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

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ARTICLE INFO

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 Brönsted acids (e.g., HF, H$_2$SO$_4$) 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 Brönsted 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 (1–5 m^2 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 m^2 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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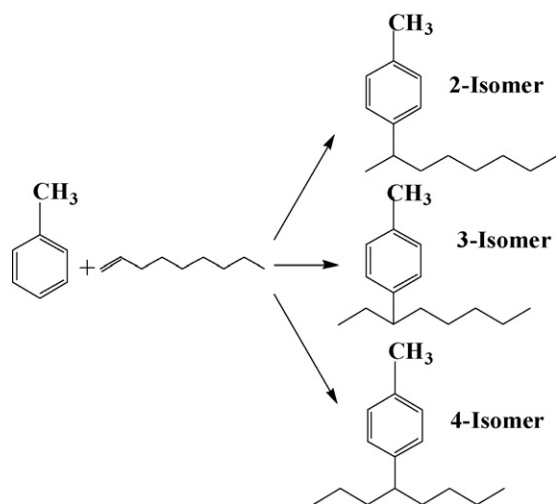*E-mail address:* linxu@nenu.edu.cn (L. Xu).

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 $H_3PW_{12}O_{40} \cdot nH_2O$ (HPW), tungstosilicic acid $H_4SiW_{12}O_{40} \cdot nH_2O$ (HSiW), molybdophosphoric acid $H_3PMo_{12}O_{40} \cdot nH_2O$ (HPMo), and molybdovanadophosphoric acid $H_4PMo_{11}VO_{40} \cdot nH_2O$ (HPMo$_{11}$V) 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 Kα radiation, λ = 1.5418 Å], FT-IR spectroscopy [Alpha centaurt FT-IR Spectraphoto-meter using KBr pellets], and thermogravimetric analyses (TGA) [PerkinElmer TGA47, under nitrogen flow with a heating rate of 10 °C min^{-1}].
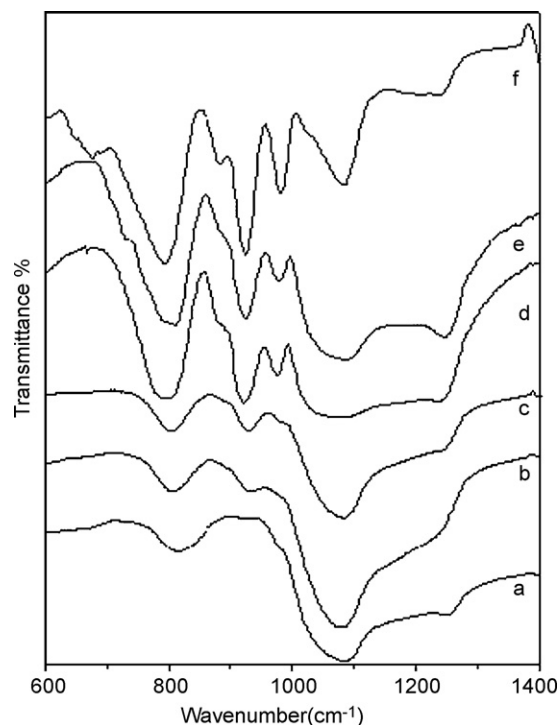

Fig. 2. FT-IR spectra of catalysts: (a) MCM-41; (b) HSiW(10)/MCM-41; (c) HSiW(30)/MCM-41; (d) HSiW(50)/MCM-41 (fresh); (e) HSiW(50)/MCM-41 (after reused five times); and (f) HSiW.

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 × 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-
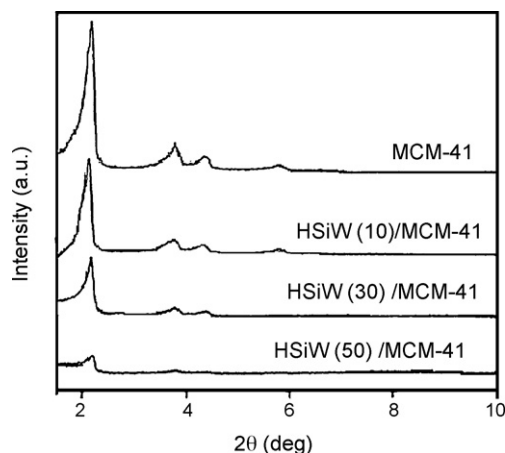
Fig. 3. XRD patterns of pure MCM-41 and HSiW(x)/MCM-41.

