Chapter 7

Conclusion

7.1. Summary and Conclusions

Zeolites have unique properties that are: well-defined microporous aluminosilicate framework; high thermal stability; ion exchange properties; high internal surface area; reusability and eco-friendly nature; thus such they are widely replacing conventional homogeneous and other heterogeneous catalysts. For this reason, zeolites are promising materials; hugely applied in miscellaneous fields such as catalysis, ion exchange, purification, separation, and drying processes. The present thesis was committed to the synthesis, modification and comparative application of zeolites and modified zeolites such as MCM-22, swelling-sonicated MCM-22, and alkali-treated MCM-22. They have difference in physico-chemical properties that impart great influence in gas phase alkylation and dehydration reactions for the production of some industrially important intermediates.

The preliminary plan was to collect raw materials, to set-up the optimized synthesis conditions, to find out types of modifications, and to do careful characterization of the zeolites. In this study, to investigate industrially vital intermediates such catalysts have been synthesized, suitably modified and thoroughly characterized. Such all processes has been described in this thesis. Further, protonic form of catalysts have been applied carefully in tubular continuous, down-flow quartz reactor for catalysis. The catalytic formation of ethyltoluenes and diethylbenzenes have been studied over zeolite MCM-22 as well as modified zeolite (SS) by alkylation reaction of toluene and ethylbenzene with ethanol. The conversion and selectivity of this reactions have been discussed. Further, this reactions have been studied with two different reaction parameters i.e., effect of temperature and effect of feed molar ratio.
In the ethylation of toluene and EB, the undesired side products formed due to dealkylation and disproportionation reactions. The flow of desired product in alkylation reaction has also been studied by theoretical findings. The comparative studies of experimental and theoretical results has been discussed in this thesis. Ethyltoluenes, Diethylbenzenes, Acrolein, and Hydroxyacetone are important for the production of many useful materials such as polymers, cosmetics, perfumery, and pesticides.

Formation of acrolein and hydroxyacetone have been studied over microporous zeolite MCM-22 as well as hierarchical alkali-treated (5 h) modified MCM-22 by glycerol dehydration reaction. For this purpose, zeolites with different structure and acidity have been used. Characterization of such zeolites by various physico-chemical techniques have been discussed. In this reaction study, diluted glycerol has been used with different molar composition. Formation of acrolein has been studied over MCM-22 and hydroxyacetone has been studied over modified zeolite.

The major findings of the thesis include:

- **Synthesis of zeolite MCM-22** with different silica sources yielded microporous materials with different crystallinity, while swelling-sonication as well as alkali-treatment in MCM-22(P) create different acidic sites and partial mesoporous properties. These are responsible for better selectivity towards para-ethyltoluene and p-diethylbenzene during ethylation of toluene as well as ethylbenzene, over MCM-22 and modified MCM-22 (SS), respectively. Further, selective dehydration of glycerol yielded acrolein over MCM-22 while hydroxyacetone is formed over modified MCM-22 (AT 5h) due to their distinct acidic sites.

- **Theoretical study** suggests that although higher entropy of meta isomer is thermodynamically more stable, the smaller dipole moment of para isomer should favor its diffusion, which is also complemented by the experimental observation for MCM-22. Experimental data shows modified MCM-22 has high selectivity towards diethylbenzene and ethyltoluene isomers than MCM-22 while para isomer selectivity was attributed by the shape selective nature of MCM-22 pore. On the other hand, modified MCM-22 having partial mesoporosity, was non-shape selective towards product distribution resulting in the formation of o- and m-isomer.
These studies conclude that the conversion of toluene decreased over modified MCM-22, while ethylbenzene conversion increased. Therefore, toluene alkylation is more favourable over MCM-22 and ethylbenzene favourable towards modified MCM-22. The optimum conditions for selective ethylation over modified zeolite MCM-22 are found to be: temperature 250 °C, feed rate 0.2 ml min⁻¹, and toluene and ethylbenzene/ethanol molar ratio 1:1.

As the time of alkali-treatment increased, the layered properties changed to agglomeration and micropores were converted to partial mesopores having hierarchical structure. It was noticeable that after modification, the gel quantity decreased and while drying, the gel was sticking to cellulose paper, which might be responsible for desilication as confirmed by EDXA. Depending on the degree of silica deposition on the MCM-22 crystals, the adsorption behavior, as well as acidic properties, were affected. This may impart great impact on its catalytic application which was justified in glycerol dehydration reaction. Among the catalysts, high selectivity of acrolein was observed due to brønsted acidity of MCM-22 while hydroxyacetone was found maximum due to lewis acidity of modified MCM-22.

7.2. Scope for Future work

The present thesis describes the formation of para isomeric products such as p-ethyltoluene and p-diethylbenzene over conventional microporous zeolite and modified hierarchical zeolite by alkylation reactions. On the other hand, using these zeolites it describes the formation of acrolein and hydroxyacetone by glycerol dehydration reaction. These investigations could be explored by selecting aromatic molecules with different substituents and examining their activity in other novel organic reactions over such kind of modified zeolites. For example, in chapter 4, formation of p-ethyltoluene was studied by alkylation of toluene with ethanol while in chapter 5, formation of p-diethylbenzene was studied by alkylation of EB with ethanol. Among the all feed ratio and reaction temperature, for alkylation reactions the conversion as well as selectivity exhibits best results at 250 °C with molar ratio 1:1. In a broader sense, aromatic alkyl substituted products can be formed by the alkylation of toluene and EB with ethanol. This kind of route has been studied by De Vos, D.E. et al. in 2002 and also described in chapter 4 & 5.
Experimental isomeric product flow has been also discussed from theoretical-thermodynamics study of product molecules using computational software. Hence, the formation of isomeric alkylated aromatic products could be formed in the same manner and various modified zeolites could be examined for this purpose to compose the optimal conjunction with acidity and pore geometry.

The effectiveness of zeolites shall be synthesized and modified for following applications: Implementation of alkali-treatment for zeolite membrane preparation; Preparation of zeolite/metal composites; materials shall be tested for the vapor phase reactions; Impact of materials over various catalytic application to improve the catalytic activity and overall efficiency of the zeolites.

7.3. References


Journal Publications and Conferences presentations

   Riddhi Thakkar and Rajib Bandyopadhyay
   *ChemistrySelect*, 2019, 4(11), pp.3047-3051

2. Development of hierarchical MCM-22 layered zeolite for selective glycerol dehydration.
   Riddhi Thakkar and Rajib Bandyopadhyay

3. Preparation, characterization, and post-synthetic modification of layered MCM-22 zeolite precursor.
   Riddhi Thakkar and Rajib Bandyopadhyay


6. Short oral on Computational and Experimental comparative studies of Ethylbenzene Ethylation over modified and parent MCM-22 by RT & RB
   Poster on Preparation, characterization and time dependent post-synthesis modification of MCM-22(p) layered zeolite by RT & RB are presented at Sofia, Bulgaria in 7th FEZA, Federation European Zeolite Association international conference and same
Poster is presented in Post-conference school, **Plovdiv, Bulgaria, Europe, July 3-9, 2017**.

7. Oral on Preparation, characterization, and postsynthetic modification of layered MCM-22 zeolite precursor by RT & RB is presented at **ICT Mumbai in APCAT-7, Asia-Pacific Congress on Catalysis** international conference, **January 17-21, 2017**.