotherms at 77 K using an adsorption porosimeter (Micromeritics, Tristar 3000). X-ray powder diffraction (XRD) data were acquired on a Philips diffractometer using Cu K α radiation. Fourier transform IR (FT-IR) spectra of fresh catalysts were recorded on a Mattson Infinity Series spectrophotometer using the potassium bromide wafer technique. Diffuse reflectance UV-VIS spectra (DRS) of as-synthesized and calcined chromium mesoporous materials were obtained under ambient conditions on a CARY-1 spectrophotometer equipped with a diffuse reflectance accessory in the wavelength range of 300-700 nm. A halon white reflectance standard was used as a reference material. Thermogravimetric analyses (TGA) were performed in air flow on a TA instrument SDT 2960 thermobalance, with a heating rate of 5° C/min up to 700 °C. Catalysts chemical composition was measured by ICP-atomic emission spectroscopy on a Varian Vista AX CD system.

Catalytic tests of ethylene polymerization were carried out in a 2 litre stainless steel stirred Autoclave Engineers apparatus. Reaction conditions were: 600 r.p.m., 85 °C, 40 bars of ethylene pressure using isobutane as solvent. The resulting polyethylene was recovered, filtered and washed with acetone.

The obtained polymer was characterized with FTIR, XRD, scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and with a melt flow indexer. SEM images of polyethylene particles were obtained with a Philips XL30 environmental scanning electron microscope. DSC analysis were recorded from 50 to 180 °C (heating rate = 10 °C/min) with a Mettler Toledo DSC822 apparatus. High load melt index values were obtained from the resultant polymers at 190 °C with a weight load of 21.6 kg with a Ceast 6542/002 extrusion plastometer. The bulk density of polyethylene was determined from the dry weight and the volume of the sample in a volumetric tube by liquid displacement.

3. Results and discussion.

The X-ray diffraction patterns of the calcined MCM-41 samples showed the main (100) reflection assigned to the hexagonal structure of the mesopores at $2\theta = 1.0\text{-}1.3^\circ$, corresponding to $d = 67 - 89 \text{ \AA}$, instead of typical values around $2\theta = 2.5^\circ$. This fact indicated that 1,3,5-trimethylbenzene incorporation in the synthesis mixture led to MCM-41 materials with enlarged pores.

Table 1 summarizes the textural properties of supports and catalysts chromium content after grafting. The Si/Al ratios determined by chemical analysis are very similar to Si/Al ratios of the synthesis gel, which means that almost all Al atoms were incorporated to the solid materials. All the samples showed type IV adsorption isotherms typical for mesoporous MCM-41. A step rise in the nitrogen adsorbed amount was observed at a relative pressure of c.a. 0.42, being caused by capillary condensation of nitrogen in the mesopores around 72 \AA of diameter. Aluminium incorporation was responsible of an increase in BET surface area and pore volume while pore size remained almost unaltered.

Chromium loading increased considerably upon aluminium incorporation. According to the literature [10], chromium anchorage on silica surface depended on OH groups

population, but the presence of aluminium in AlMCM samples, produced acid sites which may also contribute to chromium incorporation.

FT-IR spectra of as-synthesized catalysts in the characteristic region for the vibrations of the acetylacetonate ligands ($1600 - 1200 \text{ cm}^{-1}$) are shown in Figure 1. In this region, MCM-41 supports had also important absorption bands, so that the support spectrum was subtracted from each catalyst spectrum. For comparison the spectrum of bulk chromium (III) acetylacetonate is also reported. A possibility of discrimination between chromium (III) acetylacetonate and aluminium acetylacetonate surface species is based on the fact that vibrations of carbon-oxygen and carbon-carbon bonds in acetylacetonate ligands coordinated to chromium and aluminium differ [11, 12]. All spectra showed bands at 1565, 1530, 1428, 1370, and 1280 cm^{-1} which were also present in the spectrum recorder for bulk chromium (III) acetylacetonate. In the case of Si-MCM (0.26 wt% Cr) sample low intensity signals were achieved due to its reduced chromium content. Anyway, these bands can be attributed to the vibrations of the carbonyl and carbon-carbon double bonds in the conjugated chelate rings coordinated to the Cr^{3+} ion. Accordingly, the ligands of the supported complex had retained their ring structure and no aluminium acetylacetonate species were found on Al-MCM-41 samples after grafting with chromium (III) acetylacetonate, under our experimental conditions.

