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Olefin polymerizations with zirconocene supported on SiO_2 modified by MgO, NaOH and LiOH

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ABSTRACT

Silica gels modified by MgO, LiOH, and NaOH, i.e., SiO_2/MgO, SiO_2/LiOH, SiO_2/NaOH, respectively, were examined as solid supports in the ethylene and propylene polymerization reactions using dimethylsilylene-bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride (SHIZ) as the catalyst and *i*-Bu_3Al as the co-catalyst. All three were found to be equally effective for the former reaction, whereas activity was discrete for the latter reaction, with the order being SiO_2/MgO > SiO_2/LiOH > SiO_2/NaOH. For the SiO_2/MgO combination which showed the highest performance, BET and STEM studies indicated that Mg was evenly distributed in the silica gel. Acid–base measurements of all three solids indicated that SiO_2/MgO had strongly acidic sites whereas the other two did not, and in addition, SiO_2/NaOH had strongly basic sites whereas the remaining two had only weakly basic spots. These results suggested that the presence of weakly nucleophilic anionic sites is essential for high reactivity and that strongly acidic sites enhance the reactivity.

1. Introduction

The emergence of metallocene catalysts has enabled the production of polymers with a narrow molecular weight distribution and thus of uniform composition [1,2]. Furthermore, control of stereoregularity of polymers has been achieved by tuning the properties of the ligands on the metallocene complexes. Metallocene complexes of group IV elements, particularly zirconocenes, have been found to be especially advantageous for accomplishing these features.

Zirconocene catalysts utilized in polymer synthesis generally are used in a combination with co-catalysts such as borates which typically bear pentafluorophenyl groups, boranes or methylaluminoxane (MAO). Among these, MAO has been recognized to be of particular versatility. Although the precise role of co-catalysts still remains to be clarified, it is generally considered to be to function both as strong acid to assist in the generation of active cationic metal species from the zirconocene complexes and as weakly coordinating anion to provide stabilization to the cationic complexes without forming strong dative bonds that would diminish activity.

In view of the commercial production of polyolefins, it is very important to obtain the polymers as particles and also to utilize gas phase or slurry polymerization processes. In order to do so, it is usually necessary to fix the zirconocene catalysts on solid supports such as inorganic oxides [2]. Since the nature of the support is expected to affect catalyst performance, it becomes important to identify the properties of supporting materials and if possible to refine them. Thus, studies aimed at the development of efficient supported catalysts have been an active area in polymer chemistry. Previous investigations have centered on the use of solid acids in a combination with MAO. However, rather recently, examinations on the use of conventional alkylaluminiums in the place of the commonly used but less cost efficient MAO in conjunction with solid materials such as mesoporous silica [3], alumina [4], zeolites [4b,5], zirconia [6], $MgCl_2$ [4a,7], clay [8], and Ga-modified zeolites [9] have emerged. Unfortunately, besides clay, satisfactory activity has not necessarily been established in systems using trialkylaluminiums, as of yet. The reason for the lack of success with the materials previously examined is that, even if a cationic zirconocene complex were to form with the help of some acidic material, there would still be the need for weakly or better non-nucleophilic anionic species appropriate for the stabilization of the cationic species.

Although the importance of such counteranions has been recognized for quite a while [10], sufficient investigations to address this issue in relation with the solid support have not been carried out. We, also, have had interest in the use of modified solid

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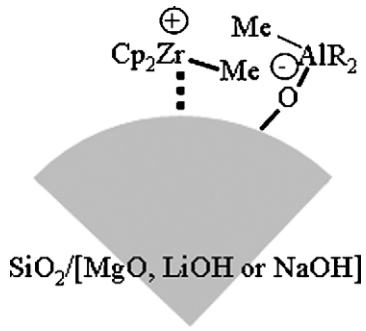

Fig. 1. Conceptional image of the base-modified SiO_2 surface.

supports for polymerization reactions [11], and decided to tackle this problem by examining the use of silica gel as the support, since its use would be favorable in terms of cost and adaptability for various processes. The surface of SiO_2 itself does not possess marked chemical properties, and therefore, it cannot function as a co-catalyst by itself. However, if it were possible to add function to silica gel by chemically modifying the surface, then there would be the possibility that the support functions also as a catalyst activator. Furthermore, the poor reactivity of the SiO_2 surface would be preferable for evaluation of the modifications based upon our concepts for useful co-catalyst design.

In order to fulfill our objective of adding activation function to the SiO_2 surface, we have examined the effects of the anionic properties endowed on the SiO_2 surface with MgO, LiOH and NaOH on polymerization activities using dimethylsilylene-bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride (SHIZ) [12] as the catalyst precursor and *i*-Bu_3Al as a co-catalyst (Fig. 1) and scavenger. For SiO_2/MgO, which was found to have the most promising activity as a co-catalyst, SiO_2 surface assessments were made using the BET method and STEM observations. Also measured were the acid–base properties of the supported surfaces of the three combinations in order to elucidate the relation between surface acidity-basicity and polymerization reactivity. Herein, we present the details.

