

Green Chemistry Oriented Synthesis of Arylmethyl Ethers by the Reaction of Phenol and Its Derivatives with Dimethyl Carbonate in the Presence of FeHYmmm Zeolite [†]

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Abstract: In recent years, Green Chemistry methods have been intensively developed to reduce the harmful effects of chemical processes on the environment. Dimethyl carbonate is an effective substitute for toxic methyl halides and phosgene. We have developed for the first time a new catalytic method for the preparation of arylmethyl ethers based on the reaction of phenol and its derivatives, as well as α - and β -naphthols with dimethyl carbonate in the presence of FeHYmmm zeolite of a hierarchical micro-, meso- and macroporous structure with a high degree of crystallinity. The optimal molar catalyst and reagents, as well as the reaction conditions for the selective synthesis of arylmethyl ethers, have been found. The nature and position of the substituent in the phenol molecule do not significantly affect the selectivity of the reaction, but affect the yield of esters. The presence of meso- and macropores in the catalyst creates conditions for effective diffusion of reactant molecules to catalytically active sites.

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Keywords: aryl methyl ethers; catalyst; dimethyl carbonate; methylation; phenols; zeolite

1. Introduction

Arylmethyl ethers are an important class of ethers. They are widely used in practice as solvents and reagents for the production of dyes, medicinal and aromatic substances, pesticides, antioxidants and stabilizers for polymers, additives for gasolines [1]. Known methods for the synthesis of arylmethyl ethers, in particular anisole, are based on the alkylation of phenol and its derivatives with dimethyl carbonate (DMC)—the reagent of “green chemistry”. The reaction is carried out in the presence of an excess of solid bases K_2CO_3 (1:1.2) or MgO under microwave irradiation [2–4] or by the reaction of phenols with DMC (40-fold excess) in the presence of a stoichiometric amount of $AlCl_3$ [5]. The use of stoichiometric amounts of activators makes these methods unattractive for a wide use due to the formation of a large amount of waste. Transition metal carbonyls ($Mn_2(CO)_{10}$, $W(CO)_6$, $Co_2(CO)_8$) catalyze methylation of phenols with dimethyl carbonate at 180 °C for 1 h but these catalysts cannot be reused [6]. This work describes highly efficient heterogeneous catalysts based on zeolites without binders to facilitate the selective methylation of phenols with dimethyl carbonate.

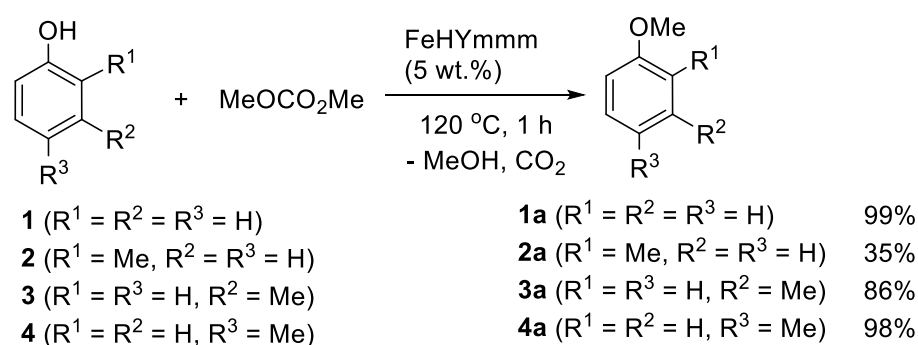
2. Results and Discussion

We found that micro-, meso-, and macroporous zeolite catalyst FeHYmmm without a binder is an effective catalyst for the selective O-methylation of phenol and its derivatives using DMC. The advantage of the catalyst is the presence of meso- and

macropores, which create conditions for effective diffusion of reactant molecules to catalytically active sites. In addition, the concentration of active sites in catalysts without binders is significantly higher than in catalysts with binders.