The removal of the acetylacetonate ligands from the chromium complexes grafted onto the surface of MCM-41 materials was studied using TGA in air flow. The number of acetylacetonate molecules released per chromium atom was 3 in all samples. Therefore, taking into account this ratio (acetylacetonate/Cr = 3) and the absence of aluminium-acetylacetonate species evidenced by FT-IR, it is reasonable to conclude that the attachment of Cr species to MCM-41 surface may result from the interaction of support hydroxyl groups with the acetylacetonate ligands through H-bonds. Besides, on Al-MCM-41, the quasi π -

electron system of the acetylacetonate ligands could interact with electron acceptor centres like Al^{3+} ions (Scheme 1) [13, 14].

Diffuse reflectance spectra of as-synthesized and calcined catalysts are shown in Figure 2. Typical Cr (III) d-d absorption bands at 327, 394 and 563 nm were observed in fresh catalysts (Figure 2 I) that, by analogy with chromium (III) acetylacetonate, can be attributed to ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ transitions respectively, in the pseudo-octahedrally coordinated chromium (III) ions [15]. Calcination of the as-synthesized samples resulted in the complete disappearance of these d-d bands (Figure 2 II) owing to Cr (III) oxidation to Cr(VI) ions. The later were characterized by two absorption bands at 350 and 460 nm which can be assigned to the $\text{O} \rightarrow \text{Cr}^{6+}$ charge transfer transitions of chromate and dichromate [16]. The absence of chromium (III) oxide band at 560 nm indicates the total oxidation of Cr^{3+} to Cr^{6+} during the calcination step.

A conventional Cr/SiO₂ catalyst (1 wt% Cr) and the AlMCM-30(0.89 wt% Cr) sample were tested in ethylene polymerization reaction in order to compare their relative activities as they presented similar chromium contents in the typical range of the Phillips catalysts employed in slurry-phase polymerization processes (0.9-2 wt% Cr).

Table 2 summarizes both catalysts activities and the properties of the obtained polymers. It is clear that the mesoporous sample was almost twice as active as the conventional Cr/silica catalyst. Besides, the catalytic performance of AlMCM-30(0.89 wt% Cr) sample was much better than those previously reported by Weckhuysen et al. (14 kg PE/g Cr h, obtained at a reaction temperature of 104 °C and 31.4 bar of ethylene pressure) using a typical Al-MCM-41 (Si/Al = 27 ; 1 wt% Cr) [8]. This difference in activity must be related to the fact that the swelled Al-MCM-41 mesoporous material has both larger pore size and pore volume than silica and typical MCM-41 samples. So, in swelled MCM-41 mesoporous

materials, the formation of polyethylene chains is less limited than in conventional MCM-41 samples where active Cr sites would be quickly blocked.

The melting temperatures (T_m) of the obtained polymers were around 135-140 °C indicating the formation of linear high-density polyethylene. The polymer product formed with AlMCM-30 (0.89 wt% Cr) catalyst showed slightly higher values of High Load Melt Index (HLMI) than the PE obtained with the conventional Cr/SiO₂ catalysts, which is related with its lower bulk density and melting temperature values.

XRD, FTIR and SEM techniques were also used to characterize polyethylene formed with Cr/SiO₂ and AlMCM-30(0.89 wt% Cr) catalysts. XRD patterns were typical of crystalline polyethylene with [110] and [200] diffraction peaks at 21.6 ° and 24° respectively. FTIR spectra presented the characteristic vibrations at 715 and 1473 cm⁻¹ assigned to the methylene groups of PE in their rocking and bending mode. Bands at 2850 and 2919 cm⁻¹ (symmetric and asymmetric methylene stretching modes of polyethylene) were also observed.

Finally, the SEM images of the resulting polymers revealed granular particles of different size depending on the catalyst used (Figure 3). As can be seen, conventional Cr/SiO₂ material produced polyethylene particles larger than those obtained with AlMCM-30(0.89 wt% Cr) sample, because polymer particles replicate the morphology of catalyst support [17].

4. Conclusions.

IR and Uv-Vis spectra of catalysts obtained by grafting of Cr(acac)₃ over swelled MCM-41 and Al-MCM-41 showed that the chromium complex retained their ring structure and no aluminium-acetylacetonate species were produced. Calcination of the as-synthesized catalysts resulted in the complete oxidation of Cr(III) to Cr(VI).

