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Preparation of 1,3,5-tribenzylhexahydro-1,3,5-triazine-$CrCl_3$ catalyst supported on SiO_2 and activity studies in ethylene polymerization

Jun Wang, Hugo Leeman, Robert A. Schoonheydt *

Centre for Surface Chemistry and Catalysis, Kasteelpark Arenberg 23, Katholieke Universiteit Leuven, 3001 Leuven, Belgium

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Abstract

In the present work, 1,3,5-tribenzylhexahydro-1,3,5-triazine-$CrCl_3$ (TAC-$CrCl_3$) complex was supported on Stöber silica and on commercial porous SiO_2. Ethylene polymerization and copolymerization were carried with methylaluminoxane (MAO) as co-catalyst. In the polymerization of ethylene, the silica-supported TAC-$CrCl_3$ catalysts exhibit activity values from 200 to 374 kg/molCr/h with Stöber silica being the best. In the co-polymerization of ethylene with 1-hexene, the yields of polymer are 34–117 kg/molCr/h; the highest value is again obtained with Stöber silica as a support. The polymers were characterized by X-ray diffraction, solid-state ^{13}C NMR, viscosimetric analysis and differential scanning calorimeter (DSC). The polymers have molecular weights of 23,000–40,000 g/mol; crystallinity varies from 60 to 68% and melting points in the range 125–131 °C.

Keywords: Chromium catalyst; Polymerization; Ethylene; Stöber silica

1. Introduction

A great deal of effort has been devoted to the synthesis and characterization of silica-supported transition metals because of their widespread catalytic applicability [1–6]. Silica-supported chromium catalysts have attracted much attention over the years because of their commercial impact in the production of high-density polyethylene [3–5]. Besides traditional amorphous and porous silica, new mesoporous silica such as MCM-41, MCM-48 and SBA-15 were used to immobilize metal catalysts [5–7]. One method to create monodisperse silica particles is the sol–gel method developed by Stöber [8]. Silica particles prepared by the Stöber process are attractive not only for sensors and opto-electronic devices but also for catalyst supports. This is because the Stöber silica particles have low impurity levels, a very well defined particles size and narrow particle size distributions [9]. The surface charge behavior of Stöber silica can be controlled by methanol washing, which leads to formation of methoxy group [10]. Recently, [(triazacyclohexane)$CrCl_3$] complexes were synthesized, and they were found to be active in ethene polymerization [11,12]. It was of interest to load these organic Cr complexes on Stöber silica particles and to investigate the influence of the support on the polymerization activity.

In this paper, the 1,3,5-tribenzylhexahydro-1,3,5-triazine-$CrCl_3$ (TAC-$CrCl_3$) complex was supported on Stöber silica and on commercial porous SiO_2, respectively. The influence of different types of silica on the catalytic activity in the ethylene polymerization and the copolymerization of ethene with 1-hexene were studied. The polymers were characterized by X-ray diffraction, solid-state ^{13}C NMR, viscosimetric analysis and differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials

Commercial porous silica (SP18-8506, GRACE GmbH, pSiO_2) was used. Methylaluminoxane (MAO), 1,3,5-tribenzylhexahydro-1,3,5-triazine (TAC) and chromium(III) chloride tetrahydrofuran complex ([$CrCl_3(THF)_3$]) were obtained from Aldrich.

* Corresponding author.
E-mail address: Robert.Schoonheydt@agr.kuleuven.ac.be (R.A. Schoonheydt).

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2.2. Synthesis of TAC-$CrCl_3$ and catalysts TAC-$CrCl_3/SiO_2$

TAC-$CrCl_3$ complex was synthesized following a literature recipe [12]. Stöber silica particles (400 nm, washed with methanol, $sSiO_2$) were prepared according to the literature [9,10]. 49.5 mg TAC-$CrCl_3$ were impregnated on 0.95 g silica particles in 50 ml chloroform. After agitation in an ultrasonic bath for 30 min, the suspensions were placed in the air to allow solvent evaporation. The loading is 0.5 wt% Cr, corresponding to 0.0962 mmolCr/g catalyst.

