Chemical Engineering Journal 147 (2009) 383–390

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Modified-sorbents for acetone adsorption: Application in ethylene polymerization process

Maria Angélica C. Gollmann [a], Larissa B. Capeletti [a], Márcia S.L. Miranda [b], João H.Z. dos Santos [a,*]

[a] Instituto de Química, UFRGS, Av. Bento Gonçalves 9500, Porto Alegre 91501-970, Brazil
[b] Braskem S.A., III Pólo Petroquímico, Via Oeste, Lote 05, Triunfo 95853-000, Brazil

ARTICLE INFO

Article history:
Received 30 August 2008
Received in revised form 3 November 2008
Accepted 14 November 2008

Keywords:
Adsorption
Poison
Ziegler-Natta catalyst
Chrysotile
Polyethylene

ABSTRACT

Ziegler-Natta catalysts are commonly employed in alfa-olefin (co)polymerization. Such systems are extremely sensitive to some organic compounds, which may act as poison, reducing polymer productivity. Among them, oxygenated compounds such as acetone can cause catalyst deactivation. In the present study, silica and chrysotile, in their pure form and after chemical modification with Cu and Ag, were characterized by a series of volumetric, spectroscopic and microscopic techniques. The results are discussed in terms of silanol group density, Lewis acid centers introduced by the metal and textural properties of the support. The resulting sorbents were evaluated in the adsorption of acetone from cyclohexane. Solvent containing acetone was percolated through the investigated sorbents and evaluated in the polymerization of ethylene using Ziegler-Natta catalysts. The best results in catalyst activity were observed in the case of silica or chrysotile modified with Cu.

1. Introduction

The term Ziegler-Natta catalyst encompasses a great variety of catalytic systems based on transition metals that are capable of polymerizing and co-polymerizing α-olefins and dienes. There are numerous polymer grades produced by Ziegler-Natta catalysts, such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), low linear density polyethylene (LLDPE), and polypropylene (PP), to mention a few [1]. Currently, polyethylene production reaches 75.2 million tons a year, with predicted expansion to about 100 million tons in 2010 [2].

Nevertheless, as in any catalyst process, poisoning is an important issue of investigation [3–5]. Specifically, in the case of the titanium-based Ziegler-Natta ($TiCl_4/MgCl_2$) polymerization catalysts, such systems are strongly inhibited by alcohol, organic amines and sulfites, as shown by Eley et al. [6], Ballard et al. [7], Grayson and McDaniel [8] and Vizen et al. [9]. For these catalysts, traces of oxygenated compounds in the parts per billion (ppb) level are enough to engender significant loss of catalytic activity, because they can compete with ethylene for the Ti active site. Chlorine mobility in titanium chlorides has also been modeled as potential responsible for Ziegler-Natta catalyst deactivation [10]. These poisons can be indirectly introduced in the polymerization process by the solvent or by the feed stocks.

In order to avoid such problems, adsorbents have shown to be an economical way to remove contaminants form industrial solvents. For these processes, there are adsorbent materials such as silica, alumina and zeolites which are used industrially for the purification of solvents [11]. In recent years, other minerals in their natural or modified forms have been investigated as alternative potential adsorbents. Examples of the use as adsorbents of chrysotile [12] and kaolin [13] have been recently reported in the literature.

In the present paper, we report the use of chrysotile, native and modified with Ag and Cu, for the adsorption of acetone from cyclohexane, which is the solvent usually employed in the polymerization process. For comparative purposes, silica-based materials were modified with the same metals. The modification of such materials with Ag and Cu (Lewis acid centers) represents an attempt to increase the interaction of acetone with the adsorbent materials, and therefore reduce the poison content in the solvent.

2. Experimental

2.1. Chemicals

All employed chemicals were analytical reagent grade. For adsorption studies, the solutions were prepared using acetone (Mallinckrodt, HPLC) and cyclohexane (VETEC). Silica (provided by Braskem, Camaçari, Brazil) was used as received. Chrysotile (generously donated by SAMA, Mineração de Amianto Ltda, mined in Uruaçu, Brazil) was used in its native form and also after acid treatment.

---

* Corresponding author. Tel.: +55 51 3308 7238; fax: +55 51 3308 7304.
E-mail address: jhzds@iq.ufrgs.br (J.H.Z. dos Santos).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.11.023

For the polymerization experiments, titanium tetrachloride (Merck), acetone and diethylaluminium chloride toluene solution (DEAC) were used without purification. Cyclohexane and toluene were purified by distillation on metallic sodium and benzophenone. Silica Grace 948 ($255\,m^2\,g^{-1}$), employed for the preparation of Ziegler-Natta catalyst, was activated under vacuum ($P < 10^{-4}$ mbar) for 16 h at 110 °C. The support was cooled to room temperature under dynamic vacuum and stored under dried argon.

2.2. Adsorbent modification

2.2.1. Acid treatment

Leached chrysotile was prepared by treating natural chrysotile (ca. 30 g) with hydrochloric acid solution ($1000.0\,mL—5.0\,mol\,L^{-1}$), following a previously reported protocol [14]. The suspension was stirred for 48 h at room temperature. Then, it was filtrated and washed abundantly with water, yielding 15.0 g of product.

