

The Influences of Structural Feature and Surface Properties of Montmorillonite on the Supported Olefin Polymerization Catalysts

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ABSTRACT: Clay minerals possess unique physical properties such as high Lewis acidity, high specific surface area, periodic layer structures, and these materials can be utilized as polyolefin catalysts supports. This work focused on the influence of structural and surface properties of montmorillonite (MMT) on the catalytic ethylene polymerization performances. The structural parameter, specific surface area and compositions of the MMTs under different chemical modification conditions were measured by X-ray diffraction (XRD) analyses, multipoint BET method and X-ray fluorescence spectrometer (XRF) methods. The basal spacing value increased when samples were treated with H₂SO₄/Li₂SO₄ combination while the value remained nearly constant when the samples were treated with H₂SO₄ solution alone. Majority of elements Ca, Mg, K are leached out after the acid treatment. Ethylene polymerization results showed that MMT treated with H₂SO₄/Li₂SO₄ combination, activated with triethylaluminum (TEA), exhibit higher polymerization activity, reached the level of methylaluminoxane (MAO) activated supports. It can be attributed to the relatively wider interlayer space which had more reactive sites for chemically anchoring metallocene catalysts.

Keywords: Montmorillonite, Triethylaluminum, Interlayer space, Ethylene polymerization

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I. INTRODUCTION

Polyolefins are the most widely used organic materials in modern society, with an annual production of around 160 million tons. These materials are mainly produced by catalytic coordination polymerization processes, or technically the Ziegler-Natta processes, utilizing transition metal catalysts supported on an inert organic or inorganic carrier material, namely the support. The supporting materials are either synthetic or natural, with highly porous structure and high surface areas. Inert organic materials such as synthetic polymers¹⁻⁶ and inorganic materials such as porous magnesium chloride⁷⁻⁹, porous silica/alumina¹⁰⁻¹², and layered natural clay minerals such as montmorillonite (MMT), hectorite, mica, kaolin, vermiculite, etc.^{13, 14} are majority of the catalyst supports.

Periodically layered natural clay minerals, especially the smectites aluminosilicates are abundant on earth, and they usually possess high acidity in nature and their layered structure can be readily exfoliated¹⁵. As a common example of clay mineral, MMT has been successfully employed as both a carrier and an activator for transition metal catalyzed olefin polymerization catalyses^{16, 17}. This later function of activating organometallic complexes without the use of large excess high cost co-catalysts activators, such as MAO¹⁸⁻²⁰ and perfluorinated

borates²¹ is a significant economic advantage for MMT serving as transition metal catalysts carrier.

Layered MMT structure consists of one octahedral sheet sandwiched between two tetrahedral sheets. The tetrahedra contains mainly Si as the central atoms with some Al substitution, while the central positions in the octahedral sheets are occupied by Al, partially substituted with Fe and Mg²². Non-equivalent substitution generates negative charges on the layers and the negative charges are balanced by hydrated exchangeable cations (mostly Ca²⁺, Mg²⁺, and Na⁺) present in the interlayers and on the crystal edges. Acid treatment of a typical MMT clay results in leaching out of the soluble metal ions, such as Al³⁺, Ca²⁺, Mg²⁺, Na⁺, and Fe³⁺ etc. from the clay lattice, and the gradual delamination of the periodical clay structure^{22, 23}. As acid treatment proceeds, changes in the surface area and the porosity of the clay, and changes in the type and concentration of ions in exchangeable sites, are all expected to affect layered structure, and eventually influence the catalyst performances. When the active catalyst metal centers anchored in such a confined environment, it will influence the catalytic polymerization behavior and the morphology of the resulting polymer.