Considering the (acetylacetonate/Cr) ratio and the absence of aluminium-acetylacetonate species, the attachment of Cr species to MCM-41 surface may result from the

interaction of support hydroxyls groups with the acetylacetonate ligands through H-bonds. Besides, on Al-MCM-41, the quasi π -electron system of the acetylacetonate ligands could interact with electron acceptor centres like Al^{3+} ions.

Mesoporous AlMCM-30 (0.89%Cr) sample showed higher polyethylene production than conventional Cr/SiO₂ catalyst and polymer obtained with both catalysts is high-density polyethylene. According to these results, swelled MCM-41 materials are promising supports to prepare new Phillips-type catalysts with high polymerization activity.

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Table 1. Textural properties of supports and chromium contents of catalysts after grafting procedure.

Support	Si/Al ^a	d [100] (Å)	S _{BET} (m ² /g)	V _{pore} (cc/g)	D _{pore} (Å) ^b	Cr (wt %) ^a
Si-MCM	∞	86.5	786	1.54	72	0.26
AlMCM-90	89.4	88.9	999	1.83	73	0.60
AlMCM-60	60	67.0	990	1.71	70	0.78
AlMCM-30	28.4	68.4	977	1.87	72	0.89

^a Determined by ICP analysis

^b Determined from the maximum of BJH pore size distribution

Table 2. Comparison of ethylene polymerization results.

Catalyst	S_{BET} (m^2/g)	V_{pore} (cc/g)	D_{pore} (\AA) ^c	Activity $\left(\frac{\text{kgPE}}{\text{gCrh}}\right)$	POLYETHYLENE PROPERTIES		
					T_{m} ($^{\circ}\text{C}$) ^d	HLMI $\left(\frac{\text{g}}{10\text{min}}\right)$	Bulk Density (g/cc)
Cr/SiO ₂ ^a (1wt% Cr) ^b	462	1.47	180	138.4	140.7	0.07	0.36
AlMCM-30 ^a (0.89%Cr) ^b	977	1.87	72	248.6	138.6	0.09	0.24
Al-MCM-41 ^c (1wt% Cr) ^b	1070	1.42	28	140.0	136	0.56	0.21

^a Reactor temperature = 85 °C, ethylene pressure = 40 bar.

^b Determined by ICP analysis

^c Determined from the maximum of BJH pore size distribution

^d Melting temperature from DSC

^e Data taken from reference [8] (Reaction temperature of 104 °C and 31.4 bar of ethylene pressure).

Figure Captions

Figure 1. FTIR spectra of (a) Si-MCM (0.26%Cr), (b) AIMCM-90 (0.6 wt% Cr), (c) AIMCM-30 (0.89 wt% Cr) and (d) Cr(acac)₃. The corresponding support spectrum has been subtracted from each catalysts spectrum.

Figure 2. DR UV-Vis spectra of as-synthesized (I) and calcined (II) catalysts: (a) Si-MCM (0.26%Cr) (b) AIMCM-90 (0.6 wt% Cr) (c) AIMCM-30 (0.89 wt% Cr).

Figure 3. SEM pictures of polyethylene formed by (a) conventional Cr/SiO₂ catalyst and (b) AIMCM-30 (0.89 wt% Cr) sample.

