Clay Catalysts in Organic Synthesis
Compiled by Vijayakumar Badathala

Vijayakumar Badathala was born in Kavali (Andhra Pradesh, India) in 1976. In 1999 he received his M.Sc., (Tech) degree in Chemistry (Petrochemicals) from Jawaharlal Nehru Technological University, Hyderabad, Andhra Pradesh, India. He is currently working towards his Ph.D. under the supervision of Professor B. S. Jai Prakash and Professor Gopalpur Nagendrappa at the Department of Chemistry, Bangalore Institute of Technology, Bangalore, India. His present research interests focus on the synthesis of industrially important esters using environmentally benign clay catalysts.

Green Chemistry Research Laboratory, 3rd Floor, Room No.301A, Bangalore Institute of Technology, K. R. Road, Bangalore 560 004, India
E-mail: badathala@yahoo.com; E-mail: reslab@sancharnet.in

Introduction

Clay minerals are made up of layered silicates. They are crystalline materials of very fine particle size ranging from 150 to less than 1 micron. There are two basic building blocks – tetrahedral and octahedral layers, which are common to clay minerals.1

A variety of organic reactions that are catalysed by Brønsted acids such as H2SO4, HCl, and other protonic acids or Lewis acids such as AlCl3, FeCl3, etc. have been shown to take place in clays, especially montmorillonite, more efficiently, i.e., under milder conditions, with greater selectivity, better yields, shorter reaction times and so on. The range of reactions that have been successfully performed on clay catalysts includes addition, dehydration, elimination, oxidation, rearrangement reactions, substitution, etc.2

Preparation of Clay Catalysts

Methods of cation exchange and the subsequent washing steps to remove excess salt are also well known for clays.3 Between the layers of a smectite, large cationic species can be inserted by cation exchange.4,5 Such bulky species act as pillars, propping apart the layers. Clayfen and claycop are simply prepared by evaporating acetone solutions of the nitrate salts onto the clay.6,7 Clayzic,8 clay-supported potassium permanganate,9 quaternary ammonium salts-exchanged montmorillonite,10 clay-surfactants composites11 and organo-clay assemblies12 have also been reported.

Abstracts

(A) The intramolecular dehydrogenation of alcohols is efficiently catalysed by both Al3+- as well as H+-exchange clays.13 Primary alcohols afford mainly dialkyl ethers with little alkene production whereas secondary and tertiary alcohols provide alkenes almost exclusively.

\[
\text{RCH}_2\text{CH}_2\text{OH} \xrightarrow{\text{Al}^{3+}, \text{Mont.}} \text{RCH}_2\text{OCH}_2\text{CH}_2\text{R} + \text{CH}_2=\text{CH}_2
\]

(B) Montmorillonite supported transition metal salts (zinc and nickel chlorides) are highly active and selective agents for the catalysis of Friedel–Crafts alkylation.14,15

\[
\text{R} + \text{RX} \xrightarrow{\text{Clay}} \text{R}\text{R}^\prime
\]
(C) Bosch et al. have accomplished the Beckmann rearrangement of ketoximes with montmorillonite K10 clay in ‘dry’ media in good yields.

\[
\begin{align*}
R^1R^2C &= \text{K10 Clay} \\
\text{NOH} &\quad \text{MW, 7-10 min.} \\
\rightarrow &\quad O \\
R^1CNHR^2
\end{align*}
\]

(D) To develop environmentally benign synthetic protocols utilising microwave irradiation under solvent-free conditions, a simple synthetic procedure has been developed that is catalysed by montmorillonite K10 clay for the preparation of imines and enamines.

\[
\begin{align*}
R^1HC &= \text{K10 Clay} \\
\text{O} &\quad \text{MW} \\
\rightarrow &\quad OH \\
R^1CNHR \\
\rightarrow &\quad H_2O \\
R^1HC &= NR
\end{align*}
\]

References