The catalyst composition with the carrier characterized with two fundamental functions: acting

asco-catalyst to activate the metallocene catalyst precursors, and serves as carrier for the activated catalyst. The layered structure of MMT also provides a convenient macroscopic system to study fundamental scientific issues²⁴. Also, it is reported that the olefin polymerization activity is improved by using an ion-exchange layered compound treated by an acid alone, or a metal salt, or a combination of an acid/metal salt as a catalyst component. Despite the large number of scientific papers dealing with the characterization of acid-activated MMT clays, only few publications report on the influence of different treatment conditions on the catalytic activity²⁴.

In the present research, in order to understand how the structural and surface properties of MMT affect the catalytic ethylene polymerization performances, MMTs are treated with sulfuric acid, or sulfuric acid/metal salt combination respectively, under different acidic strength. The treated MMT materials are applied as carrier for couple of metallocene precatalysts, and the supported catalyst components are used for ethylene polymerizations under industrial relevant conditions. The polymerization performances and the polymer properties are studied with respect to the MMT material properties.

II. EXPERIMENTAL

2.1 Materials

The MMT clay used in this work is commercial montmorillonite K10 (Sigma-Aldrich Co. LLC.). The main compositions of the original MMT was found by XRF to be SiO₂: 71.67%; Al₂O₃: 17.14%; Fe₂O₃: 2.43%; MgO: 3.86%; CaO: 3.02%. All solvents and chemicals used in the processes of catalysts preparation, treated support handling, polymerization experiments are reagent grade and supplied by Sinopharm Chemical Reagent Beijing Co., Ltd., and are purified and dried as required. All manipulations with air and moisture sensitive materials are conducted using standard Schlenk techniques under dry nitrogen in a high temperature oven dried glassware, or operated in a high purity argon atmosphere glove-box, unless otherwise noted.

2.2 Measurement

The layered structural properties of MMT are measured with X-ray diffraction (XRD) analyses, which are performed using a Panalytical X'Pert PRO Diffractometer with Cu radiation (40 KV, 40 mA). Scanning is in 0.028 steps at a speed of 2°/min. Basal spaces were calculated by use of d_{001} values.

Specific surface areas of MMT are commonly measured using gas adsorption techniques (BET method, Quantachrome Autosorb-6B surface area analyzer). Specific surface area, pore volume, and average pore diameter of clay samples are determined by multipoint BET method at liquid

nitrogen temperature. The compositions of MMT are measured by X-ray fluorescence spectrometer (ZSX Primus II, Rigaku).

DSC of polyethylene was recorded on NETZSCH DSC 204F1 differential scanning calorimeter. T_m and crystallinity of the polyethylenes are measured at a heating rate of 10°C/min from ambient temperature to 190°C, and the second heating/cooling circle is used to eliminate thermal history.

Molecular weight (M_w , M_n) and molecular weight distribution (M_w/M_n) are characterized by high temperature gel permeation chromatography (Polymer Char GPC-220). The samples are dissolved in 1,2,4-trichlorobenzene (containing 0.1% Irganox-1010 antioxidant) eluted with 1,2,4-TCB at 135°C at a flow rate of 1.0 mL/min. The columns are calibrated with monodisperse polystyrene standard, and the molecular weight values reported are absolute values.

2.3 MMT Structure Modification

The MMT clay was treated with different concentration of H₂SO₄ solution or the mixture of H₂SO₄/Li₂SO₄ solution (clay mineral: acid ratio is 1 g to 30 mL). The suspension is stirred at 90°C for 4 h and the supernatant is decanted with the aid of centrifuging, the solid residue is washed thoroughly with deionized water until the supernatants are pH-neutral. The obtained clays are first air-dried for 3 days and subsequently grounded to a fine powder followed by high vacuum (10⁻³ torr) for 6 hours.

