Mesoporous aromatic frameworks modified by metal chlorides in phenol alkylation with oct-1-ene

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Mesoporous polyaromatic frameworks (PAF) based on tetraphenylmethane were synthesized. The PAF/$AlCl_3$ and PAF/$FeCl_3$ catalysts were prepared by impregnating the synthesized products with aluminum and iron chlorides, respectively. The resulting materials were characterized by low-temperature adsorption—desorption of nitrogen, IR spectroscopy, and transmission electron microscopy. The catalytic activity of PAF/$AlCl_3$ and PAF/$FeCl_3$ was tested in the phenol alkylation with oct-1-ene. The tests showed that the use of these catalysts gave both alkylphenols (C-alkylates) and alkyl phenyl ethers (O-alkylates) in the total yields up to 78 and 65% for PAF/$AlCl_3$ and PAF/$FeCl_3$, respectively. The fraction of alkylphenols depends on both the catalyst amount and reaction temperature.

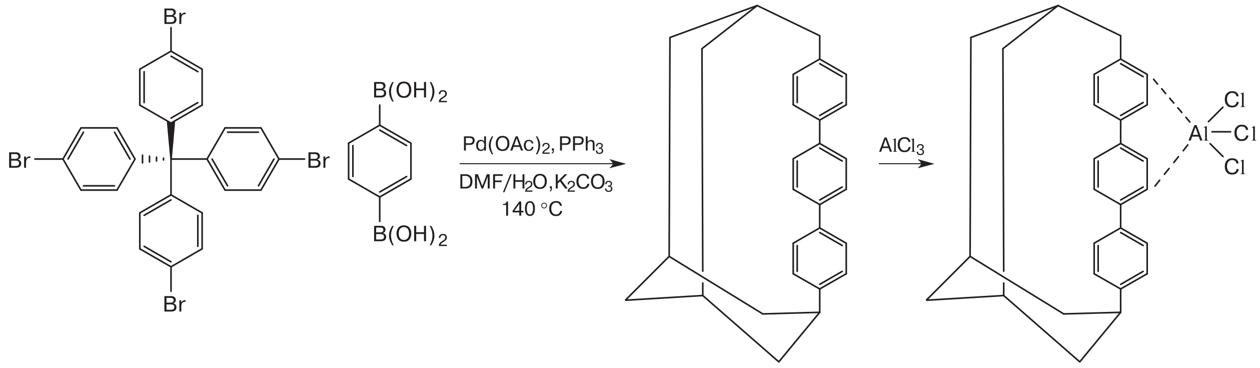
Key words: nanoporous materials, modified mesoporous aromatic frameworks, Lewis acids, alkylation, alkenes, alkylphenols, alkyl phenyl ethers.

The Friedel—Crafts alkylation with olefins, alcohols, and halogen derivatives is the main route to the synthesis of alkylaromatic compounds. The use of heterogeneous catalysts of diverse types has presently been acknowledged as the most efficient and promising method for the preparation of alkylated aromatic compounds. These catalysts are polymeric sulfonic cation-exchange resins[1]; mesoporous structured materials of the MCM-41, MCM-48, and SBA-15 types functionalized by sulfo groups; metal halides; and ionic liquids.[2—7] We have previously shown that the catalysts based on supports consisting of carbon atoms only, namely, porous aromatic frameworks (PAF) modified by sulfo groups can successfully be used in the alkylation of phenol with alkenes[8] and in the aldol condensation of furfural with carbonyl compounds.[9] The purpose of this work is to synthesize the PAF catalysts with supported Lewis acids, aluminum and iron chloride salts, and to study the activity of the obtained PAF/$AlCl_3$ and PAF/$FeCl_3$ catalysts in the alkylation of phenol with oct-1-ene.

