MECHANISM OF ALKYKLATION OF PHENOL WITH METHANOL ON ACID ZEOLITES

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Introduction

The gas-phase alkylation of phenol with methanol has been widely studied on acid catalysts but knowledge regarding the reaction mechanism and the exact requirements of acid site density and strength to efficiently promote the selective formation of cresols is still needed. A variety of products such as cresols, anisole, xylenols and methylanisoles are formed from methylation of phenol on acid catalysts [1,2]. Cresols are formed by both direct C-alkylation of phenol with methanol and conversion of anisole previously formed by O-methylation of phenol. But cresols can in turn react with methanol on acid sites to produce dialkylated compounds (xvlenols, methylanisoles). In this work, we performed a detailed study on the effect of the pore microstructure and the nature, density, and strength of surface acid sites on product distribution for the methylation of phenol with methanol on acid zeolites (zeolites HZSM5, HBEA and HMCM22). We propose a reaction mechanism that interprets the primary and secondary reaction pathways leading from phenol to mono- and dialkylated products and also explains the unique high *para*-selectivity obtained on HMCM22.

Results and Discussion

The mechanism of methylation of phenol on zeolites HZSM5, HBEA and HMCM22 was studied by: i) performing the reaction at increasing contact times; ii) using as reactants the intermediate reaction products, namely, pure anisole, anisole + CH₃OH, anisole + phenol, *o*-cresol + CH₃OH, and *p*-cresol + CH₃OH.

Results of the methylation of phenol 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 amounts of anisole than HMCM22. 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 produced from anisole dealkylation, but also by anisole disproportionation. Experiences feeding *o*-cresol and *p*-cresol with methanol showed that

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



zeolites HBEA and HZSM5. which exhibit similar amounts of Brønsted and Lewis acid sites. form mainly 2.6- and 2,4-xylenols via alkylation reactions. In contrast, zeolite HMCM22 that contains predominantly Brønsted acid sites. promotes also isomerization reactions, forming mcresol by consecutive isomerization of oand *p*-cresol isomers.

Our catalytic results are well explained by considering that the alkylation of phenol with methanol on acid zeolites occurs according to the complex reaction network proposed in Figure 1. Cresol formation rates are better promoted on wide pore zeolites containing strong surface Lewis and Brønsted acid sites, such as zeolite HBEA. Zeolite HZSM5 forms more anisole and less xylenols than HBEA because its narrow pore structure hampers the formation of bulky intermediates involved in both the cresol alkylation to xylenols and the anisole disproportionation. Zeolite HMCM22 suppresses the formation of anisole, decreases the *o*-cresol formation rate and forms *p*-cresol at high rates, thereby increasing substantially the *para*-selectivity.

References

1. M.E. Sad, C.L. Padró, C.R. Apesteguía, Catal. Today 133-135 (2008) 720.

2. M.E. Sad, C.L. Padró, C.R. Apesteguia, Appl. Catal. A: Gen. 342 (2008) 40.