2.4 Catalyst preparation

The MMT-supported catalysts were prepared by the following procedure. First, MMT (1g, treated with H₂SO₄ solution or H₂SO₄/Li₂SO₄ combination) suspension in dry toluene were activated with TEA (1.0 M solution in hexane) at 50°C for 2 h. TEA treatment not only significantly improve the supported catalyst activity, it is also possible to reduce the polymer particles agglomeration, and prevent polymer from fusing onto the polymerization reactor wall and on the stirrer^[25]. The metallocene precatalyst were treated with triisobutyl aluminium (TIBAL) at 50°C for 1 h, then the treated metallocene solution is added into the TEA pretreated MMT suspension and kept at 50°C for 2 h, followed by washing three times with dry toluene. The free-flow MMT-supported catalyst is obtained after vacuum drying at room temperature for few hours.

2.5 Ethylene polymerization

The polymerization reactions were conducted in a 10L autoclave (Meryer) with

n-hexane solvent, and the temperature and pressure control were adjusted to industrial relevant conditions. The catalyst activity was calculated as total polymer mass obtained against the catalyst mass on an average of 1 hour. In a typical polymerization experiment, the autoclave was heated to 80-90°C under a dynamic vacuum for 2 hours and the atmosphere was thoroughly replaced with dry and high purity nitrogen (three vacuum and refill circles). n-Hexane and 100 ppm of TEA (10% hexane solution) were injected into the autoclave under N₂ atmosphere, the mixture was heated to 55°C and stirred for 15 min, then cooled to room temperature. The MMT-supported catalyst and ethylene (polymerization grade) were added into the autoclave in sequence with the aid of n-hexane flow, and the polymerization initiated with heating the autoclave to the desired polymerization temperature. The polymerization reactions were typically conducted for 1 hour and are terminated by venting the monomer and injection of a methanol/HCl solution to the system. The polymer was dried to constant weight.

III. Results and discussion

3.1 Structural studies

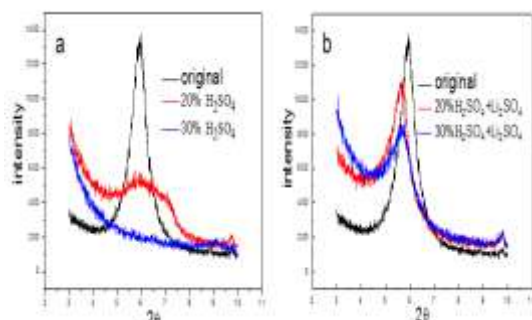


Fig.1 X-Ray diffraction analysis of MMTs treated with (a) H₂SO₄ solution (b) H₂SO₄/Li₂SO₄ solution

Fig. 1 shows the X-ray diffraction analysis of the acid and acid/salt combinations treated samples. The position of the basal (001) reflection at 205.8° indicates that the interlayer distance for this MMT is 1.52 nm. The X-ray diffraction results show that the crystallinity of the material decreased with increasing acid concentration and the (001) peak totally disappeared when the sample was treated with 30% H₂SO₄. Similar results were also obtained by C. Bieseki and co-workers²⁶, the strong decrease of the intensity of the basal (001) peak and the partial retaining of the other reflections testifying a loss of periodicity along the c direction, most likely associated with partial delamination of MMT structure. But the (001) peak still existed when the sample was treated with combination of 30% H₂SO₄ and 5% Li₂SO₄. The basal spacing value is maintained nearly constant when the sample was treated with 30%

H₂SO₄. But the value increased from 1.5 nm to 1.6 nm when the sample was treated with a mixture of 30% H₂SO₄ and 5% Li₂SO₄. In the study by Okada⁹, the X-ray diffraction analysis of MMT samples treated with H₂SO₄ also showed a decrease in (001) peak, as was the case for samples in the current study, which exhibited structural disorganization due to the excessive removal of Al³⁺, Fe³⁺ and Mg²⁺ from the structure, as seen in Table 1. When the samples were treated with a mixture of H₂SO₄/Li₂SO₄, Li⁺ take the place of Al³⁺, Fe³⁺ and Mg²⁺ to balance the charge, so as to retaining the layered structure with an increased interlayer space distances.

