

# Ethylene polymerization over chromium supported onto SBA-15 mesoporous materials

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Ethylene polymerization catalysts have been prepared by incorporation of chromium (III) acetylacetonate onto siliceous SBA-15 swelled mesoporous materials. Catalysts characterization includes DRX, FTIR, UV-vis spectroscopy, nitrogen physisorption, TGA and ICP analysis. Chromium anchorage through H-bonds was observed in Cr/SBA-15 catalyst prepared by incipient wetness impregnation. On the contrary, when catalysts were prepared by grafting, a ligand exchange reaction may occur. For similar chromium contents, catalyst prepared by grafting showed higher polymerization activity than catalyst prepared by incipient wetness impregnation. Regarding polymer properties, Cr/SBA-15 catalyst prepared by impregnation gave polyethylene with slightly higher molecular weight, polydispersity, bulk density and melting temperature than polyethylene obtained from grafted catalyst.

## 1. INTRODUCTION

In the early 1950's J.P. Hogan and R. L. Banks discovered that chromium oxide supported on silica and other carriers catalyzed the polymerization of olefins to high polymers [1]. Since then, this catalytic system has showed an important development and different varieties of chromium-based catalysts are used in the Phillips polymerization process, because of the wide variations in the polymer properties depending upon the catalyst molecular structure [2]. Today, chromium catalysts are responsible for the commercial production of more than one third of all polyethylene sold worldwide [3]. The activity of these polymerization catalysts is very sensitive to the textural properties of the supports and particularly to their porosity [4]. Therefore, an adequate control of the porous structure of the supports during their synthesis gives an opportunity to prepare new polymerization catalysts.

Recently, the synthesis of new mesoporous silica, SBA-15 has been reported under acidic conditions using triblock copolymers as structure directing agents [5]. The narrow, controlled pore size distribution of these ordered hexagonal materials as well as their large pore openings (5- 30 nm) and high surface areas (600 - 1000 m<sup>2</sup>/g) are attractive properties that make SBA-15 mesoporous materials useful as catalyst supports for polymerization processes.

Besides, the method of chromium incorporation employed could also influence on the polymerization behaviour of Phillips catalysts. Conventionally, chromium oxide systems supported on silica and alumina systems have been prepared by impregnation of the dispersed support with a solution of chromium compounds, followed by their transformation to the catalytically active phase upon thermal treatment. However, gas phase deposition and grafting of chromium complexes onto reactive surface structures are two alternatives to traditional

incipient wetness impregnation method, which allow obtaining catalytic systems with different properties [6-7].

We compare here the properties and ethylene polymerization behaviour of Cr/SBA-15 catalysts prepared by incipient wetness impregnation and grafting methods.

## 2. EXPERIMENTAL

Siliceous SBA-15 mesoporous support was synthesized in the presence of trimethylbenzene (TMB) as swelling agent, according to the process previously reported [5]. This material, after drying and calcination at 550°C, was stirred with different solutions of chromium (III) acetylacetonate, Cr(acac)<sub>3</sub>, in toluene (5, 15, 35 and 56 grams of Cr per 100 grams of solid) for 24 hours under reflux. Then, solids were recovered by filtration and intensively washed with toluene. Besides, one additional SBA-15 sample was incipient wetness impregnated with a fixed amount of Cr(acac)<sub>3</sub> in toluene to get 1 wt% chromium loading. Finally, catalysts were calcined with air on a fluidized bed reactor up to 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). Pore size was obtained from the maximum of BJH pore size distribution. X-ray powder diffraction (XRD) data were acquired on a Philips diffractometer using Cu K $\alpha$  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 measurements (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. The carbon content of the as-synthesized catalysts was determined with an elemental Vario EL III analyzer by burning at 1150 °C.

Ethylene polymerizations were carried out in a 2-litre stainless steel stirred Autoclave Engineers apparatus. Reaction conditions were 600 r.p.m., 85 °C, 35 bar of ethylene pressure, 5.0 bar of hydrogen and 0.5 mol of 1-hexene using isobutane as solvent. The resulting polyethylene was recovered, filtered and washed with acetone.

