



Toluene alkylation with 1-octene over supported heteropoly acids on MCM-41 catalysts

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ABSTRACT

The liquid phase alkylation of toluene with 1-octene catalyzed by bulk and MCM-41 supported Keggin-type heteropoly acids (HPA), such as tungstophosphoric acid (HPW), tungstosilicic acid (HSiW), and molybdophosphoric acid (HPMo), has been studied. Among these catalysts, the supported catalysts exhibited more activity than bulk HPA, especially, HSiW and HPW supported on MCM-41 (HSiW/MCM-41 and HPW/MCM-41). The conversion of 1-octene was 100% and selectivity for monoalkylation products was 99.9% after 2 h of reaction at 120 °C over HSiW/MCM-41. The studies of FT-IR, thermogravimetric analyses (TGA) and X-ray diffraction (XRD) confirmed the presence and high dispersion of HPA on MCM-41 mesoporous structure. We also examined the reusability of the supported catalysts. The catalysts retained their catalytic activity for five reaction times in the present study. These results indicate that HSiW/MCM-41 and HPW/MCM-41 are excellent catalysts for this reaction under mild conditions.

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1. Introduction

The Friedel-Crafts alkylation of aromatic compounds is the most important processes for the synthesis of alkyl aromatic compounds on an industrial scale [1]. For instance, alkylation of benzene with ethylene and propylene to produce ethylbenzene and cumene, respectively, is presently the most widely used in petrochemical industry [2–4]. Conventionally, alkylation reactions are carried out with alkylating agents by using Lewis acids (e.g., AlCl_3 , ZnCl_2) or Brønsted acids (e.g., HF, H_2SO_4) as catalysts [5,6]. However, these homogeneous processes are typically associated with problems of decomposition, corrosion, large catalyst amounts, and difficulties in the separation of catalyst [7,8]. In order to overcome these drawbacks, in recent years, considerable effort has been put into developing heterogeneously catalyzed alkylation reaction using solid acid catalysts such as zeolites [9,10], clays [11], Nafion-H [12], ion exchange resin [13,14], and heteropoly acids [15,16].

Heteropoly acids (HPA) have several advantages, such as no corrosion, strong Brønsted acidity [7,17,18], which make them extensively used as acid and oxidation catalysts for several industrial applications. Nevertheless, HPA have an extremely small surface area ($1\text{--}5\text{ m}^2\text{ g}^{-1}$) and high solubility in polar solvents (e.g., water, lower alcohol, and ketone) [7]. To improve the catalytic per-

formance of HPA, many attempts have been done. One method was dispersion HPA on neutral support, such as SiO_2 [19,20], active carbon [21], mesoporous silica [22–24], and TiO_2 [25] to enlarge the surface area, which increases the number of acidic sites on the surface and enhances catalytic activity. Among them, since Beck et al. [26] discovered the mesoporous silica of MCM-41 type, then this type of materials have played an important role in catalysts, catalyst-precursors or catalyst supports [10,19,22–24,27] due to their high thermal stability, large internal surface area ($>1000\text{ m}^2\text{ g}^{-1}$), uniform and controllable pore size. In the last decade, various acid-catalyzed processes based on HPA supported on MCM-41 had been investigated by several groups [18,22,24,27].

Long chain alkylbenzenes are important industrial intermediates for detergents and many other chemicals. In contrast to a high number of papers dealing with alkylation of benzene and toluene with propylene [10], few studies on toluene alkylation with 1-octene over cation exchange resins and zeolites have been published [10,13,14]. Although relatively active of the several reported catalysts, these reaction systems brought in a complex mixture of products. Furthermore, the lower surface area, less stable under high temperature limited the practical application of cation exchange resins.

In this work, we reported the first example of Friedel-Crafts alkylation of toluene with 1-octene (Fig. 1) catalyzed by Keggin-type heteropoly acids (HPW, HSiW, and HPMo) bulk and supported on MCM-41. The effect of reaction conditions was investigated in a detail. Emphasis is put on the optimization of catalyst performance,

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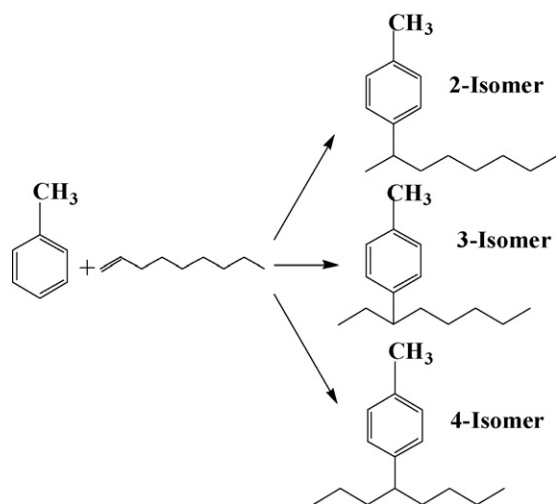


Fig. 1. Scheme of alkylation of toluene with 1-octene.

substrate conversion, product selectivity, and catalyst reusability. These catalytic results show that HPA supported on MCM-41 are superior to those for ZSM-5, zeolite beta [10].