tra of HSiW(10)/MCM-41 and HSiW(30)/MCM-41 are quite similar, except for the absorption intensity of 924 cm^{-1}, which is stronger in spectrum of HSiW(30)/MCM-41. With increasing the HSiW loading to 50 wt%, the characteristic peaks are obvious and become sharper. Although, one of the absorption bands of Keggin structure characteristic peaks at 791 cm^{-1} was not clear seen at lower loadings, the absorption bands at 924 cm^{-1}, which is assigned to the stretching vibrations of W–O_b–W was observed in all supported catalysts. These characteristic peaks of Keggin ion confirmed the presence of heteropoly acids into MCM-41 framework. A similar behavior was observed for HPW(x)/MCM-41.

3.1.2. X-ray diffraction patterns

X-ray diffraction is a strong tool to measure the crystallinity and regularity of the materials. Fig. 3 shows the XRD patterns of pure MCM-41 and HSiW(x)/MCM-41.

For pure MCM-41, four peaks at low angle corresponding to four planes, [1 0 0], [1 1 0], [2 0 0], and [2 1 0], which can be indexed on a hexagonal lattice, show the formation of an ordered hexagonal mesoporous structure [22,26]. The characteristic peak at [1 0 0] shows the long-range order of MCM-41 [26]. However, the amount of HSiW has a remarkable effect on the intensity of the [1 0 0] peak. With increase amount of HSiW on MCM-41, a significant decrease in the intensity of the [1 0 0] peak is visible in XRD patterns. It is due to the occurrence of disorder in the hexagonal structure of MCM-41 [23]. A similar phenomenon appears in HPW/MCM-41.

The supported catalysts exhibit a broad bump in the range of $2\theta = 15$–$40°$, which is ascribed to the formation of an amorphous phase. No patterns of any bulk HPA crystal phase are observed for the supported catalysts. These results indicate that the HSiW was well dispersed on the MCM-41 support at less than 50 wt% loading. Earlier researchers have confirmed the conclusion by TEM [23,24,32].

3.1.3. Thermogravimetric analyses

Typical TGA profiles for HSiW bulk and supported on MCM-41 are shown in Fig. 4. Three distinct weight loss patterns can be observed in the profiles of bulk HSiW. (i) The first weight loss of 6.6% up to 100 °C corresponds to the loss of 11-non-coordinated water (the amount depending on the number of hydration water molecules in HSiW which changed with the prepared conditions). (ii) The second weight loss of 4.8% up to 250 °C is due to the dehydration of 8H_2O molecules. The crystal structure of HSiW is formed by packing heteropolyanions into a body-centered cubic structure [7]. (iii) The third of 1.15% up to 500 °C accounting for the loss of 2H_2O molecules belongs to the loss of all acidic protons [18,22,23].
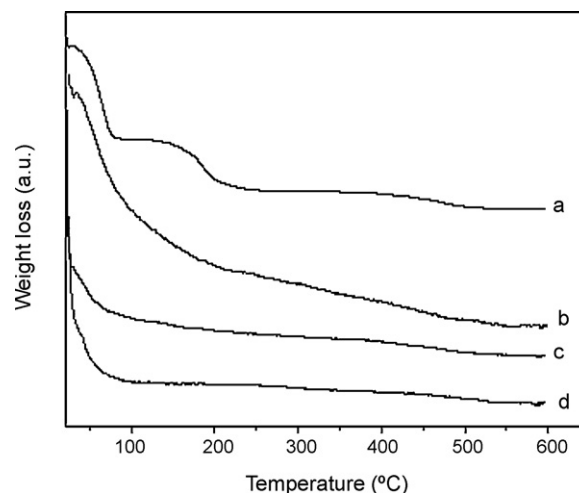

Fig. 4. TGA profiles of catalysts: (a) HSiW; (b) HSiW(10)/MCM-41; (c) HSiW(30)/MCM-41; (d) HSiW(50)/MCM-41.