In contrast to the complexes of Mn, W and Co, zeolite FeHYmmm (5 wt.%) catalyzes selective *O*-methylation of phenol **1** with dimethyl carbonate under milder conditions: 120 °C, 1 h. The yield of anisole was 99% at a molar ratio of reagents [phenol]: [DMC] = 1:2. Depending on the solubility of the phenolic substrate, the experiments were carried out using a two- or three-fold excess of dimethyl carbonate. In the case of phenol **1**, alkylation of aromatic ring and transesterification of dimethyl carbonate were not observed.

o- (**2**), *m*- (**3**), and *p*-Cresols (**4**) readily react with DMC in the presence of FeHYmmm (5 wt.%). The yields of the corresponding esters **2a**, **3a**, **4a** depend on the location of the methyl substituent (Scheme 1). The lowest ester yield was observed in the case of *o*-cresol **2**.



Scheme 1. The reaction of phenol and its derivatives with DMC in the presence of FeHYmmm zeolite.

The reaction of substituted phenols with DMC proceeds with high selectivity with the formation of exclusively arylmethyl ethers. The substituents have no significant effect on the conversion and yield of the corresponding esters. Thus, 3,4-dichlorophenol **14**, 3-aminophenol **15**, methyl 3-hydroxybenzoate **16** react with dimethyl carbonate to form 3,4-dichlorophenyl methyl ester **14a**, 1-methoxy-3-phenylamine **15a** and methyl 3-methoxybenzoate **16a** in a yield 85, 99 and 99%, respectively. On the other hand, the position of the substituent with respect to the hydroxyl group in substituted phenol has a noticeable effect on the course of the reaction. The reaction of 2-chlorophenol **13** with dimethyl carbonate at 120 °C for 3 h gives 1-methoxy-2-chlorobenzene **13a** with 34% yield. An increase in temperature to 130 °C for 2 h affords **13a** with 78% yield. The influence of the number of methyl groups in the molecule of 2,3,4,5,6-pentamethylphenol **11** on the yield of methyl ester **11a** was insignificant.

The Table 1 shows the results of the reaction of phenol and its derivatives with dimethyl carbonate in the presence of FeHYmmm.

Table 1. The reaction of phenol and its derivatives with dimethyl carbonate in the presence of FeHYmmm ^a.

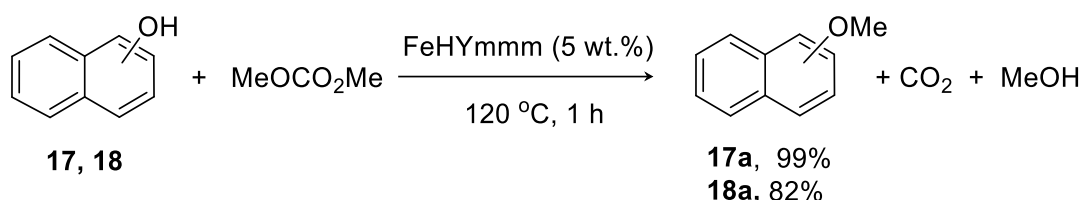
Substituted Phenol (5–16)	Reaction Conditions	Yield of Methoxybenzenes (5a–16a), %
2,3-Dimethylphenol	120 °C, 3 h	70
3,4-Dimethylphenol	120 °C, 1 h	98
3,5-Dimethylphenol	120 °C, 1 h	92
2,6-Dimethylphenol	120 °C, 1 h	75
2,3,5-Trimethylphenol	120 °C, 1 h	89
2,3,6-Trimethylphenol	120 °C, 1 h	92
2,3,4,5,6-Pentamethylphenol	120 °C, 1 h	60

2-Propylphenol	120 °C, 1 h	34
2-Chlorophenol	120 °C, 1 h	78
2-Chlorophenol	120 °C, 1 h	87
3,4-Dichlorophenol	120 °C, 1 h	96
3-Aminophenol	120 °C, 1 h	97

Methyl 3-hydroxybenzoate

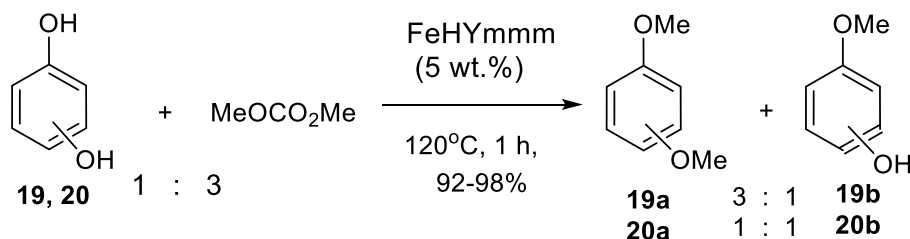
^a Molar ratio [phenol]: [DMC] = 1:3.

