Vapor phase alkylation of toluene using various alcohols over H_3PO_4/MCM-41 catalyst: influence of reaction parameters on selectivity and conversion

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A mesoporous MCM-41 molecular sieve material with a molar ratio of $SiO_2/Al_2O_3 = 70$ and loaded with H_3PO_4 was used as a catalyst for the alkylation of toluene, using various alcohols, namely methanol, *iso*-propanol, and *tert*-butanol, as alkylating agents. *Para*-alkylated toluene was the predominant product, formation of which was enhanced by moderate temperature, low amounts of the alkylating agents in the feed, and high carrier gas flow rate. Time on stream was found to exert a profound effect on the selectivity and conversion to the different products.

Key Words: Alkylation; toluene; mesoporous MCM-41; vapor phase; H_3PO_4.

Introduction

The Friedel-Crafts alkylation reaction is a very useful reaction for the synthesis of alkyl aromatic compounds both in the laboratory and on an industrial scale.[1,2] The reaction is generally carried out with alkylating reagents such as alkenes, alkyl chlorides, and alcohols by using a stoichiometric amount of Lewis and Brönsted acids.[2] Environmentally hazardous Friedel-Crafts catalysts, such as $AlCl_3$, HF, or H_2SO_4, have been employed widely.[3] In recent years, the use of heterogeneous catalysts in liquid phase reactions has greatly increased due to their advantages such as high activity and selectivity, reusability, ease of separation, and no corrosion or disposal

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of effluent problems.[4] Non-conventional solid acid catalysts such as MCM-41 have been used in this area and they showed good thermal stability.[5,6] The use of zeolites as non-conventional Friedel-Crafts catalysts, instead of the hazardous mentioned catalysts, is very interesting from both the environmental and economic points of view. No pollution problems are caused by these solid acids, whose pore structure is able to induce unique selectivity effects. Heterogeneous catalysts such as zeolites have proved to be central to this strategy, and the careful control of the reactions can maximize the selectivity and yield of a single desired product, while minimizing the formation of by-products.[6] MCM-41 is an interesting solid acid catalyst used widely in recent years. The acidity of MCM-41 is low compared with other zeolites due to the disordered wall structure.[6−9] However, the incorporation of Al-atoms into the MCM-41 structure has been known to import acidity with Brönsted acid sites corresponding to framework Al-atoms and both framework and non-framework Al-atoms contributing to Lewis acid sites.[10] Thus, Al-MCM-41 has already been proposed as an alkylation catalyst.[3,10] The combination of large pores and mild acidity in Al-MCM-41 has been exploited to carry out Friedel-Crafts alkylation and acylation of benzene with benzyl chloride.[11−20] Shape selective alkylation of 2,4-di-*tert*-butylphenol with cinnamyl alcohol and tertiary butylation of anthracene, naphthalene, and phenanthrene have also been reported over MCM-41.[12,14,18] Condon obtained 38% *ortho*, 27% *meta*, and 35% *para*-cymene by isopropylation of toluene under conditions in which dealkylation and isomerization were thought to be unimportant.[19] This distribution was obtained when the reaction was catalyzed with aluminum chloride-nitromethane in benzene as a solvent or with boron fluoride etherate at 658 °C. Simons and Hart[20] reported that hydrogen chloride catalyzed isopropylation of toluene yielded a distribution of 31% *ortho*, 25% *meta*, and 44% *para*-cymene. Schlatter and Clark[21] obtained 41% *ortho*, 26% *meta*, and 33% *para*-cymene with HF and phosphoric acid catalysts. Alkylation of toluene with isopropyl alcohol and H_2SO_4 (80%) at 708 °C furnished 35% of 2,4 *para*-cymene and diisopropyltoluene.[22] Moreover, *para*-cymene, *para*-ethyltoluene, and 4-*tert*-butyltoluene are also important chemical intermediates obtained by acid alkylation of benzene or toluene.[23]

The present work was undertaken to study the selective alkylation of toluene with methanol, isopropanol, and *tert*-butanol in the presence of MCM-41 molecular sieve, which had been modified and activated with H_3PO_4 loading on the basis of previous work[24] as a useful catalyst in vapor phase conditions.