A relatively rapid weight loss between 20 and 150 °C occurred in the profile of HSiW/MCM-41 is due to the loss of water in the channels of MCM-41 [26]. Gradual weight loss from 150 to 500 °C in the profiles of HSiW(x)/MCM-41 were observed, but rapid weight loss from 150 to 300 °C for bulk HSiW was disappeared. These types of weight loss can be attributed to the difficulty in the removal of water in HSiW molecules when they were supported on MCM-41.

3.2. Catalytic activity test in alkylation of toluene

3.2.1. Comparison of different catalysts

The catalytic performance of different catalysts in the alkylation of toluene with 1-octene was tested under similar conditions. The result is depicted in Table 1. As can be seen that parent MCM-41 has no activity for this reaction. At the same conditions, bulk HPA (HPW, HSiW, HPMo, and HPMo$_{11}$V) have very low activity as compared to supported catalysts. The conversions of 1-octene are merely 4.2, 4.5, 3.3, and 2.1% in the presence of the former bulk HPA catalysts, respectively, and the conversions of corresponding supported catalysts reach 57, 80, 19, and 10%, respectively. Although bulk HPA are strong Brönsted acid, the low surface area (1–5 m^2 g^{-1}) causes a relatively small number of acidic sites on the surface [8]. This property results in the low activity of bulk HPA. When the bulk HPA were dispersed on MCM-41, the number of acidic sites on the surface is increasing with the increase of surface area [7,8,22,23]. Consequently, the catalytic performance of supported catalysts is superior to that of bulk HPA.

In terms of selectivity, they showed high selectivity for monoalkylation products (100%). Furthermore, the reaction almost only formed 2-isomer at lower conversion. Branched isomers are result of a skeletal isomerization of 1-octene, which are undesirable due to lower biodegradability [14]. Therefore, the 2-isomer is the most preferred product.

According to the results of preliminary reactions, the alkylation reaction was further investigated with HSiW/MCM-41 and HPW/MCM-41 as catalysts.

3.2.2. Effect of toluene/1-octene molar ratio

The effect of the molar ratio of toluene to 1-octene on the conversion and monoalkylation selectivity was studied at 80 °C, HSiW(50)/MCM-41 as catalyst. The results are presented in Fig. 5. During these reactions, the amount of catalyst is a constant (1.2 wt%).

Table 1
Alkylation of toluene with 1-octene over different catalysts.

Catalyst	Conversion of 1-octene (%)	Selectivity of monoalkylation (%)	Distribution of products (%)		
			2-Isomer	3-Isomer	4-Isomer
HSiW(50)/MCM-41[a]	80	99.9	43.4	25.5	31.1
HPW(50)/MCM-41[a]	57	99.9	54	22.4	23.6
HPMo(50)/MCM-41[a]	19	99.9	95.6	4.4	–
$PMo_{11}V_1(50)$/MCM-41[a]	10	99.9	100	–	–
$H_3PW_{12}O_{40}$[b]	4.2	99.9	100	–	–
$H_4SiW_{12}O_{40}$[b]	4.5	99.9	100	–	–
$H_3PMo_{12}O_{40}$[b]	3.3	99.9	100	–	–
$H_4PMo_{11}VO_{40}$[b]	2.1	99.9	100	–	–
MCM-41[a]	–	–	–	–	–

[a] Reaction conditions: m_{catal}: 0.1 g; toluene, 8.4 mL; 1-octene, 1.5 mL; temperature 80 °C; reaction time 4 h.
[b] Reaction conditions: m_{catal}: 0.2 g; toluene, 8.4 mL; 1-octene, 1.5 mL; temperature 80 °C; reaction time 4 h.

When the molar ratio of toluene to 1-octene was increased from 1 to 10, the conversion of 1-octene greatly increased from 25.5 to 80%. Hereafter, when increased the ratio to 20, the conversion decreased to 62.5%. This phenomenon results from the low concentration of 1-octene when the molar ratio increased to 20. The selectivity to monoalkylation products was 100% at all mole ratios and 2-isomer was the main product (44%). Therefore in our reaction conditions, the best molar ratio of toluene to 1-octene is 10.

3.2.3. Effect of reaction temperature

Temperature plays an important role in alkylation of toluene with 1-octene. Fig. 6 depicts the conversion of 1-octene as a function of temperature in the presence of HSiW(50)/MCM-41.

