# Simple and Economical Synthesis of Alkyl Phenyl Ethers by the Reaction of Phenols and Alkyl Esters Using Nanocrystalline Beta

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Ⓢ *Supporting Information*

ABSTRACT: A simple, economical, and recyclable catalytic route is developed for the synthesis of alkyl phenyl ethers by the liquid phase reaction of phenol derivatives with alkyl esters using conventional and nanocrystalline zeolite Beta. A wide range of alkyl phenyl ethers can be prepared using this catalytic protocol. Nanocrystalline zeolite Beta exhibited higher activity than conventional zeolite Beta.
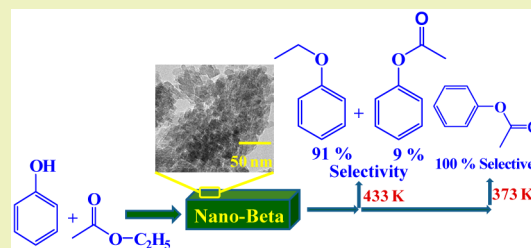
KEYWORDS: *Alkyl phenyl ether, O-alkylation, Zeolite, Nanocrystalline Beta, Solid acid catalyst*

■ INTRODUCTION

Alkyl phenyl ethers, cresol, and polyalkylated phenols are industrially important synthetic intermediates that are widely used in food, fragrances, tobaccos, beverages, toothpastes, detergents, pharmaceutical ingredients, and cosmetics.[1] The conventional Williamson synthesis route of alkyl phenyl ether requires a rigorous condition such as a strong base and high temperature.[2,3] 2-Methoxy naphthalene was obtained in an earlier report, when methyl methacrylate was reacted with 2-naphthol in the presence of sulfuric acid.[4] Under the optimized reaction conditions, other aliphatic esters (methyl methacrylate or ethyl acetate) and phenolic compounds (phenol, 1-naphthol, 4-hydroxybiphenyl 4-nitrophenol) were reacted in the presence of acid (sulfuric acid, orthophosphoric acid) or metallic sodium as the catalyst, but alkyl phenyl ethers were not obtained, as quoted in this earlier report.[4] Later, a wide variety of procedures have been developed to prepare ethers, including the use of crown ethers,[5] phase-transfer catalysts,[6] ionic liquids,[7] and the microwave method.[8] However, most of these methods are neither eco-friendly nor cost effective. To overcome these problems, heterogeneous catalyst-based eco-friendly vapor phase catalytic routes have been developed. The most widely investigated catalysts are strong Brönsted-type acid zeolite materials[9,10] and weak acid metal phosphates.[11,12] However, alkylation reactions over solid acid catalysts, especially with reactants in the gas phase, were usually accompanied by several unwanted side reactions, triggered by the same surface acidity of the catalyst, leading to a more or less rapid deactivation of the catalyst due to fouling by carbonaceous deposits.[13] Reaction of phenol with olefins leads to the formation of alkyl phenyl ethers in the liquid phase.[14,15] Alkyl phenyl ether synthesis is also reported by using solid base catalysts.[16,17] Reaction of phenol with methyl acetate in the vapor phase condition using Mg-containing zeolites lead to the formation of anisole with very low yield (low selectivity and low

phenol conversion).[18] Catalyst selectivity to O-alkylated and C-alkylated products depends on the nature of the active site (basic or acid sites) and phenol conversion. In general, solid base catalysts favor ortho-C-alkylated products, whereas solid acid catalysts favor the O-alkylation of phenol. Therefore, it is very important to develop a simple heterogeneous catalytic route that can offer high selectivity for alkyl phenyl ethers.

Solid acid (especially zeolites)-based catalytic processes are widely used in numerous industrial practices, especially in the petrochemical and fine chemical industries.[19−22] Zeolite exhibits excellent activity and selectivity in several catalytic processes due to its characteristic micropores.[23,24] However, the microporous zeolites exhibit diffusion limitation in the fine chemical industries involving large reactant/product molecules.[19−24] To overcome this problem, efforts have been made to prepare nanocrystalline zeolites containing inter/intracrystalline mesopores.[25−30] In general, top-down and bottom-up approaches are used to prepare nanocrystalline zeolites.[31,32] Soft templates and hard templates have been used to prepare nanocrystalline zeolites.[25−32] Efforts have been made by our research group to prepare nanocrystalline zeolites of different framework structures, using a variety of new series of structure-directing agents (SDA).[33−40]