Experimental

Synthesis of the catalyst

The solid used as catalyst in the present work is one of the large series of Al-MCM-41 molecular sieves and impregnated Al-MCM-41 with various amounts of H_3PO_4 which its preparation and characterization have been reported elsewhere.[24] Ghiaci et al.[24] demonstrated a modification on MCM-41 synthesis and some synthesis parameters such as the Al/Si ratio, the source of aluminum, and the temperature, were systematically modified and the different synthesis procedures can be seen in the mentioned reference. All characterizations of the catalyst samples are reported by Ghiaci et al.[24] Pyridine was used as a probe molecule to distinguish between Brønsted and Lewis acid sites.[25] Fourier transform IR spectra of adsorbed pyridine were measured using a JASCO FT/IR (680 plus) spectrometer.[26]

Synthesis of MCM-41 with $SiO_2/Al_2O_3 = 70$

First 0.050 g (0.75 mmol) of aluminum hydroxide gel was dissolved in the boiling solution of sodium hydroxide including 1.7031 g (41.73 mmol) of sodium hydroxide and some water. Water was slowly added to this solution until the total amount of water reached 23.0 g (1277.8 mmol). Then 5.5535 g (26.38 mmol SiO_2) of sodium silicate solution and 2.4219 g (23.48 mmol) of sulfuric acid were added to prepared aluminate solution. The obtained gel was stirred for 0.5 h to give a completely homogeneous mixture of reactants. Then an aqueous solution of cetyl trimethyl ammonium bromide (CTAB), prepared by dissolving of 2.3 g (6.31 mmol) of CTAB, was slowly added to the gel mixture. The resulting mixture was then stirred for 1 h at room temperature. The final pH was 10.48. Then it was kept in an autoclave at 373 K for about 1 h. The temperature was increased to 443 K and kept at that level for another 3.5 h. The obtained solid was recovered by filtration, followed by exhaustive washing with distilled water until neutral pH in the filtrate was obtained. The solid was dried at 373 K for 8 h and then the sample was calcined at 813 K for about 5 h.

Preparation of H_3PO_4/MCM-41 molecular sieves

Synthesized MCM-41 molecular sieves with 15 wt% H_3PO_4 content were prepared by impregnating a calculated amount of H_3PO_4 dissolved in distilled water on MCM-41 molecular sieves with a molar ratio of SiO_2/Al_2O_3 = 70. The impregnated catalysts were dried at 383 K for 12 h and then calcined in air at 873 K for 4 h. All the impregnated catalysts were pressed into wafers, crushed, and sieved to 20-40 mesh before use.

Characterization of the catalyst

Approximately 40-50 mg of material previously calcined in air for 4 h at 500 °C was pressed (for 3 min at 15 t cm^{-2} pressure under approximately 10^{-2} torr vacuum) into a self-supporting wafer of 15 mm diameter. The resulted wafer was treated with 26 mmHg of pyridine at 473 K for 1 h and evacuated at 473, 573, and 673 K for 1 h in a dynamic vacuum. After each treatment, an IR spectrum was recorded at room temperature. The peak areas corresponding to the concentration of Brønsted and Lewis acid sites adsorbed pyridine were collected at 1545 and 1445 cm^{-1} respectively. The extinction coefficients given by Emeis[27] (1.67 and 2.22 cm/μmol for Brønsted and Lewis acid sites, respectively) were considered. The relevant peak areas calculated for all the catalysts are presented in Table 1.

Table 1. Acidity of the catalysts used for alkylation of toluene.

