38f Zeolite-Based Friedel-Crafts Acylation of Anisole in Supercritical Carbon Dioxide: Kinetics and Mechanisms

Yusuf G. Adewuyi

Acylation of aromatics is of considerable industrial importance for making intermediates, which are used in the production of pharmaceuticals, insecticides, perfumes, agrochemicals and other fine chemicals. Pharmaceutical drug sales alone were an estimated 124.5 billion dollars in 1998. For example, the acylation of isobutylbenzene with hydrogen fluoride is currently used to manufacture 4-isobutylacetophenone, a key intermediate for the bulk active pharmaceutical ibuprofen. However, the use of large amount of hazardous catalysts (e.g., Lewis acid catalyst such as AlCl3) and solvents (e.g., nitrobenzene) in order to achieve high selectivity make most traditional Friedel-Crafts acylation processes inherently dirty and highly polluting. The development of an efficient and environmentally friendly catalytic acylation of aromatics via the Friedel-Crafts reaction remains a major challenge and a high priority for clean technology. The acylation of anisole with acetic anhydride using beta zeolite catalysts with high framework SiO2/Al2O3 ratio in the absence and presence of supercritical CO2 as a solvent has been investigated in a high-pressure 25 ml batch stainless steel (SS 316) reactor. The effects of reaction conditions (e.g., temperature, catalyst concentration, reaction time and pressure, etc.) on anisole conversion and product yield are also evaluated using 0.2-0.8g of catalyst at 60-150oC and pressures of about 1200 – 3000 psi. It is demonstrated that the zeolite and carbon dioxide based approach shows promise as a greener alternative to the inherently dirty and highly polluting traditional Friedel-Crafts acylation processes, which uses typically nonregenerable Lewis acid like aluminum chloride (AlCl3) as catalyst and nitrobenzene as solvent. The kinetics and mechanisms of the acylation of anisole in supercritical carbon dioxide will be presented. The effects of supercritical CO2, catalyst properties, and different process variables on anisole conversion and yield of the main product, 4-methyl acetophenone (4-MAP) will be presented.

References

Y.G. Adewuyi, Zeolite-Based Catalysis in Supercritical CO2 for Green Chemical Processing. In: Environmental Catalysis; V. Grassian, editor; CRC Press; A Division of Taylor and Francis, Inc. 2005, 609-626.