CHAPTER I

INTRODUCTION

1.1 The importance of olefinations and products from olefination of carbonyl compounds

Olefination of carbonyl compounds, being the transformation of the carbonyl group into the carbon-carbon double bond, is one of the most convenient and universal method for the preparation of alkenes [1]. Great diversity and accessibility of carbonyl compounds allows olefination to be used for syntheses of a wide scope of substituted alkenes. The methods for olefination have been widely reported depending on the reagent used such as Wittig reaction and its modified versions, Peterson olefination, Kocienski-Julia, and Horner-Wadsworth-Emmons reactions. Several systems employing stoichiometric organometallic reagents based on tantalum, titanium, zirconium, molybdenum, zinc and other metals have been developed. The product from olefination are indeed important in organic synthesis, agrochemical [2], pharmaceutical industries [3] and other chemical fields [4]. For example fluoroolefins, typically obtained from fluoroalkenoates and *tert*-butyl α-fluoro-α-(trialkylsilyl) acetates *via* Peterson olefination, are widely utilized in the preparation of biologically active materials like peptide isosteres [5] and enzyme inhibitors [6].

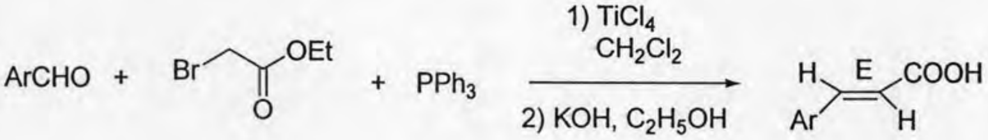
1.2 Literature review on the olefinations of carbonyl compounds

Reactions with homogeneous catalysts

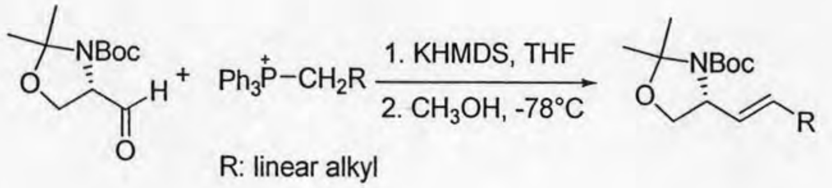
Wittig olefination or Wittig reagent allows the preparation of an alkene by the reaction of an aldehyde or ketone with the ylide generated form a phosphonium salt. In 1989 Fujimura and Honma [7] reported the stereoselective conversion of a variety of aldehydes to (*E*)-olefins by the reaction of ethyl diazoacetate and triphenylphosphine in the presence of a catalytic amount of $RuCl_2(PPh_3)_3$.

$$R^1CHO + N_2CHCO_2Et + PPh_3 \xrightarrow[ClCH_2CH_2Cl]{RuCl_2(PPh_3)_3} R^1CH=CHCO_2Et$$

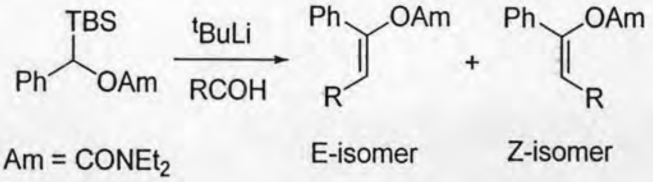
In 2002 Basavaiah and Rao [8] reported a convenient stereoselective transformation of a variety of aldehydes into (*E*)-cinnamic acids *via* the reaction with ethyl bromoacetate and triphenylphosphine under the influence of a catalytic amount of $TiCl_4$, followed by hydrolysis and crystallization. This methodology represents an alternative to Wittig olefination.