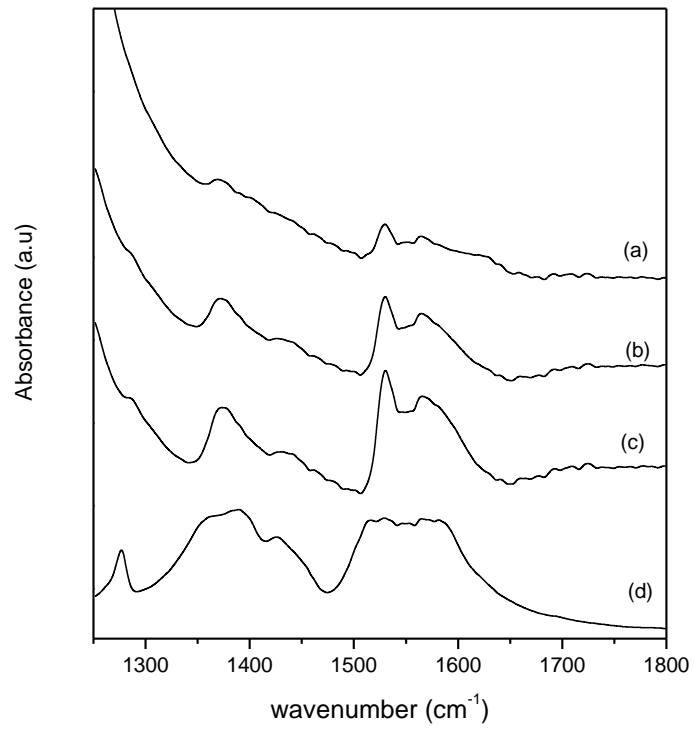


Figure 1

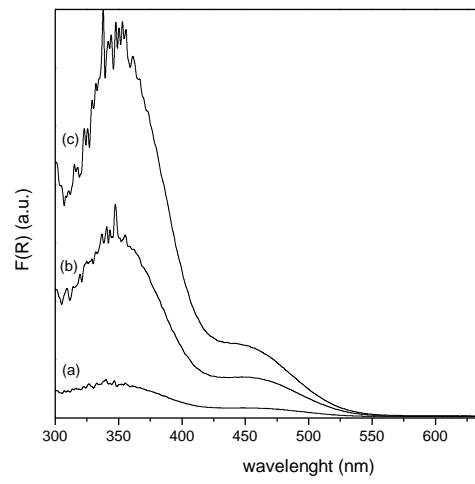
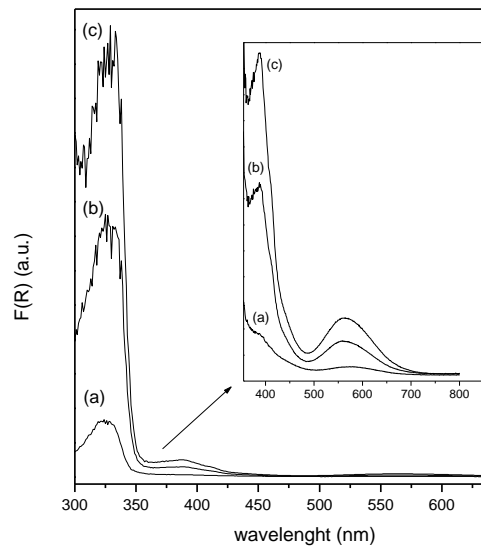


Figure 2

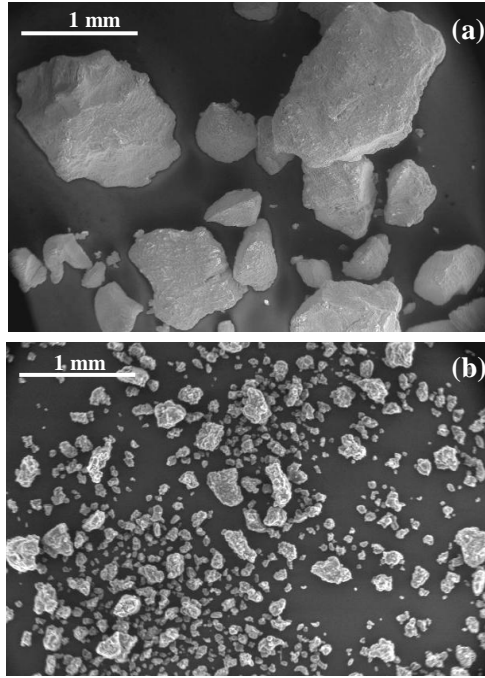
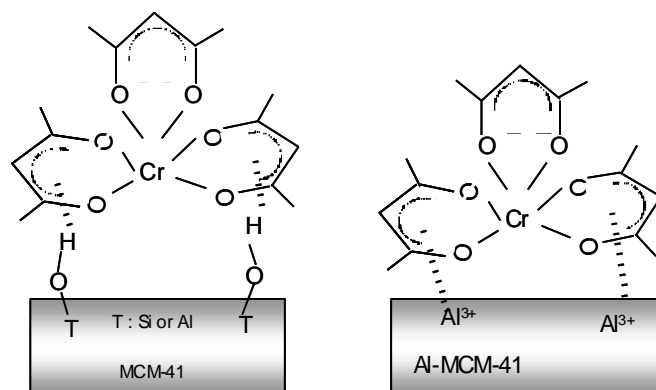


Figure 3



Scheme 1