The acid treatment is intended not only to remove impurities on the surface but also to elute a part or the whole of cations such as Al, Fe or Mg in the crystal structure. By the salt-treatment, an ion complex, a molecular complex or an organic derivative may be formed, and the surface area and the interlaminar distance may be changed²⁸.

3.2 BET results

Table.1 The Surface Area, Pore Volume and Pore Diameter of MMT Before and After the Acid and Salt Treatment

	Surface area (m ² /g)	Pore volume (ml/g)	Pore diameter (nm)
Original	59.4	0.148	3.79
30% H ₂ SO ₄	108.0	0.171	3.81
30% H ₂ SO ₄	188.1	0.281	3.83
30% H ₂ SO ₄	191.6	0.361	3.79
30% H ₂ SO ₄ +30% Li ₂ SO ₄	190.0	0.173	3.81
30% H ₂ SO ₄ +30% Li ₂ SO ₄	188.0	0.273	3.83
30% H ₂ SO ₄ +30% Li ₂ SO ₄	182.2	0.341	3.79

As shown in Table.1, a significant increase in the surface area and the pore volume was observed for samples treated with increasing acid concentration. The surface area for natural MMT is approximately 60 m²/g and it increased to 190 m²/g when treated with 30% H₂SO₄. The pore volume increased from 0.148 ml/g to 0.361 ml/g when treated with 30% H₂SO₄. At the same time, the pore diameter has a marginal change with increasing acid concentration from 10% to 20%, and no change of pore diameter when acid concentration above 20%. It was established that the surface properties such as surface area and catalytic activity has an optimum. It is known that by subjecting to the acid treatment, impurities on its surface are removed and cations such as Al³⁺, Fe²⁺/Fe³⁺, Mg²⁺ etc. in its crystal structure are eluted, thereby increasing a surface area. With the progress of the acid treatment, the surface area and pore volume are increased²⁵. The salt treatment means a treatment carried out for the purpose of exchanging cations in an ion-exchanged

layered silicate²⁵.

3.3 XRF results

Component	Content (%)		
	original	H ₂ SO ₄ -treated	H ₂ SO ₄ /Li ₂ SO ₄ -treated
SiO ₂	71.67	79.89	78.82
Al ₂ O ₃	17.14	13.39	14.43
MgO	3.86	2.39	2.65
CaO	3.92	1.26	0.76
Fe ₂ O ₃	2.43	1.54	1.68

Table.2. The Content of Main Components of MMT Before and After the Acid and Solid Treatment

The content of main components of MMT before and after the acid and acid/salt treatment, measured by XRF were shown in Table.2. The main elements of the original MMT are Si, Al, Mg, Ca, Fe in the original structure, and majority of elements Ca, Mg are leached out, Al and Fe elements are partially removed after the treatment. As a consequence, the Si content increased about 10%. The decomposition of the MMT is realized through the dissolution of the octahedral and the tetrahedral anions, and the dissolution rate of the octahedral and the tetrahedral anions are different²³. The content of Li element is not available when the MMT treated with combination of H₂SO₄ and Li₂SO₄, because the XRF method limitation on detecting heavier metallic elements than Li.

3.4 Ethylene polymerization results

Table.3. Results of Slurry Polymerization of Ethylene

Catalyst	Support	Activity (g/gZn)	MFR (g/10min)	Bulk Density (g/cm ³)	Mn	Mw	PDI
Cat1	MMT/MAO	380	0.71	0.18	187453	303611	2.33
Cat2	MMT/MAO	330	0.81	0.34	18482	246763	2.95
Cat3	MMT/TEA	78	0.77	0.26	88657	227827	2.62
Cat4	MMT/TEA	48	0.65	0.24	94647	223366	2.38
Cat5	MMT/TEA	806	1.0	0.18	127983	277894	2.17
Cat6	MMT/TEA	188	0.9	0.17	77948	177983	2.28
Cat7	MMT/TEA	58	1.0	0.35	17228	363239	2.86

Table. 3 shows the results of the ethylene polymerization with the supported catalysts from H₂SO₄ or H₂SO₄/Li₂SO₄ treated MMTs and pre-activated with either MAO or TEA, respectively.