2. Experimental

2.1. Materials

Tungstophosphoric acid $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ (HPW), tungstosilicic acid $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ (HSiW), molybdophosphoric acid $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ (HPMo), and molybdovanadophosphoric acid $\text{H}_4\text{PMo}_{11}\text{VO}_{40}\cdot n\text{H}_2\text{O}$ (HPMo₁₁V) were prepared according to the literature method [28,29]. Tetraethyl orthosilicate (TEOS), cetyl trimethylammonium bromide (CTMA-Br), toluene, and 1-octene were obtained commercially of analytical grade and were used without further purification.

2.2. Preparation of catalysts

Pure-silica MCM-41 was synthesized in our laboratory according to the literature method of Beck et al. [26]. The supported catalysts were prepared by the equilibrium impregnation technique following the procedure of Kozhevnikov et al. [30]. Typically, 1 g of MCM-41 was suspended in 30 mL methanol solution and then added a certain amount of HPA to this mixture. After stirring the suspension 24 h (overnight) at room temperature, the solvent was evaporated below 30 °C and was dried at 60 °C under vacuum, so as to obtain loadings of 10–50 wt% HPA supported on MCM-41. The catalysts were stored in a desiccator until use.

HPA supported on MCM-41 are abbreviated as HPA(x)/MCM-41, where x in parentheses denote the percentage loading (wt%) of the heteropoly acids on MCM-41.

2.3. Characterization

Heteropoly acids supported on MCM-41 were characterized by X-ray diffraction (XRD) [Siemens XRD-5005 diffractometer at a scanning rate of 4°/min, using Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$], FT-IR spectroscopy [Alpha centaur FT-IR Spectrophotometer using KBr pellets], and thermogravimetric analyses (TGA) [PerkinElmer TGA47, under nitrogen flow with a heating rate of 10 °C min⁻¹].

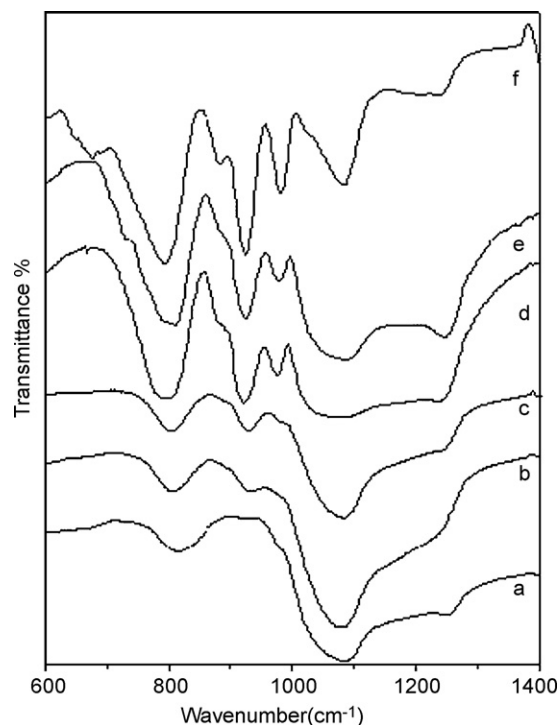


Fig. 2. FT-IR spectra of catalysts: (a) MCM-41; (b) HSiW(10)/MCM-41; (c) HSiW(30)/MCM-41; (d) HSiW(50)/MCM-41 (fresh); (e) HSiW(50)/MCM-41 (after reused five times); and (f) HSiW.

2.4. Alkylation reactions

A typical run is as follows: toluene (8.4 mL, 95.6 mmol), 1-octene (1.5 mL, 9.56 mmol), and catalyst 0.1 g (the amount of catalyst was varied in some experiments) were charged in a round-bottom glass reactor (50 mL capacity) equipped with a condenser and magnetic stirrer. The mixture of reaction was stirred rapidly and kept at 80 °C by means of a preheated oil-bath for a certain time under reflux condition. Once the reaction time was reached, the mixture was cooled to room temperature and then removed the catalyst by filtration. The liquid samples were analyzed using a GC112 gas chromatograph equipped with a hydrogen flame ionization detector system and OV-17 capillary column (15 m \times 0.25 mm). The experiment conditions were as follows: initial temperature, 70 °C (2 min); 10 °C/min; final temperature, 200 °C (15 min) with nitrogen as carrier gas. The products were also identified by gas chromatograph–mass spectrometry analysis (GC–MS) on Agilent 6890 with HP-ultra1 quartz capillary column. The conversion values of 1-octene were calculated as the mass of 1-octene which consumed during the reaction divided by the mass of 1-octene before reaction.

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. FT-IR spectra

Typical Fourier transform infrared (FT-IR) spectra of pure HSiW powder and HSiW(x)/MCM-41 powder are shown in Fig. 2, respectively. The fingerprint absorption bands in the range from 700 to 1100 cm⁻¹ ascribed to the Keggin structure [23]. It can be observed that the characteristic peaks are present in both bulk HSiW and HSiW(50)/MCM-41. Pure MCM-41 shows a strong broad absorption band in the range of 1050–1200 cm⁻¹, which partially overlaps the stretching vibration of Si–O_a in HSiW (1080 cm⁻¹) [31]. The IR spec-

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