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VAPOR-PHASE NITRATION OF BENZENE OVER POLYORGANOSILOXANES BEARING SULFO GROUPS

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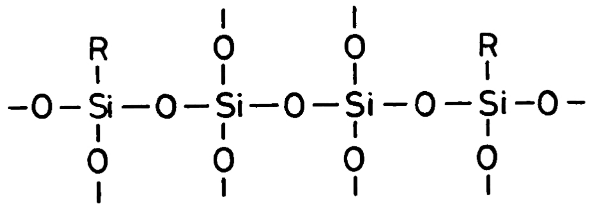
Polyorganosiloxanes with sulfo groups have the high catalytic activity for vapor-phase nitration of benzene. The polysiloxane with sulfophenyl groups showed the highest activity. The reaction rate depended greatly on the partial pressures of both benzene and nitrogen dioxide. The nitrobenzene yield of 80% was obtained at 443 K under the partial pressures of benzene and nitrogen dioxide of 20 and 40 kPa, respectively.

Nitrobenzene is an important intermediate chemical for producing dye-stuffs. It is also used as a solvent. The industrial synthesis of nitrobenzene has been carried out in a liquid phase with a mixed acid, a mixture of nitric acid and concentrated sulfuric acid. Though the process is an old one, it still has some unsolved problems such as treatment of waste sulfuric acid and disposal of waste water. The vapor phase nitration of benzene could avoid these tedious treatment of waste materials, since it produces no sulfuric acid.

$$2\ C_6H_6 + 3\ NO_2 \longrightarrow 2\ C_6H_5NO_2 + NO + H_2O$$

Since the earlier work of Mckee and Wilhelm,$^{1)}$ various solid acids like metal phosphates or zeolites have been proposed as catalysts for the vapor-phase nitration of benzene.$^{2)}$ Here, we wish to report that polyorganosiloxanes having sulfo guroups are potential catalysts for the vapor phase nitration of benzene.

The structures of the catalysts prepared are shown in Fig. 1. Three types of polyorganosiloxanes were prepared by co-condensation of tetraalcoxysilane and organotrialcoxysilane according to the method described by Unger et al.$^{3)}$ For



R = $C_6H_4SO_3H$ (SPOS A)
$CH_2C_6H_4SO_3H$ (SOPS B)
$CH_2CH_2C_6H_4SO_3H$ (SPOS C)
$(CH_2)_3SO_3H$ (SPOS D)

Fig. 1. The structures of the catalysts.

example, a polysiloxane with phenyl groups was prepared as follows: tetraethoxysilane(0.7 mol) and phenyltriethoxysilane(0.3 mol) were dissolved into 125 ml of ethanol. To the solution, 35 ml of 0.01 M hydrochloric acid was added and then the mixture was heated under stirring until the volume of the mixture became 120 ml. After cooling, 60 ml of ethanol and 90 ml of cyclohexane were added, and then under vigorous stirring, 270 ml of water and 50 ml of concentrated aqueous ammonia were added and the mixture was kept stirring for 4 h. The preciptite formed was separated by filtration and washed and dried at 393 K for 4 h in vacuo. Polysiloxanes bearing benzyl groups and 2-phenylethyl groups were also prepared by using benzyltriethoxysilane and 2-phenylethyltrichlorosilane, respectively, instead of phenyltriethoxysilane. A polysiloxane bearing 3-mercaptopropyl groups was prepared by the polyco-condensation of 3-mercaptopropyltrimetoxysilane and tetramethoxysilane. Polysiloxanes containing phenyl, benzyl, and 2-phenylethyl groups were sulfonated by refluxing a solution of chlorosulfonic acid and chloroform(1:4) containing 10 g of the polymers for 3 h. Polysiloxanes containing sulfonated phenyl, benzyl, and 2-phenylethyl groups will be designated as SPOS A (Sulfonated Polyorganosiloxane A), SPOS B, and SPOS C, respectively. The numbers of sulfo groups in the three polymers were estimated as 2.6, 3.0, and 3.2 mmol g^{-1} by the titration method. The polysiloxane having 3-mercaptopropyl groups was converted to the sulfonated polymer by oxidizing the mercapto groups with potassium permanganate.[4] The sulfonated polymer thus obtained (designated as SPOS D) has sulfo groups of 0.8 mmol g^{-1}.

The reaction was carried out in a flow-type reactor operating at atmospheric pressure. The catalysts except Amberlyst-15 were pelleted, crushed, and assorted into grains of 9-16 mesh. 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 products were accumulated in a trap kept at 273 K, withdrawn periodically and analyzed with a gas-chromatograph. Nitrobenzene was an only product, dinitrobenzenes being not detected.

