Transactions C: Chemistry and Chemical Engineering
Vol. 16, No. 2, pp. 81–88
© Sharif University of Technology, December 2009

SCIENTIA
IRANICA

A New Eco-Friendly and Efficient Mesoporous Solid Acid Catalyst for the Alkylation of Phenols and Naphthols Under Microwave Irradiation and Solvent-Free Conditions

F. Matloubi Moghaddam[1,*], **M. Akhlaghi**[1], **L. Hojabri**[1] and **M.G. Dekamin**[2]

Abstract. *The catalytic activity of a mixture of $ZnCl_2$: $AlCl_3$ supported on silica gel was evaluated for the alkylation of phenols with benzyl alcohol,* tret*-butyl alcohol and styrene under microwave irradiation and solvent-free conditions. The catalyst preparation method, its characterization and reusability, were reported. The effect of the phenol to benzyl alcohol ratio and the time of reaction on the phenol conversion and distribution of products was investigated. A conversion percentage up to 97% was achieved when hydroquinone was used. A selective ortho- directed alkylation for phenol, α-naphthol and β-naphthol was observed.*

Keywords: *Mesoporous solid acid catalyst; Alkylation; Phenols; Microwave irradiation; Solvent free.*

INTRODUCTION

Alkaylphenols are very valuable industrial chemicals among which *tert*-butylated phenols find many applications. For instance, 2-*tert*-butylphenol is an intermediate for pesticide, fragrances and other products, whereas 4-*tert*-butylphenol is used to make phosphate esters, fragrances and oil field chemicals. The alkylation of aromatic compounds has been studied extensively in the past using various Lewis acid catalysts ($AlCl_3$, BF_3, $TiCl_4$, $FeCl_3$, etc.) and protonic acid (H_2SO_4, HF, HNO_3, etc.) [1-3]. These reactions are carried out industrially, using conventional homogeneous acid catalysts, such as anhydrous $AlCl_3$, which generates a high volume of waste material. So, with the current drive towards "green chemistry", it is recognized that there is a need to replace the conventional Lewis acid catalysts with reusable environmentally friendly catalysts that generate minimal waste by-products. Furthermore, the homogeneous acid catalysts are difficult to separate from the reaction mixture. They require additional processing stages and it is necessary to use a stochiometric amount of the catalyst with respect to the alkylating agent. Finally, disposal of spent catalysts, corrosion and high toxicity are disadvantages of applying these catalysts in organic reactions. In order to overcome the difficulties of the homogeneous systems, the development and utilization of a solid catalyst is important to replace homogenous acid catalysts. Development of reusable heterogeneous catalysts having high activity and selectivity with little or no moisture sensitivity for the liquid phase Friedel-Crafts type reactions is, therefore, of great practical importance [4]. Hence, efforts have been made to replace homogeneous catalysts by heterogeneous solid acid catalysts [5-18]. Such catalysts are interesting and efficient for organic synthesis, because the catalyst is easily separated from the products. In this case, the organic reactions occur in the uniform of the solid catalyst and hence the reactivity and selectivity may be different from those in the homogeneous solutions. However, the reported catalysts require special handling conditions, safety, corrosion and waste disposal. Therefore, there is a real need for a solid acid that offers the safety, stability and recoverability advantages of traditional Lewis acid catalysts. On the other hand, the coupling of microwave irradiation with the use of catalysts or mineral supported reagents

---

1. *Laboratory of Organic Synthesis and Natural Products, Department of Chemistry, Sharif University of Technology, Tehran, P.O. Box 11155-9516, Iran.*
2. *College of Chemistry, Iran University of Science and Technology, Tehran, P.O. Box 16846-13114, Iran.*

*. *Corresponding author. E-mail: matloubi@sharif.edu*

Received 26 April 2009; received in revised form 26 July 2009; accepted 8 September 2009

under solvent-free conditions provides unique chemical processes with special attributes, such as enhanced reaction rates, higher yields, greater selectivity and ease of manipulation. In this field, we have developed a new and eco-friendly solid acid ($ZnCl_2$: $AlCl_3$: SiO_2) which could catalyze many acid catalyzed organic reactions, such as the Claisen rearrangement [19], the Fries rearrangement [20], the hetero-Fries rearrangement [21] and the dealkylation of aryl ethers.