The conversion increased with an increase in temperature and the selectivity of monoalkylation products was almost 100%. After 4 h, the conversions of 1-octene were 15, 80, and 88.9% at 60, 80, and 100 °C, respectively. The best result was achieved at 120 °C, the reaction was almost complete after 2 h and the selectivity of 2-isomer was 43%. With the increasing of the conversion the distribution of monoalkylation products was changed. 2-Isomer was found to decrease. The changes of the percentage of 2-isomer during the reaction are presented in Fig. 7. At lower temperature (60 °C), the reaction formed more 2-isomer than at higher temperature (120 °C).

3.2.4. Effect of catalyst amount

The dependence of the conversion of 1-octene on the catalyst amount was investigated ranged from 0.05 to 0.2 g using
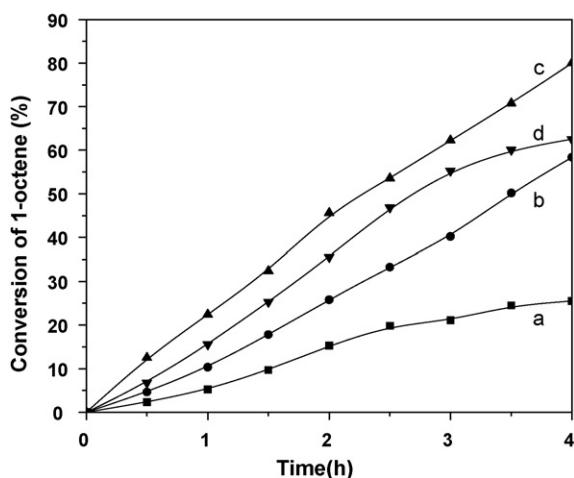

Fig. 6. Effect of reaction temperature on the alkylation of toluene over HSiW(50)/MCM-41. Toluene/1-octene = 10:1 (mol/mol); m_{catal} = 0.1 g. (a) 60 °C, (b) 80 °C, (c) 100 °C, and (d) 120 °C.

HSiW(50)/MCM-41 as the catalyst. It was found that the conversion increased with the increase of catalyst amount up to 0.2 g (Fig. 8). The alkylation almost completed within 1 h when the amount of HSiW(50)/MCM-41 was 0.2 g. This is due to the increased of the number of acidic sites. It is generally accepted that the electrophilic aromatic substitution and in particular Friedel-

Fig. 5. Influence of molar ratio of toluene to 1-octene on the conversion catalyzed by HSiW(50)/MCM-41. T = 80 °C; catalyst weigh percentage: 1.2%. (a) 1:1, (b) 5:1, (c) 10:1, and (d) 20:1.
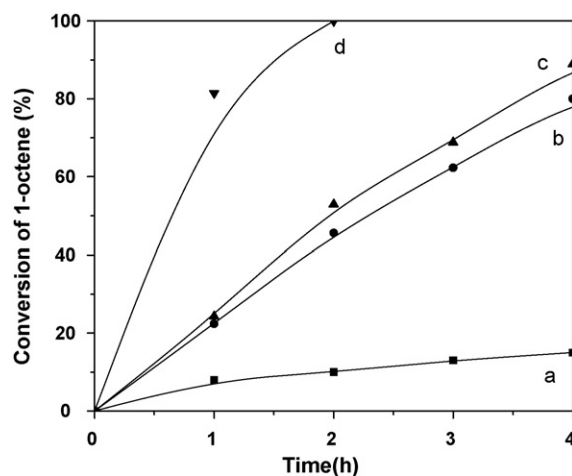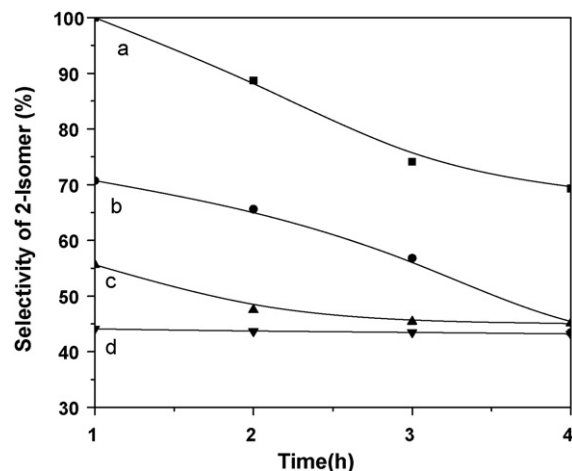

