

Study of the mechanism of methylation of phenol over acid zeolites

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Introduction

Gas phase alkylation of phenol (P) with methanol (M) has been widely studied for many years but the mechanism over solid acids remains still unresolved. A variety of products such as cresols, anisole, xylenols (X) and methylanisoles (MA) are formed when acid catalysts are used. In general, cresols can be formed both by direct C-alkylation of phenol with methanol and by conversion of the anisole formed by O-methylation of phenol. In a previous work [1], we have investigated this reaction on acid catalysts with the goal of promoting the selective synthesis of p-cresol. The para-selectivity was dramatically increased by using zeolite HMCM22, revealing that the narrow channels of this zeolite are particularly suitable for improving by shape selectivity the formation of p-cresol. In this work, we performed a detailed study of the gas-phase alkylation of phenol with methanol on samples containing both Lewis and Brønsted acid sites and different porous structure (zeolites HZSM5, HBEA and HMCM22) in order to better understand the mechanism of cresols formation. Results will show that the primary and secondary reaction pathways leading from phenol to cresols depend on both the pore microstructure and the nature, density, and strength of surface acid sites and also explain the unusual high para-selectivity obtained over HMCM22 [1].

Materials and Methods

Commercial zeolites HZSM5 (Zeocat PZ-2/54, Si/Al=20) and HBEA (Zeocat PB, Si/Al=12.5) were used. Zeolite HMCM22 (Si/Al = 15) was synthesized according to [2]. Sample acidity was determined by TPD of NH_3 preadsorbed at 373 K. The nature of surface acid sites was determined by infrared spectroscopy using pyridine as probe molecule. Gas phase reactions (alkylation of phenol with methanol, alkylation of anisole with methanol, alkylation of phenol with anisole, methylation of cresols, etc) were carried out in a fixed bed reactor at 473 K and 101.3 kPa in continuous flow of N_2 . The exit gases were analyzed on-line using an Agilent 6850 chromatograph that was equipped with a flame ionization detector and a 30 m Innowax column (inner diameter: 0.32 mm, film thickness: 0.5 μm).

Results and Discussion

Results of the methylation of phenol on zeolites HZSM5, HBEA and HMCM22 showed that the anisole yield increases with contact time and then reaches a maximum indicating that anisole is converted to secondary products. HBEA and HZSM5 formed higher amount of anisole than HMCM22. Essentially, zeolite HMCM22 suppressed the formation of anisole and also significantly decreased the o-cresol formation rate, but formed p-cresol at high rates. Our results using pure anisole and anisole with phenol as reactants suggested that on HBEA, cresols are mainly formed by alkylation of phenol with anisole, whereas on HZSM5 and HMCM22 phenol does not promote the cresols formation. All the experiences feeding anisole (pure and with phenol or methanol) showed that significant amounts of phenol were

always formed. Phenol was mainly formed from anisole dealkylation, but it was also produced by anisole disproportionation. Experiences feeding o-cresol and methanol showed that zeolites HBEA and HZSM5, which exhibit similar amounts of Brønsted and Lewis acid sites, form mainly xylenols via alkylation reactions. In contrast, zeolite HMCM22 that contains predominantly Brønsted acid sites, promotes isomerization reactions, forming preferentially p-cresol but also m-cresol by consecutive isomerization of orto and para-isomers. Our catalytic results on zeolites HBEA, HZSM5 and HMCM22 are well explained by considering that the alkylation of phenol with methanol occurs according to the reaction network proposed in Figure 1.

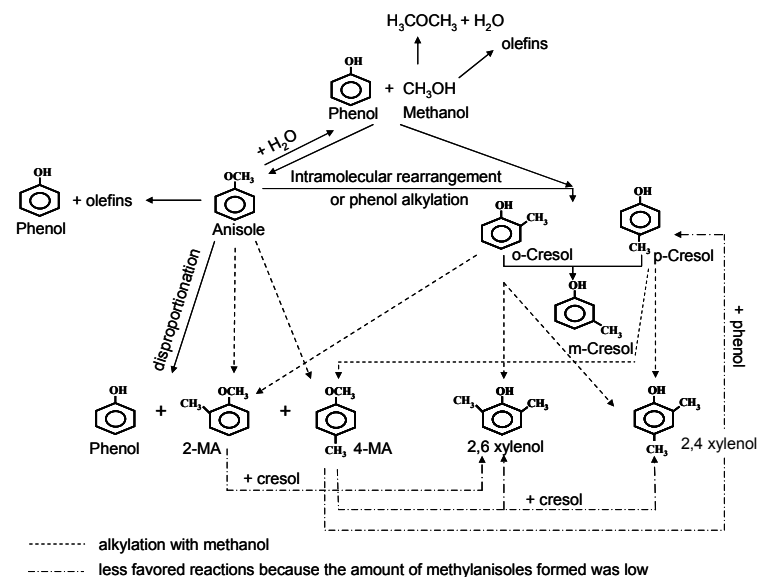


Figure 1. Reaction network for methylation of phenol on HBEA, HZSM5 and HMCM22.

Significance

Catalytic tests feeding intermediate reaction products allowed us to clarify the complex reaction network of the methylation of phenol on acid zeolites. We also concluded that both the particular porous structure and the high Brønsted/Lewis acid sites ratio of HMCM22 are responsible for the preferential formation of p-cresol on this zeolite.

References

1. Maria E. Sad, Cristina L. Padro, C. Apesteguia, Appl. Catal. A: Gen 342 (2008) 40.
2. Rubin, M.A., and Chu, P. US Patent 4,954,325, 1990.