Chapter 2

Literature review

2.1. Preamble

This chapter describes literature review on the types of zeolites and their synthesis, modifications, and catalytic applications over various organic reactions. It contains the scope of the present research based on the literature survey and research gaps.

2.2. Various catalytic applications of zeolites

There is a peculiar affinity between the oxides of aluminum and silicon. Such porous polyaluminosilicate materials have huge applications in the field of heterogeneous catalysis. However, zeolites have properties like reusability and strong active sites, called attractive materials for nanotechnology, cosmetics, pharmaceutical, and petrochemical industries. The study of various catalytic application of zeolites have been summarized in Table 2.1.

<table>
<thead>
<tr>
<th>Table 2.1 Catalytic applications of zeolites</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Title of the paper</strong></td>
</tr>
<tr>
<td>Acid-catalyzed synthesis of mono-and dialkyl benzenes over zeolites: Active sites, zeolite</td>
</tr>
<tr>
<td>Topology, and reaction mechanisms.</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>Alkylation of benzene with short-chain olefins over MCM-22 zeolite: catalytic behavior and kinetic mechanism.</td>
</tr>
<tr>
<td>Catalytic benzene alkylation over mesoporous zeolite single crystals:</td>
</tr>
</tbody>
</table>
| Literature review | Improving activity and selectivity with a new family of porous materials. | Benzene to ethene was 5.1:1.  
Catalyst: Zeolite ZSM-5  
Application: Gas-phase alkylation of benzene with ethene; the maximum conversion of benzene ca. 20%; the higher selectivities to ethylbenzene observed with mesoporous zeolite catalyst. |
|-------------------|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
Catalyst: ZSM-5 and Silylated ZSM-5  
Application: Gas-phase ethylbenzene ethylation in a fixed-bed reactor; very high para-selectivity can be achieved by the CVD of silica on ZSM-5 zeolites through selective disproportionation of toluene and aromatisation of paraffins. |
Catalyst: ITQ-22, ZSM-5, Beta/Ge, SSZ-33 zeolite  
Application: Vapour phase alkylation of benzene with ethanol and isopropanol; Zeolite ITQ-22 is an active catalyst for the synthesis of ethylbenzene and cumene while zeolite ZSM-5, Beta/Ge, and SSZ-33 present an intermediate behaviour; the selectivity to the desired products is higher over ITQ-22 than that obtained with the industrially used catalysts based on ZSM-5 and Beta. |
Application: This covers the recent achievements in acid-catalyzed transformations of aromatic hydrocarbons with a special focus on alkylation-isomerization-disproportionation reactions in petrochemistry, and acylations or condensations used mainly in synthesis of chemical specialties. |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Recent advances in reactions of alkylbenzenes over novel zeolites: the effects of zeolite structure and morphology.</td>
<td>Al-Khattaf, S., et al. 2014.</td>
<td>Application: This comprehensive review covers major reactions of mono-, di-, and tri-alkylbenzenes such as disproportionation, alkylation, transalkylation, isomerization, etc., over different zeolite-based acid catalysts. The influence of the type of acid sites, zeolite topology, and reaction conditions on the activity, selectivity and pathways of these reactions, thermodynamics and reaction kinetics of transformations of aromatic hydrocarbons are also discussed. This article covers mostly literature published during the period of 2002–2013.</td>
</tr>
</tbody>
</table>
| Mesoporous MCM-22 zeolites prepared through organic amine-assisted reversible structural change and protective desilication for catalysis of bulky molecules. | Ji, Yong-Jun, et al. 2013. | Reaction conditions: Catalyst, 0.2 g; temp, 473 K; pressure, 0.1 MPa; benzene/isopropyl alcohol molar ratio, 1.0; feed rate 1.7 mL h⁻¹; N₂, 30 mL min⁻¹; TOS = 10 h.
Catalyst: H-MCM-22 and H-Meso-MCM-22
Application: Gas-Phase Alkylation of Benzene with Isopropyl Alcohol; The meso-MCM-22 catalyst exhibited much higher cumene selectivity and benzene conversion. |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Applications of zeolites in sustainable chemistry.</td>
<td>Li, Y., Li, L. and Yu, J., 2017.</td>
<td>Catalyst: H-ZSM-5, H-Beta, CHA type zeolite Application: In the field of sustainable processes, such as biomass conversion, fuel cell, thermal energy storage, CO2 capture and conversion, air-pollution remediation, and water purification.</td>
</tr>
</tbody>
</table>
2.3. Post-synthesis modifications of zeolites

In the area of porous aluminosilicates, zeolites synthesis has been described conceptually by expert members of IZA synthesis commission. Generally, in the synthesis and post-synthesis modification of zeolites, the challenging areas have been consent by various scientist. Such research areas and fruitful actions, on which efforts should be concentrated are those have been summarized in Table 2.2 (Bellussi, G. et al. 2013). Such kind of information gives interesting topics in the field of synthesis such as designing new materials with hierarchical properties.

