AUTOCONDENSATION OF CYCLIC KETONES ON CLAY CATALYSTS

D.M.D.S. Dissanayake, S. Wijeratne and B.M.R. Bandara*

Department of Chemistry, Faculty of Scienc, University of Peradeniya

Introduction

Aldol condensation reactions are useful in carbon carbon bond formations in organic synthesis. However, the harmful and highly corrosive nature of the acid and base catalysts used in these reactions and their difficult work-up procedures led scientists to find convenient and environmental friendly green catalysts. The objective of the present project was to study the self-condensation reaction of cyclic ketones, namely cyclohexanone, cyclopentanone and cycloheptanone in the presence of montmorillonite clay exchanged with H^+, Al^{3+} and ZrO^{2+} cations in solvent free conditions. Apparently, self-condensed products of cyclohexanone can be used as a precursor for manufacturing 2-cyclohexylcyclo-hexanol (a fragrance) and in industrial synthesis of 2-phenylphenol (a bactericide) (Trakha-nov *et al.*, 2003).

Materials and Methods

Preparation and characterization of clay catalysts

The Bentonite-Aldrich montmorillo-nite clay (10 g) was stirred overnight separately with 0.5 M (400 mL) solutions of aluminium nitrate, hydrochloric acid and zirconyl chloride to get Al^{3+}-montmorillonite, H^+-montmorillonite, ZrO^{2+}-montmo-rillonite clay catalysts, respectively. The clay catalysts were then centrifuged and washed with distilled water repeatedly to remove nitrate ions or until washing showed negative test for chloride ions with aqueous $AgNO_3$. The clay samples were then allowed to dry under ambient air for a week and ground to get the fine particles. Clay catalysts prepared were then characterized with X-ray diffraction and thermogravimetric analysis.

Self-condensation reaction of cycloalkanones with modified montmorillonite clay catalysts

Cyclohexanone (29 mmol) and 0.15 g of the clay catalyst (H^+-MMT or Al^{3+}-MMT) were placed in a round-bottomed flask fitted with a drying tube. The mixture was then heated at 140-150 ^{0}C for different time intervals (1, 2, 3 and 6 h). After the reaction, the catalyst was separated by filtration. The effect of reaction time, amount of clay catalyst used (0.15 g, 0.50 g, 1.00 g), Al^{3+}-MMT clay activation (100 ^{0}C for 2 h prior to the reaction) and the usage of ZrO^{2+}-MMT catalyst on the percent conversion of cyclohexanone to the self-condensed product mixture was also investigated. The product mixture obtained with 0.15 g of Al^{3+}-MMT catalyst was distilled to remove the remaining reagent prior to NMR analysis.

The self-condensed product mixture of cyclohexanone which was obtained with 0.50 g of Al^{3+}-MMT (heated at