

Chlorination of Benzene with L-Zeolite Catalyst in the Presence of Oxygen
and Various Solvents

Tadashi NAKAMURA,⁺ Kiyonori SHINODA,^{*} and Kensei YASUDA

Toyama National College of Technology, Hongo, Toyama 939

⁺Kureha Chemical Industry, Nihonbashi Horidome, Chuo-ku, Tokyo 103

Benzene was chlorinated by using L type zeolite into p-dichlorobenzene(p-DCB) in a high yield in the presence of 1,2-dichloroethane (EDC) and oxygen.

Zeolite catalysis is known to give high para selectivity in the chlorination of substituted benzenes such as chlorobenzene and toluene. This applies particularly to L type zeolite in liquid phase chlorination.¹⁻⁴⁾ However, little is known about the chlorination of benzene with zeolite catalysts. Moreover, zeolite catalyst may induce the addition of chlorine to benzene yielding hexachlorocyclohexanes.⁵⁾ Such additional compounds may poison the active sites of the catalyst and reduce the catalyst life.

Hence, we investigated para selective chlorination of benzene by using L type zeolite(TSZ-500KOA) in the presence of various solvents and oxygen. The zeolite catalyst was heated in air for 8 h at 160 °C and held in a desiccator prior to the reaction. The reaction was carried out in a 200 ml four necked brown flask. Furthermore, the reactor was covered with a black PVC film to avoid scattering light. Two grams of the catalyst was added to 20 ml of reaction solution in the reactor, then chlorine and oxygen were introduced for 3 h at the rate of 0.25 and 0.2 mol/h, respectively. During the reaction time, the temperature was kept at 70 °C and the solution was stirred. The reaction products were analyzed by gas chromatography (Shimazu GC-8A, PEG 6000). The result of the reaction is summarized in Table 1. Moles of chlorine reacted per a mole of benzene introduced are defined as the chlorination degree. Para selectivity indicates the proportion of para isomer to total dichlorobenzenes. The use of EDC as a solvent gave higher selectivity of p-DCB than the other solvents. In particular, an excellent result was given by presence of oxygen in addition to EDC. The use of oxygen seems to accelerate the reaction rate as well as the para selectivity. It is

Table 1. Effect of reaction conditions on selectivity of p-DCB

Reaction conditions								
C ₆ H ₆	(ml)	20	20	10	10	10	10	10
Solvent	(10 ml)	-	-	EDC	EDC	CH ₃ NO ₂	CCl ₄	CF ₃ COOH
O ₂	(mol/h)	-	0.2	-	0.2	0.2	0.2	0.2
Product composition/mol%								
C ₆ H ₆		29.4	21.3	17.8	-	5.2	2.3	-
C ₆ H ₅ Cl		69.6	74.2	33.2	13.0	89.9	80.4	59.6
p-C ₆ H ₄ Cl ₂		0.8	3.8	43.3	82.3	4.4	15.1	29.1
o-C ₆ H ₄ Cl ₂		0.2	0.7	5.5	4.7	0.5	2.2	10.7
1,2,4-C ₆ H ₃ Cl ₃		-	-	0.2	-	-	-	0.6
Chlorination degree		0.72	0.83	1.31	1.87	1.00	1.15	1.41
Para selectivity		0.80	0.84	0.89	0.95	0.90	0.87	0.73

assumed that oxygen may suppress the radical reactions. Investigations still in progress suggest that oxygen also reduces the formation of the chlorine added products. Therefore, the active sites of the catalyst were not poisoned and the chlorination might be not retarded.

Botta et al.⁴⁾ reported the favorable effect of dichloromethane as a solvent in para chlorination of biphenyl. They suggest that the use of certain solvent may influence the activation of reactants or diffusion and transport processes in the zeolite channels. EDC may play a similar role. Since EDC has a higher boiling point than dichloromethane, the chlorination is able to carry out under the broad reaction conditions.

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