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Hydroxylation of Benzene with Dinitrogen Monoxide over H-ZSM-5 Zeolite

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Phenol was obtained from benzene and dinitrogen monoxide over H-ZSM-5 zeolite at 603 K, a phenol yield on a benzene basis being 8.1% at partial pressures of benzene and dinitrogen monoxide of 6.9 kPa and 51 kPa, respectively. Neither CO nor CO_2 was detected in the product.

Phenol has been synthesized by an oxidation of cumene through multistep procedures,[1)] while direct hydroxylation of benzene has long been remained highly desirable. Phenol has been obtained by a non-catalytic liquid-phase direct hyroxylation of benzene with hydrogen peroxide in the presence of superacids[2,3)] or with hydrogen peroxide or dioxygen in the presence of aqueous solutions containing sulfuric acid and Cu^+ ions.[4,5)] A catalytic hydroxylation of benzene with hydrogen peroxide has been attained by using a silica-supported Fe^{3+}-catechol catalyst.[6)]

The vapor-phase direct hydroxylation of benzene with dioxygen has been demonstrated over solid catalysts. Thus, Ikawa and Ueda[7)] obtained phenol with a 6.5% yield over a tellurium oxide catalyst, a selectivity for phenol being 70%. Umemura et al.[8)] obtained phenol with a 26% yield over oxides contaning zirconium, silver, and phosphorus, the selectivity being 62%. Iwamoto et al.[9,10)] have found that dinitrogen monoxide is also an effective oxidant for benzene to give phenol in the presence of a V_2O_5/SiO_2 catalyst at 823 K. A phenol yield was 5.0% with the selectivity of 45%.

Here, the authors wish to report a solid acid-catalyzed vapor-phase hydroxylation of benzene using dinitrogen monoxide as an oxidant. A phenol yield of 8.1% was obtained at 603 K. None of deeply oxidized compounds, CO and CO_2, were found in the product.

Reactions were carried out with a continuous flow reactor operating at atmospheric pressure. A 0.5 g portion of NH_4-ZSM-5 (SiO_2/Al_2O_3= 85) was pretreated under an air stream at 853 K for 1.5 h to be converted into the proton form of the zeolite (H-ZSM-5). Products were accumulated in a trap containing ethanol at 273 K and were analyzed by a gas chromatograph.

The catalytic activity of H-ZSM-5 was stable; thus, stationary phenol yields of 3.8% and 6.0% with on-stream time were obtained at 583 K and 603 K, respectively, under the conditions of C_6H_6= 3.5 kPa, N_2O= 51 kPa, a flow rate of the feed (reactants and nitrogen), F, of 0.079 mol h^{-1}, and a weight of catalyst, W, of 0.5 g. Above 623 K, however, the yield decreased monotonously with on-stream time. Deeply oxidized compounds, CO and CO_2, did not appear in the product at 583-623 K, but did above 673 K.

At 603 K, trace amount of catechol was detected in the product. Nitrogen was detected in the product with a N_2/phenol molar ratio of 3.8. The excess evolution of nitrogen may be attributed to decomposition of dinitrogen monoxide. The decomposition should be accompanied by an evolution of oxygen as well as nitrogen, but oxygen could not be detected in the product.

Reactions were performed at various benzene pressures (3.5-13 kPa) with constant dinitrogen monoxide pressure of 51 kPa at 603 K. The rate of phenol formation increased monotonously with the increase in benzene pressure. Figure 1

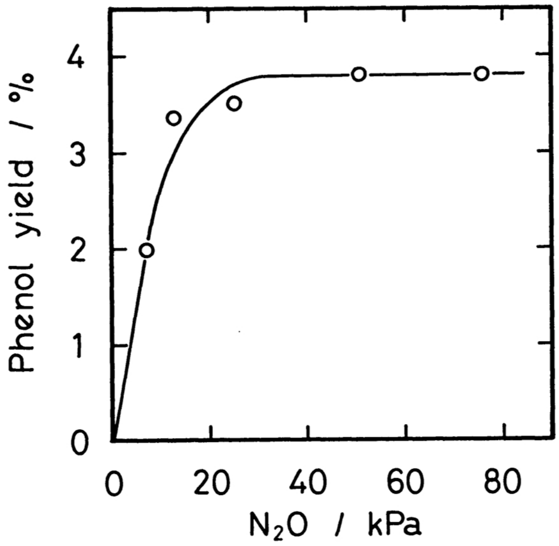

Fig. 1. Change in the phenol yield with dinitrogen monoxide partial pressure.
Reaction conditions: reaction temperature= 603 K, C_6H_6= 6.9 kPa, F= 0.079 mol h^{-1}, and W= 0.5 g.