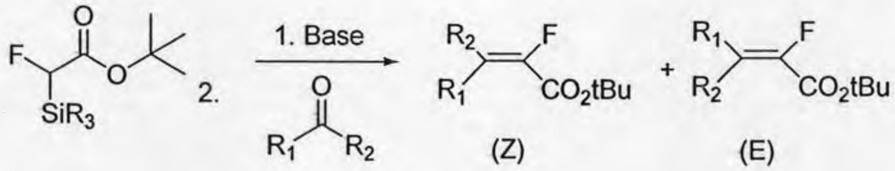
In 2004 Oh *et al.* [9] addressed that (*E*)-alkenes could be produced as a major product by quenching the reactions with a large excess of MeOH at -78°C. Even under the salt-free conditions, more than 10:1 ratio of (*E*)- to (*Z*)-alkene was attained from the ylides of a linear alkyl chain. Without addition of MeOH, usual selectivity for (*Z*)-alkene was obtained in a ratio of 94:6.



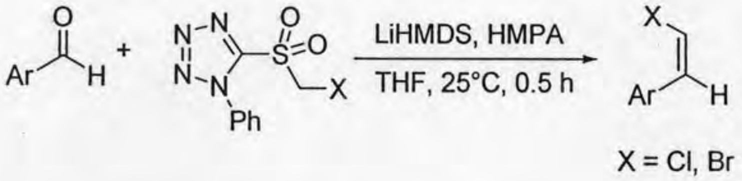
Peterson olefination or Peterson reaction is the chemical reaction of α-silyl carbanions with ketones (or aldehydes) to form β-hydroxysilane which eliminates to form alkenes. In 1997, Emslie *et al.* [10] investigated the reactivity of benzyl carbamates and its application in Peterson olefination. The products were isolated directly from the reaction of α-silylated benzyl carbamate with carbonyl compounds. This reaction gives good *Z*-selectivity when *t*-butyldimethylsilyl carbamate is used.



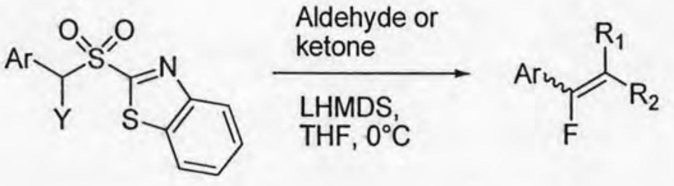
In 1998 Lin and Welch [11] reported the new silyl reagent, *tert*-butyl α-fluoro-α-(trialkylsilyl)acetate. This reagent has been employed in base-catalyzed Peterson olefination reactions with a variety of aldehydes and ketones to yield a series of new fluoroolefin compounds in moderate yields.



Julia olefination is a multistep synthesis enables the preparation of (*E*)-alkenes. The addition of a phenylsulfonyl carbanion to an aldehyde or ketone leads to an intermediate alcohol, which is esterified *in situ*. The reductive elimination with sodium amalgam to furnish alkenes takes place in the second step. In 2005, Lebrun *et al.* [12] reported the use of α-halomethyl sulfones and a variety of aldehydes affording alkenyl halides with high *E/Z* stereoselectivities. Sulfones were readily prepared in two or three steps from commercially available reagents.

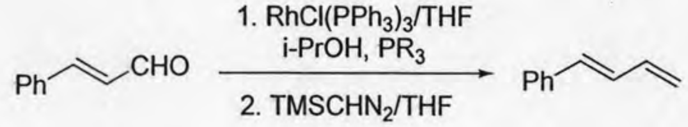


In 2006 Ghosh and Zajc [13] reported tandem electrophilic fluorination and modified Julia olefination for the synthesis of fluoroolefins. The α-fluoro-1,3-benzothiazol-2-yl sulfones were subjected to condensation with a variety of aldehydes and ketones to afford high yields of regiospecifically fluorinated olefins.

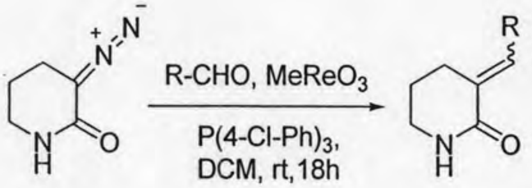


Heck reaction involved the chemical reaction of an unsaturated halide (or triflate) with an alkene and a strong base and palladium catalyst to form a substituted alkene. In 2007 Chen *et al.* [14] synthesized of Pd(II) complexes from pyridylbenzoimidazole derivatives and their catalytic activity for the Heck olefination of bromobenzene with butenyl acrylate.

