

HETEROGENEOUS REACTIONS

(Production of Value-added Chemicals by Utilizing Hydrogen Sulphide, Glycerol and Toluene)

By
Lakshmana Rao Jeeru

Abstract

The present study focuses on utilization of hydrogen sulphide (H₂S), glycerol and toluene in the production of valuable chemicals. Hydrogen sulphide, a byproduct of petroleum and hydrocarbon processing industry, was used to produce chloroanilines by reduction of the corresponding chloronitrobenzenes. Glycerol, a cheap byproduct of biodiesel industry, was successfully converted to solketal, a useful transportation fuel additive, by heterogeneous ketalization with acetone, which is also a low-cost byproduct of cumene process for phenol. Toluene (T), having very less market demand compared to benzene (B) and xylene (X) (in petrochemical industry, BTX are produced by catalytic reforming of naphtha), was converted to benzene and xylene by disproportionation over a solid acid catalyst. Triphase catalysis has been used to produce nitrotoluenes by nitration of toluene without using sulphuric acid in an environment-friendly process.

The reduction of chloronitrobenzenes (CNBs) by aqueous ammonium sulphide, obtained by absorbing H₂S in aqueous ammonia solution, was carried out using an anion exchange resin, Amberlite IR400 (Cl⁻ form) as triphase (liquid-liquid-solid) catalyst. A maximum enhancement factor of about 66 was observed with 20% (W/V) loading of the catalyst with *p*-chloronitrobenzene as the organic substrate. The reduction reactions were observed to be kinetically controlled with negligible mass transfer resistance. The triphase catalyst could be reused for four times with insignificant loss in activity.

A heterogeneous catalysis approach was employed for the synthesis of solketal using an acidic ion exchange resin (Amberlite IR120) as solid acid catalyst. The effects of various experimental conditions (stirring speed, catalyst loading, temperature, and feed composition) on the reaction rates were investigated. With intense agitation of the reaction mixture, the reaction was found to be kinetically controlled. The apparent activation energy of the reaction was determined to be about 54.34 kJ/mol. The ion exchange resin as heterogeneous catalyst was easily recovered and reused without any reactivation up to six times with comparable activity as the fresh one.

Toluene is a low-cost product formed during catalytic reforming of naphtha. In the present work, toluene having very low market demand was utilized to produce value-added (having very high demand) chemicals, benzene and xylenes by disproportionation. Disproportionation reactions were carried out in the vapor phase over modified HZSM-5 catalyst in a fixed-bed down-flow laboratory scale reactor. Modification of the pore size of HZSM-5 by silica increased *p*-xylene selectivity from 27 to 64%. The influences of various process parameters such as temperature and space-time on toluene conversion and product distribution were studied. The experiments were carried out to choose the zone in which the mass transfer effects were negligible. A suitable kinetic model was proposed and the experimental data were fitted to the model. From the kinetic constant, the activation energy of the reaction was determined to be 89.25 kJ/mole.

The liquid phase nitration of toluene with concentrated HNO₃ was carried out in presence of various solid acid catalysts. The protonated form of Y, ZSM-5, and Mordenite type zeolites as well as strongly acidic cation exchange resin (Amberlite IR-120) were used for the nitration reaction. All the three mono nitro toluene isomers (*ortho*-, *meta*- and *para*-nitro toluene) together with trace amounts of di-nitro toluene were obtained as products. Among the solid acid catalysts tried, H-Mordenite was found to be most active. The reaction was found to be free from external diffusional resistance. A pseudo-homogeneous kinetic model was tested to fit the kinetic data. From the estimated kinetic constant, the activation energy was determined to be 25.75 kJ/mol. The reusability of the catalyst was also tested by carrying out three cycles of reaction. The activity of the catalyst after third cycle of reaction was found to be close to that of the fresh one with negligible loss in activity.

Keywords: Heterogeneous Reactions; Hydrogen sulphide, Ammonium sulphide, Chloronitobenzenes, Chloroanilines, Anion exchange resin; Biodiesel, Glycerol, Acetone, Solketal, Cation exchange resin; Toluene disproportionation, *p*-Xylene, Selectivity, Zeolites, Modified HZSM-5; Nitration, Nitrotoluenes, Solid acid catalysts, H-Mordenite; Kinetics, Activation energy.