Catalyst	Brønsted acidity (mmol kg^{-1}) (desorption temperature of pyridine)			Lewis acidity (mmol kg^{-1}) (desorption temperature of pyridine)		
	473 K	573 K	673 K	473 K	573 K	673 K
Al-MCM-41	227	205	110	24	23	22
10 wt% H$_3$PO$_4$/Al-MCM-41	198	176	100	9	9	8
15 wt% H$_3$PO$_4$/Al-MCM-41	173	157	84	9	8	7
25 wt% H$_3$PO$_4$/Al-MCM-41	139	119	64	5	4	4
30 wt% H$_3$PO$_4$/Al-MCM-41	120	103	36	2	2	0

Typical procedure for the vapor phase alkylation of toluene

The catalytic reactions were carried out in a down flow fixed bed tubular glass microreactor (15 mm internal diameter and 30 cm length) at atmospheric pressure and using 0.5 g of catalyst in each run. The catalyst was compacted in a hydraulic press. The pellets were broken and then sieved to 20-40 mesh size prior to use. The reactor was placed inside a temperature controlled vertical furnace and the thermocouple tip was situated at the center of the catalyst bed. After being loaded in the reactor, the catalyst was pretreated at 723 K for 3 h and using an inert gas stream of nitrogen (40 mL/min). Solutions of each alcohol dissolved in toluene (alcohol:toluene = 0.1) were fed, using a syringe pump with an optimum rate of 0.1 mL/min. The pure inert gas (nitrogen as carrier gas) was introduced by using a mass flow controller. Time-on-stream (TOS) was usually deducted within 30 min after the start of the reaction since mass balance in the initial period was poor. Then the products were collected from the reactor every hour in an ice/water trap and analyzed off-line with a gas chromatograph equipped with a 50 m-length capillary SE-30 column and a FID detector. N-decane was used as internal standard.

Results and discussion

To understand the role of H_3PO_4 loading on the catalyst and the changes in surface acidity of the catalyst, pyridine adsorption/desorption was used. In addition, to investigate the influence of reaction parameters on the selectivity and conversion we changed several factors and measured their influences on the selectivity and conversion. These parameters, including H_3PO_4 content, reaction temperature, injection rate of the starting materials, carrier gas flow rate, and time-on-stream (TOS), were studied in detail.

Acidity measurements

The acidity of the H_3PO_4/MCM-41 samples with various amounts of H_3PO_4 was measured using FTIR spectroscopy and pyridine as a probe molecule. The results obtained from all of the samples are summarized in Table 1.

Table 1 illustrates that in all catalysts the impregnation of various amounts of H_3PO_4 leads to a decrease in the Brønsted acidity. As the percentage of impregnated H_3PO_4 goes up, the strong Brønsted sites convert to weak Brønsted acidic sites. Therefore, the number of strong Brønsted sites decreases. According to the results in Table 1, the numbers of Lewis acid sites are much lower than the numbers of Brønsted acid sites. Especially when the amount of loaded H_3PO_4 increases, the numbers of Lewis acid sites become negligible. Therefore, it would be expected that the Brønsted acid sites in this catalyst play a key role in the alkylation mechanism. As stated before, with loading H_3PO_4 on the catalyst, the numbers of strong acid sites decreased and the numbers of weak acid sites increased. It could be concluded that H_3PO_4/MCM-41 is a mild acid catalyst suitable for toluene alkylation. According to this mild acidity nature, by-products such as dehydration products and di-alkylated products are negligible in the steam products. In addition, a lower rate of catalyst deactivation, because of coke formation on the surface of MCM-41, was observed, which was related to its mild acidity.

Influence of H_3PO_4 content on the toluene alkylation

Improvement of the H_3PO_4/MCM-41 catalyst is achieved by optimizing the loaded H_3PO_4 (Table 2). Variation loaded H_3PO_4 between 0 and 30 wt% has different effects on the activity and selectivity of alkylation. The activity of the catalysts with different amounts of H_3PO_4 is compared in Table 2 for the alkylation reaction at 330 °C for a period of time-on-stream (TOS = 8 h). Alkylation of toluene was done using methanol, *iso*-propanol, and *tert*-butanol as alkylating agent. Alkylation of toluene resulted in 3 products: *para*-alkylated as a major product, as well as small amounts of *ortho*-alkylated and di-alkylated products (Scheme), while dehydration products (alkene) were not detected even as a trace.