Herein, we wish to report a simple catalytic route based on conventional and nanocrystalline zeolite Beta, which is not only a remarkable mild alternative to classical synthesis of alkyl phenyl ether but is also to the best of our knowledge the first example of alkyl phenyl ether synthesis using alkyl acetate as an economical source in the liquid phase condition. The best part of this catalytic protocol is that just by varying the reaction temperature two different synthetic intermediates can be
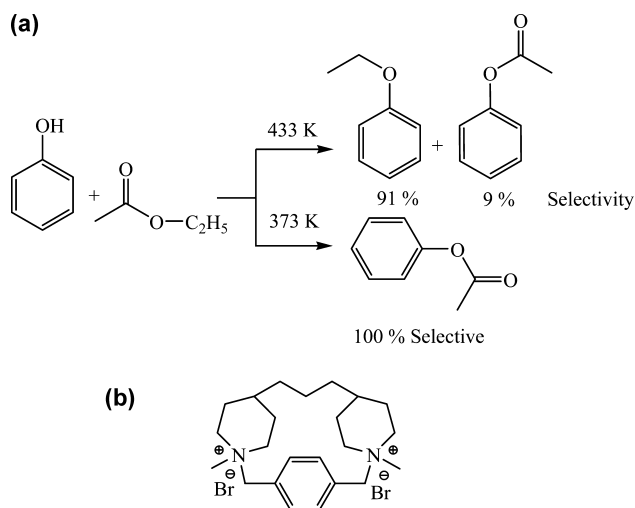
prepared by the reaction of phenol and ethyl acetate (Scheme 1a). The idea behind choosing alkyl ester is that it can be easily

Scheme 1. (a) Synthesis of Ethyl Phenyl Ether by Reaction of Phenol with Ethyl Acetate. (b) Structure-Directing Agent Used in Synthesis of Nanocrystalline Zeolite Beta.

activated by zeolite acid sites and participates in many organic transformations, for example, transesterification.

RESULTS AND DISCUSSION

Nanocrystalline zeolite Beta (hereafter represented as Nano-Beta) was prepared according to a procedure in which 4,4′-trimethylene bis(1-methylpiperidine)-based SDA (Scheme 1b) was added into an initial synthesis composition for ordinary zeolite Beta (Supporting Information). Zeolite was synthesized using sodium silicate as the silica source and $Al_2(SO_4)_3 \cdot 18H_2O$ as the alumina source. The initial gel composition was $30Na_2O:3.33\ Al_2O_3:100SiO_2:10SDA:15H_2SO_4:6000H_2O$. After aging for 6 h at room temperature, the mixture was transferred to a Teflon-coated stainless-steel autoclave and heated at 443 K for 2 days with stirring. For comparative purposes, conventional zeolite Beta was prepared by following the reported procedure.[41] It may be noted that synthesis of Beta took 15 days using tetraethylammonium bromide (TEABr),[41] whereas only 2 days was required for the formation of Nano-Beta. Nano-Beta was characterized using scanning electron micrographs (SEM), transmission electron microscopy (TEM), and a N_2-adsorption study in the same way as in our previous report.[33,34] The N_2-adsorption isotherm and TEM/SEM images of the Nano-Beta prepared in the present work were similar to those reported in our previous work,[33,34] except for a slight variation in textural properties (Table 1). To show the nanocrystalline nature, TEM images along with the selected

Table 1. Textural Properties of Various Catalysts Used in the Present Study

catalyst	Si/Al[a]	S_{BET} (m²/g)[b]	$^cV_{total}$ (mL/g)[c]	V_{meso} (mL/g)[c]
Beta	14.2	475	0.40	0.21
Nano-Beta	14.6	664	0.77	0.59

[a]Obtained by ICP analysis. [b]S_{BET} is surface area calculated using the Brunauer–Emmett–Teller equation. [c]V_{total} is total pore volume and V_{meso} is mesopore volume.

area diffraction (SAED) pattern of Nano-Beta are provided in Figure S1 of the Supporting Information. The dicationic SDA used in the synthesis of Nano-Beta is able to generate a large number of zeolite seeds when compared to their mono-ammonium analogues (TEABr) during 6 h aging. This facilitated the formation of preorganized zeolite-like assembly during the gelation process. This process reduced the nucleation time, and further crystal growth took place rapidly to form Nano-Beta in much less time.

