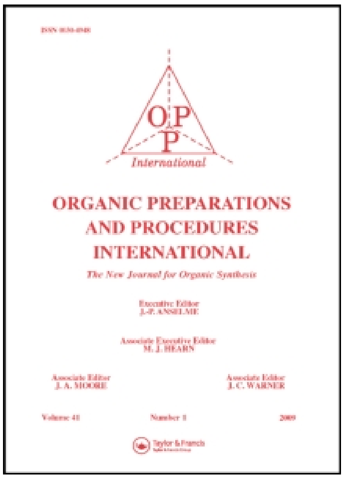

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RECENT ADVANCES IN CLAY-CATALYZED ORGANIC TRANSFORMATIONS

Milind D. Nikalje[a]; Prodeep Phukan[a]; Arumugam Sudalai[a]
[a] Process Development Division, National Chemical Laboratory, Pune, INDIA

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Milind D. Nikalje, Prodeep Phukan and Arumugam Sudalai*

Process Development Division, National Chemical Laboratory, Pune - 411008, INDIA
E-mail: sudalai@dalton.ncl.res.in

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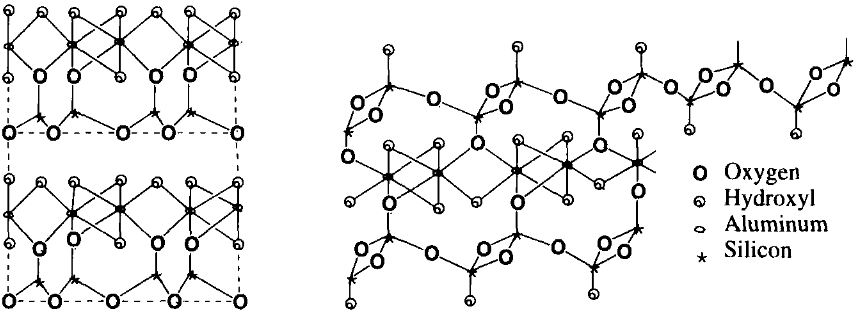
INTRODUCTION

Clays are predominantly composed of hydrous phyllosilicates referred to as "clay minerals".[1-3] These are hydrous silicates of aluminum, magnesium, potassium and iron. Clay minerals are extremely fine crystals or particles, often colloidal in size and usually plate like in shape. Many clay mineral crystals carry an excess negative electric charge owing to internal substitution by lower valent cations which increases the internal reactivity in chemical combination and ion-exchange.

Heterogeneous catalytic organic transformations using clay have been reviewed recently by Cornelis and Laszlo.[4] A few monographs on clay catalysis have also appeared recently.[5-7] The present review deals with the recent advances in various organic transformations that have been carried out using clays as catalysts since 1994.

The Al^{3+}-cations in clays are bonded to an octahedral arrangement of oxygen anions. Repetition of these AlO_6 units in two dimensions forms an octahedral layer. Likewise, a tetrahedral layer is formed from SiO_4 units. The resulting sheets are planar. These planar clay platelets stack on top of one another.



(a) Kaolinite (b) Montmorillonite

Fig. 1

The least complicated clay minerals are the 1:1 clay minerals composed of one tetrahedral (T) layer and one octahedral (O) layer. The 1:1 clay minerals are referred to as TO minerals. The TO package has a basal spacing of 0.7 nm (7Å). For example, kaolinite (*Fig. 1a*), refer to the dioctahedral (1:1)-mineral, it has Al^{3+} filling two of three octahedral sites (*Fig. 1*). Clay minerals that are composed of two tetrahedral layers and one octahedral layer are referring to as (2:1)-clay mineral or TOT mineral. The apical oxygens of the two tetrahedral sheets project into the octahedral sheets. The (2:1)-clay mineral structure has a basal spacing of 1.5nm (15Å). For example, a montmorillonite (*Fig. 1b*) is a clay mineral in which one octahedral aluminate layer is sandwiched between two tetrahedral silicate layers (*Fig. 1*).