Table 2. Influence of the H_3PO_4 loading on the conversion of the alcohols and selectivity toward different products.

H_3PO_4 (wt%)	Conversion (%)			*Para*-alkylated toluene (%)			*Ortho*-alkylated toluene (%)			Dialkylated toluene (%)		
	MeOH	i-PrOH	t-BuOH	Me	i-Pr	t-Bu	Me	i-Pr	t-Bu	Me	i-Pr	t-Bu
0	2	5	8	57	64	73	34	30	25	7	6	2
10	45	72	79	65	73	84	28	22	15	7	5	1
15	74	83	91	73	79	89	22	27	10	5	4	1
25	98	100	100	83	88	94	12	9	6	5	3	-
30	100	100	100	75	77	73	21	22	27	4	1	-

Reaction conditions: T = 330 °C; P = 1 atm; injection rate = 0.05 mL/min; carrier gas N_2; N_2 flow rate = 30 mL/min.
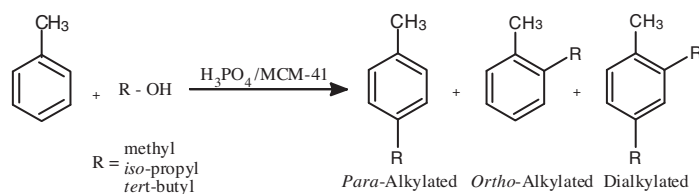
Scheme. Alkylation of toluene.

The first important result is that H_3PO_4-containing catalysts are more active than the support alone (without loaded H_3PO_4). The obtained results also show that the maximum alcohol conversion and best selectivity to *para*-alkylated toluene is recorded for the catalyst including 25 wt% H_3PO_4. Interestingly, the *para*-alkylated toluene selectivity also increases with increasing amount of loaded H_3PO_4, reaching the maximum value for the solids with 15-25 wt% H_3PO_4. Beyond this loading, selectivity to *para*-alkylated toluene decreases. According to the literature, supported H_3PO_4 on silica (silica phosphoric acid-SPA) was discovered by Ipatieff[23] and industrially developed in the 1940s. The first modified MCM-41 zeolite as the support for phosphoric acid was reported,[24] which led to the improvement of the shape selectivity of that zeolite. It is assumed[25−28] that by treating the aluminosilicate molecular sieves with phosphoric acid the bridged OH groups between Si and Al atoms are replaced by the $H_2PO_4^-$ groups. The substitution of the

Brønsted acidic hydroxyl groups by the $H_2PO_4^-$ groups implies different consequences on the strength and density of the Brønsted acid sites. Strong Brønsted acid sites are converted into weak Brønsted acid sites, and the resulting terminal hydroxyl groups have a lower acid strength than the bridged hydroxyl groups, but the number of weak acidic Brønsted sites increases twice. Therefore the catalytic activity of the catalyst increases with loading H_3PO_4. Moreover, by treating a zeolite with H_3PO_4, the areal activity of the catalyst and the theoretical surface area and accessible pore volume decrease. We think that the diffusion constraints imposed by phosphoric acid might induce new properties to the surface. In this work we loaded MCM-41 with H_3PO_4 and studied its catalytic properties in the alkylation of toluene with various alcohols. The MCM-41 without phosphoric acid shows a very low conversion and a moderate selectivity to *para*-alkylated toluene. One would expect the MCM-41 without phosphoric acid to show a low conversion. However, this catalyst has the least diffusional constraint and for this reason the molecules have more room to tumble. Therefore, it is not possible to achieve high percentages of *para*-alkylated products over MCM-41 catalyst without modifying by phosphoric acid. By increasing the amount of loaded H_3PO_4 it is clear that the conversion and selectivity increases. When the H_3PO_4 content reaches 30 wt%, the conversion remains high but the selectivity toward bulkier *para*-alkylated toluene (p-tert butyl toluene) decreases to some extent. The increase in the amount of the *ortho*-alkylated toluene, when the H_3PO_4 content is further increased, is probably due to blocking of the pore network of the support by phosphoric acid. Therefore, the reaction is presumably occurring on the external surface of the catalyst, which does not induce any shape selectivity.