EXPERIMENTAL

Materials and Instruments

All solvents, reagents and silica gel (Art. No. 1.07734, 0.063-0.2 mm), $AlCl_3$ and $ZnCl_2$ were purchased from Merck (pro analysis). The microwave-assisted reactions were performed in a single-mode microwave cavity (Ethos, MR, 2.45 GHz, maximum power 1000 W), producing controlled irradiation. Reaction temperatures were determined and controlled via the built-in, on-line sensor. The microwave synthesis reactor was equipped with a water-cooled condenser. The analysis of products and catalyst was carried out by H-NMR (Bruker DRX - 500), FT-IR (ABB Bomem MB-100), GC-Mass (Hewlett-pakard 5973 MSD) and IR DRIFT (Bruker 55 FT IR). The surface area and porosity were determined by micrometrics ASAP 2010.

Preparation of Heterogeneous Catalyst

The catalyst was prepared by a well established procedure in this laboratory. It was prepared by impregnating silica gel (500 g) with a mixture of $ZnCl_2$ (100 g) and $AlCl_3$ (300 g) in aqueous solution. Activation of the catalyst was carried out in two steps: Activation at 120°C for 24 h and then activation at 320°C for 6 h in a vacuum oven. The catalyst was stored in desiccators until use. The weight ratio of silica: $AlCl_3$: $ZnCl_2$ was 5:3:1.

Catalyst Characterization

Pyridine is a useful probe molecule for the determination of Lewis and Bronsted acid sites by FTIR spectroscopy [22]. Using this methodology, the activated catalyst exhibited Bronsted (IR DRIFT peaks at 1632, 1530, 1480 cm^{-1}, a characteristic of pyridinum ion), as well as Lewis acidity (peaks at 1601, 1450 cm^{-1}, a characteristic of coordinated pyridine to the Lewis acid sites) (Figure 1). The prepared catalyst possesses a high surface area (N 276.36 m^2 g^{-1}) determined by the BET method and a narrow pore size distribution (73.06 A°) in the mesoporous range. The ^{27}Al MAS-NMR spectrum (Figure 2a) of the activated catalyst sample exhibits three peaks; peaks at 50 ppm and 34 ppm are characteristic of trivalent aluminum in the tetrahedral framework with two or one chlorine atom coordinated, respectively [23].

The third signal at 0 ppm, however, appears to be due to octahedral aluminum, which may probably be generated during activation. The ^{29}Si MAS-NMR spectrum (Figure 2b) shows two peaks at -100 and -110 ppm, characteristic of the tetrahedral framework for silicon with one hydroxyl group and without a hydroxyl

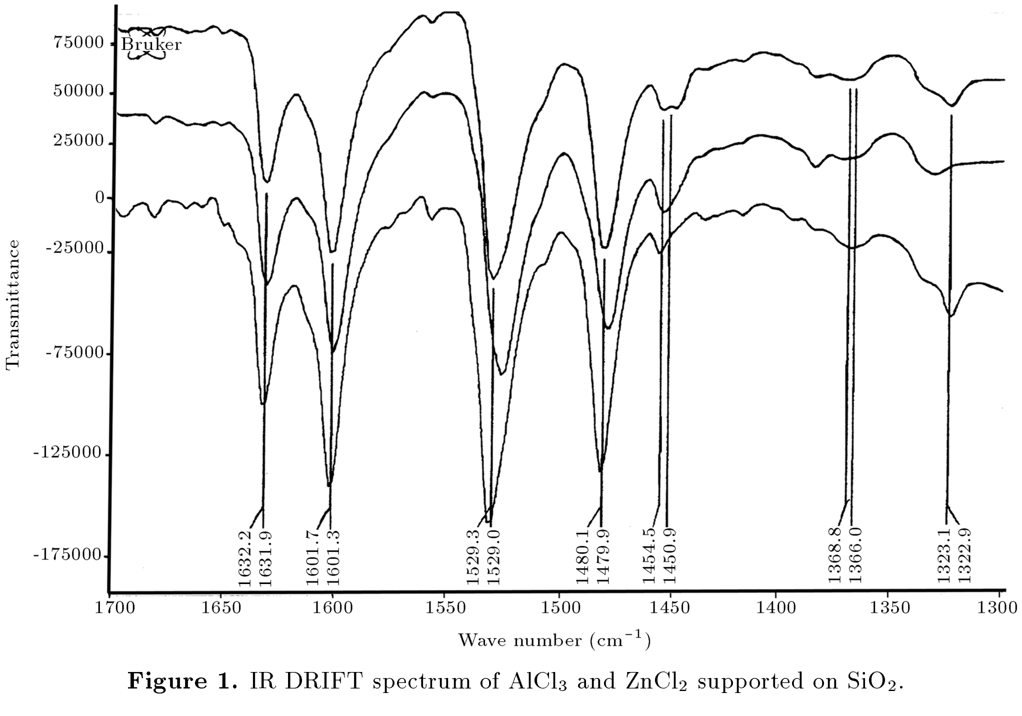
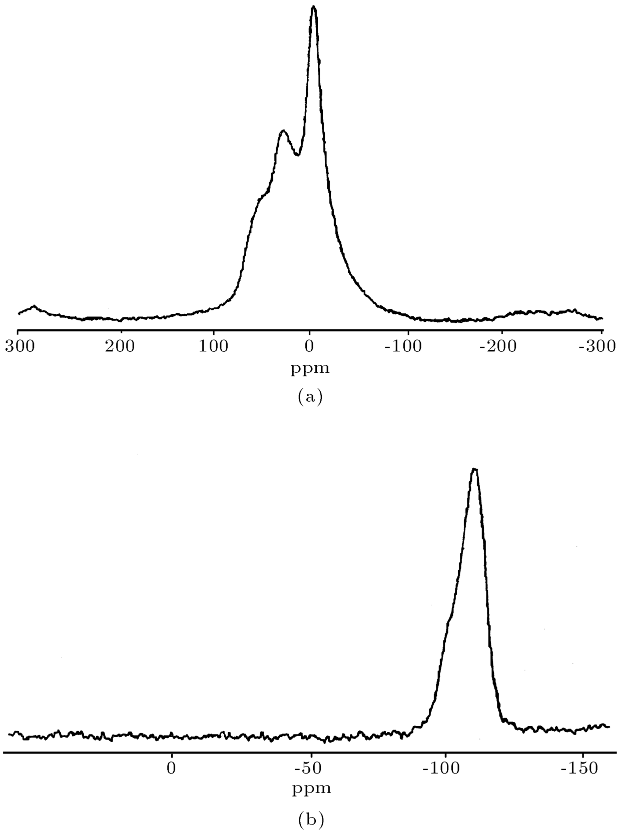


