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A MOF-supported chromium catalyst for ethylene polymerization through post-synthetic modification

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ABSTRACT

Isoreticular metal-organic framework-3 (IRMOF-3) has been post-synthetically modified to generate a Cr(III)-based heterogeneous catalyst (IRMOF-3-SI-Cr) for ethylene polymerization, which has been characterized by a variety of physical methods. The XRD analysis indicated that the structure integrity of the final solid was preserved after the functionalization with the imine and the subsequent coordination to chromium. The BET surface area of the final solid was slightly reduced as determined by N_2 adsorption–desorption experiments. The material exhibited a unique behavior for ethylene polymerization upon activation with various alkylaluminium co-catalysts, and the polyethylenes formed featured high molecular weights and broad molecular weight distributions.

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1. Introduction

Metal-organic frameworks (MOFs) [1–4], a class of porous materials have aroused great interest for their unique properties, which consist of metal ions (or clusters) and multidentate organic molecules. On one hand, their pore size, shape, dimensionality, and chemical environment can be well controlled by the judicious selection of the structural unit (metal and organic linker) [5]. On the other hand, the presence of strong metal–ligand interactions can confer the permanent porosity, so it is possible for appropriate guest molecule to freely get in and out without structure collapse [6]. Over the past decade, MOFs possess a wide array of potential applications in chemical engineering, chemistry, and materials science [7–15], especially in heterogeneous catalysis [16–18].

In general, the coordination sphere of the metal ions in MOFs is completely blocked by the organic linkers; therefore there are no free positions available to interact/activate with the reactants, which could limit the possibilities of MOFs for catalysis [19]. The new synthetic strategies have been developed to overcome the above drawbacks and prepare MOFs with unsaturated metal sites, such as the introduction of labile ligands during the synthesis of MOFs [19–21]. Another approach is available to prepare MOFs with active metal sites by using metal complexes as linkers that further react with a second metal to form frameworks [22,23].

In recent years, the covalent post-synthetic modification of MOFs has received great interest [24–26]. IRMOF-3 [27], as a derivative of the canonical MOF-5, consists of octahedral Zn_4O clusters linked by 2-aminoterephthalate ligands, in which the aromatic amino groups do not participate in binding to the tetranuclear Zn_4O nodes and thereby provide the opportunities for the post-synthetic modification. The amino groups of IRMOF-3 were firstly modified with alkyl anhydrides [28]. The condensation reaction between amino groups in IRMOF-3 and salicylaldehyde afforded the formation of a salicylidene moiety (R—N=C—C_6H_4OH), which activated the framework toward metal sequestering, demonstrated by heterogenizing a vanadyl complex (IRMOF-3-V$_{sal}$) for the oxidation of cyclohexene with t-BuOOH [29]. Similarly, a MOF-containing gold(III) Schiff-base complex lining the pore walls was prepared by the post-synthetic modification and found to be highly active, selective and reusable for domino coupling and cyclization reactions in liquid phase [30]. The observed catalysis did provide a proof of principle that, via the sequential functionalization, porous MOFs can be chemically transformed to introduce useful ligating groups, activating the material toward metal complex binding and producing catalytically active MOFs.

The heterogenization of homogeneous catalysts for gas and slurry polymerization of olefins is a highly desirable objective because of slower deactivation of catalysts, less co-catalyst required, better polymer morphology, avoidance of reactor fouling in heterogeneous polymerization [31]. Many materials have been used as catalyst supports, such as silica and alumina, magnesium chloride, zeolites, polymers, and so on [32]. Recently, MOFs appear

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as particularly good candidates for catalytic heterogeneous polymerization [33–37], as they can exhibit well-defined catalytic sites (accessible metal sites) and pores with various sizes and shapes. For instance, the Nd-based MOFs had been used as precatalysts for the selective polymerization of isoprene in the presence of Al-based co-catalyst and the residual Nd material with unchanged structure was found in the polymer [36,37]. Therefore, MOFs have been considered to be introduced as supports into heterogeneous catalysts for ethylene polymerization. In this study, we prepared a MOF-supported chromium(III) phenoxy-imine complex (IRMOF-3-SI-Cr) as an active heterogeneous catalyst for ethylene polymerization on treatment with various alkylaluminium co-catalysts, producing polyethylenes with high molecular weights and broad molecular weight distributions.

2. Experimental

2.1. General procedures

All manipulations of air- and/or moisture-sensitive compounds were performed under nitrogen using standard Schlenk and glove-box techniques. The solvents for synthesis and polymerization, THF, n-hexane, diethyl ether, and toluene were refluxed over metallic potassium/sodium with benzophenone as an indicator and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M in toluene) was purchased from Akzo Nobel Corp. Trimethylaluminum (TMA, 1.0 M in heptane), triethylaluminum (TEA, 1.0 M in hexane), triisobutylaluminium (TIBA, 1.1 M in toluene) were purchased from Acros Chemicals. 2-Aminoterephthalic acid (H_2ATA), $Zn(NO_3)_2 \cdot 6H_2O$, aniline, salicylaldehyde and $CrCl_3(THF)_3$ were obtained from J&K Scientific Ltd. and used as received. Polymerization-grade ethylene (TOPGRAND Petrifaction Industry Gas. Ltd.) was purified by passing it through columns of CuO catalyst and 3 Å molecular sieves. All other chemical chemicals were obtained commercially and used without further purification unless otherwise stated.