The change in the nitrobenzene yield with time on stream over the four sulfonated polyoganosiloxanes at 443 K is shown in Fig. 2, where were also given the time courses for Amberlyst-15 (ion-exchange resin with surfo groups), dodecatungstophosphoric acid (30wt%) supported on silica, and ZSM-5 zeolite for comparision. Every polyorganosiloxane having sulfo groups showed high activity for the vapor phase nitration after some induction time. The highest activity was observed with the polysiloxane with sulfophenyl groups (SPOS A). ZSM-5 zeolite showed a high activity at the beginning, but the activity decreased gradually with time on stream. Amberlyst-15 has a negligible activity for the nitration. Since Amberlyst-15 has more sulfo groups (4.4 mmol g^{-1}) than SPOS A, the higher activity of the latter cannot be ascribed to the number of acid centers. Actually, the ion-exchanger has a higher activity than the sulfonated polysiloxanes for the dehydration of 2-propanol or ethyl alcohol. Using SPOS A catalyst which showed

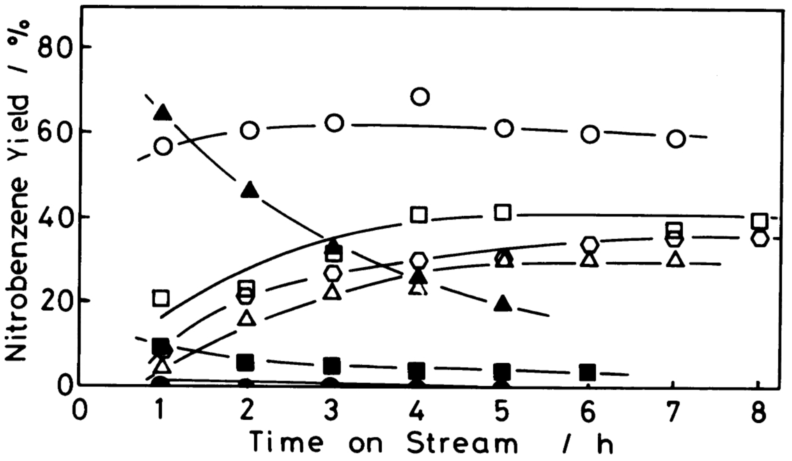


Fig. 2. The change in the nitrobenzene yield with time on stream over various catalysts.
Reaction temperature : 443 K, W/F = 8.1 g h mol^{-1},
NO_2 = 9.1 kPa, C_6H_6 = 4.5kPa
○:SPOS A, □:SPOS B, ⬡:SPOS C, △:SPOS D,
●:Amberlyst-15, ▲:NH_4ZSM-5 ($SiO_2/Al_2O_3=36$),
■:12-tungustophosphoric acid 30 wt% on Silica

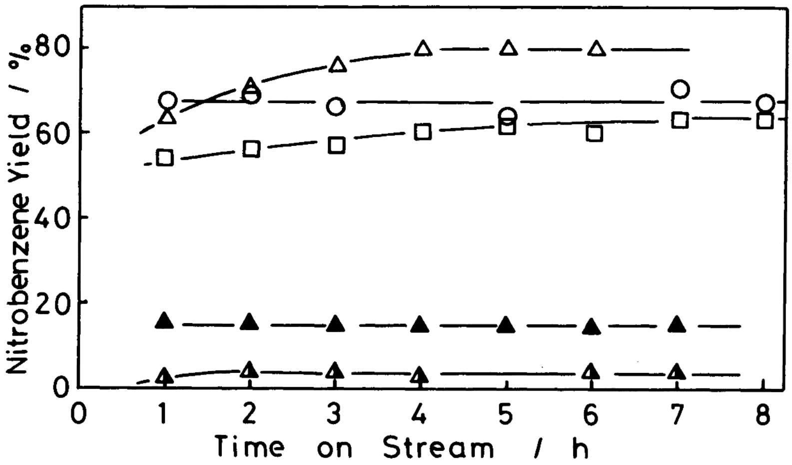


Fig. 3. The effects of the partial pressures of nitrogen dioxide and benzene on the nitrobenzene yield.
Catalyst : SPOS A, 443 K, W/F = 17.8 g h mol^{-1},
△: NO_2= 40 kPa, C_6H_6= 20 kPa, ○: NO_2= 40 kPa, C_6H_6= 10 kPa
□: NO_2= 40 kPa, C_6H_6= 6.65 kPa, ▲: NO_2= 20 kPa, C_6H_6= 20 kPa
▲: NO_2= 10 kPa, C_6H_6= 20 kPa

the highest activity among the sulfonated polyorganosiloxanes studied, the effects of the partial pressures of nitrogen dioxide and benzene on the nitrobenzene yield were examined. As is seen in Fig. 3, the yield of nitrobenzene depended very greatly on the partial pressure of nitrogen dioxide. Thus, the nitrobenzene yields were 4, 15, and 80% at the nitrogen dioxide pressure of 10, 20, and 40 kPa, respectively. The nitrobenzene yield increased also with benzene partial pressure. The nitrobenzene yield of 80% was obtained at the partial pressures of benzene and nitrogen dioxide of 20 and 40 kPa, respectively, at 443 K, and no decay of the activity was observed under the reaction conditions.

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