Figure 1. IR DRIFT spectrum of $AlCl_3$ and $ZnCl_2$ supported on SiO_2.



(a)

(b)

Figure 2. a) ^{27}Al NMR spectrum of catalyst; b) ^{29}Si NMR soectrum of catalyst.

group, respectively. The ^{27}Al MAS-NMR spectrum indicates the Lewis acid sites, while the ^{29}Si MAS-NMR spectrum confirms Bronsted acid sites of the support. These results are in good agreement with the data obtained by IR DRIFT spectroscopy.

The proposed surface structure is illustrated in Scheme 1.

Products Characterization

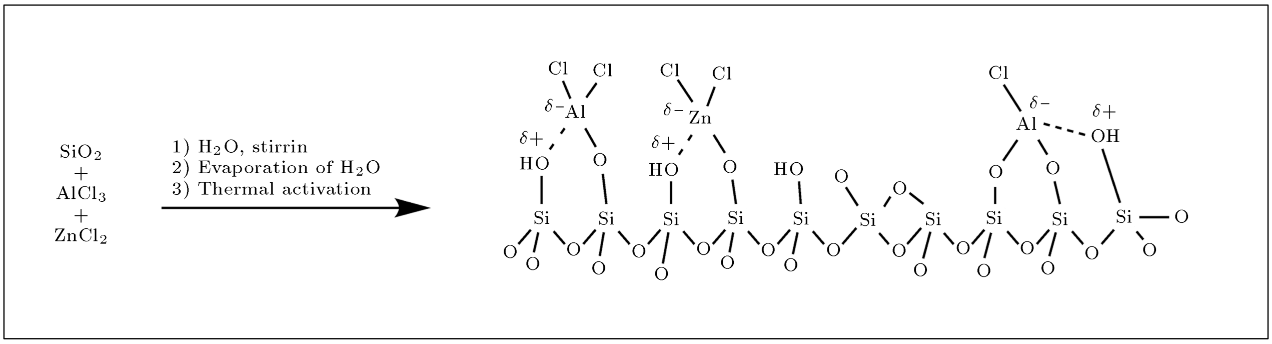
H-NMR, FT-IR and GC-Mass were used to characterize products. The compounds that were synthesized in this research are all known and the achieved spectral data was compared with data from the Merck index [24], The Atlas of spectral data and physical constants for organic compounds [25], The SDBS integrated spectral database system for organic compounds [26], The Aldrich library of NMR spectra [27] and the Sigma-Aldrich on-line product catalog [28].