Fig. 7. Selectivity of 2-isomer as the function of temperature over HSiW(50)/MCM-41. Toluene/1-octene = 10:1 (mol/mol); m_{catal} = 0.1 g. (a) 60 °C, (b) 80 °C, (c) 100 °C, and (d) 120 °C.
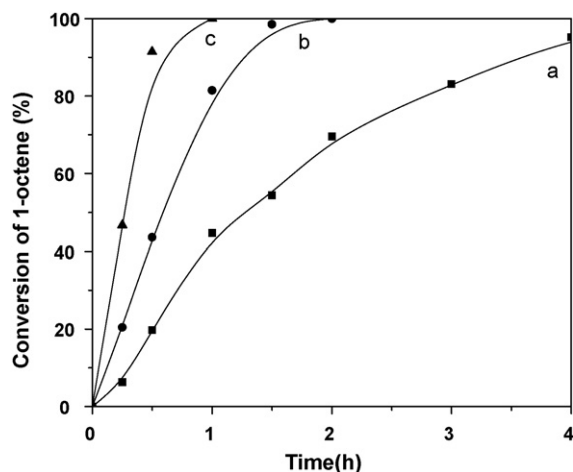
Fig. 8. Effect of the catalyst [HSiW(50)/MCM-41] amount on the conversion of 1-octene. Toluene/1-octene = 10:1 (mol/mol); T = 120 °C. (a) 0.05 g, (b) 0.1 g, and (c) 0.2 g.

Fig. 9. Effect of the catalyst [HSiW(x)/MCM-41] loadings on the conversion of 1-octene. Toluene/1-octene = 10:1 (mol/mol); m_{catal} = 0.1 g; T = 120 °C. (a) 10 wt%, (b) 30 wt%, and (c) 50 wt%.

Crafts reaction occurs with the formation of carbenium ion as the intermediate [19,33]. With an increase in the catalyst amount, the number of acidic sites and surface area increased leading to the formation of more carbenium ions per unit of time, which directly increases the reaction rate. The composition of isomer in the monoalkylation products remains with higher selectivity for 2-isomer (44%).

3.2.5. Influence of HPA loading

We also examined the influence of the HSiW loadings on MCM-41 at 120 °C (Fig. 9). When the loadings are changed from 10 to 30 wt%, the catalytic performance increased rapidly. When the loading reaches to 50 wt%, the conversion of 1-octene has a slight drop as compared to 30 wt% loading at the same reaction time. Dispersing HPA on solid support with high surface area can enhance the catalytic activity of HPA. However, earlier studies have reported the fact that tiny crystallite formation of HPA occurs at higher loadings such as 50 wt% [22,32].

It has been known that the BET surface area and pore volume of HPA supported on MCM-41 decreased with increase in the loadings of HPA [22,23]. The BET surface area of HPW(30)/MCM-41 is 646 m² g⁻¹ [22], but when increased the loading to 50 wt% the area decreased to 403 m² g⁻¹. The pore volume of the HPW supported on MCM-41 also exhibited similar trends. So HSiW(30)/MCM-41 is a little higher activity than HSiW(50)/MCM-41 may be due to the former has higher surface area and better dispersion of HPA. Although HSiW(10)/MCM-41 has higher surface area than HSiW(30)/MCM-41, the loading of HPA is too small, so the number of acidic sites is relatively small too. The low activity of HSiW(10)/MCM-41 can be attributed to this reason. The conversion of 1-octene shows that
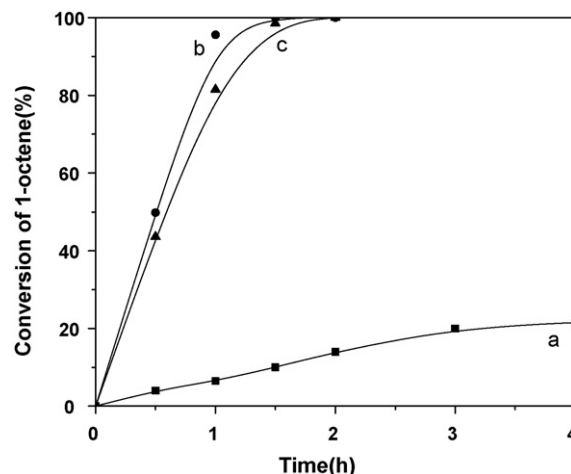
HSiW(30)/MCM-41 has the highest catalytic performance for the alkylation of toluene with 1-octene under our reaction conditions among the three catalysts.