To optimize the reaction condition, phenol was reacted with conventional zeolite Beta (hereafter represented as Beta) at different temperatures in the range of 373−473 K. It was surprising to note that when the reaction was performed at 373 K, only phenyl acetate was obtained. However, by increasing the temperature to 433 K or higher, ethyl phenyl ether was formed as a selective product along with a small amount of phenyl acetate (Scheme 1b). Because the aim of the present investigation was to develop a synthesis protocol for alkyl phenyl ether, the reaction condition was optimized to obtain a high yield of ethyl phenyl ether (Table 2). Acetic acid was also

Table 2. Optimization of Reaction Condition Using Conventional Beta Shown in Scheme 1a*
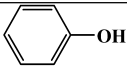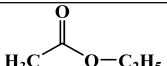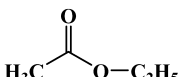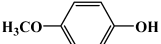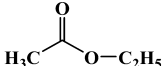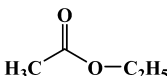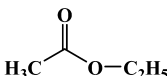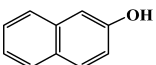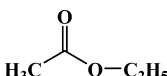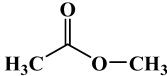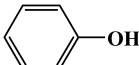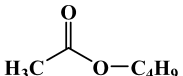
catalyst amount (g)	temp. (K)	ethyl acetate (phenol)	phenol conv. (%)	ethyl phenyl ether selec. (%)[a]
0.4 g	433	5:1	15.8	50.2
0.4 g	433	10:1	40.4	85.2
0.4 g	433	20:1	55.2	91.6
0.4 g	433	40:1	50.5	89.7
0.4 g	403	20:1	27.2	56.2
0.4 g	453	20:1	64.8	90.9
0.4 g	473	20:1	72.0	90.5
0.2 g	433	20:1	52.4	79.4
0.1 g	433	20:1	38.0	65.3

*Reaction conditions: phenol (5 mmol) and reaction time (6 h). [a]Other product is phenyl acetate.

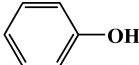formed during the reaction, which can be easily removed by extracting the product with water. It was found that with an increase in the ethyl acetate to phenol ratio up to 20:1, the conversion of phenol as well as selectivity of ethyl phenyl ether was increased. A further increase in the ethyl acetate amount and a decrease in the selectivity of ethyl phenyl ether were obtained. It is also noted that with an increase in the reaction temperature, the phenol conversion was increased but the ethyl phenyl ether selectivity was marginally decreased (Table 2). Reaction time plays a very important role. By prolonging the reaction, Fries rearrangement of phenyl acetate took place, which leads to the formation of a number of products (Figure S2, Supporting Information). In the beginning of the reaction, the reaction rate was high. With an increase in the reaction time, phenol conversion as well as ethyl phenyl ether selectivity was increased. With a further increase in time, not much of an increase in the phenol conversion was observed, but the number of products was observed due to the Fries rearrangement (Figure S2, Supporting Information). The amount of catalyst also plays an important role in obtaining higher selectivity. With 400 mg of catalyst, the highest selectivity toward ethyl phenyl ether was obtained (Table 2). Nano-Beta was found to be more active than conventional zeolite Beta (Table 3). The high activity of Nano-Beta can be correlated to its high surface area, small particles size, and inter/intracrystal-

Table 3. Synthesis of Alkyl Phenyl Ether Using Beta and Nano-Beta*

Phenols	Alkyl acetate	Beta		Nano-Beta	
		Conv. (%)	Selec. (%)	Conv. (%)	Selec. (%)
phenol / ethyl acetate		55.2 (50.8)[a]	91.6 (90.4)[a]	70.5 (68.2)[a]	93.0 (92.5)[a]
4-methylphenol / ethyl acetate		57.0	87.0	75.6	90.1
4-methoxyphenol / ethyl acetate		85.2	80.8	97.0	85.6
4-nitrophenol / ethyl acetate		9.0	100	14.6	100
1-naphthol / ethyl acetate		66.0	47.6	85.0	55.2
2-naphthol / ethyl acetate		42.7 (24.2)[a]	79.6 (60.5)[a]	65.2 (62.3)[a]	81.4 (80.2)[a]
phenol / methyl acetate		25.6	70.5	31.1	72.3
phenol / butyl acetate		94.0	91.8	99.2 (99.0)[a]	92.7 (92.0)[a]
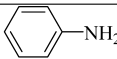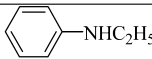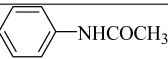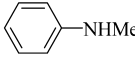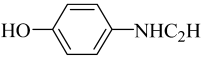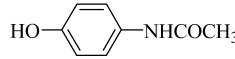
*Reaction conditions: phenol (5 mmol), alkyl acetate (100 mmol), temperature (433 K), catalyst (0.4 g), and reaction time (6 h). [a]Catalytic data obtained after 5 recycles of the catalyst.