<table>
<thead>
<tr>
<th>Zeolites (Reference)</th>
<th>Modification</th>
<th>Variant</th>
<th>Outcome</th>
</tr>
</thead>
</table>
Currently, prime objective of research is modified the morphological and textural characteristics of zeolites. The development of modification in synthesis procedures able to produce solid in the form of nanocrystals or hierarchical crystals or aggregate crystals. This is helpful to overcome the diffusion limitations of organic molecules during processing of zeolite catalysts that usually effective on their productivity and overall life (Bellussi, G. et al. 2013). Some of literatures for synthesis and modification of zeolites are listed in Table 2.3.

<table>
<thead>
<tr>
<th>Title of the paper /Book</th>
<th>Author Name</th>
<th>Outcome</th>
</tr>
</thead>
</table>
| Molecular Sieves: Principles of Synthesis and Identification | Szostak, Rosemarie Reference book (1989) | • It address such important items as hydrothermal synthesis, gel composition, synthesis parameters, and post-synthesis modifications such as ion exchange, dealumination, swelling and desilication.  
• Characterization by all kinds of chemical and physico-chemical methods including spectroscopic techniques, acidity and basicity, surface properties, sorption and diffusion.  
• The text is divided into five chapters: (1) Molecular Sieves for Use in Catalysis (2) |
<table>
<thead>
<tr>
<th>Literature review</th>
</tr>
</thead>
<tbody>
<tr>
<td>• The catalytic flavour is strongest in Chapter 1, where structure and acidity introduce the concept of shape selectivity.</td>
</tr>
<tr>
<td>• Chapter 2 gives a good account of the practicalities of hydrothermal synthesis and the influence of reaction variables. The method of treatment is to present and attempt to rationalise experimental observations, rather than to adopt a more fundamental approach.</td>
</tr>
<tr>
<td>• To some extent this is balanced by devoting an entire Chapter (3) to reviewing the literature on purported zeolite precursors and proposed mechanisms of formation. This is a worthwhile exercise, but it is important to realise that the ratio of conjecture to proof in much of this work is high.</td>
</tr>
<tr>
<td>• In Chapter 4, the present volume scores over earlier books in providing an account of the burgeoning area of nonaluminosilicate molecular sieves. However, in this chapter (as in the next), the coverage of the subject is influenced by the author's particular interests, and the balance of material is not ideal.</td>
</tr>
</tbody>
</table>
| • The final Chapter deals with characterization methods, and concentrates on traditional (e.g.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• In this article it discussed on various possibility of zeolites synthesis and different types of modifications. This is an opportunity for designing new materials with improved properties. It mainly focused on layered zeolites.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• It gives all kind of information, in which some inventions have been done in past, some doing in present and some will be done in future in the field of synthesis and modification of microporous materials.</td>
<td></td>
</tr>
</tbody>
</table>

Fig 2.1 shows that different type of modifications can be possible from 2D layered microporous zeolites precursor. There are possibility of doping zeolites with alkali, alkaline earth and transition metals that can be resulted to differ in various structural and morphology properties. Another possibility is to modify framework of the zeolite by synthesizing zeolites with alkali-treatment that can be resulted to agglomeration of layers. The 3D zeolite can be obtained by calcination of its 2D precursor while it can be delaminated via post-synthesis treatment like aging, change in pH, or ultrasonication. Such kind of modification in zeolites impart distinct properties to its further applications as catalyst.
The discovery of layered zeolites was a fundamental breakthrough that created unprecedented opportunities because of inherent strong acid sites that make them very active catalytically. Porosity through the layers and Bridging of 2D and 3D structures.

From all above studies the more interesting zeolite is MCM-22 and first layered zeolite precursor MCM-22(P) was prepared by Mobil researchers in 1990. The gel composition of MCM-22(P) has mole ratio of the organic template to the aluminosilicate is greater than 2.0. The solid is composed of stacking layers which already contain the bidimensional 10-ring channels. Structure directing agent (SDA- hexamethylenimine) molecules are housed in the interlayer space of the as-prepared material. The possibility of delaminating this solid while maintaining the layers’ crystalline structure would be another long expected breakthrough in the field of acidic catalysis with aluminosilicates. Thus, the MCM-22(P) precursor can be calcined, forming the MCM-22 material which has a good thermal stability and an acidity controlled by the aluminium content. Delamination of the swollen MCM-22 leads to ITQ-2 material. Moreover, MCM-22(P) has been exfoliated using post-synthesis treatment like high temperature with high pH.
2.4. Vapor phase organic reactions over zeolites

Some literatures of vapor phase organic reactions over zeolites have been summarized in Table 2.4.