Influence of reaction temperature on the toluene alkylation

Temperature has a paramount effect in the product distribution for alkylation of toluene. The effects of the reaction temperature in the toluene alkylation with alcohols over 25 wt% H_3PO_4/MCM-41 in the range 250-370 °C are summarized in Table 3 and selectivity of the catalyst at these temperatures is given in the Figure. The molar ratio of alcohol to toluene is 0.1. In all the studies, the major product was *para*-alkylated toluene, which increased with increasing temperature to 330 °C, and at higher temperature *para* selectivity decreased.
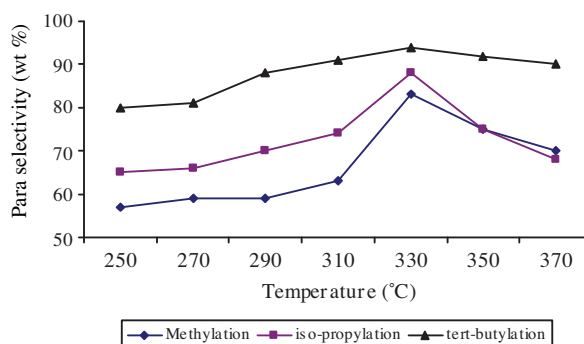
Figure. Influence of the reaction temperature on conversion of alcohols and product selectivity. Reaction conditions: P = 1 atm; injection rate = 0.05 mL/min; carrier gas N_2; N_2 flow rate = 30 mL/min.

The selectivity toward the dialkylated products remained less than 7% in the temperature range of the study. It can be seen from Table 3 that the conversion of alcohols at 250-310 °C and over 25 wt% H_3PO_4/MCM-41 was around 42%-88%, reaching 100% at higher temperatures. For experiments at higher temperatures, i.e.

above 310 °C, the formation of dialkylated products increased. Despite this increase we observed higher conversion and *para*-selectivity above 310 °C. Thus, 330 °C was the most favorable temperature for this reaction. Therefore, the other experiments were carried out at this temperature.

Table 3. Influence of the reaction temperature on the conversion of the alcohols and selectivity toward different products.

Temperature (°C)	Conversion (%)			*Para*-alkylated toluene (%)			*Ortho*-alkylated toluene (%)			Dialkylated toluene (%)		
	MeOH	i-PrOH	t-BuOH	Me	i-Pr	t-Bu	Me	i-Pr	t-Bu	Me	i-Pr	t-Bu
250	42	40	62	57	65	80	40	35	19	3	-	-
270	53	58	73	59	66	81	40	32	18	1	1	-
290	69	73	89	59	70	88	39	29	10	2	-	-
310	88	97	98	63	74	91	35	24	7	2	1	1
330	98	100	100	83	88	94	12	9	6	5	3	-
350	100	100	100	75	75	92	22	20	4	3	3	1
370	100	100	100	70	68	90	23	24	4	7	4	2

Reaction conditions: P = 1 atm; injection rate = 0.05 mL/min; carrier gas N_2; N_2 flow rate = 30 mL/min.

Influence of injection rate on toluene alkylation

Table 4 demonstrates the influence of injection rate on the conversion of alcohols. Increasing the injection rate of the feed, resulting in reduced contact time of reactant over the catalyst, and diffusion in the catalyst channels

Table 4. Influence of the injection rate of the starting materials on the conversion of the alcohols and selectivity toward different products.