line mesoporosity. The short diffusion paths provided by the inter/intracrystalline mesopores facilitate the diffusion of reactant/product molecules, and therefore, high activity was observed in the case of Nano-Beta.

Having found the optimized reaction condition, a wide range of phenols were reacted with ethyl acetate in the presence of Beta and Nano-Beta (Table 3). Catalytic results show that substituent influences phenol conversion and product selectivity. More yield of the product was obtained when the electron-donating group (for example, −OCH$_3$) is attached to phenol ring, whereas much less yield of the product was obtained when the electron-withdrawing substituent (for example, −NO$_2$) is attached to the phenol ring (Table 3). Not only substituted phenols but bulkier phenol derivatives such as naphthols were also reacted with ethyl acetate to give ethyl naphthyl ether.

However, the naphthol conversion and ethyl naphthyl ether selectivity were less when compared to the reaction of phenol with ethyl acetate (Table 3). Because the electron-withdrawing substituent retards the reaction rate, low reactivity of naphthol was anticipated because an additional aromatic ring in naphthol when compared with phenol acts as an electron-withdrawing substituent. It may be noted that ethyl β-naphthyl ether (neroline) is widely used in perfumery products. Not only ethyl phenyl ether but m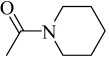ethyl phenyl ether and butyl phenyl ether were also prepared using the same protocol, when phenol was reacted with methyl acetate and butyl acetate, respectively (Table 3). It was observed that with an increase in the aliphatic chain length in the alkyl acetate, high reactant conversion and high selectivity of the alkyl phenyl ether were obtained. Here, we only show the comparative catalytic data at an identical

Table 4. Catalytic Data for Reaction of Amines and Heterocyclic Compounds with Ethyl Acetate over Beta and Nano-Beta*

| Reactant	Reactant conversion (%)	Product selectivity (%)	
⌬—NH₂ (aniline)	36.2[a] / 55.7[b]	⌬—NHC₂H₅ (43.2)[a] (48.9)[b]	⌬—NHCOCH₃ (56.8)[a] (51.1)[b]
⌬—NHMe	Nil	-	-
HO—⌬—NH₂	72.1[a] / >99[b]	HO—⌬—NHC₂H₅ (6.1)[a] (11.5)[b]	HO—⌬—NHCOCH₃ (93.9)[a] (88.5)[b]
pyrrole (HN)	Nil	-	-
imidazole (HN–N)	Nil	-	-
piperidine (HN)	84.6[a] / >99[b]	N-acetyl piperidine (100)[a,b]	
pyrrolidine (NH)	75.6[a] / >99[b]	N-acetyl pyrrolidine (100)[a,b]	

*Reaction conditions: reactant (5 mmol), ethyl acetate (100 mmol), temperature (433 K), catalyst (0.4 g), and reaction time (6 h). [a]Catalytic data obtained using Beta. [b]Catalytic data obtained using Nano-Beta.

condition. Product yield can be improved by performing the reaction at a higher temperature or using a higher amount of catalyst. It may be noted that this reaction condition was good for the synthesis of alkyl phenyl ether but not for alkyl alkyl ether. For example, when 1-octanol (5 mmol) was reacted with ethyl acetate (20 mmol) in the presence of Beta, 100% conversion for 1-octanol was observed, but only 12% selectivity for ethyl octyl ether was obtained. In this reaction, octyl acetate was obtained as a major product (75% selectivity). Researchers would be interested to know whether this protocol is only applicable to phenols or it can be extended to aromatic amines and heterocyclic compounds. When aniline was reacted at the optimized reaction conditions, in addition to N-ethyl aniline (selectivity = 43.8%), a significant amount of acetanilide (selectivity = 56.2%) was obtained (Table 4). When 4-amino phenol was reacted with ethyl acetate under optimized reaction conditions, no etherification of phenol took place, and instead large amount of amide product (selectivity = 93.9%) was obtained (Table 4). Piperidine and pyrrolidine produced selectively monoacetylated products using these catalysts (Table 4). Furthermore, no reaction took place under the optimized condition when pyrrole, imidazole, and N-methyl aniline were reacted with ethyl acetate. The catalytic process reported here can be easily scalable to 100 g or more. The importance of Nano-Beta was observed during the recycling of the catalyst. Conventional Beta was found to be recyclable only for small molecules such as phenol (Table 3). When 2-naphthol was used as a reactant, a progressive decrease in the catalytic activity was observed during the recycling process over Beta (Figure S3, Supporting Information), whereas catalytic activity

