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A method for obtaining 2,3,6-trimethylphenol by gas-phase catalytic methylation over iron oxide

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Gas-phase alkylation of *meta*-cresol, 2,5-xylenol and 2,3-xylenol by methanol over a catalyst containing iron oxide as the main component was studied. The reactions were carried out in a continuous process at atmospheric pressure in the temperature range of 573–663 K. The yield of 2,3,6-trimethylphenol increases in the series: *meta*-cresol $<$ 2,3-xylenol $<$ 2,5-xylenol. In the case of 2,5-xylenol, the yield of 2,3,6-trimethylphenol reached over 99% in the temperature range of 635–650 K.

Keywords: 2,3,6-trimethylphenol, alkylation, iron catalyst

2,3,6-trimethylphenol is an important intermediate in the synthesis of vitamin E (α-tocopherol) [1], which is used as a medicine and an antioxidant in stabilization of foodstuff, cosmetics and plastics. 2,3,6-trimethylphenol is formed during catalytic methylation of phenol or 2,6-xylenol in the 570–670 K temperature range in processes run under atmospheric or increased pressure [2,3]. Its separation from and purification of other products of the methylation is complicated [4], which significantly increases the production cost of vitamin E.

Durgakumari et al. [5] carried out studies obtaining 2,3,6-trimethylphenol, using *meta*-cresol as the raw material and MgO as the catalyst. The methylation reactions were conducted in the temperature range of 773–833 K, under pressure of 1–30 bar. The maximum yield of 2,3,6-trimethylphenol, reaching 90%, was obtained at 773 K and 20–30 bar. The by-products of the reaction were 2,3- and 2,5-xylenols. Higher yields of 2,3,6-trimethylphenol (95.5%) obtained by *meta*-cresol methylation in the presence of Fe oxide–V oxide/SiO_2 catalysts are claimed in [6].

We have recently published a series of papers concerning C alkylation of phenol, naphthols and some of their derivatives with methanol, run in a continuous process in the gas phase at atmospheric pressure in the presence of an iron catalyst [7–12]. *ortho*-methyl derivatives, in relation to the hydroxyl group, were obtained with high yield and selectivity. We also proposed a pathway of alkylation of hydroxyarenes with alcohols [8]. For that reason, it was interesting to examine the possibility of applying that catalyst to obtain 2,3,6-trimethylphenol from *meta*-cresol, 2,3- and 2,5-xylenols.

The course of *meta*-cresol methylation in relation to reaction temperatures is shown in figure 1. Beginning at the temperature of 573 K, 2,3- and 2,5-xylenols started to develop, the contents of which in the products of reaction were reaching maxima at the temperature of 628 K, amounting to 15.0 and 48.8%, respectively. The contents of those derivatives decrease later in the course, and mainly the desired product, i.e., 2,3,6-trimethylphenol, is formed. Depending

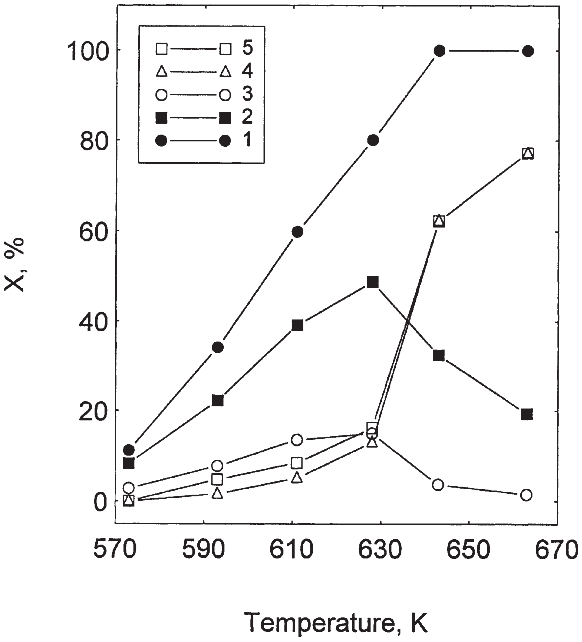

Figure 1. Alkylation of *meta*-cresol with methanol. Molar ratio *meta*-cresol : methanol : water $=$ 1 : 5 : 1; catalyst load $=$ 1.0 h^{-1}; $X =$ conversion of *meta*-cresol (curve 1), yield of 2,5-xylenol (curve 2), yield of 2,3-xylenol (curve 3), yield of 2,3,6-trimethylphenol (curve 4), selectivity of 2,3,6-trimethylphenol (curve 5).

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Table 1
Methylation of 2,5-xylenol with methanol.[a]

T (K)	Conversion of 2,5-xylenol (%)	Samples composition (%) 2,3-xylenol	2,3,6-trimethylphenol	others	Selectivity of 2,3,6-trimethylphenol (%)
573	54.6	–	50.5	4.2	92.4
591	56.5	–	56.4	traces	∼100
611	73.3	–	73.1	traces	∼100
623	82.0	–	81.9	traces	∼100
636	100	–	>99	traces	∼100
651	100	–	>99	traces	∼100
658	96.8	2.4	94.4	traces	97.5

[a] Molar ratio of reagents 2,5-xylenol : methanol : water = 1 : 5 : 1; catalyst load 1.0 h^{-1}.

on the reaction temperature, 0.9–3.3% of unidentified by-products are formed. The alkylation reaction of *meta*-cresol runs similarly, as it was observed by Durgakumari et al., over a MgO catalyst at 1 bar, but at a temperature by 110 °C lower.