3.2.6. Catalytic activity of HPW(x)/MCM-41

Detailed studies on the catalytic performance of HPW(x)/MCM-41 were done in this work, too (Table 2). Although HPW(x)/MCM-41 showed a similar behavior as HSiW(x)/MCM-41 when changed the reaction conditions involved reaction temperature, catalyst amount, and HPA loadings, the catalytic activity was a little lower in comparison with HSiW(x)/MCM-41 under the same conditions. When the molar ratio was 10, temperature was 120 °C, and catalyst [HPW(30)/MCM-41] amount was 0.1 g, the alkylation reaction reached the maximum conversion (100%) within 2 h. From Fig. 9 we can see that, at the same conditions HSiW(30)/MCM-41 reached the maximum conversion after 1.5 h. It is likely that the difference in activity is not only caused by the difference in acid strength. Generally, HPW is considered to be slightly stronger acidic than HSiW [7], but HPA protons play an important role in the catalytic activity of acid catalyzed. Apparently, HSiW contains four protons per Keggin unit, compared with HPW, which has only three. Moreover, small interaction between HPA and MCM-41 might cause the difference in activity [34,35]. Furthermore, like the condition of HSiW(x)/MCM-41, HPW(30)/MCM-41 showed more activity than that of HPW(50)/MCM-41.

3.2.7. Reusability of catalysts

Recycling experiments were investigated over HSiW(50)/MCM-41 and HPW(50)/MCM-41. The results are presented in Table 3.

Table 2
Detailed studies on the catalytic performance of HPW(x)/MCM-41.

Catalyst	m_{catal} (g)	T (°C)	Time (h)	Conversion of 1-octene (%)	Selectivity of monoalkylation (%)	Distribution of products (%)	
						2-Isomer	3-Isomer
HPW(50)/MCM-41	0.1	60	4	10.1	99.9	68	17.7
HPW(50)/MCM-41	0.1	80	4	57	99.9	54	22.4
HPW(50)/MCM-41	0.1	100	4	80	99.9	43.6	25.1
HPW(50)/MCM-41	0.1	120	4	100	99.9	43.7	24.7
HPW(50)/MCM-41	0.05	120	4	93.1	99.9	43.8	25.1
HPW(50)/MCM-41	0.2	120	1.5	100	99.9	43.3	24.7
HPW(10)/MCM-41	0.1	120	4	9.5	99.9	100	–
HPW(30)/MCM-41	0.1	120	2	100	99.9	44.1	24.4

Table 3
Recycling of HSiW(50)/MCM-41 and HPW(50)/MCM-41 for the alkylation of toluene with 1-octene[a].

Catalyst	Time (h)	Conversion of 1-octene (%)	Selectivity of monoalkylation (%)	Distribution of products (%)		
				2-Isomer	3-Isomer	4-Isomer
HSiW(50)/MCM-41	1	100	99.9	43	24.7	32.3
	2	95	99.9	44.2	25.2	30.6
	3	93	99.9	45	24.6	30.4
	4	92.7	99.9	45.1	24.3	30.6
	5	93	99.9	44.9	25	30.1
HPW(50)/MCM-41	1	96.5	99.9	43.8	24.9	31.3
	2	95.7	99.9	43.3	25	31.7
	3	95	99.9	43.2	24.4	32.4
	4	94.7	99.9	43.5	24.3	32.2
	5	94.5	99.9	44	24.5	31.5

[a] Reaction conditions: toluene/1-octene, 10:1 (mol/mol); m_{catal}: 0.1 g; temperature 120 °C; reaction time 2 h.

Table 4
Comparison of the catalytic activity of different solid acids in the alkylation of aromatic compounds with olefins.