Injection rate mL/min	Conversion (%)			*Para*-alkylated toluene (%)			*Ortho*-alkylated toluene (%)			Dialkylated toluene (%)		
	MeOH	i-PrOH	t-BuOH	Me	i-Pr	t-Bu	Me	i-Pr	t-Bu	Me	i-Pr	t-Bu
0.025	100	100	100	58	69	88	40	27	10	2	2	1
0.050	98	100	100	83	88	94	12	9	6	5	3	-
0.075	100	94	100	61	72	90	37	27	7	2	1	1
0.100	97	91	96	55	67	85	43	30	10	2	2	4

Reaction conditions: T = 330 °C; P = 1 atm; carrier gas N_2; N_2 flow rate = 30 mL/min.

we observed a decrease in *para* selectivity of alkylation and a decrease in the conversion of alcohol. The yield of *para* product was highest when the injection rate was 0.05 mL/min. On the basis of this finding, we applied an injection rate of 0.05 mL/min in further experiments to investigate the influence of other parameters.

Influence of the carrier gas flow rate on toluene alkylation

The influence of the carrier gas flow rate on the conversion of the alcohols and the selectivity to the *para*-substituted isomers during toluene alkylation reaction is shown in Table 5. It can be seen that increasing the flow rate of the carrier gas (N_2) results in an increase in the *para* selectivity and a decrease in the conversion of alcohol, probably due to the shorter residence time of the starting materials on the catalyst surface and hence lower conversion but higher selectivity. An increase in the carrier gas flow to 30 mL/min leads to an increase in the yield of *para*-alkylation products.

Table 5. Influence of the flow rate of the carrier gas on the conversion of the alcohols and product selectivity.

Flow rate mL/min	Conversion (%)			*Para*-alkylated toluene (%)			*Ortho*-alkylated toluene (%)			Dialkylated toluene (%)		
	MeOH	i-PrOH	t-BuOH	Me	i-Pr	t-Bu	Me	i-Pr	t-Bu	Me	i-Pr	t-Bu
10	100	100	100	45	55	78	54	41	21	1	0.5	-
20	100	100	100	52	64	84	46	34	15	2	0.5	-
30	98	100	100	83	88	94	12	9	6	5	3	-
40	96	78	80	58	69	89	40	30	10	2	-	-

Reaction conditions: T = 330 °C; P = 1 atm; injection rate = 0.05 mL/min; carrier gas N_2.

Influence of TOS on toluene alkylation

Time-on-stream (TOS) studies were carried out over the 25 wt% H_3PO_4/MCM-41 catalyst under the conditions previously selected as optimum (330 °C, injection rate of 0.05 mL/min, and flow rate of 30 mL/min) with the molar ratio of alcohol:toluene as 1:10. The study was conducted for 8 h and the results are presented in Table 6. As shown, a decrease in conversion with an increase in TOS was observed. In part, this might be due to the blocking of active sites of the catalyst by coke. Surprisingly, this study indicated that alkylation of toluene did not result, even after 8 h on-stream. The increase in selectivity of *ortho*-derivatives with time is because of fast deactivation due to coke formation and pore blockage, which facilitated the forming of *ortho* products over the surface of the catalyst instead of inside the pores in comparison to other derivatives.

Leaching studies of H_3PO_4/MCM-41

The catalysts were recycled 5 times, by calcination at 500 °C in a flow of air, in order to test their activity at 330 °C for the title reaction (Table 7). It was observed that there was no significant loss in activity of the

catalyst for this reaction and hence the deactivation must be due to coke formation, which was removed during reactivation (regeneration) of catalyst. From the experiments on leaching studies using H_3PO_4/MCM-41, no leaching of H_3PO_4 was observed from the catalyst after the catalytic reaction (Table 7).

Table 6. Influence of time on stream on the conversion of the alcohols and on the selectivity toward different products.

Time-on-steam (h)	Conversion (%)			*Para*-alkylated toluene (%)			*Ortho*-alkylated toluene (%)			Dialkylated toluene (%)		
	MeOH	i-PrOH	t-BuOH	Me	i-Pr	t-Bu	Me	i-Pr	t-Bu	Me	i-Pr	t-Bu
1	98	100	100	83	88	94	12	9	6	5	3	-
2	98	100	100	83	88	94	13	9	6	4	3	-
3	97	99	99	85	90	95	12	10	5	3	-	-
4	94	95	97	87	92	96	11	8	4	2	-	-
5	93	94	96	85	90	93	11	9	6	4	1	1
6	91	90	92	75	72	89	23	28	11	2	-	-
7	84	85	87	73	70	85	21	29.5	15	6	0.5	-
8	80	79	81	70	70	81	28	30	19	2	-	-

Reaction conditions: T = 330 °C; P = 1 atm; injection rate = 0.05 mL/min; carrier gas N_2; N_2 flow rate = 30 mL/min

Table 7. Recycling of 25 wt% H_3PO_4/Al-MCM-41 catalyst in alkylation of toluene with *tert*-butanol.