2.2.2. Chemical modification of silica and chrysotile

Silica (initially heated at 110 °C for 8 h), chrysotile or leached chrysotile was treated with $CuCl_2$ or $AgNO_3$ aqueous solutions (5–50 wt %) for 4 h at room temperature. Then, the solvent was removed under heating and the resulting material was calcinated in air at 450 °C for 8 h.

2.3. Adsorbent characterizations

2.3.1. X-ray diffraction spectroscopy (XRD)

The crystal structure and phase composition of the adsorbents were analyzed by powder X-ray diffraction, using a Rigaku X-ray diffractometer, model DMAX, with Cu Kα radiation ($\lambda = 0.154178$ nm), at an accelerating voltage of 40 kV. Samples were analyzed as powders.

2.3.2. Scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDX)

Grain morphology and metal distribution in the adsorbents was determined by a JEOL JSM-5800 scanning electron microscope. The samples were placed on an aluminum stub using double-sided adhesive tape and then coated with gold to avoid charging under the electron beam. An accelerating potential of 20 kV and a current of 18 mA were used during the measurement.

2.3.3. Nitrogen adsorption/desorption

Specific pore size distributions, surface area, and pore volume were calculated by the BET and BJH methods after nitrogen adsorption/desorption using a Gemini 2375 (Micromeritics) analyzer. Prior to the analysis, the samples were degassed at 150 °C at 10^{-2} mbar for 4 h.

2.3.4. Diffuse reflectance infrared Fourier transmission spectroscopy (DRIFTS)

DRIFTS measurements were performed on a Bomem instrument, in reflectance mode. The spectra were obtained by coadding 32 scans at a spectral resolution of $4\,cm^{-1}$. Samples were analyzed as powders.

2.4. Equilibrium adsorption studies

A glass column ($L = 15$ cm; Ø0.5 cm) was packed with adsorbent (10 g). The column was loaded with a solution (10 mL) of solvent contaminated with a known concentration of acetone (range 1–200 ppm) in cyclohexane that was percolated through the column under an equilibrium time of 20 min.

2.5. Polymerization

2.5.1. Synthesis of the supported Ziegler-Natta catalyst

In the preparation of the Ziegler-Natta catalyst, activated silica was impregnated with a toluene slurry containing $MgCl_2$ corresponding to 50 wt% $MgCl_2/SiO_2$, at 80 °C for 30 min under reflux. Solvent was removed under vacuum and a $TiCl_4$ cyclohexane solution (corresponding to 3.0% Ti/SiO_2) was added. The resulting slurry was stirred for 1 h at room temperature and filtered through a fritted disk. More details are reported elsewhere [15].

2.5.2. Polymerization reactions

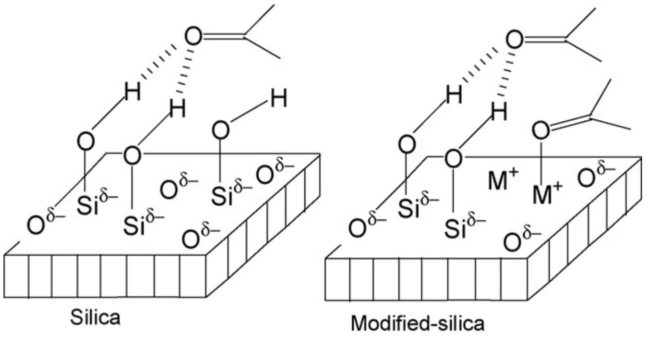
Ethylene polymerization reactions were performed in a 300 mL Pyrex glass reactor. The reactions were performed under Ar atmosphere using cyclohexane as the solvent (150 mL) in 1.6 atm of ethylene for 20 min at 60 °C. DEAC was employed as the cocatalyst (Al/Ti = 200). For the non-supported $TiCl_4$ catalyst system the following conditions were employed: $[M] = 10^{-3}$ mol/L and Al/Ti = 5, while for the supported ones: $[M] = 10^{-5}$ mol/L and Al/Ti = 200. After distillation, cyclohexane was contaminated with acetone (0–80 ppm). In the reactions using adsorbents, the contaminated solvent (50 ppm) was percolated through the adsorbent (2.0 g) column under inert atmosphere and transferred into the reactor. Replicates in polymerization reactions were performed up to reach standard deviation lower than 6%. Catalyst activity was calculated taking into account the dried mass of the resulting polymer expressed in terms of metal present on the polymerization medium, either in terms of soluble catalyst or present on the supported catalyst.

2.5.3. Polymer characterization

The resulting polymers were characterized by differential scanning calorimetry (DSC). Polymer melting points (T_m) and crystallinities (X_c) were determined on a Thermal Analysis Instruments DSC-2010 calibrated with Indium, using a heating rate of $10\,°C\,min^{-1}$ in the temperature range of 40–180 °C. The heating cycles were performed twice, but only the second was taken into account, since the first cycle was influenced by the mechanical and thermal history of the samples. The samples (ca. ≅5 mg) were put into an aluminum pan and hermetically sealed.

Table 1
Metal crystallite size of the chemically modified chrysotile and silica.

Sample	Particle size (nm)
LC Cu 50	10.1
LC Ag 50	10.4
S Cu 50	10.4
S Ag 50	10.3



Scheme 1. Interaction of carbonyl with (a) silica and (b) metal modified silica surface.