Clay particles generally give well defined X-ray diffraction patterns from which the mineral composition and the basal distances are determined. They are so finely divided that clay properties are often controlled by the surface properties of the minerals rather than by bulk chemical composition. Particle size, shape, nature and the distribution of amount of both mineral and organic impurities, nature and amount of exchangeable ions and degree of crystal perfection are all known to affect the properties of clays profoundly. Clays are classified according to the relative number of tetrahedral and octahedral layers.

Along with the high Bronsted acidic surfaces, the catalytic sites are edge sites where the platelets break off, offering coordinately-unsaturated Al^{3+}-sites; Fe^{2+} and Fe^{3+}-centers arising often from substitution of Al^{3+} in the octahedral layer. Furthermore, dehydrative activation of clay through heating in an oven at 150-300° results in generation of surface radical sites of the O_3SiO silyloxy type. Due to planar topology and the geometrical constraint of insertion between the parallel plates of two adjacent clay layers, substrate molecules are restricted in their orientation as they chemisorb on to catalytic sites.

The Bronsted acidity stems from the terminal hydroxyl groups and from the bridging oxygens. High acidity especially due to the latter. It is measured using a standard set of dye indicators by Hammett H_0 acidity function. These surface acidity for natural clays with Na^+ or NH_4^+ as interstitial cations range from +1.5 to -3. Simple washing of the clay with mineral acid exchanging the interlamellar Na^+, K^+, NH_4^+-cations with proton brings their surface acidity to H_0 values between -5.6 to -8 which is between that for conc. nitric acid (H_0=-5) and that for conc. sulfuric acid (H_0= -12).

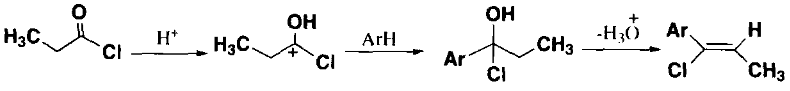
Most commonly, the modification of clays is carried out either by exchanging the cations present in the clay with any other suitable cations like Fe, Zn, Pd, Cu, Ru, Rh, Ce, *etc.* or by increasing the interlameller space by pillaring.[3] Cation-exchanged clays were prepared by stirring a mixture of the clay and a metal salt in aqueous medium or aqueous acetone at room temperature or above. Pillared layered structures (PLS) are ultralarge pore materials consisting of layered structures with pillars in the interlamellar region. Smectite is one of the families of minerals that can be used as pillared material.[3] Montmorillonite is most widely used smectites for the preparation of PLS. The general procedure for preparing these clays consists of exchanging the cations in the interlamellar position with larger inorganic hydroxymetal cations. These hydroxy species are polymeric or oligomeric hydroxyl metal cations formed by the hydrolysis of metal salts of Al, Zr, Ga, Cr, Si, Ti, Fe, *etc.* and mixtures of them. When the exchanged samples are subjected to a thermal treatment, dehydration and dehydroxylation occur, forming stable metal oxide clusters which serve to separate the layers, creating a two dimensional opening (space length > 1.0nm). Among the advantages of pillared smectic clays over faujasite-zeolites is that their pore size can be made larger and under controlled pillaring condition, the pore size can be adjusted to suit a particular application.

I. APPLICATION TO ORGANIC SYNTHESIS

1. Alkylation

Friedel-Crafts reactions are of great interest due to their importance and common use in synthetic and industrial chemistry. The major disadvantages encountered in the use of anhydrous $AlCl_3$ include corrosion, unfriendliness to the environment, stoichiometric requirement of large excess of reagent thereby generating large amount of waste.