Results and Discussion

Synthesis and characterization of the supports and catalysts. The PAF polymer was synthesized by the cross-coupling of tetrakis(4-bromophenyl)methane and *para*-benzeneboric acid as shown in Scheme 1. The material was characterized by low-temperature adsorption—desorption of nitrogen and IR spectroscopy. Its more detailed

Scheme 1



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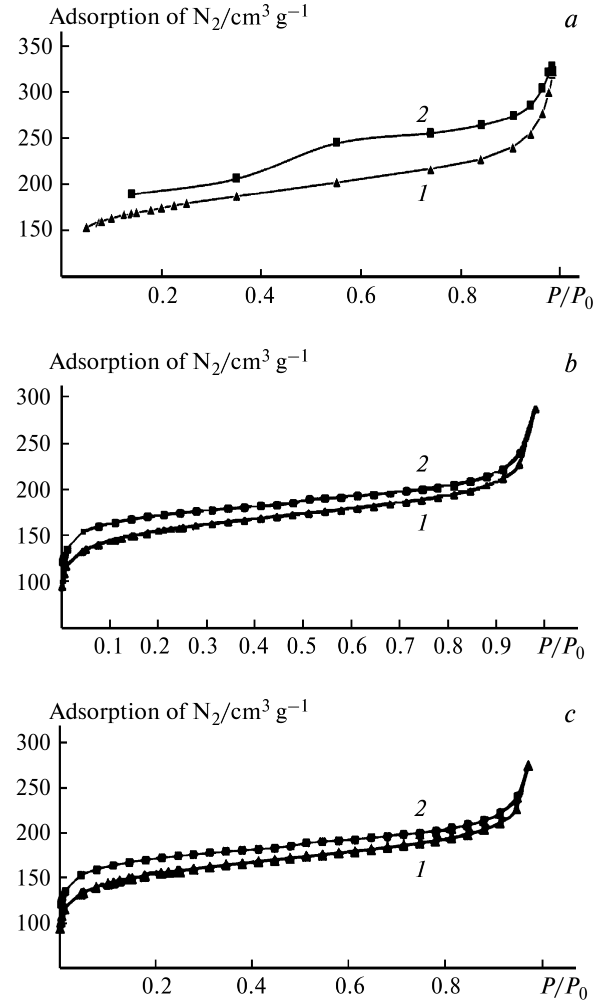

Fig. 1. Isotherms of adsorption—desorption of N_2 on the mesoporous materials PAF (*a*), PAF/$AlCl_3$ (*b*), and PAF/$FeCl_3$ (*c*); *1*, adsorption and *2*, desorption.

characteristics (obtained by transmission electron microscopy (TEM) and ^{13}C NMR spectroscopy) were described earlier.[8,9]

Table 1. Results of analysis of the mesoporous polymers before and after modification by low-temperature adsorption—desorption of nitrogen

Sample	S_{sp} /m^2 g^{-1}	Total pore volume /cm^3 g^{-1}	Average pore diameter /nm	Content of metal (wt.%)
PAF	584	0.32	4.9	—
PAF/$FeCl_3$	455	0.18	4.0	16.1
PAF/$AlCl_3$	471	0.19	4.1	15.8

According to the data of low-temperature adsorption—desorption of nitrogen (Table 1, Fig. 1, *a*), the PAF material has a high specific surface area (584 m^2 g^{-1}) and an average pore diameter of 4.9 nm. The material structure contains micropores, which is indicated by a sharp nitrogen uptake in the low-pressure range (P/P_0 = 0—0.05). The hysteresis loop confirms the mesoporous structure of the material, which is consistent with published data.[10,11]

The IR spectrum of the PAF material (Fig. 2) exhibits signals characteristic of aromatic compounds: an intense band of bending vibrations of C—H bonds at 809 cm^{-1} and less intense bands with absorption maxima at 1486 and 1600 cm^{-1} attributed to stretching vibrations of C—C bonds for *para*-substituted phenyl fragments.

The PAF polymer was modified by aluminum and iron chlorides using the impregnation method. According to the elemental analysis data, the metal content in the samples was 15.8 wt.% for PAF/$AlCl_3$ and 16.1 wt.% for PAF/$FeCl_3$. After the metal salts were introduced into the PAF material, the obtained catalysts PAF/$AlCl_3$ and PAF/$FeCl_3$ were studied by low-temperature adsorption—desorption of nitrogen, IR spectroscopy, and TEM.