The results of the methylation of 2,5-xylenol are given in table 1. The reaction was studied within the same range of temperatures as the *meta*-cresol methylation. Alkylation occurred with high yield and selectivity. In the 630–650 K temperature range, the yield of 2,3,6-trimethylphenol is nearly quantitative. The formation of three additional compounds (that were not identified) was observed only at lower temperature (573 K). Products of reaction obtained at higher temperatures, however, contained small amounts of 2,3-xylenol, formed as a result of 2,5-xylenol isomerization.

Methylation of 2,3-xylenol was carried out under the same conditions. The reaction runs similarly as in the case of 2,5-xylenol, however, with lower yield and selectivity. The maximum yield of 2,3,6-trimethylphenol was obtained in the 625–650 K temperature range, and it amounted from 90 to 96%. The yields of 2,3,6-trimethylphenol depending on the applied raw material in the whole range of the studied temperatures is shown in figure 2. It reveals that the best substrate for obtaining 2,3,6-trimethylphenol, as far as the yield and selectivity of the process are concerned, is 2,5-xylenol, although *meta*-cresol is the cheapest raw material.

As a result of the studies carried out, it has been shown that the iron catalyst is an efficient and selective catalyst for the methylation of *meta*-cresol, 2,3- and 2,5-xylenols. Those reactions can be carried out at atmospheric pressure and they occur at temperatures lower than the alkylation of *meta*-cresol over MgO. We believe that the mechanism occurring on the surface of an iron catalyst is also in this case similar to that proposed in paper [8].

The catalyst we used consisted of Fe, Si, Cr and K oxides in the molar ratio of 100 : 2 : 1 : 0.1. Silicon and chromium were used as additives to prevent sintering, while potassium acts as an activator. The catalyst was obtained by coprecipitation at room temperature from the aqueous solution of iron and chromium nitrates and sodium silicate with ammonia aqueous solution (1 : 1) until pH 7 was reached. The precipitate was filtered off and washed with distilled water to remove nitrate ions, then impregnated with an aqueous solution of potassium carbonate. The precipitate was dried at 383 K, ground and pelletized with a 3% addition of graphite. The pellets were calcined in air at 743 K for 5 h and crushed. In the experiments, the catalyst of 0.6–1.2 mm grain size was used. The fresh catalyst was α-Fe_2O_3 ($S_{BET} \approx 60$ m^2/g) and during the reactions it underwent reduction to magnetite Fe_3O_4 ($S_{BET} \approx 40$ m^2/g). The properties of the catalyst are described in greater detail in papers [9,13].

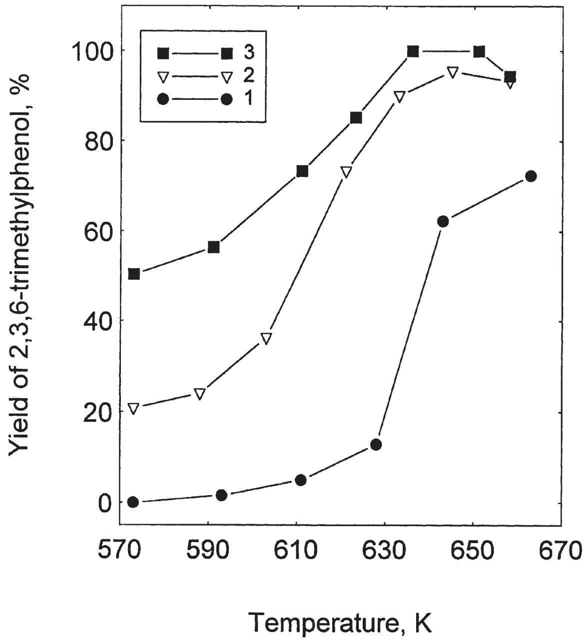

Figure 2. Yield of 2,3,6-trimethylphenol obtained during methylation of *meta*-cresol (curve 1), 2,3-xylenol (curve 2) and 2,5-xylenol (curve 3).

The methylation reactions were carried out in a standard flow system at atmospheric pressure. A vertical quartz reactor of 6 mm inner diameter filled with 3 cm^3 of the catalyst was used. The substrates, solutions of an appropriate methylphenol with methanol and water in the molar ratio of 1 : 5 : 1, were introduced through the top of the reactor using a micropump, applying the load of 1.0 h^{-1}. The alkylation reactions were started at 573 K and studied as a function of increasing temperature up to 663 K. However, at pre-chosen temperatures, after stationary equilibrium had set in (after approximately 1 h), the condensed products were collected and analysed by gas chromatography and mass spectroscopy. The gas chromatograph HP 6890 was equipped with a FID detector and a capillary column HP-5 (30 m × 0.32 mm filled with phenyl methyl silicone). Helium was used as the carrier gas. The identification of products was carried out by the comparison of their retention times to the standards and also by mass spectroscopy (HP MSD 59). After a series of experiments, the catalyst was regenerated with air at a temperature up to 743 K.

Methylation of *meta*-cresol, 2,3- and 2,5-xylenols over an iron catalyst carried out at atmospheric pressure is an efficient method for obtaining 2,3,6-trimethylphenol. During the reaction, no resin- and tar-type deposits are formed on the catalyst. 2,3,6-trimethylphenol is obtained with a high yield, especially when 2,5-xylenol is used as the raw material. The proposed method of synthesis 2,3,6-trimethylphenol may be an inexpensive source of this product. Before its application in further synthesis, the obtained 2,3,6-trimethylphenol does not require costly purification.

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