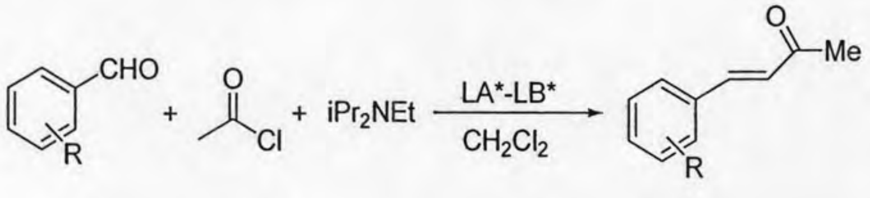
In addition, olefination based on metal complex has been developed. In 2003 Lebel and Paquet [15] reported the use of rhodium-catalyzed methylenation of aldehydes. The synthetic potential is highlighted allowing the preparation of terminal alkenes with yields up to 99%.



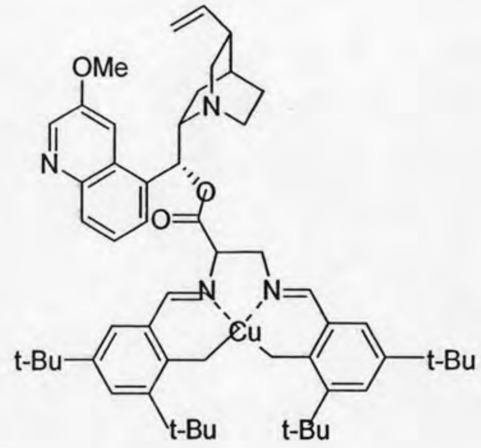
The new conditions have been developed for the olefination of diazo compounds catalyzed by methyl trioxorhenium. The new system is suitable for unreactive diazo compounds and its utility is demonstrated by the olefination of 3-diazopiperidin-2-one with a range of aromatic, heterocyclic and alkylaldehydes. [16]



Recently, Salen-quinine mixed ligand and Lewis acid-Lewis base bifunctional catalysts has been developed for olefination. In 2007 Lin *et al.* [17] discovered a new catalytic reaction for converting aldehydes into *E* enones exclusively, using acetyl chloride as a vinylating reagent for this olefination reaction. The new Cu(II) catalyst formally converts two molecules of acetyl chloride into the synthetic equivalent of an 'acetyl vinyl' group that olefinates aldehyde carbonyl groups.