DSC analysis of the obtained polymers were recorded from 50 to 180 °C (heating rate = 10 °C/min) with a Mettler Toledo DSC822 apparatus. High load melt index (HLMI) values were determined at 190 °C with a weight load of 21.6 kg using 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. Molecular weights and molecular weight distributions of the polymers were determined by size-exclusion chromatography at 145°C on a Waters 150C Plus instrument, using 1,2,4-dichlorobenzene as a mobile phase. The column set consisted of one PL-Gel 10 $\mu$ m Mixed B (300 x 7.5 mm) and another Polymer PL-Gel 10  $\mu$ m 10E6A (300 x 7.5 mm).

## 3. RESULTS AND DISCUSSION

### 3.1 Catalysts Characterization

The X-ray diffraction pattern of calcined SBA-15 support prepared with TMB showed a (100) peak and (110), (200) and (210) signals at d spacings of 132, 105, 98 and 74 Å,

respectively. These reflections are associated with p6mm hexagonal symmetry typical of SBA-15 materials [5], although the presence of TMB as a swelling micelle agent, leads to structures less organized as evidenced by weak XRD peaks [8]. The prepared catalysts are listed in Table 1, they are denoted as SBA-nG or SBA-nI for grafted or impregnated samples, respectively. The number designed by “n” corresponds to the chromium loading (wt %) of each catalyst.

TABLE 1  
Grafting efficiencies and textural properties of Cr/SBA-15 catalysts

Catalysts	Grafting solution $\left(\frac{g\ Cr\ (solution)}{g\ support}\right) \times 100$	Chromium content (wt %)	Grafting Efficiency (%)	Surface Area (m <sup>2</sup> /g)	Pore Volume (cc/g)	Pore Size (Å)
SBA-15	--	--	--	613	2.20	249
SBA-0.24G	2.5	0.24	9.6	593	2.10	249
SBA-0.42G	15	0.42	2.8	n.d	n.d	n.d
SBA-0.72G	35	0.72	2.1	523	1.94	249
SBA-0.92G	56	0.92	1.6	518	1.96	252
SBA-0.99I	--	0.99	--	537	1.99	247

n.d. = not determined

It can be observed that the chromium anchored onto the calcined SBA-15 supports increased with the initial chromium amount contained in the grafting solution, although chromium incorporation degrees (grafting efficiencies) were always below 10 %. This fact can be explained taking into account that the affinity of  $M^{n+}(acac)_n$  complexes from the liquid phase with the silica surface depends on the shape, stability and metal ions in the complex [9]. In this case, chromium acetylacetonate is an octahedral complex having a high thermal stability and consequently low chemical reactivity towards the support. Besides, the octahedral geometry should generate steric hindrance for bonding to silica surface. The nitrogen adsorption/desorption isotherms at 77 K for calcined SBA-15 support and chromium catalysts (Fig. 1) belonged to type IV typical for mesoporous materials, with a sharp inflexion at a relative pressure around 0.9. Textural properties summarized in Table 1, pointed to a little decrease in both surface area and pore volume with chromium incorporation, while pore size remained almost unaltered.

UV-Vis diffuse reflectance spectra of the as-synthesized SBA-15 chromium supported catalysts are compared with bulk chromium (III) acetylacetonate spectrum in Fig. 2(I). SBA-0.99I sample, prepared by incipient wetness impregnation, and bulk  $Cr(acac)_3$  presented the same colour (violet) and similar spectra with typical Cr (III) d-d absorption bands centred at 325, 390 and 560 nm which can be attributed to  ${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$ ,  ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$  and  ${}^4A_{2g} \rightarrow {}^4T_{2g}(P)$  transitions in the pseudo-octahedral coordinated chromium (III) ions, respectively [10]. Nevertheless, catalysts prepared by grafting (SBA-0.92G and SBA-0.72G) showed a greenish colour and the band placed at 390 nm had almost disappeared from the DRS UV-Vis spectra. Both differences indicated a change in chromium electron configuration [11]. The same trend was observed for SBA-0.42G, and SBA-0.24G catalysts (not shown).

