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Enhanced activity of clays and its crucial role for the activity in ethylene polymerization

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ABSTRACT

This paper presents a study of the effects of different treatments on the polymerization activity of modified clays as cocatalysts. To achieve this goal, an intercalating cation was introduced into two smectites and these clays were then modified with trimethyl aluminium. The results for ethylene polymerization, when a zirconocene complex was used as catalyst, and the structure analysis, allow us to obtain interesting deductions about the generation mode of the active species. All active materials employed as support activators presented aluminium in a pentahedral environment together with acidic hydrogen atoms. These two features were detected only after TMA treatment and they seem to be crucial elements in active cocatalyst generation. Moreover, a material without structural aluminium displayed the best activity pointing to the new aluminium species generated in the solid matrix as the determining factor for the activity. We proposed a synergic effect between Lewis acid aluminium centres and acidic Brönsted protons that generate the SiOHAl groups that activate the zirconium compound.

1. Introduction

α-Olefin polymerization catalyst systems that combine a Group IV metallocene complex and methylaluminoxane (MAO) as cocatalyst [1] were largely studied because these systems produce polyolefins with defined microstructures by selecting the appropriate structure of the metallocene complex [2–4]. Although the complex role of MAO in the polymerization reaction has not been fully elucidated yet; it is well known [5–8] that the active species must be obtained by an activator (cocatalyst) with acidic properties. On the basis of these findings, a large number of materials with Lewis or Brönsted-acidic sites have been tested as activators for the development of a MAO free catalyst system [9–11]. Recently, we have reported [12] the use of commercial materials (K10 and K30) chemically modified with AlR_3 (R = Me, TMA; R = Et, TEA) as supports and activators, dubbed “support activators”. In the presence of group 4 metal precatalyst compounds, these catalytic systems were active for ethylene polymerization. However, it was not possible to establish a correlation between activity and structural features due to the high level of impurities in the K10 and K30 materials. Therefore, the aim of this research work was to select a set of pure clay minerals as starting materials in order to establish this good correlation.

The selected clay minerals were smectite-types and belonged to the family of 2:1 phyllosilicates [13]. Their crystalline structure is composed of stacked layers made of two silica tetrahedrons fused to an edge-shared octahedral sheet of aluminium or magnesium hydroxide. The isomorphic substitutions origin negative charges in the layers and their electroneutrality results from the cations residing in the interlayer space. In order to understand the properties of clays that govern their catalytic properties[14–16], the study of two smectites (montmorillonite and hectorite), both octahedrally charged, with different compositions has been included. The most straightforward way to change the acid strength and concentration of the acid centres is to substitute the interlayer cations (smectite/M^{n+}). Moreover we treated these materials with TMA and consequently we generated different support activators (smectite/M^{n+}/TMA).

In this study, we show the effect of the intrinsic nature of the material, the effect of the exchanged cations intercalated into the clay mineral layers before polymerization, and the result of TMA treatment on the acidic properties and catalytic performance on

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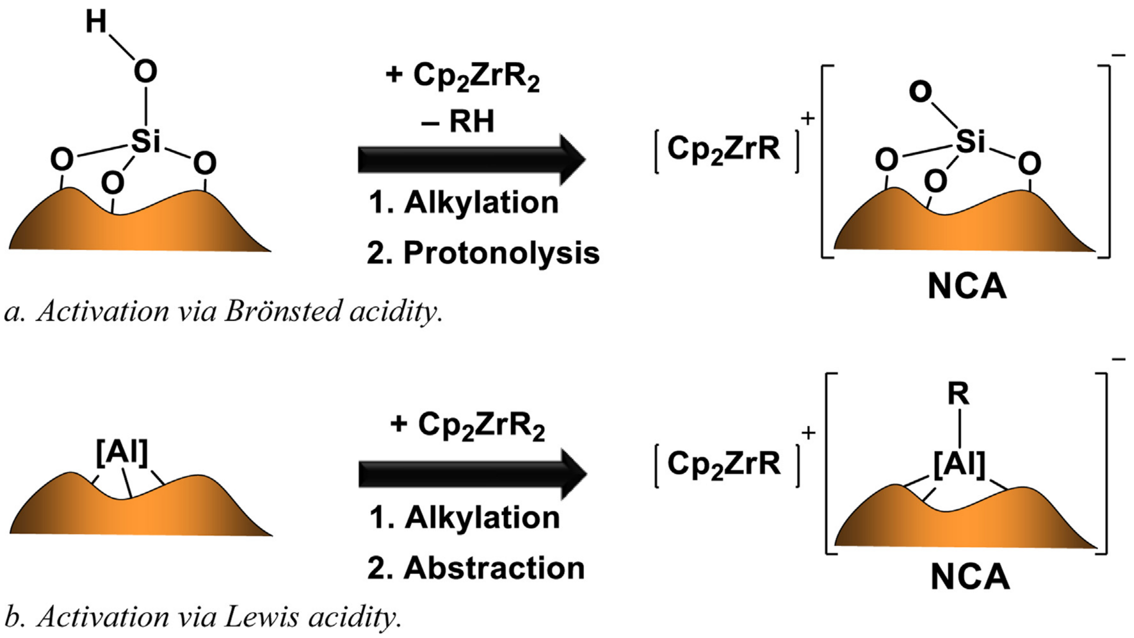