LA*-LB* =



Reaction with heterogeneous catalysts

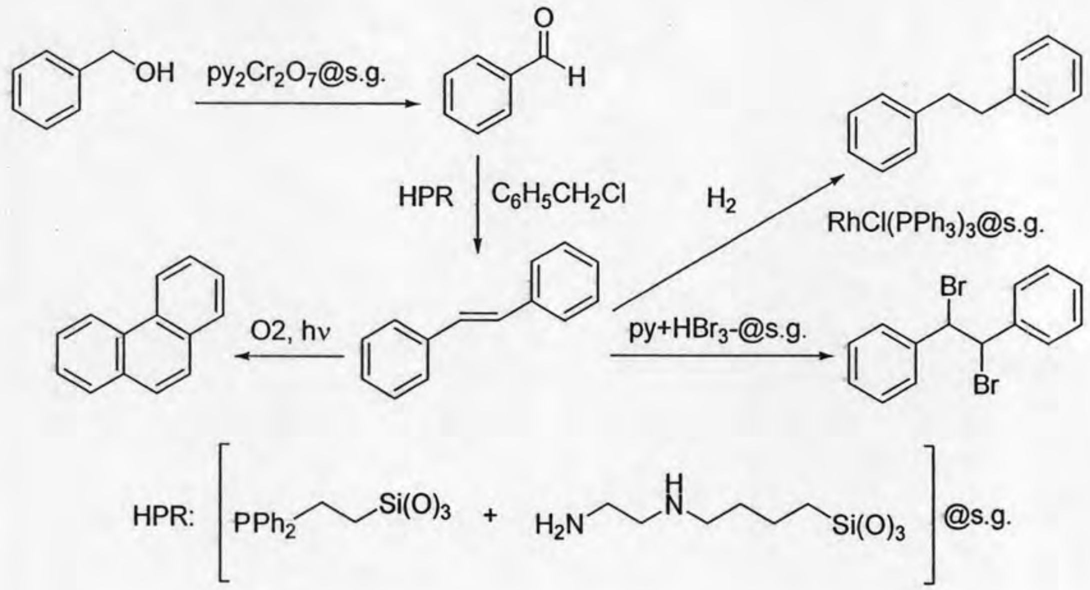
Pillared interlayered clays (PILCs) have been extensively studied in the past few years. They constitute one of the families of new microporous materials developed by molecular engineering, prepared by a multi-step synthesis process which may be divided into various steps:

(i) preparation of bulky inorganic polyoxocations by polymerization of cations of some metallic elements.

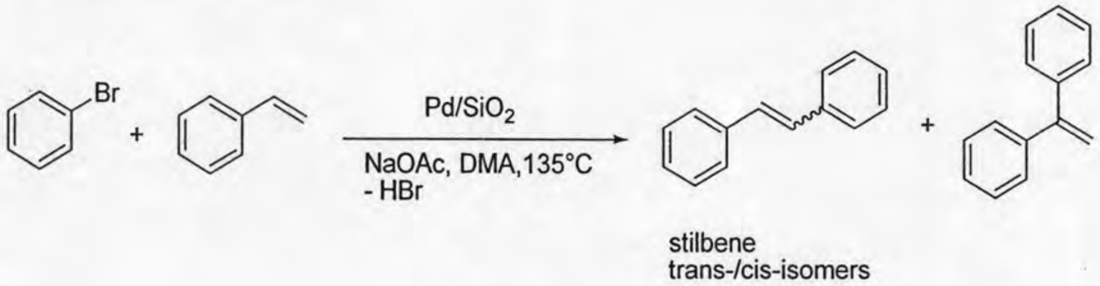
(ii) exchange of the exchangeable charge balancing cations of smectitic clays by these polyoxocations, forming intercalated solids.

(iii) immobilization of the intercalated solids by calcinations. Heterogeneous catalysts are increasingly playing an important role in organic synthesis compared to homogeneous catalysts.

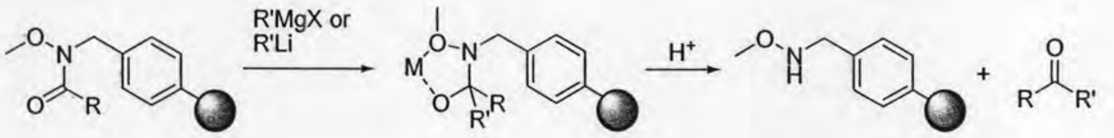
In 2006 Hamza and Blum [18] expressed that the application of sol–gel technology, co-polycondensation of tetramethoxysilane, 2-diphenyl(phosphino) ethyltri(ethoxy)silane, and *N*-2-(aminoethyl)-3-aminopropyltri(methoxy)silane forms a heterogenized tertiary phosphine reagent (HPR) to Wittig reaction. The reaction of benzyl chlorides with aldehydes yielded alkenes. This Wittig condensation could be coupled, as a one-pot process, with hydrogenation, oxidation, bromination or photocyclization.