General Procedure for Benzylation of Phenols

A phenolic compound (4.8 mmol) and benzyl alcohol (4.8 mmol) were dissolved in 10 ml acetone. The solution was added to a catalyst (2.5 g) and then acetone was evaporated in a vacuum rotary pump at 20°C. Microwave irradiation was carried out using a temperature controlled program; raising the temperature up to 120°C in 3 min and remaining constant for 7 min, then cooling the reaction vessel for 3 min. Separation of the products from the catalyst was carried out by washing the catalyst with a polar solvent, such as acetone and methanol. Purification of products was carried out using solid- liquid chromatography, when silica gel was employed as the solid phase of chromatography.

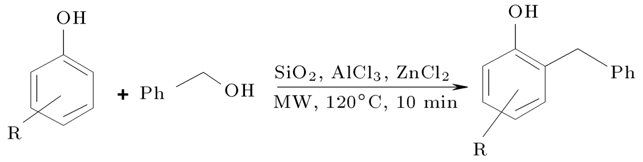
General Procedure for *tert*-Butylation of Phenols

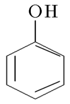
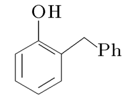
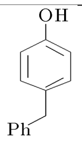
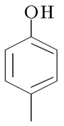
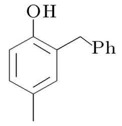
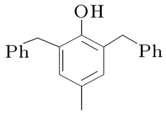
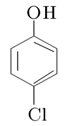
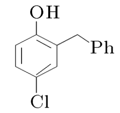
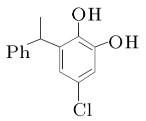
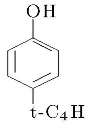
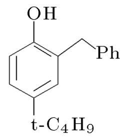
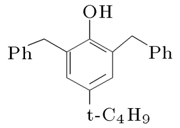
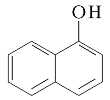
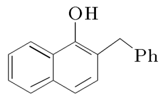
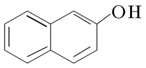
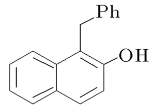
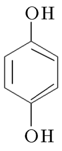
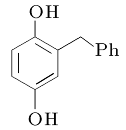
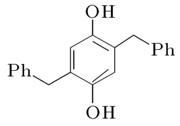
A phenolic compound (9 mmol) was dissolved in 10 ml acetone. The solution was added to a catalyst (5 g), then the acetone was evaporated in vacuum rotary pump at 20°C. Tert-butyl alcohol (90 mmol) was added in three portions to the reaction vessel during irradiation (time = 0, 3, 6 min). Microwave irradiation was carried out at a temperature controlled program in three steps; raising temperature up to 120°C in 3 min and remaining constant for 7 min, then cooling the reaction vessel for 3 minutes. Separation of products from the catalyst was carried out by washing the catalyst with a polar solvent, such as acetone and methanol. Purification of products was carried out using solid-liquid chromatography and silica gel as the solid phase of chromatography.



Scheme 1. Proposed structure of $AlCl_3$ and $ZnCl_2$ supported on SiO_2.

Table 1. Conversion percentage of phenols and distribution of products.



Entry[a]	Phenols	Conversion of Phenols[b] (%)	Products and Its Distribution (%)
1		77	 (39),  (34), di and tri benzyl phenols (27%)
2		85	 (81),  (19)
3		70	 (69),  (31)
4		75	 (73),  (27)
5		87	 (71), other alkylated products (29)
6		82	 (67), other benzylated products (33)
7		90	 (94),  (6)

[a]: Reaction conditions: Benzyl alcohol (4.8 mmol), catalyst (2.5 g), phenol (4.8 mmol), 120°C, 10 min.

[b]: GC conversion of phenols.

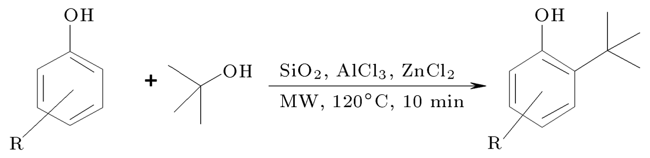
General Procedure for Alkylation of Phenols with Styrene