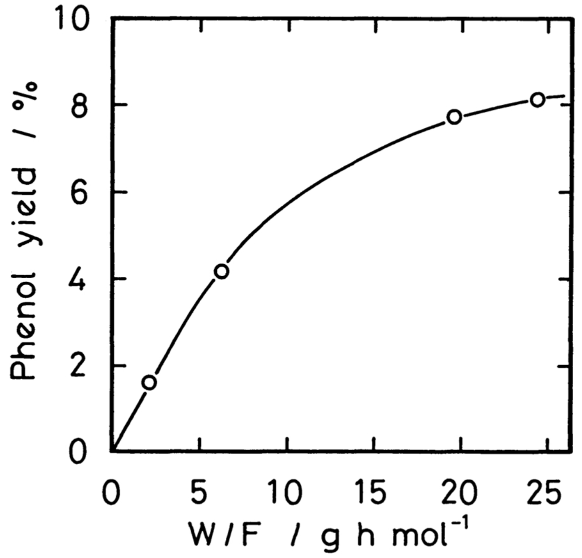

Fig. 2. Change in the phenol yield with contact time.
Reaction conditions: reaction temperature= 603 K, C_6H_6= 6.9 kPa, and N_2O= 51 kPa.

shows the effect of dinitrogen monoxide pressure on the phenol yield on a benzene basis, with a constant benzene pressure of 6.9 kPa. The phenol yield increases with the increase in the dinitrogen monoxide pressure and approaches to a constant value of 3.8%.

The reactions were carried out at different contact times. Here, the contact time is expressed by W/F. As is shown in Fig. 2, phenol yield increased with the increase in the contact time and was 8.1% at W/F= 24 g h mol^{-1}.

The H-ZSM-5 zeolite was found to be an effective catalyst also for the hydroxylation of chlorobenzene. Thus, chlorophenols (ortho=58% and meta + para= 42%) were obtained with a 6.7% yield on a chlorobenzene basis at 603 K, C_6H_5Cl= 3.9 kPa, N_2O= 76 kPa, F= 0.079 mol h^{-1}, and W= 0.5 g.

Phenol was not produced at all by using a Na-ZSM-5 zeolite in place of H-ZSM-5 zeolite. This suggests that acid sites on H-ZSM-5 zeolite particitate in the vapor-phase hydroxylation of benzene in the present work. Iwamoto et al.$^{10)}$ have suggested that, in the vapor-phase hydroxylation of benzene with dinitrogen monoxide over a V_2O_5/SiO_2 catalyst, oxygen radical (O^-) is an active species; the O^- ions abstract hydrogen atom from a benzene ring to yield a phenyl radical or the O^- ion adds directly to benzene ring. In the hydroxylation of benzene over H-ZSM-5 zeolite, the possibility may be excluded that oxygen radicals are formed over a transition metal impurity of the zeolite and that the radicals are involved in the reaction, since phenol was not obtained at all by using a Co^{2+} or a Cu^{2+}

cation-exchanged ZSM-5 zeolite in place of a H-ZSM-5 zeolite.

Olah et al.$^{11)}$ suggested that acid-catalyzed oxyfunctionalization of aromatic hydrocarbons with hydrogen peroxide involves electrophilic hydroxylation with protonated (or Lewis acid complexed) hydrogen peroxide ($^{+}OH_2$-OH). Thus we propose a plausible mechanism that dinitrogen monoxide might undergo a protonation to form hydroxy diazonium ion ($^{+}$N=N-OH), which yields hydroxyl cation ($^{+}$OH) to attack benzene molecules.

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