Fig. 1. Possible pathways to active species generation.

ethylene polymerization of different clays. The support activators obtained were fully characterized by several techniques including, XRD, XRF, FTIR and MAS-NMR. Their physical properties were correlated with the catalytic activity of the systems generated.

The choice of these types of materials as support activators is warranted because of their laminar structure. The active species can be stabilized in the interlaminar space because of its cationic nature and the swelling capacity of these materials allows the polymer chain to grow.

Because acidity[17–19] is fundamental to the behaviour of these clay minerals as cocatalysts, it is interesting to note the expected surface acidity may be explained in terms of structure. Clay mineral Lewis acidity generally arises from exposed Al^{3+}, Mg^{2+} or other ions at the edges and dominates when the interlayer water is largely removed. Brönsted acidity arises from silanol structural groups or from protons formed by the dissociation of interlayer water caused by the polarizing effect of aluminium cations present in this space. In the cases of acid treatment it also arises from the exchange with H^+ ions.

With this in mind, the different treatments were chosen to influence the inherent acidity of these materials with the assumption that the mechanism for the generation of the active specie responsible for the polymerization would be similar to that proposed in homogeneous systems (Fig. 1) [20].

2. Experimental

2.1. Starting materials and general conditions

The smectite samples montmorillonite SAz-2 (MMt) and hectorite SHCa-1 (Hect) were supplied by the Source Clays Repository of Clay Minerals Society. Fractions smaller than 2 μm were extracted [21], and the inorganic and organic matter [22,23] were eliminated to give the starting materials, a montmorillonite termed MMt (cationic exchange capacity CEC = 156 meq/100 g) and a hectorite termed Hect (CEC = 245 meq/100 g), respectively [24]. The samples were tested in different steps; with their natural interlaminar cations, when they were homoionized to obtain the cation-exchanged derivatives, and finally after TMA treatment.

$[Zr(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_9H_6SiMe_2(CH_2CH{=}CH_2)\}Cl_2]$ was synthesized according to literature procedures [25]. All manipulations involving air sensitive compounds and materials were performed under argon (Air Liquid, with O_2 and H_2O content below 3 ppm), using standard Schlenk and vacuum line techniques or in a MBraun Model 150-BG glove box continuously purged with high purity dry nitrogen (O_2 and H_2O content less than 1 ppm). Solvents were purified by distillation under argon using appropriate drying agents.

2.2. Preparation of cation-exchanged smectites

Exchanged smectites were prepared by a cation-exchange reaction using NH_4Cl, $AlCl_3$ or H_2SO_4 solutions, respectively. To obtain smectite/M^{n+} ($M^{n+} = NH_4^+$ or Al^{3+}); 10 g of the desired smectite was suspended in an aqueous solution of the chosen salt with a concentration of 10 times the CEC of the smectite. After stirring for 8 h at room temperature, the suspension was centrifuged at 10 °C with a velocity of 16,000 rpm for 20 min. The supernatant liquid was removed and the procedure was repeated four times. The smectite/Al^{3+} was repeatedly washed and filtered until the filtrate was Cl^- free. Samples were dried at room temperature for one week and finely hand ground in an agate mortar.

Acid treatment was achieved by preparing a suspension of 10 g of the desired smectite (smectite/H^+) in 50 ml of H_2SO_4 1.5 M, which was then heated at 80 °C over 4 h for MMt and 3 h for Hect. The resulting solid was washed, until it was free of sulphate ions, with hot distilled water, collected by centrifugation and then dried at room temperature for 1 week.

2.3. Support activator preparation

A suspension of 5 g of the desired smectite in 150 ml of toluene was prepared in a 250 ml round-bottom flask fitted with a tap. A dropping funnel containing trimethylaluminium (TMA 2M in toluene, Aldrich) in a proportion of 17.3×10^{-3} Al mol/1 g of smectite was connected to the round-bottom flask, and the system was closed using a gas bubbler to follow gas evolution. TMA solution was added dropwise to the suspension and the resulting mixture was stirred for 3 h at room temperature. The solid sample was then