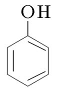
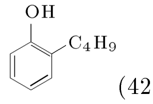
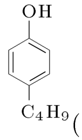
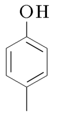
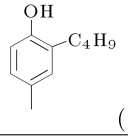
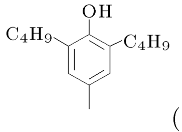
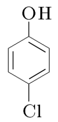
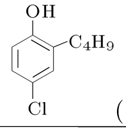
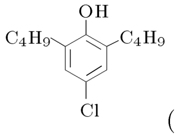
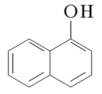
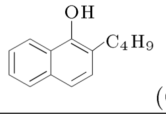
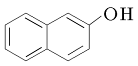
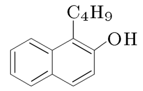
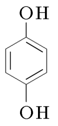
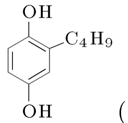
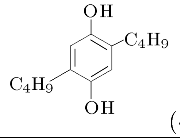
Styrene (5 mmol) and solid support (1.04 g) were added into a solution of phenol (5 mmol) in dry dichloromethane (15 ml). Then, solvent was removed under reduced pressure and the residue was exposed to microwave irradiation under temperature programming; raising temperature up to 150°C in 5 minutes and remaining constant for 5 minutes. The reaction mixture was washed by acetone and the products were separated by column chromatography.

RESULT AND DISCUSSION

The present work was undertaken to find the efficiency of the prepared mesoporous solid acid catalyst for the alkylation of phenols and naphthols with *tert*-

Table 2. Tert-butylation of phenols.



Entry[a]	**Phenols**	**Conversion of Phenols**[b] **(%)**	**Products and Its Distribution (%)**
1		64	 (42),  (37) Di and Tri *tert*-butyl phenols (21)
2		62	 (87),  (13)
3		70	 (73),  (27)
4		81	 (62), other alkylated products (38)
5		78	 (57), other alkylated products (43)
6		84	 (96),  (4)

[a]: Reaction conditions: *tert*-butyl alcohol (90 mmol), catalyst (5 g), phenol (9 mmol), 120°C, 10 min.

[b]: GC conversion of phenols.

butanol and benzyl alcohol, as well as styrene as alkylating reagents under solvent free conditions and under microwave irradiation. The phenolic compounds, such as phenol, *p*-cresol, *p*-chlorophenol, *p*-*tert* butyl phenol, α-naphthol, β-naphthol, hydroquinone and *p*-nitrophenol were used for the benzylation reaction.

The conversion percentage of benzyl alcohol was 100% for all phenolic compounds. Table 1 presents the conversion percentage of phenolic compounds along with the distribution of products.

Hydroquinone has the highest conversion with 94% yield for the mono benzylated compound (entry 7). P-nitrophenol did not participate in the benzylation reaction. The catalyst showed selective activity for mono-benzylation of *para* substituted phenols and benzylation at the ortho position for phenol, α-naphthol and β-naphthol. The results of the *tret*-butylation of phenolic compounds along with the conversion percentage of phenolic compounds and the distribution of products are listed in Table 2.

Hydroquinone has the highest conversion (entry 6), while this process failed when *p*-nitro phenol was used (entry 7). The catalyst showed selective activity for mono *tert*-butylation of *para*-substituted phenols and also *tert*-butylation in the ortho position of the hydroxyl group of phenol, α-naphthol and β-naphthol (entries 1, 4 and 5).

The reaction of phenols with styrene progressed with the electron-donating group. The rate of reaction was accelerated in the presence of the electron-donating