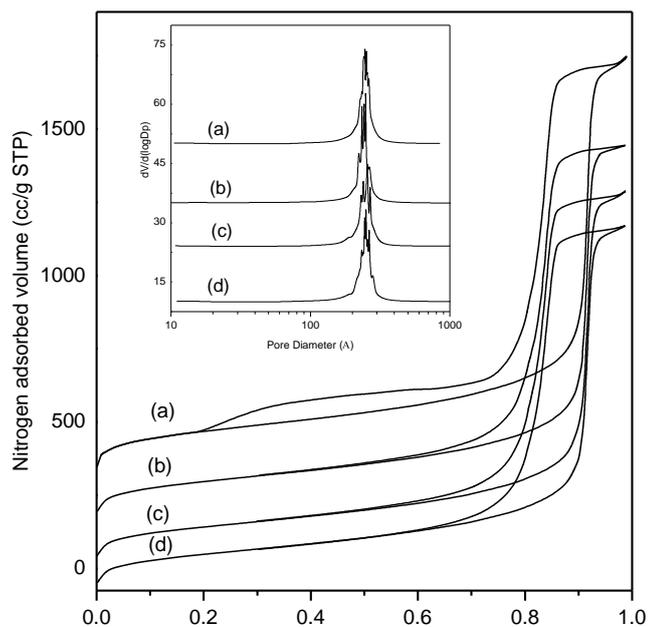


Fig.1. N<sub>2</sub> adsorption/desorption isotherms of: (a) SBA-15 support, (b) SBA-0.99I, (c) SBA-0.92G, (d) SBA-0.72G.

The calcination of the as-synthesized samples resulted in the complete disappearance of d-d bands (Fig. 2 (II)) caused by the oxidation of Cr (III) species to Cr(VI). Hexavalent chromium species were characterized by two absorption bands centred at 350 and 460 nm, which can be assigned to the O $\rightarrow$ Cr<sup>6+</sup> charge transfer transitions of chromate and dichromate species [12]. The absence of Cr<sub>2</sub>O<sub>3</sub> bands at 560 nm indicated the total oxidation of Cr<sup>3+</sup> to Cr<sup>6+</sup> during the calcination step.

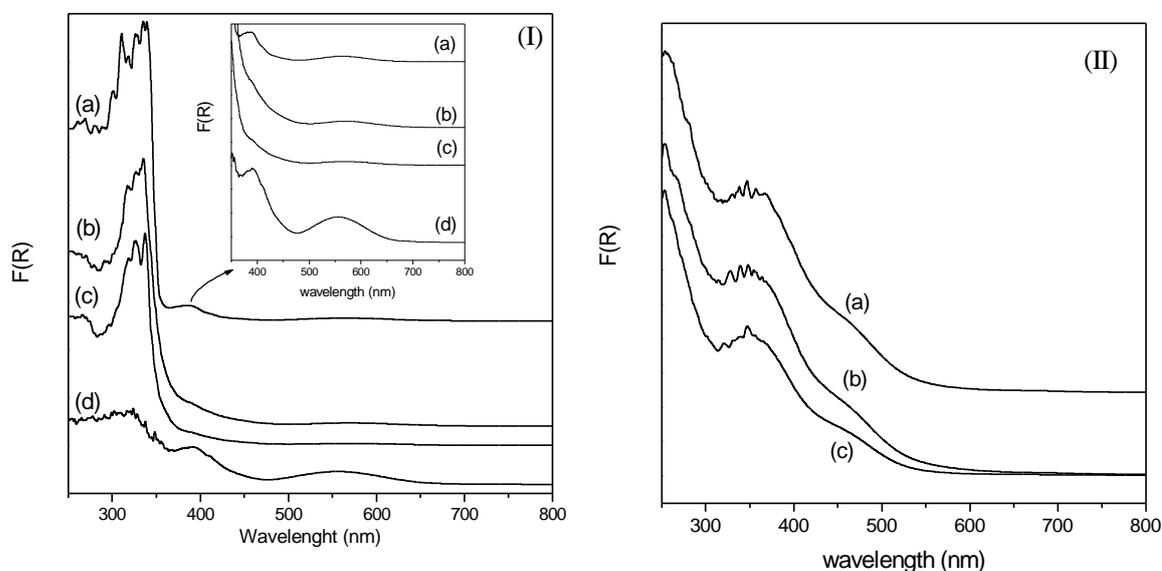


Fig.2. DRS UV-Vis spectra of as-synthesized (I) and calcined (II) catalysts: (a) SBA-0.99I (b) SBA-0.92G (c) SBA-0.72G (d) Cr (acac)<sub>3</sub>.

