

Abstract/Synopsis

The research work in the present Thesis emphasizes the development of green catalytic routes for the synthesis of fine and commercially important chemicals using eco-friendly heterogeneous catalysts via hydroformylation, condensation and isomerization reactions. Chapters from second to fourth of this thesis are related to the development of multi-functional catalyst to reduce the multi-steps processes into a single pot for the synthesis of higher carbon chain length aldehydes/alcohols starting from low carbon number alkene as a reactant. For example, 2-ethylhexanal and 2-ethylhexanol, which are the commercially important intermediates for the synthesis of dioctylphthalate (DOP), are synthesized industrially from propylene in three steps process. The existing commercial processes for the manufacturing of C₈ aldol derivatives have drawbacks like, i) being a multi-step process, ii) use of hazardous liquid base KOH or NaOH in stoichiometric amount for aldol condensation reaction, iii) involving post synthesis work-up in the separation of spent KOH or NaOH from product mixture, iv) lower selectivity of product, corrosion of reactors and storage vessels. Therefore, the main focus was on the replacement of liquid bases, which are being used in stoichiometric amount, by the eco-friendly heterogeneous catalyst to carry out all three steps into a single pot by altering the reaction conditions.

The multi-functional [HF/HT] catalyst system was synthesized by the impregnation (Chapter 2) and intercalation (Chapter 3 and 4) of rhodium complex [HF] onto/into the interlayer space of hydrotalcite [HT] and its multi-functional potential was evaluated for the single pot selective synthesis of C₈ aldol derivatives (aldehydes/alcohols) from propylene. The Mg/Al ratio of [HT], amount of [HF] complex and [HT], and reaction temperature showed pronounced effect on the selectivity of C₈ aldol derivatives. Aldol condensation temperature T₂ played a significant role in the formation of 2-ethylhexanol in a single pot. As Mg/Al molar ratio and amount of [HT] increased, the selectivity of 2-ethylhexanal also increased due to the enhancement in the basicity of the catalyst. From kinetic experiments, it was observed that the rate of formation of 2-ethylhexanal is dependent on the rate of aldol condensation which is catalyzed by hydrotalcite present in the [HF/HT] catalyst.

Other commercial examples are the synthesis of perfumery chemicals such as, jasminaldehyde by the condensation of heptanal with benzaldehyde; *trans*-anethole and *trans*-isoeugenol by double bond isomerization of methyl chavicol and eugenol, respectively, using liquid KOH or NaOH in stoichiometric amounts. With increased environmental awareness, replacement of stoichiometric technologies by atom efficient greener catalytic routes with low E factor (kg of byproducts generated per kg of desired product) and substitution of toxic and/or hazardous solvents/reagents with cleaner alternatives is today's demand. Therefore, it is desirable to find solid base catalysts which could substitute liquid bases.

The hydrotalcite samples of varied Mg/Al molar ratio were used as catalysts for synthesis of 2-methylpentenal by aldol condensation of propanal (Chapter 5) and jasminaldehyde in solvent free condensation of 1-heptanal with benzaldehyde (Chapter 6). 97% conversion of propanal with 99% selectivity of 2-methylpentenal was achieved using activated hydrotalcite of Mg/Al molar ratio 3.5. From the kinetic data for aldol condensation of propanal using activated hydrotalcite (Mg/Al molar ratio 3.5), the initial rate of reaction was observed to increase on increasing the amount of catalyst. The activation energy for propanal condensation was calculated by Arrhenius plot and found to be 58 kJ/mol. The catalyst was recycled upto six cycles without loss in its activity. The selectivity of jasminaldehyde was observed to increase on increasing the M(II)/Al molar ratio of as-synthesized as well as activated hydrotalcite. The maximum selectivity of jasminaldehyde (86%) with 98% conversion of 1-heptanal was observed using as-synthesized Mg-Al hydrotalcite of Mg/Al molar ratio of 3.5 as a catalyst. The effect of activation of as-synthesized Mg-Al hydrotalcite samples of varied Mg/Al molar ratio on catalytic activity was studied and correlated with their basicity as determined from the model test reaction. The rate of reaction was calculated as 11.6×10^{-4} mol/(g_{cat} min) at optimum reaction conditions and catalyst was reused several times for the synthesis of jasminaldehyde..

The regioselective synthesis of *trans*-anethole from methyl chavicol via double bond isomerization of methyl chavicol using RuCl₂(PPh₃)₃ and RuCl₃(AsPh₃)₂.CH₃OH complexes with detailed kinetics has been studied in Chapter 7. The incorporation of ruthenium in the hydrotalcite matrix was also carried out for double bond isomerization of perfumery related chemicals such as, methyl chavicol, eugenol, saffrole, allylbenzene, dimethoxy allylbenzene, 3-carene. 98% conversion of methyl chavicol with 88% selectivity of *trans*-anethole was observed in 1 h reaction time. The effect of reaction temperature showed 41% conversion of methyl chavicol and 74% selectivity of *trans*-anethole at 100 °C which increased to 98% with 88% selectivity of *trans*-anethole on increasing temperature to 210 °C using Ru-Mg-Al as a catalyst. The activity of Ru-Mg-Al was compared with the various ruthenium impregnated catalysts such as, Ru-HT, Ru-MgO, Ru-CaO, Ru-SiO₂ and Ru-alumina. The Ru-Mg-Al catalyst was recycled upto fourth cycle without loss of its activity.