Catalyst	Conversion of 1-octene (%)	Selectivity of monoalkylation (%)	Distribution of products (%)		Reference
			2-Isomer	3-Isomer	
HSiW(50)/MCM-41[a]	100	99.9	43	24.7	This work
HPW(50)/MCM-41[a]	96.5	99.9	43.8	24.9	This work
HSiW(30)/MCM-41[b]	100	99.9	44.1	24.8	This work
HPW(30)/MCM-4[b]	100	99.9	44.1	24.4	This work
Amb15[c]	75	100	56	17.3	[13]
Amb35[d]	100	90	44	49	[14]
Zirconia[e]	100	94	43	–	[36]
Filtrol-24[f]	85	–	22	47	[37]
Zeolite Beta[g]	25	100	–	–	[10]
ZSM-5[g]	20	100	–	–	[10]

[a] Toluene/1-octene, 10:1 (mol/mol); m_{catal}: 0.1 g; temperature 120 °C; reaction time 2 h.
[b] Toluene/1-octene, 10:1 (mol/mol); m_{catal}: 0.1 g; temperature 120 °C; reaction time 1.5 h.
[c] Toluene/1-octene, 10:1 (mol/mol); temperature 80 °C; reaction time 4 h.
[d] Toluene/1-octene, 10:1 (mol/mol); catalyst: 0.04 g/cm³; temperature 110 °C; reaction time 4 h.
[e] Benzene/1-octene, 10:1 (mol/mol); m_{catal}: 1 g.
[f] Benzene/1-dodecene, 10:1 (mol/mol); temperature 150 °C; catalyst: 0.05 g/cm³; autoclave.
[g] Toluene/1-octene, 10:1 (mol/mol); m_{catal} = 1 g; temperature 120 °C; reaction time 3 h.

The catalysts were separated from the reaction mixture by filtration after the reaction finished and washed with methanol and then reused after drying at 100 °C overnight. There were losses during handling due to the particle size was very small. We changed the molar of substrate to keep the weight percentage of catalyst constant.

It is seen that the conversions of 1-octene only have a slightly drop during the five times reactions. Fig. 2d and e showed the FT-IR spectra of HSiW(50)/MCM-41 fresh and after reused five times, respectively. There is a little difference between these. These results indicate that these two catalysts had excellent reusability. Under the reaction conditions no significant deactivation of HPA immobilized on MCM-41 occurred. Therefore, it can be a viable alternative for substituting the traditional acid catalysts.

Comparison of the composition product mixture of different processes over different catalysts is presented in Table 4.

The data show that the catalytic of HSiW/MCM-41 and HPW/MCM-41 is comparable to that of commercial Amberlyst-35. The conversion of 1-octene were 100% at 120 °C using HPA(30)/MCM-41 as catalysts, whereas, using ZSM-5 as catalyst the conversion of 1-octene was 20% [10]. Apparently, the catalytic activity of HPA/MCM-41 is superior to non-zeolitic catalysts. The fact can be attributed to the strong Brönsted acidity of HPA and well dispersion on MCM-41. Mesoporous molecular sieves exhibited lower conversion, which is due to the relatively low acid strength. This study has demonstrated that HPA supported on MCM-41 could be used as an efficient catalyst in alkylation of toluene with 1-octene under rather mild conditions.

4. Conclusion

HSiW(30)/MCM-41 and HPW(30)/MCM-41 are efficient solid acid catalysts for the liquid phase alkylation of toluene with 1-octene. The reaction yielded only monoalkylation products and the conversion of 1-octene is nearly 100% in the reaction conditions explored. Furthermore, 2-isomer is the major product. Among the catalysts studied in this work, supported catalysts presented better performance as compared to that of bulk HPA. It is can be attributed to the difference of surface area of bulk HPA and supported catalysts. The catalytic activity for alkylation depended on the type of heteropoly acids, and HSiW supported on MCM-41 had the highest activity among the catalysts studied in our work. The catalyst can be reused after a simple work up. Recycling experiments indicate that no significant deactivation of HSiW(50)/MCM-41 and HPW(50)/MCM-41 occurred during the reaction.

In conclusion, the liquid phase Friedel-Crafts alkylation of toluene with 1-octene can be successfully catalyzed by Keggin-type heteropoly acids supported on MCM-41. Supported HPA onto mesoporous silica MCM-41 is an efficient method to enhance the catalytic activity of bulk HPA. The material could be used as an excellent catalyst in the alkylation of aromatic compounds with long chain olefins under relatively mild conditions.

Acknowledgements

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