FTIR spectra of chromium supported catalysts and bulk chromium acetylacetonate are shown in Fig. 3. Both grafted and impregnated samples showed typical acetylacetonate ligands bands centred at  $1525\text{ cm}^{-1}$  due to the vibration of the C=C bonds, bands at  $1378$  and  $1577\text{ cm}^{-1}$  corresponding to vibration of the C=O bonds and one band located at  $1425\text{ cm}^{-1}$  related to the vibration of C-H bonds present in  $\text{CH}_3$  groups [13-14]. Therefore, acetylacetonate ligands retained their ring structure during the interaction with SBA-15 support surface.

Removal of acetylacetonate ligands from the chromium complexes anchored onto the siliceous mesoporous support was studied by TG analysis in airflow (Fig. 4).

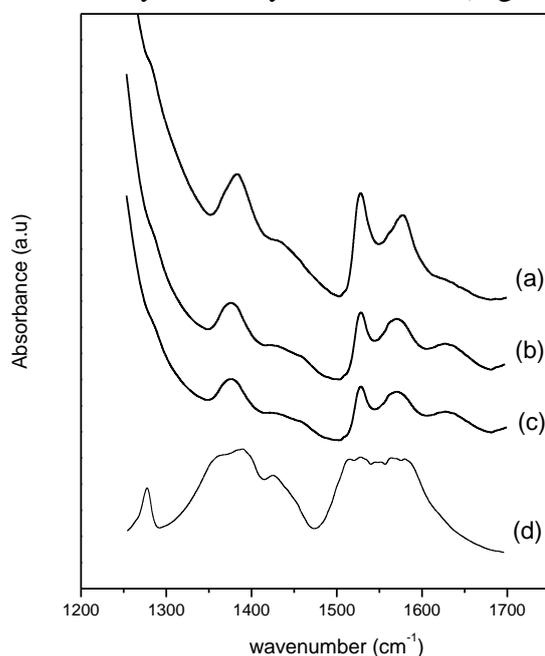


Fig.3. FT- IR spectra of (a) SBA-0.99I (b) SBA-0.92G (c) SBA-0.72G (d)  $\text{Cr}(\text{acac})_3$ .

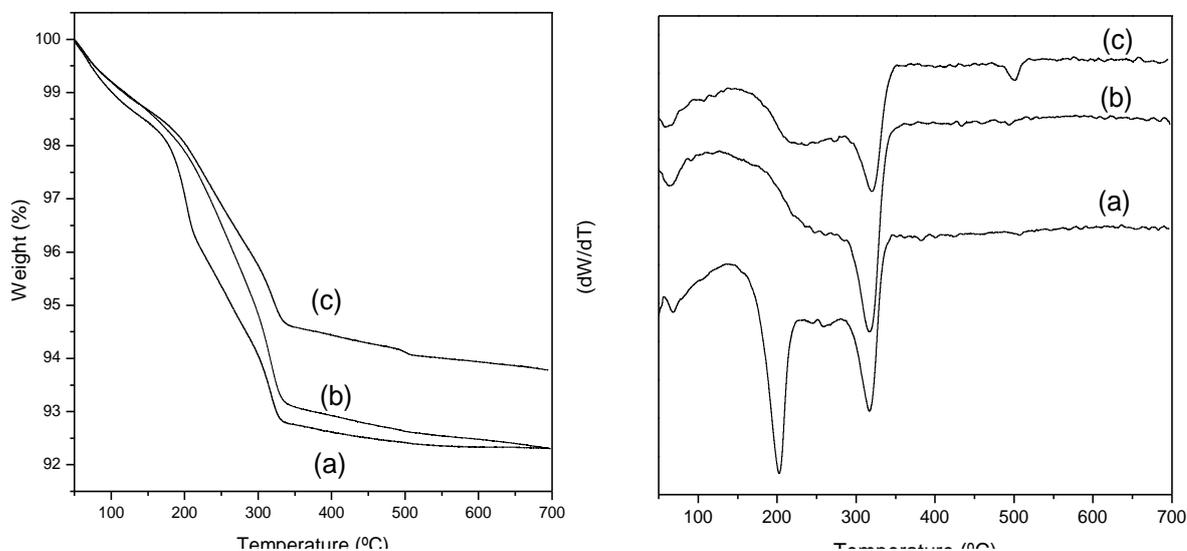
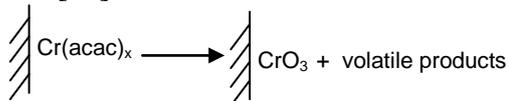


