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Catalytic Methylation of Phenol

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Abstract—Attempt was made to methylate phenol with methyl formate in the presence of a zeolite-supported palladium and a ruthenium-titanium catalyst.

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Analysis of published data on methylation of phenols shows that these processes are for the most part studied in order to obtain methyl derivatives of phenol and, in particular, anisole, xylenols, and trimethylphenols. Representatives of various classes of organic compounds have been examined as methylating agents: methyl halides, methanol, formaldehyde, dimethyl ether, methyl formate, and sulfonic acid salts having methylol groups in their structure [1–4].

As catalysts have been used chlorides, oxides of various metals and their combinations, natural and synthetic aluminosilicates, zeolites and their modified forms, acids, superacids, and supported heteropolyacids [2, 5–8]. It is known [3] that, in the presence of $ZnCl_2$ and ZnO, methyl formate methylates phenol to anisole with good selectivity.

EXPERIMENTAL

We made an attempt to methylate phenol with methyl formate in the presence of a Pd-zeolite and a ruthenium-titanium catalyst (RTC). An H-form of high-silica zeolites (HSZ) (zeolite family of the ZSM-5 type) was obtained in several stages from the Na-form by ion exchange, with the zeolite treated with a 0.1 N ammonium chloride solution at 75°C. Before the ion exchange, the zeolites were calcined at 540°C for 12 h. After the ion exchange was complete, the zeolite was washed and thermostated at 120°C for 4 h. The resulting ammonium form of the zeolite contained 0.04–0.08% sodium. H-forms of HSZs were produced by calcination of the ammonium forms at 540°C for 6 h. A sample of the H-form was mixed with a hydrogel of aluminum oxide in a 3 : 1 mass ratio, thoroughly agitated, molded, granulated, dried at room temperature, and calcined at 300 and 540°C for 3 h at each temperature.

Palladium was deposited onto the H-forms of HSZs by their impregnation with a palladium tetraaminochloride solution.

The ruthenium–titanium catalyst was fabricated by a special procedure used in the electrochemical industry. The catalyst was composed of ruthenium and titanium oxides in a 0.43 : 1 mass ratio.

Experiments were carried out in an 60-cm^3 electrically heated stainless steel autoclave with a reflux, pressure gage, and sampling valve. The temperature in the reaction zone was monitored with a thermocouple connected to a potentiometer.

The reaction products were analyzed with a Khrom-5 chromatograph with a heat-conductivity detector and a packed column (3.6 m × 4 mm) with dimenthylphthalate as the liquid phase supported in an amount of 18 wt % by Chromosorb W.

Dimenthylphthalate was synthesized by an accelerated procedure, developed by the authors, from special-purity menthol and phthalic anhydride.

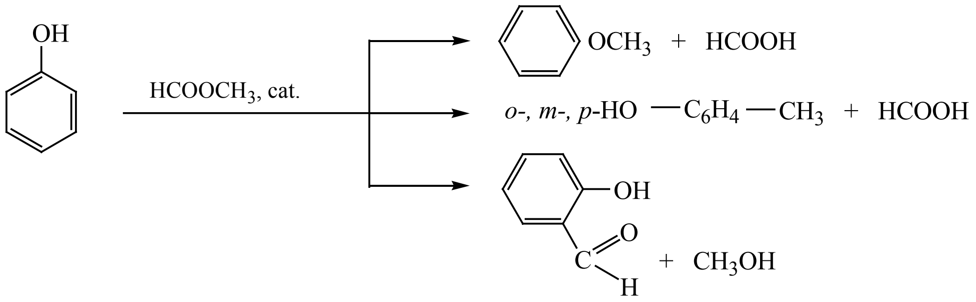
An effective analysis of difficultly separable methylphenols and, in particular, *meta*- and *para*-

isomers can be made on dimenthylphthalate having the liquid-crystalline structure (133–134°C). With this temperature mode changed, the efficiency of the chromatographic separation of isomeric methylphenols is partly impaired. A chromatographic analysis of gaseous products was made using 13X molecular sieves and NaX zeolite.