<table>
<thead>
<tr>
<th>Title of the paper</th>
<th>Author Name</th>
<th>Outcome</th>
</tr>
</thead>
</table>
| Layered Materials with Catalytic Applications: Pillared and Delaminated Zeolites from MWW Precursors | Urbano Diaz (2012) | • The preparation of this open type-zeolites family is based on the modification of, previously synthesized, zeolitic precursors which are preexpanded to obtain the final modified zeolites which exhibit very different physicochemical properties compared with the starting precursors.  
• The MWW-type zeolitic materials considered as the most relevant and high accessible.  
• Their nature, characteristics, and reactivity has been shown in the function of the employed synthesis method. |
| Two-Dimensional Zeolites: Current Status and Perspectives | Wieslaw J. Roth et al. (2014) | They includes:  
• Early Discoveries Relevant to Layered Zeolite Materials; Layered Zeolite Materials: General Overview; Synthesis of Layered Zeolite Precursors Structure of Lamellar Materials; Postsynthetic Modification of Layered Zeolite Precursors; Zeolites in Catalysis: Challenges and Opportunities; Application of computational |
<table>
<thead>
<tr>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions</strong></td>
</tr>
<tr>
<td>• He discussed solid acid catalysis involves the largest amounts of catalysts used and the largest economical effort in the oil refining and chemical industry.</td>
</tr>
<tr>
<td>• From a research point of view, zeolites and zeotypes have represented a revolution in the field of acid catalysis, not only because of the rationalization on the nature of the acid sites achieved, but also because of the practical catalytic results achieved with these materials.</td>
</tr>
<tr>
<td>• Zeolites as Acid Catalysts for Hydrocarbon Reactions and Interaction between Hydrocarbons and Acid Sites.</td>
</tr>
<tr>
<td><strong>MWW-type catalysts for gas phase glycerol dehydration to acrolein</strong></td>
</tr>
<tr>
<td>• They described the advantage of catalysts derived from MWW-type precursors are active and selective in gas phase dehydration of glycerol to acrolein.</td>
</tr>
<tr>
<td>• The delaminated material ITQ-2 showed higher selectivity to acrolein because of the improved textural properties when compared to MCM-22.</td>
</tr>
<tr>
<td>• The pillared material MCM-36 presented higher glycerol conversion, but lower selectivity to acrolein, as a combined result of acid sites density decreases and obstruction of sites by SiO2 pillars.</td>
</tr>
<tr>
<td>Literature</td>
</tr>
<tr>
<td>------------</td>
</tr>
</tbody>
</table>
| Organic catalysis over zeolites: a perspective on reaction paths within micropores | Paul B. Venuto et al. (1993) | - They described the advantage of field of organic catalysis over zeolites and related microporous materials has shown enormous international expansion.  
- They also described the depth of understanding of the catalytic chemistry, reaction conditions, and structure-reactivity relationships has shown dramatic growth.  
- Further, the utilization of ZSM-5 and related medium pore zeolites has truly enabled a revolution in shape-selective control of reaction selectivity.  
- Broad classification and survey of organic chemistry over zeolites is reported in the same article. |
| Heterogeneous catalysis in zeolites, mesoporous silica, and metal–organic frameworks. | Liang, Jie, et al. (2017) | - In this review, they highlight recent research advancements in heterogeneous catalysis using zeolites, ordered mesoporous silica, and MOFs.  
- They provided their catalytic property in gas/liquid-phase organic reactions (acid, base, oxidation, and hydrogenation). |
| Hierarchical zeolites: synthesis and catalytic properties. | Feliczak-Guzik, A. (2018) | - In this review, he described various routes for synthesis of hierarchical zeolites and their application in catalytic reactions such as alkylation of aromatics and dehydration of glycerol. |
| Catalytic performance of modified beta zeolite on the synthesis of styrene and xylene: a kinetic study. | Raparia, Y., Halder, G., Arya, R. and Barman, S., 2019. | • In general, Styrene and xylene are commercially important products in the petrochemical and polymer industries.  
• They explained catalytic performance of K-modified zeolite beta (Kβ) for the synthesis of industrially important products styrene and xylene by alkylation of toluene with methanol. |

### 2.5. Scope of the research

In this thesis, among various zeolites, one of the layered zeolite MCM-22 has been explored for further research. Rather than focusing merely on the preciosity of the zeolites used as catalysts in this thesis, our main objective was to investigate various organic reactions over these synthesized and post-synthesis modified materials. First, the formation of alkylated products has been studied by alkylation reactions over MCM-22 and modified MCM-22 zeolites. The catalytic performance of these zeolites has been compared in the alkylation of toluene with ethanol, and ethylbenzene with ethanol. Glycerol dehydration is another organic reaction has been explored for the selective formation of acrolein and hydroxyacetone over microporous MCM-22 and hierarchical modified MCM-22. In short, in this research work the synthesis and modification of MCM-22 has been synthesized, and thoroughly analyzed by using various physico-chemical techniques, and its catalytic application has been implemented in vapor phase organic reactions.

Synthesis of MCM-22 precursor with two different silica sources were explored, namely: colloidal silica and silicic acid followed optimization and proper characterization. The significant results have been explored in this study: Successful synthesis of MCM-22 and modified MCM-22 have been confirmed by its physico-chemical characterization techniques; Vapor phase organic reactions have been successfully optimized and output of work has been published; Experimental results of alkylation reactions have been compared with theoretical study using Gaussion09 computational software; and described in further detail in following chapters.
2.6. References


Literature review


Literature review