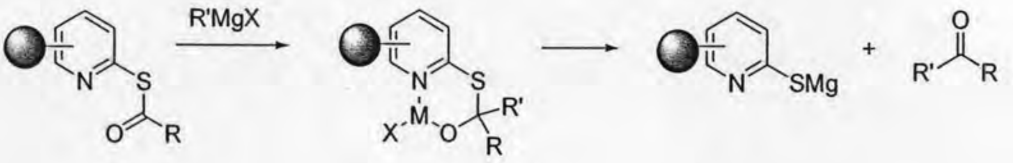


Huang *et al.* [19] studied a ligand-free heterogeneous metal catalyst system (represented as Pd/SiO_2 (O)) derived by calcination of $Pd(acac)_2/SiO_2$ in air and its catalytic properties toward the Heck coupling of bromobenzene (PhBr) and styrene. X-ray photoelectron spectroscopy (XPS) and catalytic results demonstrated that most of Pd^{2+} was reduced to Pd^0 on SiO_2 by *N,N*-dimethylacetamide (DMA) during Heck reaction and that the resulting Pd^0/SiO_2 was active for Heck reaction, the remaining Pd^{2+}/SiO_2 was not responsible for the high activity. Pd/SiO_2 (O) possessed incomparable advantages over a heterogeneous homolog (represented as Pd/SiO_2 (H)) prepared by reduction of $Pd(acac)_2/SiO_2$ in H_2 as a pre-catalyst in both activity and catalyst recycling. The activity over Pd/SiO_2 (O) was comparable to that over a homogeneous Pd system.



Tanner *et al.* [20] synthesized two new solid-supported reagents and tested in the formation of carbonyl compounds. The solid-supported Weinreb amides gave the corresponding carbonyl compounds. Likewise, the addition of phenylmagnesium bromide to the solid-supported *S*-(2-pyridyl) thiolates resulted in the corresponding carbonyl compounds.



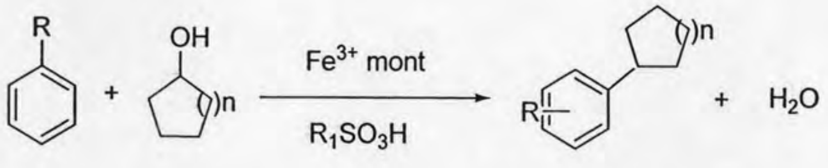


1.3 Literature review on clay catalysts

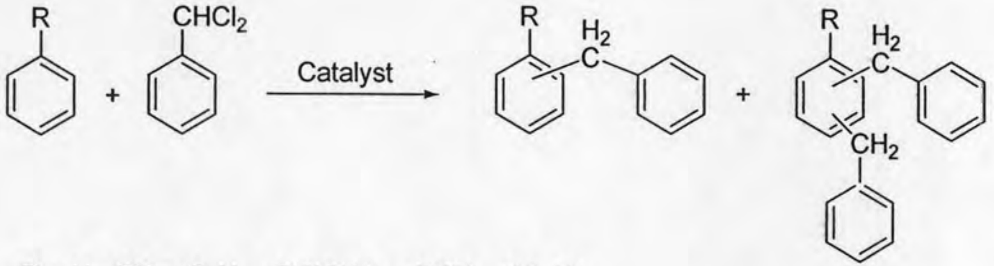
Clays have a long history in industrial sorption and catalysis, which for some time has veered towards possible clean technology applications. They are also still of interest catalytically, given the absence of a single detailed reaction mechanism for organic reactions on their surfaces. For both pillared clays and restructured clays (*i.e.* clays in which the layer structure has been partially destroyed by acid treatment), the major reason is the absence of detailed structures that the structure of montmorillonite itself is essentially an extrapolation of that for mica. Clay catalysis may function as Bronsted or Lewis acids. Organic reactions that take place under acid catalysis can be very efficiently carried out using clay catalysts. These reactions are more efficiently, under milder conditions, with greater selectivity, better yields and shorter reaction times. Moreover, the work up and purification procedures are simple as the catalyst can be filtered or centrifuged out from the reaction mixture. The range of reactions successfully performed on clay catalysts include Friedel-Crafts reaction [21-22], oligomerization [23], esterification [24], isomerization [25], Diels-Alder reaction and rearrangement reactions [26].

