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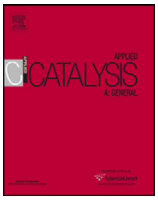

Selective synthesis of *p*-cresol by methylation of phenol

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ABSTRACT

The selective synthesis of *p*-cresol by gas-phase alkylation of phenol with methanol was studied on SiO_2–Al_2O_3 and zeolites HBEA, HZSM5 and HMCM22. Cresols were formed from phenol alkylation of methanol via two parallel pathways: the direct *C*-alkylation of phenol and the conversion of anisole intermediate obtained by *O*-alkylation of phenol. Methylation of *o*- and *p*-cresol led to the formation of 2,6- and 2,4-xylenols while anisole produced methylanisoles either by alkylation with methanol or by disproportionation. Regarding the cresol isomers distribution, *p*- and *o*-cresol were the major products on all the samples while *m*-cresol formation remained always lower than 6%. SiO_2–Al_2O_3, HBEA and HZSM5 exhibited similar initial *p*-cresol:*o*-cresol ratios, between 0.6 and 0.8. In contrast, *p*-cresol was the predominant product on HMCM22 because the narrow sinusoidal 10-membered ring channels of this zeolite were particularly suitable for improving by shape selectivity the formation of *p*-cresol. Thus, we report here that *p*-cresol yields of 55% and *p*-cresol:*o*-cresol ratios of 4 are obtained on HMCM22 by gas-phase alkylation of phenol with methanol at 473 K, atmospheric pressure and contact time of 350 g h/mol phenol.

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1. Introduction

p-Cresol is widely employed for the synthesis of pharmaceuticals, herbicides, antioxidants, agrochemicals and dyes. For example, alkylation of *p*-cresol with *tert*-butanol is used for the production of 2,6-di-*tert*-butyl-*p*-cresol, commercially known as butylated hydroxy toluene (BHT), which is extensively employed in the manufacture of phenolic resins, antioxidants, and polymerization inhibitors [1,2]. *p*-Cresol is also used to produce *p*-hydroxybenzonitrile (*p*-HBN) that is an important product used in agrochemicals [3], and anisaldheyde, a key intermediate for the synthesis of pharmacological products such as the coronary therapeutical Diltiazem or the chemotherapeutical Trimethoprim [4].

p-Cresol is commercially produced by toluene oxidation via sulfonation with sulphuric acid in a four reaction step process that entails concerns related to corrosion and disposal of spent base materials because it employs strong liquid acid catalysts and forms significant amounts of sodium sulfite as subproduct [4]. Thus, the development of a novel ecofriendly process using solid catalysts is a highly desirable technological target for the *p*-cresol synthesis. In particular, the alkylation of phenol with methanol using solid basic or acid catalysts has been widely studied in an attempt to develop less harmful processes to obtain cresol isomers. Basic and redox catalysts such as MgO and CeO_2, respectively, have been reported to selectively alkylate phenol in *ortho*-position, producing essentially *o*-cresol and 2,6-xylenol at temperatures between 673 and 773 K [5–9]. In contrast, solid acids such as zeolites HY, H-mordenite, HZSM5, and HBEA [10–14], silica–alumina [15], Nafion-H and Kieselguhr-supported phosphoric acid [16], convert phenol to anisole, cresols, xylenols and methylanisoles, at relatively low temperatures (473–523 K). However, the obtained *para*-:*ortho*-cresol ratio on amorphous acid catalysts or wide pore zeolites such as HBEA, HY, and H-mordenites was always lower than 0.7, showing that the formation of *o*-cresol is favored also on acid catalysts. Recently, it was reported that *para*-:*ortho*-cresol ratios of up to 1.2 are reached by using narrow pore zeolites HZSM5 and HMCM22 in liquid phase [17].

In this paper we have investigated the gas-phase methylation of phenol with the specific goal of significantly improving the selective synthesis of *p*-cresol. We report the results obtained using SiO_2–Al_2O_3 and zeolites HBEA, HZSM5 and HMCM22. Data will show that the reaction pathways leading from phenol to *p*-cresol depend on both the pore microstructure and the nature, density, and strength of surface acid sites, but the *para*-selectivity is only dramatically increased by using zeolite HMCM22. *p*-Cresol was, in fact, the predominant product only on HMCM22, revealing that the narrow channels of this zeolite are particularly suitable for improving by shape selectivity the formation of *p*-cresol.

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2. Experimental

2.1. Catalyst preparation

Zeolite HMCM22 was synthesized according to [18], by using sodium aluminate (Alfa Aesar, Technical Grade), silica (Aerosil Degussa 380), sodium hydroxide (Merck, >99%), hexamethyleneimine (Aldrich, 99%) and deionized water as reagents. The molar composition of the synthesis gel was $SiO_2/Al_2O_3 = 30$, $OH/SiO_2 = 0.18$, hexamethyleneimine/$SiO_2 = 0.35$ and $H_2O/SiO_2 = 45$. The gel was transferred to a Teflon lined stainless steel autoclave, rotated at 50 rpm, and heated to 423 K in an oven for 7–10 days. After crystallization, the solid was washed with deionized water, centrifugated, dried at 373 K, and finally heated in air at 773 K for 15 h. Commercial zeolites HZSM5 (Zeocat Pentasil PZ-2/54) and HBEA (Zeocat PB), and SiO_2–Al_2O_3 sample (Ketjen LA-LPV) were calcined in air at 723 K.

