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Mendeleev Commun., 1993, 3(1), 28–29

Mendeleev Communications

Preparation of Phenol over Dehydroxylated HZSM-5 Zeolites

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The influence of the pretreatment temperature of zeolites on their activity in oxidation of benzene to phenol using N_2O has been investigated. Dehydroxylation of HZSM-5 zeolites has been found to lead to a significant increase in phenol yield over these zeolites.

The application of zeolites for the preparation of fine chemicals has been reviewed.[1] Recently, oxidation of benzene and its derivatives to phenols over ZSM-5 zeolites using N_2O has been described by Y. Ono *et al.*[2] by M. Gubelmann *et al.*[3] and by G. I. Panov *et al.*[4] Brönsted acidic sites of HZSM-5 zeolite[2] or iron impurities[4] are considered as active centres in this reaction.

Earlier we reported that decomposition of N_2O over dehydroxylated HZSM-5 zeolites results in chemisorption of O-atoms and the formation of N_2.[5,6] The chemisorption of O-atoms on HZSM-5 zeolites leads to the formation of new sites Z–O* which are very likely to be active in oxidation reactions. Concentration of the Z–O* sites increases with increasing zeolite pretreatment temperature up to 1120 K. In this communication the influence of the zeolite pretreatment temperature on its activity in the oxidation of benzene to phenol using N_2O is reported.

The catalytic activity of different zeolites was determined using a flow-bed microreactor connected on-line to a gas chromatograph. Benzene was oxidized by N_2O at 620 K over zeolites according to a procedure outlined elsewhere.[6] Experimental conditions were similar to the optimum conditions reported by Y. Ono *et al.* in ref. 2, *i.e.* benzene partial pressure 6.8 kPa, N_2O partial pressure 39.5 kPa, flow rate of the feed (reactants and helium) 0.015 mol h^{-1} and mass of catalyst 0.2 g. The results obtained with time-on-stream of 10 min are illustrated in Fig. 1.

Fig. 1 shows that benzene oxidation to phenol proceeds only

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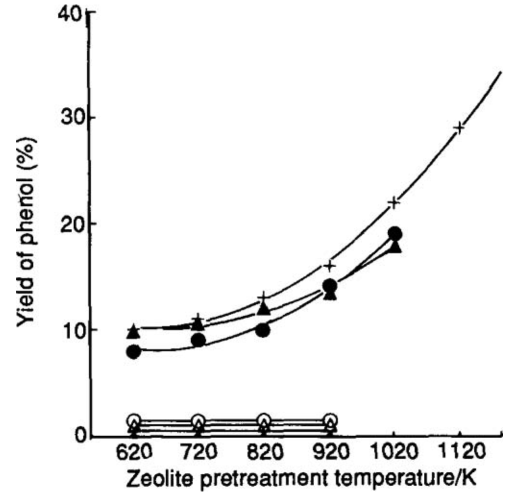

Fig. 1 Yield of phenol as a function of zeolite pretreatment temperature: + HZSM-5 (Si/Al = 20, 0.04% mass Fe_2O_3); ▲ HZSM-5 (Si/Al = 50, 0.01% mass Fe_2O_3); ● HZSM-5 (Si/Al = 19, 0.02% mass Fe_2O_3, steamed 1 h at 770 K); ○ mordenite (Si/Al = 5, 0.25% mass Fe_2O_3); △ dealuminated mordenite (Si/Al = 10, 0.005% mass Fe_2O_3); × amorphous silica-alumina (15% mass Al_2O_3)

over HZSM-5 zeolites. The selectivity of phenol formation over HZSM-5 zeolites is 95–100%. No phenol is formed if mordenite, dealuminated mordenite, Y zeolite or amorphous silica–alumina are used as catalysts. Moreover, dealumination due to steaming of HZSM-5 zeolite leads to a decrease of the phenol yield. The most important feature of the results presented in Fig. 1 is that the dehydroxylation of HZSM-5 zeolite leads to an increased phenol yield over these zeolites without a loss in the selectivity. Indeed, the yield of phenol is *ca.* 29% over HZSM-5/20 activated at 1120 K. It should be noted that samples of HZSM-5 zeolite with relatively low level of the iron impurities were used.

The same reaction was realized for the direct oxidation of chlorobenzene and fluorobenzene. Preliminary results show that increasing the activation temperature of HZSM-5 zeolites raises the yield of corresponding phenols. The effects of shape-selectivity for these substrates are also observed.

The results obtained indicate that centres other than bridged OH-groups are active in oxidation of benzene to phenol using N_2O. The formation of these centres is characteristic for HZSM-5 zeolites only. Possibly these sites of defective nature are formed during zeolite dehydroxylation at high temperature and are similar to those suggested by Kazansky *et al.*[7] The participation of the Fe–Al sites postulated in ref. 8 or of iron impurities[4] also cannot be excluded.

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Received: Cambridge, 3rd June 1992
Moscow, 23rd June 1992; Com. 2/03304F