Vapor-Phase Hydrolysis of Monochlorobenzene over Cu-ZSM-5 Catalyst Prepared By Solid-State Ion Exchange

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Introduction

Phenol is one of the most widely used chemical feedstock and usually manufactured via the cumene process. The Raschid-Hooker process combining the oxychlorination of benzene to chlorobenzene and the vapor-phase hydrolysis of chlorobenzene produces phenol from benzene and oxygen without co-products. Copper-promoted phosphates or zeolites have been disclosed to be useful catalysts, however, the reported phenol yields were relative low and catalyst-stability wasn't satisfied[1-3]. Herein we report that Cu-ZSM-5 prepared by solid-state ion exchange (SSIE). was served as efficient catalyst for chlorobenzene hydrolysis and extremely high yield and selectivity of phenol was obtained.

Materials and Methods

H-ZSM-5 (SiO_2/Al_2O_3 ratio =30) was mixed with CuCl (Cu/Al =1 in moles) and small amounts of ether was added. The mixture was finely ground and then calcined at 773K in air. Other catalysts were also prepared with an impregnation method for comparison. The vapor-phase hydrolysis of chlorobenzene to phenol was performed in a conventional quartz tube reactor. The reactants, chlorobenzene and water, were fed by syringe pumps, and nitrogen was introduced in the feed to elute the products of reaction. Condensable products were collected in a cold trap at 273 K and analyzed by a GC using toluene as internal standard. Gaseous products of H_2, CO, and CO_2 were analyzed online by another GC. Characterizations including XRD, H_2-TPR, nitrogen adsorption and IR were performed to investigate the structure-activity relationship of Cu-ZSM-5 catalyst and the cause of catalyst deactivation.

Results and Discussion

Table 1 summarizes the performances of chlorobenzene hydrolysis over different catalysts. As can be seen, ZSM-5 zeolite showed much better activity than other carriers including hydroxyapatite, lanthanum phosphate and Y zeolite. Even without the copper promoter, H-ZSM-5 obtained a phenol yield of 11.9%. The addition of copper greatly improved the activity of catalyst. Benzene, carbon deposits, hydrogen and CO_x were the main side products. The activity of chlorobenzene hydrolysis over Cu-ZSM-5 is sensitive to reaction factors including temperature and water/chlorobenzene feed ratio. In the range of 723~833K the yield of phenol remarkably increased with the increase of temperature. However, the higher the temperature, the faster is the rate of catalyst deactivation. High water/chlorobenzene feed ratio is appreciated to obtain high conversion. An extremely high phenol yield of 93% and selectivity of 97.6% was obtained over Cu-ZSM-5 with a copper loading of 7.8% prepared by

the method of solid-state ion exchange under the optimized conditions of 773 K, nitrogen GHSV of 1200 ml.g^{-1}.h^{-1}, chlorobenzene flux of 1 ml.g^{-1}.h^{-1} and water/chlorobenzene mole feed ratio of 60. Figure 1 shows that the activity of chlorobenzene hydrolysis over Cu-ZSM-5 decreased with time-on-stream. Regeneration by air-burning only partially restored its initial activity and the regenerated Cu-ZSM-5 deactivated more quickly than the fresh one.

The results of IR spectroscopy of adsorbed pyridine showed that the amounts of Lewis acid sites increased markedly after the copper was introduced into H-ZSM-5 zeolite by SSIE, while the Brønsted acid sites decreased. Powder XRD characterization revealed that no obvious changes were found between the fresh, deactivated and regenerated Cu-ZSM-5 catalysts, whereas, surface area and micropore volume of the deactivated Cu-ZSM-5 decreased obviously. Regeneration by air-burning didn't restore surface area, pore volume and the amounts of Lewis and Brønsted acid sites to its initial level, indicating an irreversible change of Cu-ZSM-5 structure occurred. Elemental analysis also revealed an obvious loss of copper on Cu-ZSM-5 occurred in the run of hydrolysis. Further experiments are under way of progress.

Table 1 Chlorobenzene hydrolysis performances over different catalysts [a]

Carrier Promoter	Preparation method	Conv. (%)	Select. (%)		
			Phenol	Benzene	others
H-ZSM-5	-	13.4	88.6	10.4	1.0
1.6%Cu-ZSM-5	Impregnation	79.1	99.1	0.4	0.5
1.6% Cu-ZSM-5	SSIE	76.4	99.0	0.4	0.6
1.6%Cu-HY	Impregnation	85.7	7.4	90.1	2.5
1.6%Cu- hydroxyapatite	Impregnation	18.4	94.2	5.1	0.7
1.6%Cu-LaPO4	Impregnation	15.1	98.5	0.6	0.9
7.8%Cu-ZSM-5	SSIE	86.8	98.9	0.7	0.4

[a] Reaction conditions: T=773K, nitrogen *GHSV*=1200 ml.g^{-1}.h^{-1}, chlorobenzene flux=2.0 ml.g^{-1}.h^{-1}, water/chlorobenzene mole feed=18.
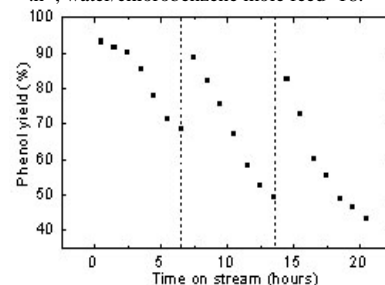

Figure 1. Stability and regeneration test over 7.8%Cu-ZSM-5 (SSIE). Regeneration by 2 h air-burning at 773 K was carried out every 6.5 h of time-on-stream. Reaction conditions: water/chlorobenzene mole feed ratio =60, others is the same as table 1.

Significance

Cu-ZSM-5 with high exchange levels of Cu$^+$ cations by SSIE displays excellent catalytic activity for chlorobenzene hydrolysis to phenol. The application and structure-activity relationship of Cu-ZSM-5 on the hydrolysis of organic halides are worth further study.

References
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