Friedel-Crafts reaction

In 2002 Choudary *et al.* [21] developed an efficient method for alkylation of aromatic compounds with secondary alcohols by *in situ* generation of alkyl sulfonates using catalytic amount of sulfonic acid and Fe^{3+}-montmorillonite in one pot.



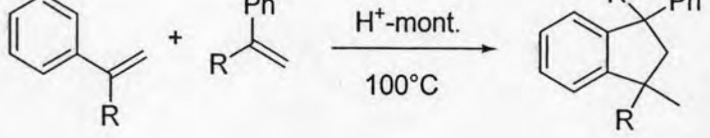
In 2003 Singh and Samant [22] modified Montmorillonite K10 with pillaring solutions of Fe, Al and Zr (K10-MPLS). The resultant catalysts were used for Friedel–Crafts benzylation of benzene with benzyl chloride under mild experimental conditions. Amongst them, K10-FePLS120 catalyst showed both high activity and selectivity for the benzylation reaction at RT (28°C). The catalyst can also be reused in the benzylation for several times. The activities of these catalysts were compared with those of Fe^{3+}-, Al^{3+}- and Zr^{4+}-exchanged montmorillonite K10 and Fe-, Al- and Zr-pillared bentonite catalysts.



R= -H, $-CH_3$, $-C_2H_5$, $-CH(CH_3)_2$, $-OCH_3$, -Cl, -Br

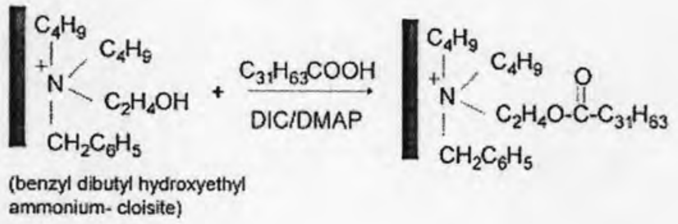
Oligomerization reaction

Tsunashima *et al.* [23] reported that alkenes underwent oligomerization in the presence of acid-treated or ion-exchanged montmorillonites. The reaction involved protonation to generate a stabilized carbocation that reacted with other alkenes to give dimers as well as oligomers after deprotonation. The polymerization of styrene has been catalyzed by acid-treated montmorillonites.



Esterification

In 2007 Mittal [24] modified montmorillonite platelets with ammonium ions of different chemical architectures in order to study the effect of ammonium ions on the extent of surface reactions with long chain fatty acids. Varying number of hydroxyl groups and the presence of octadecyl chains in the ammonium modifications were attributed.

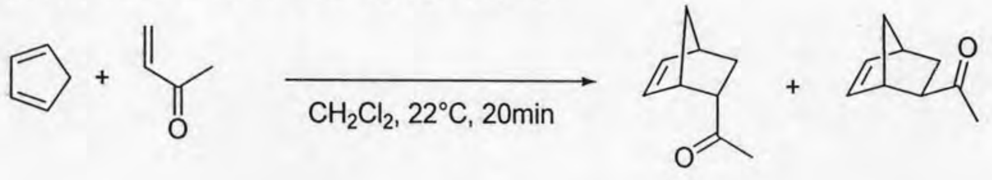


Isomerization

In 2008 Moronta *et al.* [25] synthesized pillared clays for the isomerization of 1-butene as the ion-exchanged clays. Ion-exchanged pillared clays showed the same catalytic behaviour as the parent pillared clays. The best catalyst for the reaction was Al-pillared clay and the efficiency was related to its high acidity and surface area. The total conversion was correlated with the acidity values determined by TPD of ammonia. No pillar formation was detected in Fe-treated clays in spite of the high metal content found by XRF, so it is believed that only metal oxide deposition occurred.