The mesoporous structures of the polymer materials PAF/$AlCl_3$ and PAF/$FeCl_3$ remained unchanged after PAF modification, which is indicated by the shapes of the nitrogen adsorption—desorption isotherms (Fig. 1, *b*, *c*). Their specific surface areas (see Table 1) as the total volume and average pore diameter decreased as compared to

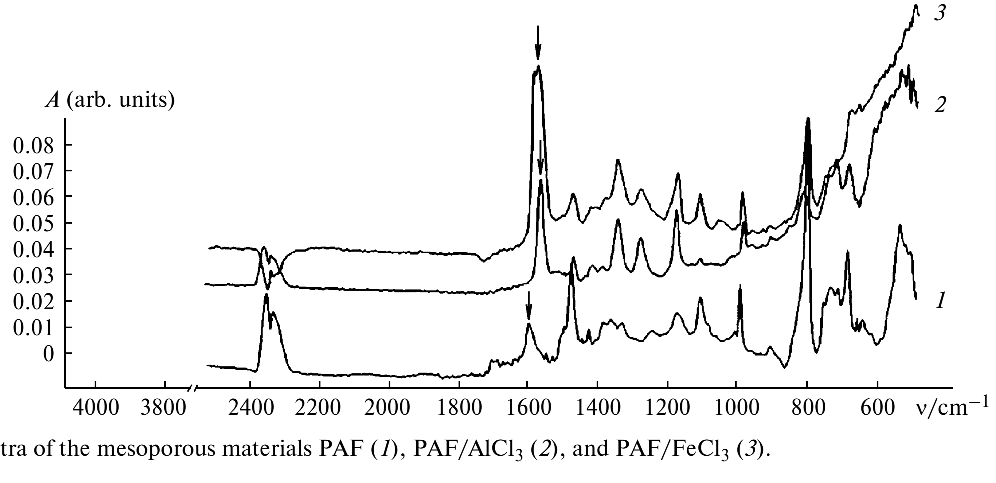

Fig. 2. IR spectra of the mesoporous materials PAF (*1*), PAF/$AlCl_3$ (*2*), and PAF/$FeCl_3$ (*3*).

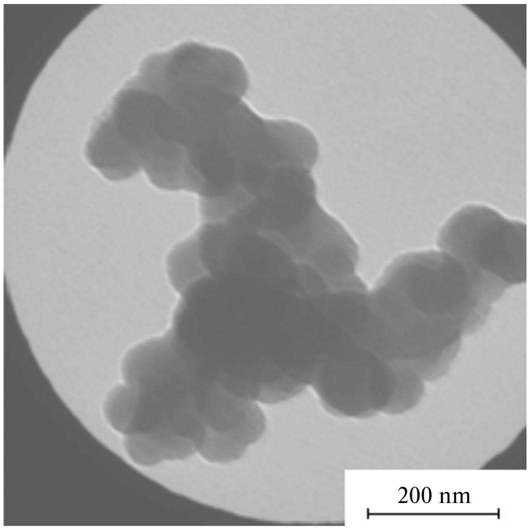

Fig. 3. TEM image of the PAF/AlCl$_3$ sample.

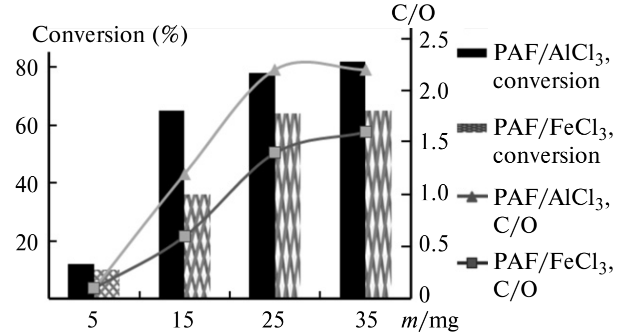

Fig. 4. Alkylation of phenol with oct-1-ene in the presence of the catalysts PAF/AlCl$_3$ and PAF/FeCl$_3$ (*m* is the catalyst mass, C/O is octylphenol/ether). Reaction conditions: octene 0.32 mmol, phenol : octene = 6 : 1, 90 °C, 6 h.

those of the initial material. It appears that the supported aluminum and iron salts partially occupy pores of the framework and block the surface.