The reaction of 2-naphthol **17** with DMC in the presence of FeHYmmm at 120 °C for 1 h proceeds with the formation of 2-methoxynaphthalene **17a** in quantitative yield. The reaction of 1-naphthol **18** with DMC in the presence of FeHYmmm zeolite gives 1-methoxynaphthalene **18a** in 82% yield (Scheme 2).



Scheme 2. Methylation of 1- and 2-naphthols using DMC in the presence of FeHYmmm.

Resorcinol **19** reacts with DMC (1:3) in the presence of FeHYmmm to give products of partial and complete methylation. Hydroquinone **20** reacts with DMC in a similar way. In experiments with resorcinol and hydroquinone, an increase in DMC concentration ([**19**, **20**]: [DMC] = 1:4) has little effect on the ratio of isomers **19a**, **19b**, **20a**, **20b** (Scheme 3).



Scheme 3. Methylation of resorcinol and hydroquinone using DMC in the presence of FeHYmmm.

3. Conclusions

Methylation of phenol, its derivatives, 1- and 2-naphthols using dimethyl carbonate was carried out to obtain arylmethyl ethers in 34–98% yields. The reaction is catalyzed by a FeHYmmm zeolite catalyst without binders. The advantages of the Fe-zeolite catalyst are availability, high selectivity of the reaction with respect to arylmethyl ethers, ease of isolation of reaction products, and the possibility of reuse. The presence of meso- and macropores in the zeolite creates conditions for the effective diffusion of molecules of reactants to catalytically active sites. The concentration of active sites in the FeHYmmm zeolite without binders is much higher than in zeolites with binders, which makes it possible to use them in catalytic amounts (5 wt.%).

4. Experimental Part

Commercially available reagents were used. The binder-free zeolite catalyst (FeHYmmm) was prepared as described in procedure [7]. The reactions were carried out in a dry argon atmosphere. ¹H and ¹³C NMR spectra were recorded on Bruker Avance 400 spectrometer (100.62 MHz for ¹³C and 400.13 MHz for ¹H). When recording the ¹H and ¹³C NMR spectra, SiMe₄ and CDCl₃ were used as an internal standards, respectively. Mass

spectra were measured using Finnigan 4021 instrument with an ionizing electron energy of 70 eV and an ionization chamber temperature of 200 °C. The elemental analysis of the samples was determined on Carlo Erba elemental analyzer, model 1106.

General procedure for the methylation phenol and its derivatives with dimethyl carbonate.

The reaction was carried out in a glass ampoule ($V = 10$ mL) placed in a 17 mL stainless steel microautoclave. The catalyst FeHYmmm (5 wt.%), 10 mmol of phenol and 20–30 mmol of dimethyl carbonate were placed in the ampoule, the ampoule was sealed and placed in an autoclave, which was hermetically sealed, and the reaction mixture was heated at 120 °C for 1–3 h with constant stirring. After the completion of the reaction, the autoclave was cooled to room temperature and opened. The reaction mixture was filtered through a layer of Al_2O_3 . Unreacted dimethyl carbonate was distilled off, the remainder of the reaction mixture was distilled at atmospheric pressure or in a vacuum, or crystallized from an ethanol-hexane mixture (1:4).

The FeHYmmm catalyst does not lose its activity upon repeated use within 4–5 cycles. After five experiments the conversion of phenol the selectivity of the reaction gradually decreases. When the used catalyst is calcined at 450 °C for 3 h, its activity is restored.

The progress of the reaction and the purity of the obtained compounds were monitored by GLC.

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Conflicts of Interest: The authors declare no conflict of interest.

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