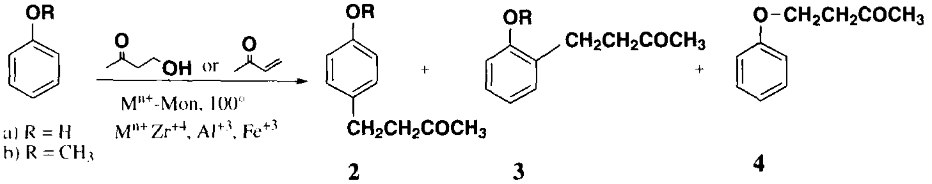
The acid-treated $FeCl_3$-montmorillonite catalyst has been found to promote both acylation as well as alkylation.[8] During the acylation of aromatic compounds with acid chlorides such as propionyl chloride in presence of clayfec type catalyst, the formation of an unusual product *i. e.* chlorostyrene (**1**) in low yield (<10%) along with the major acylated product was observed (*Scheme 1*). The alkylation of toluene with ethyl bromide has been investigated over a series of Thuan Hai clays obtained by exchanging the original Na^+-cations with Fe^{3+}, Zn^{2+}-cations.[9]



Scheme 1

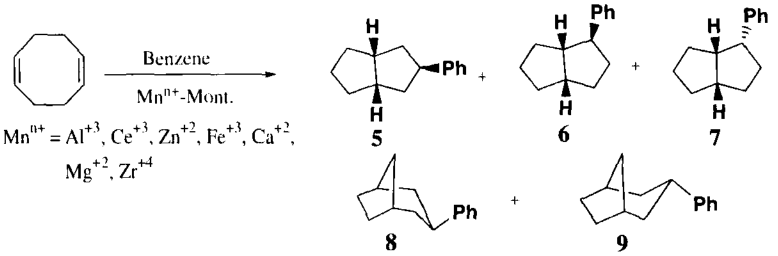
Vanadia-montmorillinite is found to be useful for the monoalkylation of aniline.[10] The propene alkylation of biphenyl has been studied at 250° and 140psi using two mesoporous clays *viz.* acid-treated montmorillonite K10 and aluminas-dealuminated-laponite.[11] A series of 3b-arylcholestenes were synthesized by Friedel-Crafts alkylation of cholesterol with arenes catalyzed by montmorillonite K-10.[12] The mesoporous clays exhibit reactivities and selectivities towards monoalkylated product that are substantially different from those exhibitted by microporous alumina pillared clays. The differences in reactivity and selectivity are explained in part by the effect of pore structure on the diffusion controlled reaction. A recent patent[13] discloses that the dialkylation of hydroquinone in 92% yield with C6-C10 olefins at <150° in the presence of 3wt% activated clay. These dialkylated hydroquinones are important polymerization inhibitor and stabilizer. Another report also discloses the synthesis of alkyl substituted hydroquinones from hydroquinone and C6-C30 olefins with activated clay.[14] Alkylation of phenol with C16-C18 olefins was also reported in the presence of activated clay and monohydric alcohols in 94% yield.[15] A new method for the preparation of pillared clays by exchanging the cation by ammonium ion, calcium ion or by metal oxide has been reported for the alkylation process.[16] Synthesis of alkylamines such as tertiary butylamine over montmorillonite clay or other catalysts is carried out using NH_3 and isobutylene as the olefin.[17] This constitutes the commercialized way to synthesize tertiary amines which are difficult to obtain by normal alkyl halogen substitution method.

A process for the preparation of styrenate phenol through catalytic alkylation of phenol with oxalic acid and activated clay was reported.[18] The reaction was carried out under mild conditions with less water and the yield of styrenate phenol can reach 99.3%. Alkylation of phenol, anisole and methoxynaphthalene with 4-hydroxybutan-2-one or methyl vinyl ketone in the presence of Zr^{+4}, Al^{+3} or Fe^{+3}-montmorillonite clay produces raspberry ketone (**2**) and several pharmaceutically active compounds (**3-4**) in low yield (*Scheme 2*).[19]