The morphology of PAF/AlCl$_3$ and PAF/FeCl$_3$ was studied using the TEM method. All samples have the structure of typical porous polymers and consist of globules 100—150 nm in diameter (Fig. 3), which was also observed for the initial PAF material.

In the IR spectra of the materials PAF/AlCl$_3$ and PAF/FeCl$_3$ (see Fig. 2), the absorption peak at 1600 cm^{-1} shifts to a range of 1580 cm^{-1} for PAF/FeCl$_3$ and 1570 cm^{-1} for PAF/AlCl$_3$ and its intensity increases. This possibly indicates a certain interaction of the π-electron clouds of the benzene rings with the orbitals of the aluminum and iron atoms, which is consistent with published data.[12]

Catalytic experiments. The obtained catalyst was tested in the alkylation of phenol, and oct-1-ene was chosen as the substrate (Scheme 2).

The alkylation products contain octyl phenyl ethers (O-alkylates) and *o*- and *p*-substituted monooctylphenols (C-alkylates). In addition, oct-1-ene undergoes isomerization under the reaction conditions to form linear isomers: oct-2-ene, oct-3-ene, and oct-4-ene. These isomeric octenes can also enter into the alkylation reaction, the products of which are isomeric octylphenols and isomeric octyl phenyl ethers as reported in our earlier studies.[8]

The influence of the catalyst amount (5—35 mg) on the conversion of octenes and the distribution of the products (ratio of the amounts of octyl phenyl ethers and octylphenols, C/O) are presented in Fig. 4. The maximum conversions of octenes at 90 °C within 6 h (80% for PAF/AlCl$_3$ and 64% for PAF/FeCl$_3$) were achieved when using 25 mg of the catalysis in both cases. In these cases, the yields of the target products (octylphenols, C) were 54% for PAF/AlCl$_3$ and 38% for PAF/FeCl$_3$. This optimum amount of the catalyst (25 mg) corresponds to 40 mol.% of the amount of oct-1-ene taken into the reaction for the PAF/AlCl$_3$ catalyst and to 20 mol.% for the PAF/FeCl$_3$ catalyst. This amount of the catalyst was used in further experiments.

An attempt to increase the yield of the alkylation products by increasing reaction temperature to 120 °C did not result in a significant increase in the conversion of octenes (Fig. 5): it was 88 and 67% for PAF/AlCl$_3$ and PAF/FeCl$_3$, respectively, but the fraction of octylphenols in the products increased (the C/O ratio became ~2.5 in both cases). For example, when PAF/AlCl$_3$ was used, octylphenols were obtained in a yield of 64% with 72%

Scheme 2

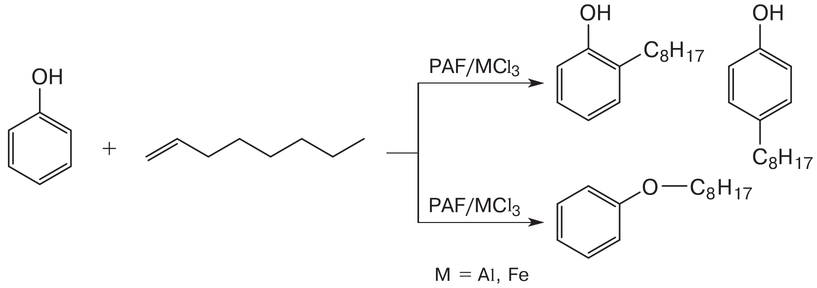

Table 2. Alkylation of phenol with oct-1-ene with repeatedly using the catalysts PAF/$AlCl_3$ and PAF/$FeCl_3$