Methyl formate was synthesized from methanol in the presence of water and a cobalt-ferrite catalyst at 350–370°C [9]. It is known [10] that this compound is formed in small amounts in alkylation of phenol with methanol on this catalyst by a parallel scheme and is a by-product of methanol conversion.

Before the reaction, formic acid methyl ester produced from methanol was boiled over anhydrous $MgSO_4$ and distilled with a reflux condenser.

The interaction of phenol with methyl formate yields catalyzates of various compositions. Anisole, isomeric cresols, salicylic aldehyde, methanol, formic acid, and carbon(II) oxide were found in the reaction products. This gives reason to assume that the following reactions occur under the process conditions:



The results of the catalytic interaction of phenol with methyl formate are listed in the table. Analysis of the data obtained shows that salicylic aldehyde is formed in small amounts over the catalysts under study, especially in the presence of RTC. As temperature is raised, its formation ceases. Thermodynamic factors hinder formation of salicylic aldehyde under these conditions. With the fact that $\Delta G^0_{298} \approx 0$ and data of [11] take into account, occurrence of the reaction can only be judged on the basis of additional experiments. Low temperatures partly provide thermodynamically favorable conditions for formylation; with increasing temperature, the thermodynamic hindrance becomes more pronounced.

The data in the table suggest that the formation of anisole is the main process direction. The alkyl–O bond

Results of the reaction of methyl formate with phenol over Pd-HSZ and RTC catalysts. Reaction conditions: phenol : methyl formate molar ratio 1 : 6, reaction duration 3 h

Catalyst	Reaction conditions		Phenol conversion, %	Selectivity, %					
	T, °C	*P*, MPa		anisole	cresol			salicylic aldehyde	other products
					ortho-	*meta-*	*para-*		
Pd-HSZ	240	0.8	10.2	90	–	–	–	9.5	–
	280	0.8	25.1	55.0	20.5	4.6	12.0	5.6	–
	320	1.0	30.2	50.0	20.0	14.6	15.0	–	–
	340	1.0	43.5	30.0	25.0	20.0	18.0	–	6.0
RTC	240	0.8	8.3	96.0	2.5	–	–	1.2	–
	280	0.8	20.0	79.0	13.0	–	6.5	–	–
	320	1.0	22.5	62.0	18.0	5.0	11.0	–	2.0

in an ester is only ruptured in the case when the carbon atom of the alkyl or aralkyl radical has groups that can stabilize the intermediately formed carbonium ion [12]. The observed alkylation can be accounted for by hydrolysis of methyl formate with admixture of water and by the interaction of phenol under acid catalysis conditions with CH_3OH being formed. However, it is also probable that the mobility of the methyl group increases upon adsorption of methyl formate on active centers of the catalysts and its methylating capacity in interaction with phenol from the bulk grows.

It can be seen in the table that the highest activity in the reaction of phenol with methyl formate is exhibited by the Pd-HSZ at 320°C. The type of interaction of phenol with methyl formate differs from that of the reaction of phenol alkylation by methanol. Primarily, a noticeable presence of anisole in catalyzates even at 320°C is observed. Under similar conditions, anisole is formed on the given catalyst from phenol and methanol, with a selectivity of 18.0%; mixture of isomeric cresols, with selectivities with respect to *ortho-, meta, and para-*isomers of 55.0, 1.0, and 20.0%, respectively; and di- and trimethylphenols, with a selectivity of 23.0%. In the case of methyl formate, there no di- and trimethylphenols, and the isomeric composition of cresols strongly differs from that specified above (see table).