2.2. Catalyst characterization

Surface areas (S_g) and pore volumes were measured by N_2 physisorption at 77 K using the BET method and Barret–Joyner–Halender (BJH) calculations, respectively, in an Autosorb Quantochrome Instrument 1-C sorptometer. Micropore volumes were determined by both the Dubinin–Radushkevich [19] and *t*-plot [20] methods. The *t*-plot was obtained using the Harkins–Jura equation [21]. Before adsorption, the samples were treated at 623 K under vacuum for 8 h. Elemental compositions were measured using atomic absorption spectroscopy.

The crystal structure of the samples was determined by powder X-ray diffraction (XRD) methods using a Shimadzu XD-D1 diffractometer and Ni-filtered CuKα radiation. The diffraction patterns were scanned in the 2θ of 2–45°.

The morphology of zeolite HMCM22 was observed by scanning electron microscopy (SEM) using a JEOL JSM-35C microscope. As samples were insulators, they were covered by a gold coating prior to analysis.

Sample acidity was determined by temperature-programmed desorption (TPD) of NH_3 preadsorbed at 373 K. Samples (100 mg) were treated in He (60 cm^3/min) at 723 K for 2 h and then exposed to a 1% NH_3/He stream for 40 min at 373 K. Weakly adsorbed NH_3 was removed by flushing with He at 373 K during 2 h. Temperature was then increased at a rate of 10 K/min and the NH_3 concentration in the effluent was measured by mass spectrometry in a Baltzers Omnistar unit.

The nature of surface acid sites was determined by infrared (IR) spectroscopy by using pyridine as probe molecule and a Shimadzu FTIR-8101M spectrophotometer. The spectral resolution was 4 cm^{-1} and 50 scans were added. Sample wafers were formed by pressing 20–40 mg of the catalyst at 5 ton/cm^2 and transferred to a sample holder made of quartz. An inverted T-shaped Pyrex cell containing the sample pellet was used. The two ends of the short arm of the T were fitted with CaF_2 windows. All the samples were initially outgassed in vacuum at 723 K for 4 h and then a background spectrum was recorded after cooling the sample at room temperature. Spectra were recorded at room temperature, after admission of pyridine, adsorption at room temperature and sequential evacuation at 298, 423, 573, and 723 K. Different spectra were obtained by subtracting the background spectrum recorded previously.

Coke formed on the catalysts during reaction was measured by temperature-programmed oxidation (TPO). Samples (20–50 mg) were heated in a 2% O_2/N_2 stream at 10 K/min from room temperature to 1073 K. The evolved CO_2 was converted to methane by means of a methanation catalyst (Ni/kieselghur) operating at 673 K and monitored using a flame ionization detector.

2.3. Catalyst testing

The gas-phase alkylation of phenol (Merck, >99%) with methanol (Merck, 99.8%) was carried out in a fixed bed reactor at 473 K and 101.3 kPa in continuous flow of N_2. Samples (particles with 0.35–0.42 mm diameter) were pretreated in-situ, at 723 K in air flow for 2 h before reaction. Methanol (M) and phenol (P) were fed (M/P = 2:1 molar) using a syringe pump and vaporized into flowing N_2 to give a $N_2/(P + M)$ molar ratio of 26.8. Catalytic runs were carried out at different contact times (W/F_P^0), between 5.6 and 560 g h/mol. The exit gases were analyzed on-line using an Agilent 6850 chromatograph that was equipped with a flame ionization detector, temperature programmer and a 30 m Innowax column (inner diameter: 0.32 mm, film thickness: 0.5 μm). Samples were collected every 20 min during 4 h. Main reaction products were cresols (*o*-, *m*- and *p*-cresols), anisole, xylenols (dimethylphenols) and methylanisoles (MA); dimethyl ether produced by methanol dehydration was also detected.

Phenol conversion (X_P) was calculated as: $X_P = \Sigma Y_i/(\Sigma Y_i + Y_P)$, where ΣY_i is the molar fraction of products formed from phenol, and Y_P is the outlet molar fraction of phenol. The selectivity to product i (S_i, mol of product i/mol of phenol reacted) was determined as: $S_i = [Y_i/\Sigma Y_i]$. Yields (η_i, mol of product i/mol of phenol fed) were calculated as $\eta_i = S_i X_P$.

3. Results and discussion

3.1. Catalyst characterization

The physicochemical properties of the samples used in this work are shown in Table 1. Silica–alumina and zeolites HBEA and HZSM5 were commercial samples while zeolite HMCM22 was synthesized in our laboratory and detailed characterized by different techniques. Fig. 1 shows the X-ray diffractograms corresponding to the HMCM22 precursor, i.e. the as-synthesized sample, and calcined zeolite HMCM22. The positions and intensities of peaks of both diffractograms are in good agreement

Table 1
Physicochemical properties of the catalysts used in this work

Catalyst	Si/Al	Surface area[a] S_g (m^2/g)	Pore diameter $\bar{d}_p$ (Å)	Pore volume[b] (cm^3/g)	Micropore volume (cm^3/g)		Ultramicropore volume[c] (cm^3/g)	External surface area S_e (m^2/g)
HBEA	12.5	560	6.6 × 6.7 5.6 × 5.6	–	0.168[c]	0.24[d]	–	304
HZSM5	20.0	350	5.1 × 5.5 5.3 × 5.6	–	0.155[c]	0.18[d]	–	73
HMCM22	15.0	400	4.0 × 5.5 4.1 × 5.1	–	0.169[c]	0.21[d]	0.10	68
SiO_2–Al_2O_3	11.3	560	45[b]	0.70	–	–	–	–

[a] Determined by the BET method.
[b] Determined by the BJH method.
[c] Determined by the *t*-plot method.
[d] Determined by the Dubinin–Radushkevich method.

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