Cycle	PAF/$AlCl_3$			PAF/$FeCl_3$		
	Conversion of octenes	Yield of octylphenols	Octylphenol/ether (C/O)	Conversion of octenes	Yield of octylphenols	Octylphenol/ether (C/O)
	%			%		
1	78	54	2.2	64	38	1.4
2	70	42	1.5	59	31	1.1
3	63	32	1.0	55	21	0.6
4	26	6	0.3	19	3	0.2
5	12	—	Only ether	5	—	Only ether

Note. Reaction conditions: octene 0.32 mmol, phenol : octene = 6 : 1, catalyst 25 mg, 90 °C, 6 h.

selectivity, whereas the yield of octylphenols was 46% and selectivity was 71% when PAF/$FeCl_3$ was used.

The possibility of the repeated use of the catalyst plays an important role in catalytic processes. After the reaction, the catalyst was separated by centrifugation followed by decantation. The repeated alkylation cycles were carried out on the used portion of the catalyst without additional loading. As can be seen from Table 2, the total conversion of octenes in the first three catalytic cycles is significant (78—55%) and substantially decreases in the subsequent two cycles. The yield of alkylphenols also decreased sharply in each subsequent cycle: to 32 and 21% for PAF/$AlCl_3$ and PAF/$FeCl_3$, respectively. Evidently, the catalysts can be used repeatedly until metal chlorides would be hydrolyzed under the action of moisture.

A comparison of the obtained catalysts with the Lewis acids (aluminum and iron(III) chlorides) traditionally used in the alkylation of aromatic compounds showed that the PAF-based catalysts modified by these chlorides exhibit somewhat lower activity than that of free $AlCl_3$ and $FeCl_3$ (Table 3): the conversion of octenes is lower (78 and 64%), the yields of octylphenols is also lower, but the selectivity to the C-products is higher, namely, 69% for PAF/$AlCl_3$ (60% for free $AlCl_3$) and 59% for PAF/$FeCl_3$ (48% for free $FeCl_3$).

Table 3. Alkylation of phenol with oct-1-ene using various catalysts

Catalyst	Conversion of octenes	Yield of octylphenols	Octylphenol /ether (C/O)
	%		
$AlCl_3$[a]	99	60	1.5
PAF/$AlCl_3$	78	54	2.2
$FeCl_3$[b]	79	38	0.9
PAF/$FeCl_3$	64	38	1.4

Note. Reaction conditions: octene 0.32 mmol, phenol : octene = = 6 : 1, catalyst 25 mg, 90 °C, 6 h.

[a] The weight of $AlCl_3$ was 19 mg.

[b] The weight of $FeCl_3$ was 12 mg.

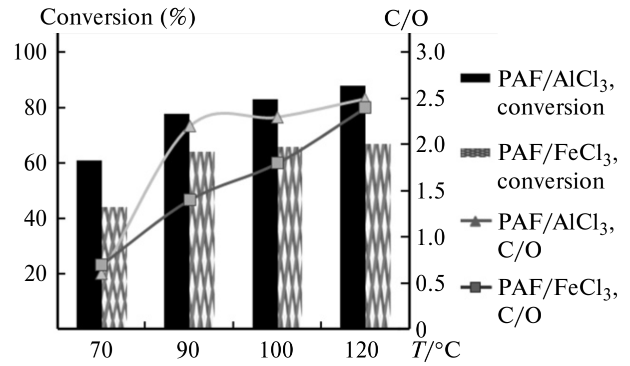

Fig. 5 Alkylation of phenol with oct-1-ene in the presence of the catalysts PAF/$AlCl_3$ and PAF/$FeCl_3$ at various temperature (C/O is octylphenol/ether). Reaction conditions: octene 0.32 mmol, phenol : octene = 6 : 1, catalyst weight 25 mg, 6 h.

