Synthesis of intermediates for fine chemicals: Alkylation of phenol to *p*-cresol

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Abstract

The gas-phase methylation of phenol was studied on samples containing only strong Brönsted acid sites (HPA/SiO_2), or both Lewis and Brønsted acid sites of either strong (zeolites HZSM5, HBEA and HMCM22) or moderate (SiO_2-Al_2O_3) strength. Zeolites HBEA, HZSM5 and HMCM22 were more active than SiO_2-Al_2O_3 or HPA/SiO_2. At 50% phenol conversion, the selectivity to cresols was clearly higher on HMCM22 (90%) than on HBEA, or HZSM5; HPA/SiO_2 formed predominantly anisole. The distribution of cresol isomers on HBEA, HZSM5, and SiO_2-Al_2O_3 was similar, being *o*-cresol the predominant product (*p*:*o* ratios between 0.7 and 0.8). In contrast, the *p*:*o* ratio increased to 3.4 on HMCM22. Thus, results 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, but the *para*-selectivity is only dramatically increased by using zeolite MCM22, because the narrow channels of this zeolite are particularly suitable for improving by shape selectivity the formation of *p*-cresol. Specifically, the *p*-cresol yield and the *para*-/*ortho*-cresol ratio on HMCM22 for 93% phenol conversion were about 58 % and 3.4, respectively, the highest values reported up to now for the *p*-cresol formation from methylation of phenol.

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