2.2. Synthesis of IRMOF-3-SI-Cr, $\{Zn_4O[SITA\text{-}CrCl_2(THF)_2]_{0.09}(ATA)_{2.91}\}$
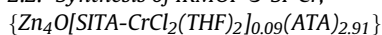
IRMOF-3, $[Zn_4O(ATA)_3]$ and IRMOF-3-SI, $[Zn_4O(SITA)_{0.09}(ATA)_{2.91}]$ (SITA = 2-salicylideneimine terephthalate) were prepared according to the literature [30].

The IRMOF-3-SI (2 g) was dispersed in THF (30 mL) after it was degassed under vacuum (50 °C, 6 h). To this slurry a solution of $CrCl_3(THF)_3$ (164 mg, 0.43 mmol) in THF (30 mL) was dropwise added at room temperature and the mixture was stirred for an additional hour. The yellowish green solid (2.06 g) was collected by filtration, washed once with THF and twice with CH_2Cl_2, and dried in vacuo. Elemental analysis for $Zn_4O[SITA\text{-}CrCl_2(THF)_2]_{0.09}(ATA)_{2.91}(C_4H_8O)$ (corresponding to 3% amine functionalization and quantitative chromium uptake): Calculated: C 38.21%, H 2.54%, N 4.96%. Found: C 38.39%, H 2.56%, N 4.95%. The amount of chromium in the final solid was determined by ICP-AES. Calculated: Cr 0.51%. Found: Cr 0.47%.

2.3. Ethylene polymerization

Ethylene polymerization was carried out in 250 mL glass reactor with a mechanical stirrer under atmospheric pressure. After it was dried under vacuum, purged 3 times with nitrogen and replaced twice with ethylene, the reactor was full of ethylene, and then placed into a water bath set at the operating temperature. Toluene (100 mL) and the required amount of co-catalyst were introduced to the reactor. Subsequently a prescribed amount of catalyst was added through a connected ampoule to start the

polymerization. After the desired time, the acidified ethanol (1 wt% HCl) was injected into the reactor to terminate the polymerization. The large amount of acidified ethanol was added to the mixture and stirred overnight. The polymers were collected, washed with ethanol, and dried in vacuo overnight at 60 °C.

The polymerization reactions under high pressure of ethylene were carried out in a 500 mL stainless steel autoclave with a mechanical stirrer and a temperature controller. Except for 200 mL of toluene used, the same procedure was employed as that under atmospheric pressure.

2.4. Compared experiments

IRMOF-3-SI-Cr was allowed to react with 300 equiv. of TIBA in 100 mL of toluene at 50 °C for 30 min. The mixture was filtered, and yellowish green precipitation was washed three times with toluene for testing. The filtrate was collected for ethylene polymerization under atmospheric pressure.

2.5. Characterization

Elemental analysis was performed on a Flash EA1112 micro-analyzer. The crystallinity of the materials was characterized by powder X-ray diffraction (XRD) on a PANalytical B.V.-Empyrean diffractometer using Cu-Kα radiation source. Thermogravimetric analysis (TG) was carried out using Perkin-Elmer Pyris 1 TGA instrument in flowing air with a heating rate of 10 °C min^{-1}. Nitrogen adsorption–desorption isotherms were measured at 77 K using a Quantachrome Autosorb-1-C instrument. Prior to the BET analysis, the samples were degassed at 100 °C for 24 h. ICP were performed on an IRIS Intrepid 2 XSP. Samples were first slowly heated to 500 °C, dissolved in hydrochloric acid after 5 h, and finally diluted to the preset volume. The molecular weight and molecular weight distribution of PE samples were measured at 150 °C in 1,2,4-trichlorobenzene with a PL-GPC220 coupled with an in-line capillary viscometer. The melting temperatures of PE samples were measured with a Perkin-Elmer DSC 7 instrument in a standard mode. The samples were first heated to 150 °C at 20 °C min^{-1} to eliminate thermal history and held constant for 2 min at 150 °C. The samples were then cooled to 30 °C at 10 °C min^{-1} and held constant for 2 min at 30 °C, before heated to 150 °C at 10 °C min^{-1}.

3. Results and discussion

3.1. Synthesis and characterization

The starting material (IRMOF-3) was synthesized from 2-aminoterephthalic acid (H_2ATA) and $Zn(NO_3)_2 \cdot 6H_2O$ in the presence of triethylamine at room temperature according to a reported procedure [30]. The covalent post-synthetic modification of IRMOF-3 with salicylaldehyde afforded the formation of salicylideneimine (IRMOF-3-SI), in which ca. 3% of the total NH_2 groups were functionalized without losing the framework integrity. Subsequently, the desolvated IRMOF-3-SI was treated with the excess of $CrCl_3(THF)_3$ to generate the MOF-supported Cr(III) catalyst (IRMOF-3-SI-Cr). During the reaction, a color change of the solid was observed from yellow to yellowish green. On the contrary, the mixture of IRMOF-3 and $CrCl_3(THF)_3$ under the same conditions remained unchanged, which indicated that the coordination reaction occurred between chromium and nitrogen atom of imine group rather than amine group (Scheme 1).

The XRD patterns of IRMOF-3 and IRMOF-3-SI were coincident with those reported in the literature [30]. In comparison, no apparent loss of crystallinity was observed after the coordination to chromium, although the incorporation of chromium resulted in a slight variation in the intensity of the diffraction peaks (Fig. 1).