2. Experimental

2.1. General

SiO_2 (P-10), SiO_2 (P-6), and SiO_2 (P-3) were purchased from Fuji Silysia Chemicals Co. SHIZ was prepared according to a reported procedure [12]. All organic solvents were dehydrated and water was deionized. MgO, LiOH, and NaOH were of high grade and were used as received.

2.2. Surface modification of SiO_2

2.2.1. SiO_2 modification with MgO in H_2O (SiO_2/MgO-1)

One gram of SiO_2 (P-10) and 0.12 g of MgO were mixed in 20 mL of H_2O; the mixture was refluxed for 1 h. Then the mixture was heated to 150 °C using an oil bath to remove H_2O, furnishing a white solid. The solid was dried for an additional 2 h at 200 °C in vacuo and the resulting solid was stored under nitrogen.

2.2.2. SiO_2 modification with MgO using a mortar (SiO_2/MgO-2)

One gram of SiO_2 (P-10) and 0.12 g of MgO were hand-mixed in a mortar for 10 min. Then the mixture was dried for 2 h at 200 °C in vacuo and the resulting solid was stored under nitrogen.

2.2.3. SiO_2 modification with LiOH or NaOH in H_2O (SiO_2/LiOH and SiO_2/NaOH)

One gram of SiO_2 (P-10) and a specified amount of LiOH or NaOH (see Table 3) were mixed in 20 mL of H_2O and the mixture was refluxed for 4 h. Then the mixture was heated to 150 °C with an oil bath to remove H_2O, furnishing a white solid. The solid was dried for an additional 2 h at 200 °C in vacuo and the resulting solid was stored under nitrogen.

2.3. Polymerization

2.3.1. Ethylene polymerization

Into a dry 1.5 L autoclave were introduced 500 mL of dehydrated toluene. Then 0.4 mmol of *i*-Bu_3Al diluted in toluene (0.5 mmol-Al/mL), a specified amount of surface treated SiO_2 dispersed in toluene, and 3 μmol of SHIZ diluted in toluene (2.0 μmol-Zr/mL) were added. After the internal temperature of the autoclave was raised to 70 °C, ethylene and 50 mL of hydrogen at the pressure of 0.8 MPa were introduced and the pressure was maintained throughout the polymerization. The polymerization reaction was terminated by the addition of EtOH.

2.3.2. Propylene polymerization

Into a dry 1.5 L autoclave were introduced 500 mL of dehydrated toluene. Then 0.4 mmol of *i*-Bu_3Al diluted in toluene (0.5 mmol-Al/mL), a specified amount of surface treated SiO_2 dispersed in toluene, and 3 μmol of SHIZ diluted in toluene (2.0 μmol-Zr/mL) were added. After the internal temperature of the autoclave was raised to 70 °C, propylene at the pressure of 0.5 MPa was introduced and the pressure was maintained throughout the polymerization. The polymerization reaction was terminated by the addition of EtOH.

2.4. Measurements of surface area, pore volume, pore diameter distribution and average pore diameter

After the surface treated SiO_2 was dried at 200 °C in vacuo for 2 h, the surface areas were determined by the Brunauer–Emmett–Teller (BET) method [13] (Quantachrome Instruments, Autosord-3B). Pore volumes, pore diameter distributions and average pore diameters were determined by the Barrett–Joyner–Halenda (BJH) method [14].

2.5. TEM measurements [15]

After an appropriate amount of a sample was imbedded in an epoxy-resin, a slice containing a section of the solid support particle was obtained by slicing with an ultra-microtome. TEM observations of the particle sections were carried out with a FEI TECNAI G2 F20 and determinations of the atomic compositions of the sections were carried out by the STEM-EDX method using an EDAX Phoenix S-UTW semiconductor detector. Particle section views were obtained as HAADF-STEM (high-angle annular dark-field scanning transmission electron microscopy) images. The contrast of the image can be correlated with the concentration of the components with this method.

2.6. Characterization of acid and base properties [16,17]

One-tenth of a gram of surface treated SiO_2 dried at 200 °C in vacuo for 2 h was immersed in 2 mL of dry toluene in a vial. One-tenth of a milliliter of a 0.2 wt% toluene solution of a Hammett indicator was added to the SiO_2/toluene slurry. The color change of the indicator on the solid surface was judged after 10 min.

3. Results and discussion

3.1. Evaluation of SiO_2 treated with MgO

MgO modification of a wide pore SiO_2 (P-10) sample was conducted by two methods. One method involved heating the two