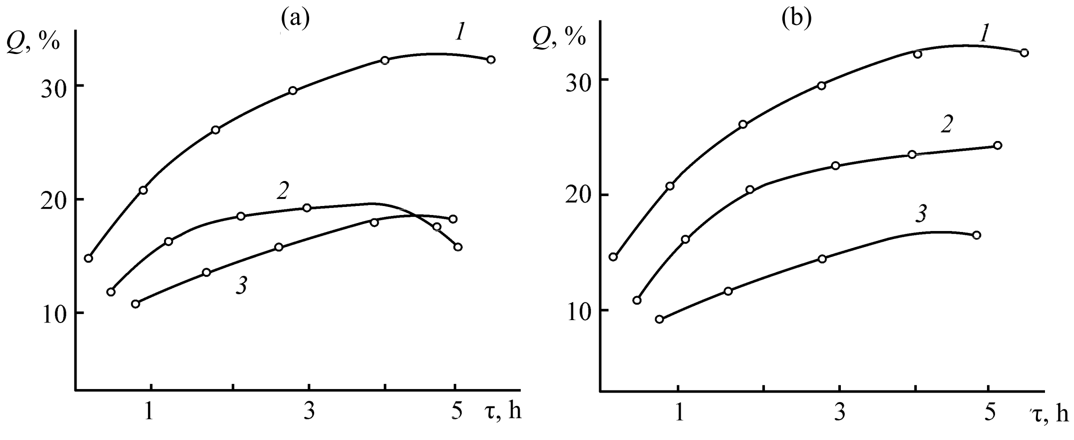
Comparison of the results obtained for the interaction of phenol with methyl formate (see table) and methanol [3] over RTC reveals their noticeable difference: in alkylation of phenol with methanol at 320°C, its conversion exceeds by 12.0% that in the interaction of phenol with methyl formate.

Under the conditions of alkylation with methanol, phenol hardly forms any anisole, and *meta-* and *para-*cresols, and the reaction mainly yields *ortho*-derivatives of phenol (*ortho*-cresol and 2,6-xylenol). It can be seen in the table that, in contrast to the aforesaid, mostly anisole and a mixture of isomeric cresols are formed from phenol and methyl formate over RTC at 320°C.

At the same time, similar effects are observed when phenol is reacted with methanol and methyl formate. First, the reaction selectivity with respect to anisole decreases with increasing temperature and that with respect to cresols grows. This relationship is less pronounced in the case of methyl formate, compared with phenol alkylation by methanol. Despite this circumstance, the probability of isomerization of anisole produced in the interaction of phenol with methyl formate into isomeric cresols cannot be ruled out. However, a special study is necessary for confirming this assumption.

The reaction duration affects the conversion of phenol and yields of anisole and cresols similarly for both the catalysts. Making the reaction longer raises the conversion of phenol over Pd-HSZ and RTC and, after 3–4 h, this parameter nearly stabilizes. A similar behavior is observed in plots describing how the yield of anisole and cresols depends on the process duration (see figure). These yields grow as the reaction duration is raised to 3 h and then, by the fourth hour of the reaction, the yield of anisole somewhat decreases (by 2.5% in the case of Pd-HSZ and by 1.5% over RTC), whereas the yield of cresols remains nearly unchanged.

Raising the temperature (>320°C) and the reaction duration (>4 h) fails to improve the process parameters,



Effect of the reaction duration τ on (*1*) conversion of phenol and (*2, 3*) yields *Q* of (*2*) anisole and (*3*) cresols per reacted phenol. Conditions: $T = 320°C$, $P = 1.0$ MPa. Catalyst: (a) Pd-HSZ and (b) RTC and, simultaneously, the decomposition of formic acid to CO and H_2O is enhanced and dimethylphenols and condensation products are partly formed.

CONCLUSIONS

(1) Methyl formate methylates phenol to anisole with high selectivity in the presence of such catalysts as palladium on high-silica zeolite and ruthenium-titanium catalyst.

(2) As temperature is raised to above 320°C, the reaction selectivity with respect to cresols grows, and that with respect to anisole decreases when the reaction is carried out in the presence of palladium on high-silica zeolite and ruthenium-titanium catalyst by factors of 2 and 3, respectively.

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