Fig.4. TGA analysis of (a) SBA-0.99I (b) SBA-0.92G (c) SBA-0.72G

Weight losses associated with acetylacetonate elimination were observed in all samples in the 150 – 350 °C temperature range. Taking into account that acac ligands removal was accompanied by oxidation of  $\text{Cr}^{3+}$  ions to  $\text{Cr}^{6+}$ , the observed weight losses can be described as follows [15] :



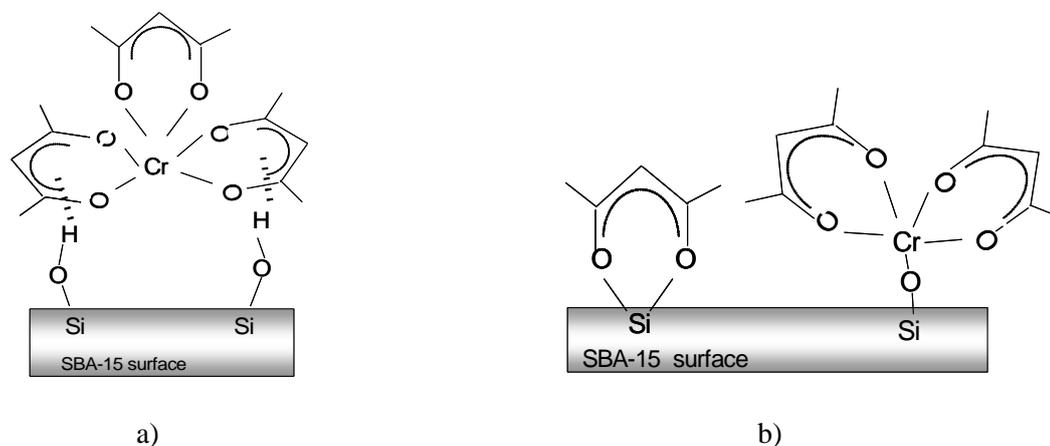
So it is possible to determine “x” values corresponding to the (acac ligands/chromium ions) ratios in the chromium species anchored to the solid surface. These molar ratios determined by TGA and by elemental analysis, are presented in Table 2.

TABLE 2.  
(Acac/Cr) molar ratios calculated by TG and elemental analysis.

Sample	TG Analysis		Elemental Analysis	
	(Acac/Cr) molar ratio	DTG Peaks (°C)	Carbon (wt %)	(Acac/Cr) molar ratio
SBA-0.24G	3.35	250 ; 318	0.82	2.95
SBA-0.42G	3.18	250 ; 318	n.d.	n.d.
SBA-0.72G	2.97	250 ; 318	2.46	2.96
SBA-0.92G	3.18	250 ; 318	3.24	3.05
SBA-0.99I	3.00	207 ; 318	3.73	3.23

n.d. not determined

DTG profile of SBA-0.99I catalysts presented two peaks at 207 and 318 °C, with an (acac/Cr) ratio was close to 3. According to the literature [13-14], the peak at 207 °C can be attributed to the elimination of acac ligands involved in hydrogen bonding with surface hydroxyls groups, while the second peak could be assigned to the thermal decomposition of acac ligands unfavourably oriented for the interaction with support surface. Therefore, the interaction of  $\text{Cr(acac)}_3$  with SBA-15 support by the incipient wetness impregnation method, may occur through a H-bonding mechanism between support hydroxyl groups and the quasi  $\Pi$ -electron system of the acac ligands (Scheme 1a) [13-14]. This result was in agreement with the preservation of  $\text{Cr(acac)}_3$  structure deduced from UV-vis spectra (Fig. 2 Ia).



Scheme 1. Proposed mechanisms for the interaction between  $\text{Cr(acac)}_3$  and SBA-15 surface: a) H-bonding, b) Covalent bonding.

On the other hand, samples prepared by grafting showed a DTG profile with only one peak at 318 °C and a shoulder at 250 °C. Again, the (acac/Cr) ratios found were close to 3. In these catalysts, the absence of the low temperature peak (207 °C) and the greenish colour observed, pointed to no acac ligands hydrogen bonded with surface silanol groups. Based on these evidences, Scheme 1b was proposed to describe the interaction of Cr(acac)<sub>3</sub> with SBA-15 support during the grafting process. Here, chromium is covalently bonded to the SBA-15 surface because of a ligand exchange reaction between acetylacetonate and surface OH groups [13,16].

