

Selective synthesis of p-ethylphenol by gas phase ethylation of phenol.

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Introduction

p-Ethylphenol (p-EP) is raw material for the production of p-vinylphenol, which is a valuable chemical used in resins preparations, synthesis of pharmaceuticals and dyes. p-EP is commercially produced by ethylbenzene sulfonation followed by alkaline fusion using corrosive acids and bases. This process poses serious environmental concerns because of the generation of significant amount of wastes. Therefore, the development of an alternative route for obtaining p-EP becomes highly desirable. Ethylphenols can be obtained by gas phase phenol alkylation with ethanol. In fact, the selective synthesis of o-ethylphenol and 2,6-diethylphenol by alkylation of phenol with ethanol using $\text{SiO}_2\text{-Al}_2\text{O}_3$ and Fe_2O_3 catalysts has already been reported [1]. p-Selective alkylation of phenol with ethanol has been claimed on pore size tailored HZSM5 zeolite at 673 K and phenol/ethanol ratio of 2, however the highest p-EP yield obtained was less than 7% [2]. In this work we studied the gas phase ethylation of phenol on zeolites HZSM5 and HMCM22 in order to obtain higher yields of p-ethylphenol and thus developing a technological alternative route for the efficient production of p-EP.

Materials and Methods

Commercial HZSM5 (Zeocat Pentasil PZ-2/54, Si/Al = 20) and zeolite HMCM22 (Si/Al=15) prepared in our laboratory were used. Zeolite surface areas were measured by N_2 physisorption at 77 K. Sample acidity was determined by TPD of NH_3 preadsorbed at 373 K. The nature of surface acid sites was studied by infrared spectroscopy using pyridine as probe molecule. Gas phase alkylation of phenol (P) with ethanol (EtOH) was performed at 523 K and 101.3 kPa in a fixed bed reactor in continuous flow of N_2 . Reactants and products were analyzed on line using an Agilent 6850 gas chromatograph.

Results and Discussion

Main characterization results are summarized in Table 1. Surface area and total density of de acid sites were similar for both catalysts; however, the Brønsted (B) to Lewis (L) ratio for HMCM22 was about three times higher than the B/L ratio for HZSM5.

Table 1. Characterization of catalysts

Catalysts	S_{BET} (m^2/g)	Mean pore size (Å)	TPD NH_3 ($\mu\text{mol}/\text{g}$)	IR of pyridine (Area/g)		
				L Sites	B Sites	B/L
HZSM5	350	5.1x5.5; 5.3x5.6	475	341	337	1
HMCM22	400	4.0x5.5; 4.1x5.1	470	176	560	3.2

Reactants conversions and selectivities values obtained at times zero and 3 h are given in Table 2. Phenol conversion was similar on both catalysts and decreased with time on stream. At time zero only ethylphenols and dialkylated products from C-alkylation of phenol were formed, but with the progress of the reaction the S_{EPE} (from O-alkylation) increased at expenses of the ethylphenols. A remarkable difference in ethylphenols distribution was observed. In fact, on

Table 2: Catalytic results. Conversions and Selectivities for gas phase phenol ethylation

Catalyst	X_{P}		X_{EtOH}		S_{EPE}		$S_{\text{o-EP}}$		$S_{\text{p-EP}}$		$S_{\text{m-EP}}$		S_{dialk}	
	t=0	3h	t=0	3h	t=0	3h	t=0	3h	t=0	3h	t=0	3h	t=0	3h
HZSM5	40.2	16.9	100	95	0	30	51.3	31.4	16.5	22.3	24.2	9.7	8	6.6
HMCM22	42.6	19.0	99	70	0	12.6	16.5	27.1	53.4	46.2	19.9	8.9	10.2	5.2

[523 K, EtOH/P 1:, $W/F_p^0 = 99.3 \text{ g h/mol}$]

HMCM22 the p-isomer was the main product ($S_{\text{p-EP}}^0 = 53.4\%$) with a p/(o+m) ratio of 1.5 while on HZSM5 this ratio was only 0.2 ($S_{\text{p-EP}}^0 = 16.5\%$). These results revealed that the narrow channels of HMCM22 are particularly suitable for improving the formation of p-EP by shape selectivity. Ethanol was totally converted on both zeolites at the beginning of the reaction but X_{EtOH} then decreased with time on stream. The main products formed from ethanol were ethylene and diethyl ether. It has been proposed that aromatic alkylation with ethanol proceeds by reaction of activated ethylene (formed from ethanol dehydration) on the zeolite acid sites [3] Ethylene can also be transformed by parallel reaction with another ethanol to form heavier oligomers that could be involved in catalyst deactivation.

The effect of contact time on the product distribution was determined on HMCM22. The nonzero initial slope of the yield curves confirmed that o-EP, p-EP and EPE are primary products (Figure 1), while m-EP and dialkylated were formed from these primary products as is depicted in the Scheme 1. Furthermore, the o-EP and p-EP can be formed from EPE and a maximum in the yield of this product was observed. At $W/F_p^0 = 200 \text{ g h/mol}$ the p-EP yield achieved was 40% and a p/(o+m) ratio of 1.9.

Scheme 1

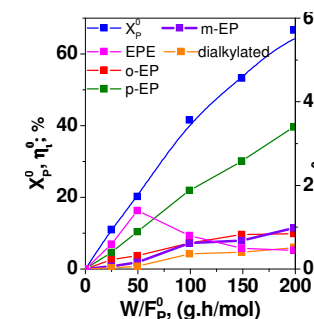
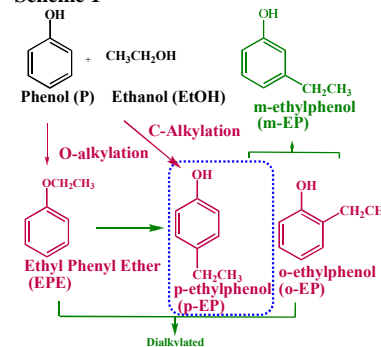


Figure 1: Phenol conversion and yields at time zero vs. contact time

Significance

We report the selective formation of p-EP on HMCM22 at 523K by ethylation of phenol. p-EP yields of 40% and p/(o+m) ratios of about 2 were achieved thereby indicating that this reaction is an interesting alternative route to the commercial process.

References

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