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Vapor-phase Nitration of Benzene over Silica-supported Benzenesulfonic Acid Catalyst

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Silica-supported benzenesulfonic acid has a high catalyst activity for the title reaction. A nitrobenzene yield on benzene basis and on nitrogen dioxide basis attained to 93% and 70%, respectively, at 443 K under partial pressures of benzene and nitrogen dioxide of 9.3 kPa and 19 kPa, respectively.

Nitrobenzene has been synthesized industially in liquid phase with a mixed acid, a mixture of nitric acid and concentrated sulfuric acid. However, this process has the disadvantage of requiring treatments of waste acid and of waste water. The vapor-phase process (Eq. 1) can afford nitrobenzene without these treatments.

$$2C_6H_6 + 3NO_2 \longrightarrow 2C_6H_5NO_2 + NO + H_2O \qquad (1)$$

Several solid catalysts for the vapor-phase process have been disclosed in patent literatures; WO_3-MoO_3,[1)] SiO_2-Al_2O_3,[2)] SiO_2-Al_2O_3 containing $SO_4{}^{2-}$ ion,[3)] metal phosphates,[4)] metal sulfates,[5)] and ZSM-5 zeolite.[6)] Over these catalysts, however, the nitrobenzene yield on benzene basis was 4-50%. The authors have reported on the vapor-phase nitration over polyorganosiloxane, the maximum nitrobenzene yield being 80%.[7)]

Bezenesulfonic acids have been examined as catalyst for a liquid-phase nitration of toluene[8)] or m-xylene.[9)] Here, we wish to report that bezenesulfonic acid supported on silica is a superior catalyst for the vapor-phase nitration of benzene.

Benzenesulfonic acid was supported (30wt%) on the "Micro Bead Silica Gel" supplied from Fuji-Davison Chemical Ltd. (specific surface area and average pore diameter being 115 m^2 g^{-1} and 30 nm, respectively, and particle size ranging from 30 to 200 mesh) by an impregnation method. The reactions were performed with a continuous flow reactor operating at atmospheric pressure. Nitrogen dioxide was fed by passing nitrogen through a saturator containing dinitrogen tetroxide kept at 273 K. Benzene was fed with a motor-driven syringe into a preheating zone of the reactor. The product was trapped at 273 K and analyzed by gas chromatograph.

Figure 1 shows the dependence of nitrobenzene yield on reaction temperature. With increasing reaction temperature up to 443 K, the yield increases slightly, followed by a drastic decrease at 463-483 K, and remains constant above 503 K. A maximum in the yield of nitrobenzene appeared at 443 K, being 77%. Dinitro-

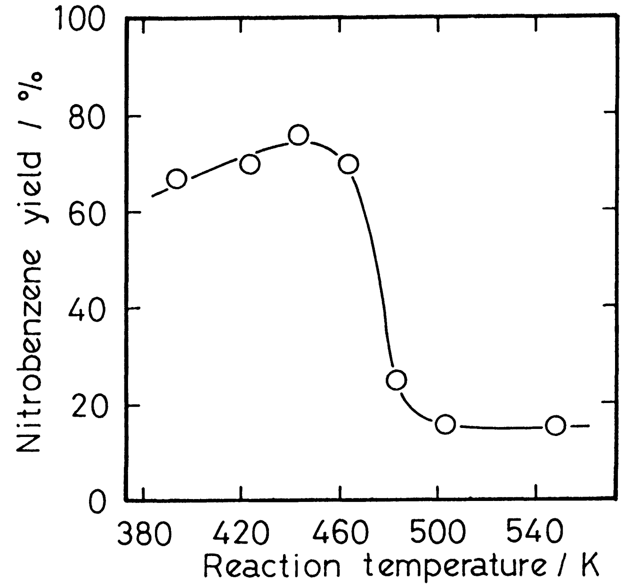

Fig. 1. Reaction temperature dependence of nitrobenzene yield (on benzene basis).
Reaction conditions: C_6H_6= 4.7 kPa, NO_2= 9.3 kPa, and W/F= 8.1 g h mol^{-1}.

benzene was not found in the product. The nitrobenze yield at 443 K was constant during a time on stream examined here (1-5 h). The decrease in the nitrobenzene yield above 463 K may be ascribed to vaporization loss of benzenesulfonic acid from the silica support.

The effects of the partial pressure of the reactants on the rate of the nitration were examined at 443 K and W/F= 8.1 g h mol^{-1}. Under a constant partial pressure of nitrogen dioxide, the benzene partial pressure (4.7-24 kPa) did not influence on the rate of nitrobenzene formation. Under a constant partial pressure of benzene, the rate of nitrobenzene formation sharply increased with the partial pressure of nitrogen dioxide (9.3-19 kPa). Thus, nitrobenzene was obtained with 93% and 70% yields on benzene and nitrogen dioxide basis, respectively, under the partial pressures of C_6H_6= 9.3 kPa and NO_2= 19 kPa.

In conclusion, silica-supported benzenesulfonic acid was found to be an effective catalyst for a vapor-phase nitration of benzene.

References

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