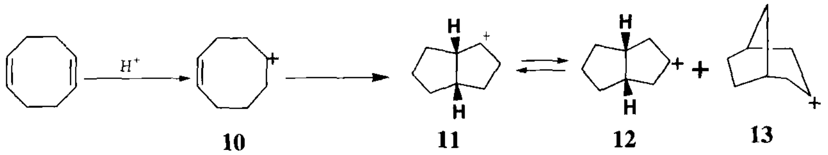
Scheme 2

The transannular alkylation of benzene with (Z, Z)-1,5-cyclooctadiene in the presence of a cation-exchanged montmorillonite K10 has been reported to give five isomers of phenyl bicyclooctane (**5-9**)[20] (*Scheme 3*). If $M^{n+}= Fe^{3+}$, isolated yields of 45% in the ratio of 35%, 24%, 10%, 19% and



Scheme 3

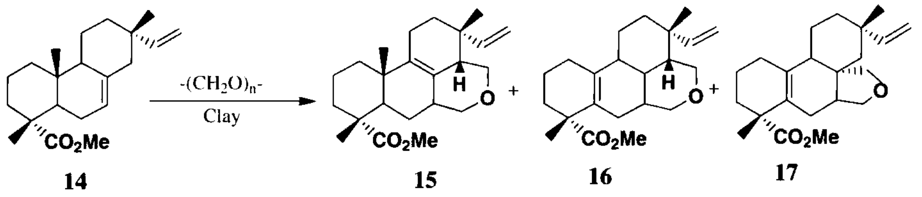
14% for compounds (**5-9**) respectively are obtained. In this alkylation, the initially produced electrophile is probably a *cis*-bicyclo[3,3,0]octyl cation (**11**), which may isomerize to the cation (**12**) and (**13**) (*Scheme 4*). These cations, stabilized by the negative charge of oxygens present on the surface of M^{n+}-montmorillonite, attack of the aryl nucleus, to produce compounds (**5-9**). Similar work has also been reported by Sabu *et al.*[21]



Scheme 4

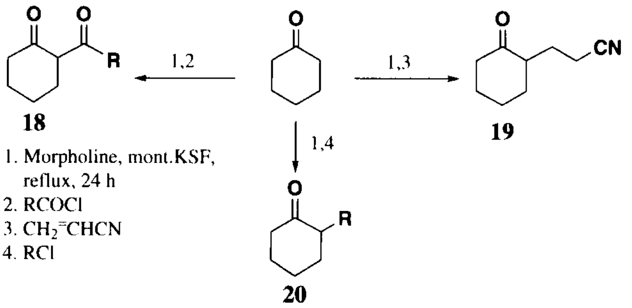
The alkylation of benzene with olefins using pillared clays to give detergent range low molecular weight alkylbenzene has been reported.[22] Also alkylation of naphthalene with *t*-butanol over alumina or zirconia-pillared montmorillonite catalyst has been reported for the formation of 2,6-

di(*tert*-butyl)naphthalene in high yield.[23] Methyl isopimarate (**14**) underwent the Prins reaction with paraformaldehyde in the presence of askanite-bentonite clay to give tetrahydropyrans (**15**) and (**16**) and tetrahydrofurans (**17**) (*Scheme 5*).[24]



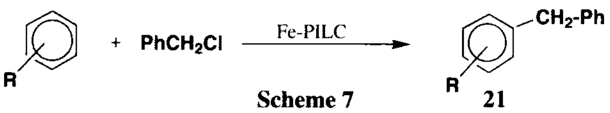
Scheme 5

A single step Stork's alkylation and acylation of cylclohexanone without isolation of enamine in the presence of montmorillonite KSF (KSF) clay as catalyst has been studied to give alkylated products (**19**) and (**20**) and acylated product **18** (*Scheme 6*).[25]



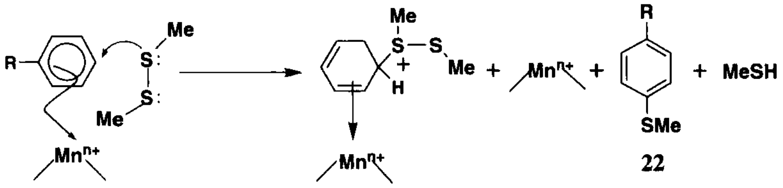
Scheme 6

Iron-pillared-clays (FePILCs) were found to be most efficient catalysts for the benzylation of aromatic compounds producing quantitative conversion of benzylated derivatives (**21**) in less reaction times.[26] Their efficiency is attributed to a higher Fe^{3+} content in the catalyst and the pillaring effect (*Scheme 7*).