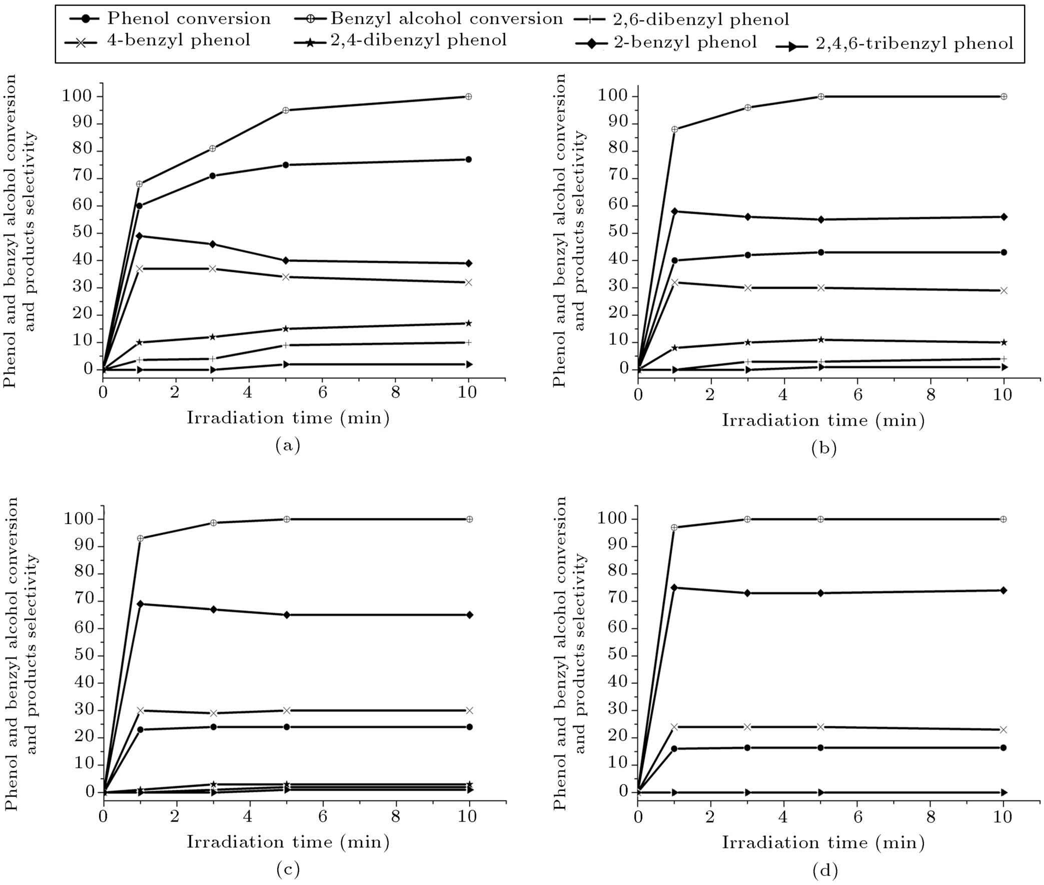


Figure 3. Phenol and benzyl alcohol conversion and products distribution vs. irradiation time.

group on the phenyl ring (Table 3). A better conversion percentage was obtained in the case of *para* methoxy phenol in comparison with *para* toloul (entries 1 and 2). The best reactivity is related to hydroquinone (entry 4). The reaction was quite slow in the presence of electrons with drawing groups, such as chloro, bromo and cetoxy on the phenol substrates. There was no product in the presence of *para*-nitro phenol.

The effects of the phenol to benzyl alcohol ratio and reaction time on the conversion of phenol and benzyl alcohol, as well as the distribution of products, have been investigated (Figure 3). The Phenol to benzyl alcohol molar ratios were 1, 2, 4 and 6. The interval time for sampling was 1, 3, 5 and 10 minute. The results are shown in Figure 4. Results show that the selectivity of 2-benzyl phenol increases when the molar ratio of phenol to benzyl alcohol is increased.

To demonstrate the efficiency of the catalyst, it was reused three times for the benzylation of phenol. After each use, the catalyst was treated with dichloromethane to remove unreacted phenol and then dried in a vacuum oven at 150°C for 3 h. It was found that the catalytic activity was only decreased a few percent up to three runs (Figure 5). Reusing the catalyst showed that the selectivity of 2-benzyl phenol and 2, 6-dibenzyl phenol are decreased, while the selectivity of 4-benzyl phenol and 2, 4-dibenzyl phenol are increased.

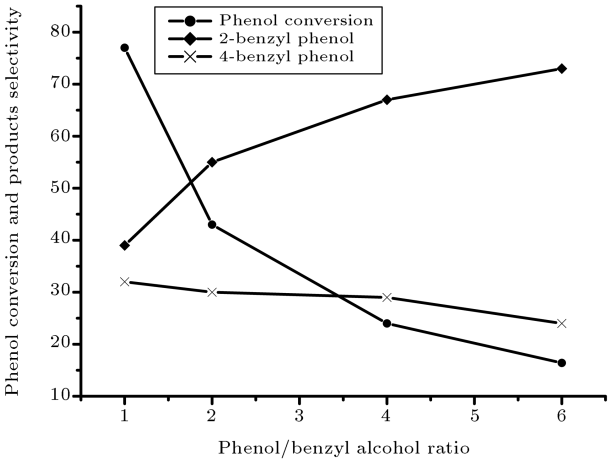
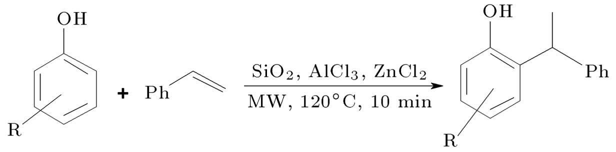
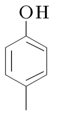
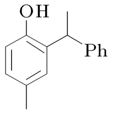
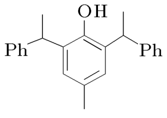
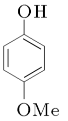
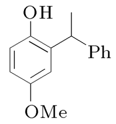
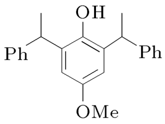
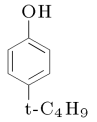
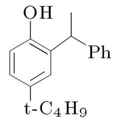
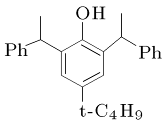
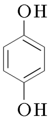
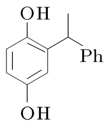
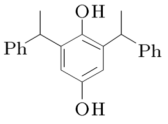
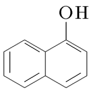
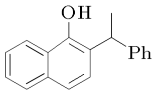
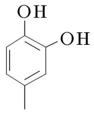
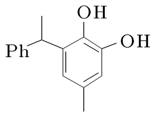