Cycle	Conversion of *tert*-butanol (%)	Product selectivity (%)		
		4-*tert*-butyl toluene	2-*tert*-butyl toluene	Di-alkylated product
Fresh	100	94.0	6.0	-
1st	99.8	94.0	6.0	-
2nd	99.7	93.7	6.1	0.2
3rd	99.8	92.6	6.7	0.7
4th	95.3	91.4	6.4	2.2
5th	90.1	91.1	6.0	2.9

Comparison with other solid acid catalysts

Table 8 shows the comparison between the catalyst used in the present study and other solid catalysts reported in the literature for toluene alkylation. As can be seen from these data, the 25 wt% H_3PO_4/MCM-41 catalyst shows high *para* selectivity, very low dialkylated and *ortho*-alkylated toluene as well as excellent conversion for alcohols in the optimum conditions.

Table 8. Catalytic activity in the vapor phase reaction of toluene with various alcohols over different catalysts.

Catalyst	Reagent	Molar ratio (toluene/alcohol)	Conversion of toluene (%)	Conversion of alcohol (%)	Product selectivity (%)			Ref.
					Para- alkylated (%)	*Ortho-* alkylated (%)	Dialkylated	
Hβ (25)	*tert*-butyl alcohol	4/1	21.1	-	62.3	-	0.3	[28]
HY (30)	*tert*-butyl alcohol	4/1	21.9	-	79.9	-	0.6	[28]
HMCM-22 (52)	*tert*-butyl alcohol	4/1	15.3	-	85.2	-	0.4	[28]
MCM-22	methanol	5/1	5.4	65.8	40.4	32.5	-	[29]
P-MCM-22	methanol	5/1	3.8	54.0	78.5	6.3	-	[29]
ITQ-2	methanol	5/1	2.3	33.6	23.6	59.1	-	[29]
P-ITQ-2	methanol	5/1	0.6	36.0	83.0	9.7	-	[29]
Zn–Al–MCM-41(75)	*tert*-butyl alcohol	1/2	99.45	-	60.73	-	2.0	[30]
Zn–Al–MCM-41(380)	*tert*-butyl alcohol	1/2	72.8	-	52.74	-	9.0	[30]
10% Pr/ZSM-	methanol	5/1	4.5	-	51.5	13.4	-	[31]
10% B/ZSM-5	methanol	5/1	5.5	-	99.9	0	-	[31]
H_3PO_4/MCM-41	methanol	10/1	-	98	83	12	5	This work
H_3PO_4/MCM-41	2-propanol	10/1	-	100	88	9	3	This work
H_3PO_4/MCM-41	*tert*-butanol	10/1	-	100	94	6	-	This work

Conclusion

High activity of 25 wt% H_3PO_4/MCM-41 catalyst was exhibited toward the alkylation of toluene with methyl, isopropyl, and *tert*-butyl groups, using the corresponding alcohols as alkylating agents. High selectivity to the *para*-substituted derivatives was observed, mainly for isopropylation and *tert*-butylation; the higher selectivity was found when the bulkier alcohol and *tert*-butanol were employed. *Ortho*-derivatives were found in lower amounts, and dehydration products were not detected in the products for isopropylation and *tert*-butylation. Influences of the critical reaction parameters were studied and an optimized condition finally applied to measure the activity of the catalyst during 8 h of reaction. The selectivity toward di-alkylated products remained less than 7% in our study. Surprisingly, this study indicated that the alkylation of toluene did not result, even after 8 h on-stream.

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