2.3. Polymerization

All polymerization experiments were carried out in 1000 ml glass flasks equipped with mechanical stirrer, thermocouple and gas inlet tube. Two hundred and fifty milliliters of toluene and 15.5 μmol Cr catalysts were added to the reactor, and N_2 was introduced into the reactor through the inlet tube. After the solution was heated to 40 °C, the MAO solution (Al:Cr = 320:1) in toluene was added. Then 20 l/h of ethylene were bubbled through the solution for one hour. In the co-polymerization experiment, 5 ml of hexene was added before and 25 ml (addition funnel, 15 min) during the addition of ethylene. The reaction was stopped by addition of a mixture of conc. HCl (15 ml) and methanol (50 ml). In addition, 250 ml methanol was added into the reaction mixture. The polymer was collected by filtration and washed with methanol, then dried at 70 °C for 10 h.

2.4. Characterization techniques

Solid-state ^{13}C NMR spectra were recorded on a Bruker AMX300 apparatus. The spinning frequency of the rotor was 5.0 kHz. Melting points of the polymers were by determined by differential scanning calorimetry (DSC). X-ray diffraction measurements were performed at room temperature using a D5000 Matic X-ray diffractometer with Cu Kα radiation. The molecular weights of the polymers were determined by viscosimetric analysis using decalin as solvent at 135 °C. UV–vis spectra were recorded on a Perkin-Elmer Lambda 12 apparatus and UV–vis–NIR in the diffuse reflectance mode (DRS) on a Varian Cary 5.

3. Results and discussion

3.1. Characterization of the catalysts

Fig. 1(a) show the UV–vis spectrum of TAC-$CrCl_3$ in chloroform. Three absorption bands are visible: an intense band at 273 nm and two weak ones around 510 and 710 nm. The band at 273 nm is attributed to the π–π* transition of the TAC ligand. The bands at 510 and 710 nm are the characteristic peaks of Cr^{3+} species, attributed, respectively, to the $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ transitions of Cr^{3+} in pseudo-octahedral coordination environment [13]. Diffuse reflectance spectra (DRS) of TAC-$CrCl_3$/p(s)SiO_2 in the UV–vis region are presented in Fig. 1(b and c). The DRS of the catalysts TAC-$CrCl_3$/p(s)SiO_2 show the characteristic bands of Cr^{3+} at 500 and 710 nm corresponding, respectively, to the $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ transitions, indicating that the structure of the TAC-$CrCl_3$ complex on silica is retained. In the UV region, the bands are broad and complex. This is due to the overlapping of the π–π* transition of TAC-$CrCl_3$ with the background due to silica.

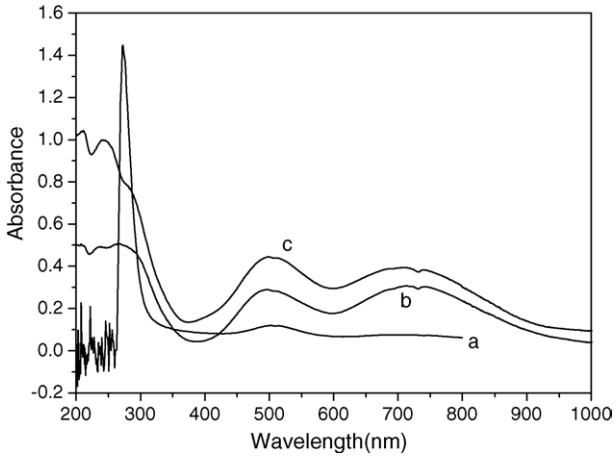

Fig. 1. (a) UV–vis of TAC-$CrCl_3$ in $CHCl_3$ solution, (b) DRS of TAC-$CrCl_3$/$sSiO_2$ and (c) DRS of TAC-$CrCl_3$/$pSiO_2$.