### 3.2. Activity results in ethylene polymerization.

Comparative ethylene polymerization reactions were carried out using two catalysts with similar chromium content as SBA-0.99I and SBA-0.92G, prepared by impregnation and grafting methods respectively. Table 3 summarizes catalysts activities and properties of the obtained polymers. It can be observed that polymerization activities clearly depend on catalysts preparation method. So the SBA-0.99G sample prepared by grafting presented similar activity in comparison with conventional Cr/SiO<sub>2</sub> catalysts [17-18]. However, the catalyst prepared by impregnation exhibit a lower activity.

TABLE 3.

Comparison of ethylene polymerization results between impregnated and grafted catalysts

Catalyst	Activity (g PE/g cat h)	POLYETHYLENE PROPERTIES				
		Mw	Mw/Mn	HLMI (g/10 min)	Bulk Density (g/cc)	T <sub>m</sub> (°C) <sup>a</sup>
SBA-0.99I	1493	426210	37.58	4.1	0.33	131.8
SBA-0.92G	3187	362400	34.20	4.2	0.32	131.5

<sup>a</sup> Melting temperature measured by DSC

According to the literature [2, 17-19], the differences in activity of both types of catalysts may be related with the presence of lower hydroxyl population and/or more reducible chromium species on the SBA-0.92 G catalyst surface, since both catalysts (impregnated and grafted) presented very similar textural properties after calcination at 600 °C. Table 3 evidences that the impregnated catalyst led to a polymer with higher molecular weight and consequently lower HLMI than polyethylene obtained with grafted catalyst. On the other hand, melting temperatures (T<sub>m</sub>) of the obtained polymers were slightly lower than typical values of high-density polyethylene (135-140 °C). This fact can be explained by the effect of 1-hexene and hydrogen over polyethylene properties [18].

XRD and FTIR (not shown) were also used to characterize the obtained polyethylene with SBA-0.99I and SBA-0.92G catalysts. In both cases, XRD patterns were typical of crystalline polyethylene with [110] and [200] diffraction peaks at 21.6 ° and 24° respectively, [20]. FTIR spectra indicated the characteristic vibrations at 715 and 1473 cm<sup>-1</sup> assigned to the methylene groups of PE in their rocking and bending mode. Bands at 2850 and 2919 cm<sup>-1</sup> (symmetric and asymmetric methylene stretching modes of polyethylene) were also observed [21].

## 4. CONCLUSIONS.

Ethylene polymerization catalysts have been prepared by grafting and impregnating chromium (III) acetylacetonate onto siliceous SBA-15 swelled mesoporous material.

Textural properties of the catalysts pointed to a little decrease in surface area and pore volume with chromium incorporation, while pore size remained almost unaltered. The amount of chromium anchored onto the SBA-15 surface increased with grafting solution concentration although low grafting efficiencies (<10%) were achieved. The fresh impregnated sample showed the same colour (violet) and UV-vis spectrum, with Cr (III) d-d bands centred at 325, 390 and 560 nm, than the bulk Cr(acac)<sub>3</sub>. Nevertheless, uncalcined samples prepared by grafting showed a greenish colour and UV-vis spectra, where the 390 nm band had almost disappeared. Calcination of the as-synthesized catalysts resulted in the complete disappearance of d-d bands due to the oxidation of Cr(III) to Cr(VI) species.

The interaction of chromium acetylacetonate molecules with the SBA-15 support surface occurs without a loss of acac ligands since the (acac/Cr) ratios found in the chromium complexes fixed to SBA-15 surface were around three for all the prepared catalysts. The attachment of Cr species to SBA-15 surface depends on preparation method. Chromium acetylacetonate may preserve its structure in catalyst prepared by impregnation. In this case, the interaction with the support may occur through an H-bonding between support hydroxyl groups and the quasi  $\pi$  electron system of the acac ligands. On the contrary, a ligand exchange reaction may occur during grafting process.

Polymerization activity also depends on catalyst preparation method. For similar chromium content, catalyst prepared by grafting is much more active than catalyst prepared by impregnation. Regarding polymer properties, Cr/SBA-15 catalyst prepared by impregnation leads to polyethylene with slightly higher molecular weight, polydispersity, bulk density and melting temperature than the polyethylene obtained with the grafted catalyst.

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