The supported catalysts Cat1 and Cat2 are from H₂SO₄ treated MMTs and pre-activated with MAO; the supported catalysts Cat3, Cat4 and Cat7 are from H₂SO₄ treated MMTs and pre-activated with TEA; the supported catalysts Cat5 and Cat6 are from H₂SO₄/Li₂SO₄ treated MMTs and pre-activated

with TEA. From polymerization activities of catalysts supported on different MMTs, the MMTs treated with combination of H₂SO₄/Li₂SO₄ have a remarkably higher activity than those treated with H₂SO₄ alone, and the activity level is similar to using costly MAO activated MMTs (Cat1 and Cat2). The enhanced ethylene polymerization activity for the MMTs treated with combination of H₂SO₄/Li₂SO₄ has an economic significance in industrial point of view. It eliminates the use of MAO, which is uneasy to handle in practical industrial processes, and is supplied from few technically monopolized overseas companies. In comparison, treatment of MMTs with TEA is easily adaptable for practical continuous industrial polymerization processes.

The enhanced ethylene polymerization activity for the MMTs treated with combination of H₂SO₄/Li₂SO₄ can be attributed to the relative bigger interlayer distance (Figure 1). Fixation of the activated metallocene catalysts in the MMT interlayers clearly depended on the existence of reactive sites among the galleries for chemically anchoring metallocene catalysts and the gallery height, which makes the ease of catalyst cations approach to the reactive sites^{28, 29}. The polydispersity index (PDI) of the polyethylene products were all between 2~3, which is normal for the metallocene single site catalysts. The polymers all had a comparatively lower bulk density (BD) and MFR (Table 3). The low BD indicates that the layered MMTs are readily exfoliated by the growing polymer chains and the interlayer confinement force is too weak to compress the growing polymer chains into dense massed morphologic matter.

The gallery of MMT is a specific space having one dimension in nanometer size scale. When polymerization occurs in such a confined environment, it will influence the polymerization and the morphology of resulted polymer²⁴. It is considered that the exfoliation of the MMT sheets take place in the process of the polymerization and results in the formation of new active sites from the metal complexes placed in the depths of the interlayer space³⁰. Fine polymer particles and agglomeration of polymer particles occurred during polymerization. Therefore, the methods of chemical modification of the MMT structure must be further improved.

IV. CONCLUSIONS

The acid treatment leads to an increase of specific surface area and number of acid centers, along with partially elimination of lower ionic potential and lower Lewis Acidic elements such as Ca, Mg, Fe, etc. Depending on the conditions used, MMT clays have an altered chemical composition and structure, due to a partial dissolution of cations such as Al, Fe or Mg in the crystal structure.

The crystallinity of the material decreased with increasing acid concentration and the (001) lattice collapsed when the sample was treated with 30% H₂SO₄ and the (001) diffraction peak vanished (figure 1(a)). The (001) crystal lattice retained when the sample was treated with the combination of 30% H₂SO₄ and 5% Li₂SO₄, and at the same time, the basal spacing value increased (Figure 1(b)).

MMT treated with H₂SO₄/Li₂SO₄ combination exhibited remarkably higher ethylene polymerization activity, reached the level MAO activated supports under industrial relevant conditions, compared with those treated with H₂SO₄ alone. The enhanced ethylene polymerization activity is attributable to the relatively wider interlayer space.

Combination of acid and salt treated clays, which have good thermal stability, high surface area and suitable porosity, are potential economic advantageous single site organometallic catalyst supports for olefin polymerizations. The chemical modification processes are, however, largely improvable to increase the interlayer confinement force, to avoid the formation of fine polymer particles and agglomeration of polymer particles, and to enhance the morphology control during polymerization.

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