3.2. Catalyst activity

The yields of the homogeneous (TAC-$CrCl_3$) and heterogeneous catalysts (TAC-$CrCl_3/sSiO_2$ and TAC-$CrCl_3/pSiO_2$) for ethylene polymerization and copolymerization are given in Table 1. One observes that for the polymerization of ethylene TAC-$CrCl_3/sSiO_2$ is the best catalyst, while TAC-$CrCl_3/pSiO_2$ gives the same yield as the homogeneous catalyst. In the copolymerization of ethylene with 1-hexene, the activity is less. This is in agreement with the literature [14]. The yields follow the order: TAC-$CrCl_3/sSiO_2$ > TAC-$CrCl_3/pSiO_2$ > TAC-$CrCl_3$. Thus, immobilization of catalytically active complex has a positive effect on the polymer production. The reason for this behavior is not fully clear. The commercial SiO_2 ($pSiO_2$) is porous, while Stöber silica ($sSiO_2$) is a nonporous material [9]. In addition, washing with methanol gives methoxy groups, thus decreasing the amount silanol groups on the silica surface [10]. As a consequence, TAC-$CrCl_3$ is primarily immobilized on the external surface of Stöber silica, while it is partially located in the pores of $pSiO_2$. In the former case, all TAC-$CrCl_3$ is available for reaction, which is not the case for TAC-$CrCl_3$/$pSiO_2$. If this reasoning is true, then the activity of the homogeneous complexes similar to that of TAC-$CrCl_3/pSiO_2$ must be ascribed to aggregation of Cr species in solution during reaction. In fact, different parameters may change the activity in the presence of silica, such as the interaction of MAO with Cr and with silica. This explanation is hypothetical and more in depth characterization is necessary. In any case, when the reaction is stopped with methanol and HCl, and the polymer is filtered off, a strong absorbance at 365 nm indicative of Cr can be found in the remaining solution by UV–vis. When the

Table 1
Yield and properties of polymers

	Yield (kg/molCr/h)	Yield (g/gSiO_2/h)	Number of polymer chain/Cr/h	mp (°C)	Crystallinity (%)	MW ($\times 10^{-4}$)
Polymer 1 catalyst: TAC-$CrCl_3$	213	–	9.26	125.8	68	2.3
Polymer 2 TAC-$CrCl_3$/pSiO_2	200	20.2	7.14	127.8	62	2.8
Polymer 3 TAC-$CrCl_3$/sSiO_2	374	37.8	12.06	127.5	63	3.1
Polymer 4 TAC-$CrCl_3$	34	–	0.85	131.0	64	4.0
Polymer 5 TAC-$CrCl_3$/pSiO_2	65	6.57	2.41	127.0	60	2.7
Polymer 6 TAC-$CrCl_3$/sSiO_2	117	11.83	4.03	127.3	63	2.9

Polymer 1–3 (polymerizations of ethylene), polymer 4–6 (co-polymerizations of ethylene with 1-hexene).

reaction is stopped by decreasing temperature to room temperature without addition of HCl and methanol, and the polymer is separated from the solution, the polymer became light green in the air. This is indicative for a physical mixture of catalyst with Cr and polymer. The remaining solution did not show activity. When MAO was added to a toluene suspension containing TAC-$CrCl_3$/sSiO_2, and the white suspension was filtered off, no Cr absorbance could be detected in the solution by UV–vis. If, first MAO is added, then HCl, to TAC-$CrCl_3$/sSiO_2 suspension, a solution with two phases was formed. The upper layer was colorless and transparent, and the bottom layer was yellow, indicative of Cr species, and silica particles deposited on the wall of the glass. We conclude from the experiment that HCl is needed to detach Cr from the catalyst particles into solution. In the absence of air and in catalytic condition, the catalyst is heterogeneous.

3.3. Characterization of polymers

The polymers were characterized by X-ray diffraction, DSC and viscosimetric analysis The XRD spectrum of polymer 3 (see Fig. 2) shows two main peaks at $2\theta = 21.6^\circ$ and 24.0°. The crystallinity was determined by the Gaussian decomposition, considering the two peaks, ascribed to the crystalline phase, and the broad area under the peaks, ascribed to the amorphous phase [15]. A crystallinity of 60–68% is obtained, irrespective of the type of catalyst and type of polymer. The data are shown in Table 1 together with the DSC data. The polyethylene obtained with the homogeneous catalyst has the lowest meting point (mp), while the copolymer obtained with the homogeneous catalyst has the highest meting point. The molecular weights are also listed in Table 1. The molecular weights (MW) of the polymers lie in the range 23,000–40,000. It is found that the TAC-$CrCl_3$/pSiO_2 and TAC-$CrCl_3$/sSiO_2 system can increase the molecular weight of polyethylene from 23,000 to, respectively, 28,000 and 31,000 in the polymerization of ethylene. In the copolymerization, the copolymer obtained with TAC-$CrCl_3$ catalyst have higher molecular weight (40,000) than those obtained with TAC-Cr/p(s)SiO_2 catalysts (27,000 and 29,000, respectively). There is a clear relation between melting points and molecular weight: the highest melting points being associated with the polymer of the highest molecular weight.