Thus, polymeric mesoporous organic frameworks (PAF) based on the tetraphenylmethane core were synthesized. The PAF/$AlCl_3$ and PAF/$FeCl_3$ catalysts were prepared by the impregnation of the synthesis products. It is found that the use of 40 mol.% PAF/$AlCl_3$ and 20 mol.% PAF/$FeCl_3$ (with respect to octane taken into the reaction) in phenyl alkylation with oct-1-ene affords octylphenols (C-alkylates) and octyl phenyl ethers (O-alkylated) in the total yields up to 65—80% at 90 °C within 6 h. The fraction of octylphenols accounts for about 60—70% in the total yield of the reaction products and increases as temperature increases to 120 °C. The synthesized catalysts based on porous aromatic frameworks with supported aluminum and iron chlorides are characterized by somewhat lower activity than Lewis acids, non-supported metal salts, but alkylphenols are formed with a higher selectivity in this case.

Experimental

Trityl chloride, isoamyl nitrite, hypophosphorous acid (50% solution in water), 1,4-phenylenediboric acid, triphenylphosphine, palladium(II) acetate, phenol, oct-1-ene, iron(III) chloride, and aluminum chloride (all Aldrich) were used.

Analysis by GLC was carried out on a Hewlett-Packard chromatograph (Hewlett-Packard, USA) with a flame-ionization detector and a temperature programmable capillary column (30 m) packed with the SE-30 phase and heated from 60 to 230 °C using helium as a carrier gas and *n*-undecane as an internal standard.

The IR spectra of the obtained samples were recorded in a range of 4000—400 cm^{-1} on a Nicolet IR-2000 instrument (Thermo Scientific, USA) by the multiple attenuated total reflection method using a Multi-reflection HATR attachment containing the ZnSe crystal (angle 45°) for various wavelength ranges with a resolution of 4 nm.

TEM analysis was conducted with a LEO912 AB OMEGA microscope (Carl Zeiss, Germany; magnification from 80× to 500000×, image resolution 0.2—0.34 nm). The electron beam potential was 100 eV. The images were processed and the average particle size was calculated using the ImageJ program.

The isotherms of adsorption—desorption of nitrogen were detected at –193 °C (77 K) with a Gemini VII 2390 instrument (Micromeritics, USA). Prior to measurements, the samples were degassed at 130 °C for 6 h. The Brunauer—Emmett—Teller (BET) method was used for the calculation of the surface area (S_{BET}) from the adsorption data in the range of relative pressures P/P_0 = 0.04—0.2. The total volume and average pore diameter were determined using the Barrett—Joyner—Halenda model.

Polymer PAF was prepared from brominated tetraphenylmethane and benzene-1,4-diboric acid according to previously described procedures.[7,8]

Catalysts PAF/FeCl$_3$ and PAF/AlCl$_3$. The metal salts were introduced onto the PAF support by impregnating the support with solutions of aluminum and iron(III) chlorides in toluene. The typical procedure includes the dissolution of aluminum or iron chloride (0.5 g) in toluene (50 mL) at 75—80 °C in a round-bottom flask preliminarily purged with an argon flow. After the salt was dissolved, the PAF polymer (0.25 g) was rapidly added to the obtained solution. The prepared suspension was stirred at this temperature for 3 h and then at room temperature for 18 h more. The black powder was filtered off, washed with toluene, and dried *in vacuo* at 70 °C for 6 h. The weight fractions of aluminum and iron in the obtained materials PAF/AlCl$_3$ and PAF/FeCl$_3$ were 15.8 and 16.1%, respectively.

PAF/AlCl$_3$: IR, ν/cm^{-1}: 1580 (C=C$_{\text{Ar}}$).

PAF/FeCl$_3$: IR, ν/cm^{-1}: 1570 (C=C$_{\text{Ar}}$).

Catalytic experiments. The calculated amounts of the catalyst, phenol, oct-1-ene, and undecane as an internal standard were placed in a steel autoclave equipped with a magnetic stirrer. The autoclave was sealed and placed into a thermostat. The reaction mixture was stirred at certain temperature for specified time. After cooling, the autoclave was depressurized, ether (1 mL) was added, and the catalyst was separated by filtration. The mixture was analyzed using GLC, and the total conversion of octenes, yields of octylphenols, and the ratio of amounts of octylphenols and octyl phenyl ethers (C/O) were calculated.

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