Diels-Alder reaction

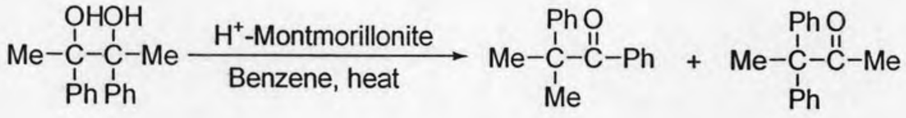
Although Diels-Alder reaction is a thermally allowed [4+2] cycloaddition process, it does not occur spontaneously with all dienes and dienophiles. The rates of these slow reactions can be greatly accelerated when they are carried out using clay catalysts even under very mild conditions. The catalytic character of clays in these reactions is due to their acidic property [26].



Fe^{3+}-K-10	9	:	1(97% yield)
Cr^{3+}-Vermiculite	2.5	:	1(47% yield)

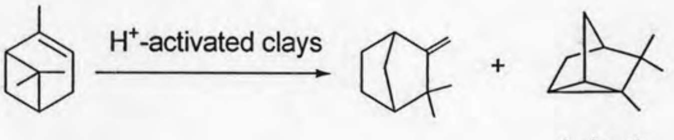
Rearrangement reaction

A good number of rearrangement/isomerization reactions have been carried out using clay catalysts. For example, pinacol-pinacolone reaction is a common reaction of tertiary 1,2-glycols catalyzed by acids, in which an alkyl or an aryl group migrates to an adjacent position [26].



$$\mathrm{Me{-}\overset{OH}{\underset{Ph}{C}}{-}\overset{OH}{\underset{Ph}{C}}{-}Me \xrightarrow[\text{Benzene, heat}]{\text{H}^+\text{-Montmorillonite}} Me{-}\overset{Ph}{\underset{Me}{C}}{-}\overset{O}{\overset{\|}{C}}{-}Ph + Me{-}\overset{Ph}{\underset{Ph}{C}}{-}\overset{O}{\overset{\|}{C}}{-}Me}$$

For example, the isomerizations of α-pinene to camphene and longifolene to isolongifolene have been carried out in good yields on acid-treated montmorillonite.



(minor)

Petroleum cracking is an important industrial application in petrochemical processing. Pillared clays could be used in this process since they are more stable at high temperature. Catalytic reforming and isomerization of *n*-alkanes to branch-chain alkanes increases the octane number. Conversion of methanol to alkanes and of synthesis-gas to hydrocarbons has also been achieved.

$$C_4\text{ -to- }C_7 \xrightarrow{\text{Ni, Co-H}^+\text{-Montmorillonite}} C_4\text{ -to- }C_7 \text{ iso-alkanes (60\% yield)}$$

$$CH_3OH \xrightarrow[350^\circ C]{\text{Al}^{3+}\text{-Montmorillonite}} C_2 - C_4 \text{ alkanes}$$

$$CO + 2H_2 \xrightarrow[175^\circ C]{\text{Co-Montmorillonite}} C_5 - C_{12} \text{ alkanes and alkenes}$$

Dehydration reactions

Primary amines are converted to dialkylamine by loss of ammonia while thiols afford dialkyl thioethers by elimination of hydrogen sulfide [26].

$$\mathrm{RCH_2XH} \xrightarrow[\mathrm{-H_2X}]{\mathrm{Al(III)^{+}\text{-}mont.}} \mathrm{RCH_2XCH_2R}$$

X = NH, O, S

Although several synthetic methods for olefination reaction have been developed, there was no report on the synthesis of alkene catalyzed by copper oxide-pillared clay. This procedure represents a new approach to the transformation of the C=O bond into the C=C bond using heterogeneous system.

1.4 The objectives of this research

1. To synthesize the efficient copper oxide-pillared clay catalyst for olefination of carbonyl compounds.
2. To study the optimum conditions for olefination of carbonyl compounds using aldehyde as a model substrate and the copper-oxide-pillared clay as a catalyst.
3. To apply the optimum conditions for olefination of some selected halogenated reagents.