Figure 4. Conversion of phenol and distribution of products vs. phenol to benzyl alcohol ratio.

To investigate the effect of microwave irradiation on the rate of reaction, the benzylation reaction of phenol was carried out in an oil bath at 120°C. After 3 hours, only a small fraction of phenol has participated

Table 3. Alkylation of phenols with styrene.



Entry[a]	Phenols	Conversion of Phenols[b] (%)	Products and Its Distribution (%)
1		77	 (73),  (27)
2		84	 (79),  (21)
3		75	 (68),  (32)
4		97	 (94),  (6)
5		67	 (84), other alkylated products(16)
6		85	 (96), other alkylated products (4)

[a]: Reaction conditions: styrene (5 mmol), catalyst (1.04 g), phenol (5 mmol), 150°C, 10 min.

[b]: GC conversion of phenols.

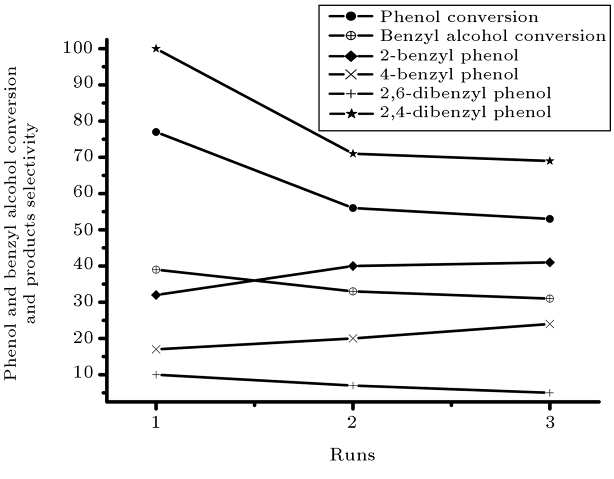


Figure 5. Reusability of catalyst.

in the benzylation reaction. Clearly, the reaction time is reduced drastically and the conversion percentage is much higher by controlled microwave heating than conventional heating (7 min./77% versus 180 min./< 10%).

CONCLUSION

In summary, we have developed a new and eco-friendly mesoporous solid acid catalyst for solvent-free alkylation of phenols and naphthols under microwave irradiation. The catalyst is selective for ortho-directed products for some substrates. This method is fast and has advantages, such as having solvent-free conditions, being a readily available medium; having ease of work-up and the reusability of the catalyst for several runs.

