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Aluminum chloride grafted mesoporous molecular sieves as alkylation catalysts

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Abstract

The aim of this work is to study the influence of different mesoporous molecular sieves (MMSs) type and the effect of pore diameter on MMSs silica grafted aluminum chloride catalysts and their activity in benzene alkylation by 1-dodecene. Four samples (two hexagonal and two wormhole like structures with different pore diameters) were prepared by post-synthesis grafting reaction in moisture free conditions (Schlenk technique). The physico-chemical properties were monitored by N_2 adsorption, XRD, atomic adsorption, ^{29}Si and ^{27}Al MAS NMR. Acidity data were obtained by TPD of ammonia, and FTIR of adsorbed pyridine. The alkylation of benzene is carried out in a Schlenk tube under dry conditions at room temperature. The products were analyzed by GC-MS. Grafting aluminum chloride on MMSs increases the yield of monoalkylated products.

Keywords: Aluminum chloride; Mesoporous materials; Lewis acid; Solid acid catalyst; Alkylation reaction

1. Introduction

For decades, linear alkylbenzenes (LABs) have been the precursors of sulfonated alkyl benzenes, which are significant commercial detergents. The process to synthesize them is usually carried out by Friedel-Craft alkylation of linear olefins using hydrogen fluoride or aluminum chloride as homogeneous catalysts. The use of these catalysts presents severe problems. For example, aluminum chloride is difficult to separate after reaction and produces a large amount of waste effluent. To solve these problems, attempts have been made to chemically support aluminum chloride on mesoporous molecular sieves (MMSs) silica type [1]. Aluminum chloride can be easily grafted onto the surface of such solids to produce very active catalysts. Drago et al. grafted aluminum chloride on silica gel for applications in cracking, isomerization reactions, dehydrochlorination and hydrodechlorination [2–5]. Another study used the same catalyst for work on the accelerating effect of ultrasonic vibration on the reaction of benzene alkylation with cyclohexene [6]. Clark et al. proposed an alternative for the cationic polymerization of styrene [7,8]. They used the Lewis acid catalyst supported on a porous silica support. The immobilized aluminum chloride on mesoporous MCM-41 silica is a substitute catalyst for liquid-phase isopropylation of naphthalene [9]. Recently, several researchers have been using aluminum chloride grafted or impregnated mesoporous support for different applications [10,11]. Enhanced selectivity in the preparation of linear alkylbenzenes using HMS silica supported aluminum chloride was presented by Clark et al. [12]. Another group investigated the pore size engineering on MCM-41 over the monoalkylation selectivity [13]. Aluminum chloride grafted on SBA-15 and MCM-41 silica supports were compared for their

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catalytic activities for benzene alkylation [14]. This study deals with the characterization of the aluminum chloride species grafted on different MMSs and their catalytic activity in the alkylation of benzene with 1-dodecene.

2. Experimental

2.1. Preparation of MMSs

The designation of the catalysts reflects three characteristics of the material. Letters, H or WH, are attributed to the structure type of MMSs (H = hexagonal and WH = wormhole like). The number after the type of structure gives average pore diameter of the MMS expressed in Angstroms and the final term indicates the molecule grafted on the MMS. For example, WH26-$AlCl_3$ is an aluminum chloride grafted on a wormhole like MMS with a pore diameter of 26 Å.

2.1.1. Sample WH26

WH26 was obtained by following the synthesis procedure reported by Tanev and Pinnavaia [15]. Dodecylamine was used as the template in a solution of ethanol:water and tetraethyl orthosilicate was the silicon source ($I^0/S^0 = 4$). Dodecylamine (1.8 g) was added to a solution of distilled water (90 ml) and ethanol (34 ml). Once the template was dissolved, tetraethyl orthosilicate (8.2 g) was added under vigorous stirring. The reaction mixture was aged at ambient temperature for 20 h. The product was filtered and washed with three portions of distilled water (300 ml) and then calcined at 600 °C for 6 h.

2.1.2. Sample WH50

WH50 was obtained following the synthesis procedure reported by Stucky and coworkers [16]. Poly(alkene oxide) block copolymer (Pluronic P-123) was used as the template in ethanol and silicon tetrachloride was the silicon source. Pluronic P-123 (2.5 g) was added in 25 ml of ethanol. Once the template was dissolved, silicon tetrachloride (4.2 g) was added under vigorous stirring for 0.5 h. The resulting product was gelled in a Petri dish at 60 °C for 3 days. WH50 was calcined at 600 °C for 6 h.

2.1.3. H33 and H55

H33 and H55 were obtained following the synthesis procedure reported by Trong On et al. [17] Poly(alkene oxide) block copolymers, BRIJ-56 and P-123, were used as template in distilled water for H33 and H55 respectively. The silicon source used was a sodium silicate solution (28.7% SiO_2, 8.9% Na_2O). The templates (16 g) were dissolved in 380 g of distilled water at 40 °C for 2 h. When the mixture was clear, 37 g of sodium silicate solution was added at room temperature with magnetic stirring for 1 h. To this solution, 48 g of sulfuric acid 98% was added with vigorous stirring for 18 h and heated for 48 h at 80 °C. H33 and H55 were filtered and washed with three portions of distilled water. The H33 and H55 were calcined at 600 °C for 6 h.

2.2. Grafting procedure (Schlenk technique)

The support (2.5 g) was dried at 400 °C under vacuum (overnight) and kept under dry argon in a Schlenk tube. The support was added to 100 ml of benzene (sodium dried) in the reaction tube under a dry argon atmosphere. To this solution was added 1.5 g of aluminum chloride stored in a Schlenk tube. The mixture was refluxed for 3 h under dry argon and then filtered and washed three times in a Schlenk tube with dry benzene (100 ml). The grafted support was stored in a Schlenk tube under a dry argon atmosphere.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a SIEMENS D5000 or a PHILIPS diffractometer using CuKα radiation ($\lambda = 1.5406$ Å). Diffraction patterns were recorded with a step scan of 0.02° for 2θ between 1° and 10°.

Nitrogen adsorption/desorption isotherms were measured at liquid nitrogen temperature using a QUANTACHROME NOVA 2000 instrument. Before adsorption, the samples were evacuated at 200 °C for 4 h. Specific surface area was calculated using the multi-point BET method in the relative pressure range of 0.05–0.3. The pore diameter was estimated from the peak position of BJH pore size distribution. Sample compositions were measured by atomic adsorption using a PERKIN ELMER model 1100B after dissolution of the catalyst in a diluted mixture of HCl and HF at 60 °C.

Adsorbed pyridine infrared spectra (IR-pyridine) were recorded on a BIO-RAD FTS-60 FTIR spectrometer. The wafers were prepared in a glove box under a dry argon atmosphere. The self-supporting wafers were evacuated in situ in an IR cell at 250 °C overnight. Pyridine was permitted to desorb at 25 °C and 120 °C. The spectra were recorded after cooling at room temperature.

The ammonia desorption experiment (TPD-NH_3) was performed on a RXM 100 multicatalyst testing and characterization system (Advanced Scientific Design Inc.). The catalyst was prepared in a glove box under dry argon atmosphere. For TPD-NH_3, 15 mg of catalyst was treated at 25–300 °C (ramp = 10 K/min) and 1 h isotherm at 300 °C under a He flow of 20 ml/min. The catalyst was cooled down to room temperature under flowing helium. The catalyst was saturated with ammonia at 120 °C under a flow of He (15 ml/min) and NH_3 (5 ml/min) for 5 min. The set up was stabilized for