We investigated the copolymer obtained with TAC-$CrCl_3$/sSiO_2 by solid-state ^{13}C NMR (Fig. 3a). It shows that main peak (CH_2) at 33 ppm is strong and the peak of methyl groups (15.5 ppm) is very weak. This indicates that copolymers were obtained with very low co-monomer content. The similar phenomena were observed by others [14]. The solid-state ^{13}C NMR spectrum of the polyethylene obtained with TAC-$CrCl_3$/sSiO_2 is shown in Fig. 3b. The observations are the same as those with the copolymer. It indicates that polyethylene is linear and that there are very few methyl branches incorporated in the polyethylene backbone. It follows that there is no observable difference between polymer and copolymer. Thus, there is little co-monomer branch incorporated in the polymer.

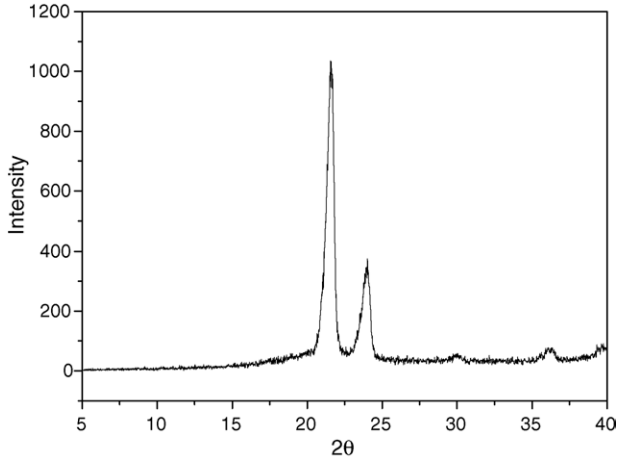

Fig. 2. X-ray spectrum of polymer 3.

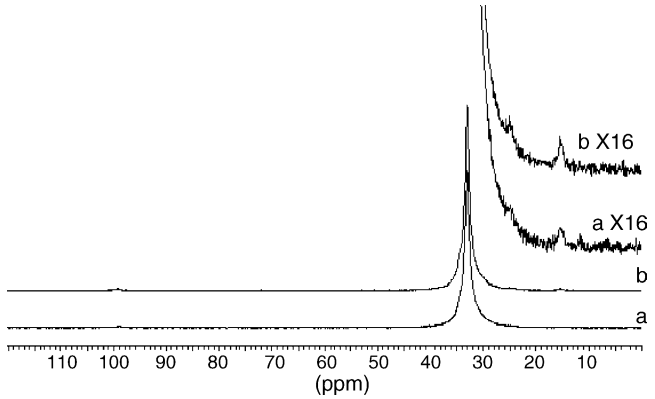

Fig. 3. Solid ^{13}C NMR (a: polymer 6, b: polymer 3, catalyst: TAC-$CrCl_3$/sSiO_2).

4. Conclusions

The aim of the work was centered on the characterization of TAC-$CrCl_3$/SiO_2 catalysts and on the influence of the SiO_2 support on the activity in the polymerization of ethylene and copolymerization of ethylene with 1-hexene. The complex TAC-$CrCl_3$ can be heterogenized on different silicas. The catalysts obtained are active polymerization catalysts, with TAC-$CrCl_3$/sSiO_2 being the most active. This can be attributed to the distribution of TAC-$CrCl_3$ over the outer surface of sSiO_2. The catalysts are heterogeneous catalysts. The polymers have molecular weights in the range 23,000–40,000, crystallinity between 60 and 68% and the melting points between 125 and 131 °C, the highest melting point being associated with the highest molecular weight.

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