was almost retained when Nano-Beta was used (Table 3). Synthesis time for the preparation of zeolite Beta can be reduced using promoters,[42] but the resultant materials exhibited textural properties similar to that of conventional Beta. Therefore, it will deactivate similar to conventional Beta. Hence, Nano-Beta has merits over conventional Beta.

As discussed above, when the reaction between phenol and ethyl acetate was performed at 373 K, only phenyl acetate was obtained. To confirm whether the −COCH₃ from the ethyl acetate was inserted to the phenol to produce phenyl acetate, some control experiments were performed. In the control experiments, phenol was reacted with methyl acetate and butyl acetate. In these cases also, phenyl acetate was observed as the product. This experimental observation confirmed that −COCH₃ group from the ester was inserted into the phenol to produce phenyl acetate at low temperature. The proposed mechanism for the formation of ethyl phenyl ether from phenol and ethyl acetate using zeolite Beta involves the ethoxylation of phenol using ethyl acetate followed by removal of acetic acid. This reaction is expected to be mediated through a carbocation (Scheme 2). The lone pair of electrons available at the oxygen of the phenol attacks the carbocation, followed by the removal of acetic acid and a proton that leads to the formation of ethyl phenyl ether. Following are some note worthy features of this catalytic process: (1) It is a simple synthetic route. (2) It involves a heterogeneous catalyst, which can be easily separated and recycled. (3) It is a solvent-less catalytic process. (4) Excess alkyl acetate can be easily separated and recycled. (5) Products can be easily separated due to the large differences in boiling

Scheme 2. Proposed Mechanism for Formation of Alkyl Phenyl Ether Using Zeolite Beta
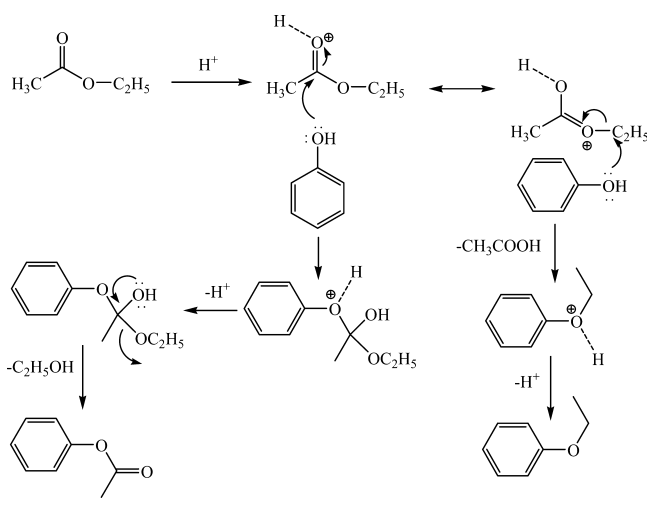
points of the reactant and product. (6) It is easily scalable to a desired quantity. (7) It follows the green chemistry principles.

CONCLUSION

In conclusion, a nanocrystalline zeolite Beta mediated, user-friendly process for the synthesis of alkyl phenyl ether is described. By using a combination of alkyl acetate as the alkyl source and Beta as the catalyst, a range of alkyl phenyl ethers were synthesized. The short diffusion paths provided by the inter/intracrystalline mesopores and large external surface area are responsible for the high activity of Nano-Beta. On the basis of these preliminary results, a detailed research work is underway to develop a more efficient catalytic process for the synthesis of alkyl phenyl ether.

ASSOCIATED CONTENT

S **Supporting Information**

Details of zeolite synthesis, characterization, and catalytic measurements. TEM images of Nano-Beta, optimization of reaction as a function time, and recyclability data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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