REFERENCES

1. Olah, G.A., *Friedel-Craft and Related Reactions: General Aspects*, **1**, Wiley/Interscience, New York (1963).
2. Olah, G.A., *Friedel-Crafts Chemistry*, Wiley/Interscience, New York (1973).
3. Olah, G.A. et al., *Superacids*, Wiley/Interscience, New York (1985).
4. Jana, S.K. "Recent developments of heterogeneous solid catalysts for liquid-phase friedel-crafts type benzylation reaction", *Catal. Surv. Asia*, **9**(1), pp. 25-34 (2005).
5. Liao, X. et al. "Synthesis, characterization of COK-5 with different Si/Al ratios and their catalytic properties for the *tert*-butylation of phenol", *Micropor. Mesopor. Mater.*, **124**(1-3), pp. 210-217 (2009).
6. Bachari, K. et al. "Catalytic properties of Ga-HMS-n materials in the tertiary butylation of phenol", *J. Mol. Catal. A: Chem.*, **294**(1-2), pp. 25-34 (2008).
7. Bhatt, N. et al. "Supported 12-tungstophosphoricacid: An efficient and selective solid acid catalyst for *tert*-butylation of phenol and cresols", *Catal. Commun.*, **9**(7), pp. 1545-1550 (2008).
8. Kumbar, S.M. and Halligudi, S.B. "Tungstophosphoric acid supported on titania: A solid acid catalyst in benzylation of phenol with benzylalcohol", *Catal. Commun.*, **8**(5), pp. 800-806 (2007).
9. Choudhary, V.R. et al. "Benzylation of benzene by benzyl chloride over Fe-modified ZSM-5 and H-β zeolites and Fe_2O_3 or $FeCl_3$ deposited on micro-, meso- and macro-porous supports", *Micropor. Mesopor. Mater.*, **56**(1), pp. 65-71 (2002).
10. Salavati-Niasari, M. et al. "Alumina-supported $FeCl_3$, $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, and $ZnCl_2$ as catalysts for the benzylation of benzene by benzyl chloride", *J. Mol. Catal. A: Chem.*, **209**(1-2), pp. 209-214 (2004).
11. Shinde, A.B. et al. "*tert*-butylation of phenols using *tert*-butyl alcohol in the presence of $FeCl_3$-modified montmorillonite K10", *Appl. Catal. A: Gen.*, **276**(1), pp. 5-8 (2004).
12. Kurian, M. and Sugunan, S. "*tert*-butylation of phenol catalysed by metal exchanged iron pillared montmorillonites", *Catal. Commun.*, **7**(6), pp. 417-421 (2006).
13. Devassy, S.B.M. et al. "Phenol *tert*-butylation over zirconia-supported 12-molybdophosphoric acid catalyst", *J. Mol. Catal. A: Chem.*, **247**(1-2), pp. 162-170 (2006).
14. Karthik, M. et al. "Characterization of Co, Al-MCM-41 and its activity in the t-butylation of phenol using isobutanol", *Appl. Catal. A: Gen.*, **268**(1-2), pp. 139-149 (2004).
15. Selvam, P. and Dapurkar, S.E. "Tertiary butylation of phenol over mesoporous MeMCM-48 and MeMCM-41 (Me = Ga, Fe, Al or B) solid acid catalysts", *Catal. Today*, **96**(3), pp. 135-141 (2004).
16. Nandhini, K.U. et al. "t-butylation of phenol over mesoporous aluminophosphate and heteropolyacid supported aluminophosphate molecular sieves", *J. Mol. Catal. A: Chem.*, **223**(1-2), pp. 201-210 (2004).
17. Xu, B. et al. "Alkylation of hydroquinone with *tert*-butanol over AlSBA-15 mesoporous molecular sieves", *Catal. Lett.*, **100**(1-2), pp. 95-100 (2005).
18. Kischel, J. et al. "A convenient $FeCl_3$-catalyzed hydroarylation of styrenes", *Org. Lett.*, **8**(1), pp. 19-22 (2006).
19. Matloubi Moghaddam, F. et al. "Tandem Fries reaction-conjugate addition under microwave irradiation in dry media", *J. Chem. Res. (S)*, **9**, pp. 574-575 (1999).
20. Matloubi Moghaddam, F. and Dakamin, M.G. "Thia-Fries rearrangement of aryl sulfonates in dry media under microwave activation", *Tetrahedron Lett.*, **41**(18), pp. 3479-3481 (2000).
21. Matloubi Moghaddam, F. and Ghaffarzadeh, M. "Microwave assisted rapid hydrolysis and preparation of thioamides by willgerodt-kindler reaction", *Synth. Commun.*, **31**, pp. 317-321 (2001).
22. Parry, E.P. "An infrared study of pyridine adsorbed on acidic solids. Characterization of surface acidity", *J. Catal.*, **2**(5), pp. 371-379 (1963).
23. Reddy, K.M. and Song, C. "Synthesis of mesoporous molecular sieves: influence of aluminum source on Al incorporation in MCM-41", *Catal. Lett.*, **36**(1-2), pp. 103-109 (1996).
24. ONeil, M. et al. "The Merck index: An encyclopedia of chemicals, drugs, and biologicals", Merck & Co., Whitehouse Station, NJ (2006).
25. Grasselli, J.G. and Ritchey, W.M., *Atlas of Spectral Data and Physical Constants for Organic Compounds*, CRC press, Cleveland (1975).
26. SDBS: Integrated spectral database system for organic compounds, world wide web: http://www.aist.go.jp/RIODB/SDBS/cgi-bin/cre_index.cgi
27. Pouchert, C.J., *Aldrich Library of NMR Spectra*, Aldrich Chemical Co., Milwaukee, WI (1983).
28. Sigma-Aldrich on-line product catalog, world wide web: http://www.sigmaaldrich.com