Scheme 7

A method for the direct thioalkylation of thiophenol and benzothiophene by reaction with an alkyl disulfide using $ZnCl_2$-modified montmorillonite clay has been reported.[27] The direct introduction of $-SCH_3$ group into activated aromatic and heteroaromatic compounds producing S-alkylated products (**22**) has been achieved by reaction with dimethyl disulfide over a $MnCl_2$ promoted montmorillonite K10 clay.[28,29] The Mn-promoted clay appears to promote the reaction by coordination of the aromatic substrate at the active site followed by the attack of the disulfide at the activated aromatics (*Scheme 8*).

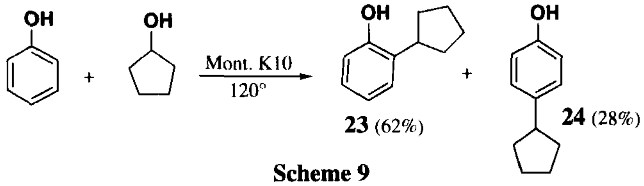


22

Scheme 8

Bisphenol-A is an important raw material for the synthesis of epoxy resins and other polymers. Recently the use of a novel catalyst based on dodecatungstophoric acid supported on montmorillonite K10 clay has been reported for the production of bisphenol-A from phenol and acetone.[30]

Another interesting observation of clay alkylation was found in our laboratory for the synthesis of cyclopentylphenol.[31] Alkylation of phenol was carried out with cyclopentanol using montmorillonite K10 clay as catalyst without the use of solvent. Interestingly, *o*-substituted product (**23**) was found to be predominant, the *ortho/para* ratio being 2.1 (*Scheme 9*). However, such *ortho* selectivity was not observed in the case of alkylation of phenol with cyclohexanol.



23 (62%) **24** (28%)

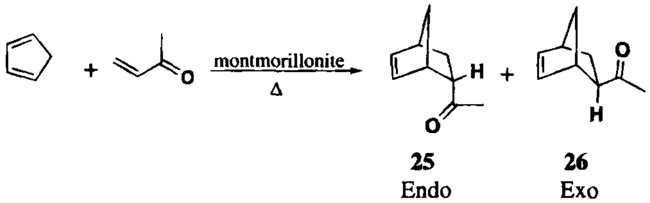
Scheme 9

Vapor phase catalytic activity of montmorillonite pillared with aluminum polyoxy-cations, in the alkylation of toluene with methanol to produce xylenes was studied.[32] The catalytic activity and selectivity of montmorillonite pillared with Al13 and GaAl12-polyoxycations were investigated at 573-673° for the gas-phase microcatalytic alkylation of toluene with MeOH.[33] At 573°, the reaction products contained 69-74% xylenes with the balance 1,2,4- and 1,2,3-trimethylbenzenes. The xylene isomer distribution was *o* > *p*> *m*. The influence of toluene concentration in methanol on conversion and selectivity also was investigated. An increase in toluene molarity produced a decrease in toluene conversion and an increase in xylene selectivity for both catalysts. Toluene methylation activity was also studied using zirconium-pillared montmorillonite and vermiculite clay catalysts.[34] The methylation activity is dependent on the preparative method and zirconium concentration of the catalysts. A recent patent describes high yield (70%) preparation of aryl substituted fatty acids by reaction of mono-unsaturated fatty acids with aromatic compounds over various clay catalysts.[35]

Alkylation of benzene with benzyl chloride under reflux was studied with natural kaolinitic clay metakaolinized at 550° and activated separately with H_2SO_4, HNO_3 and $HClO_4$.[36] The chemical composition, BET surface area, acidity distribution as well as the alkylation activity of these activated metakaolinites were studied. The SiO_2/Al_2O_3 molar ratio, surface area and the number of strong acid sites increased with increasing acid concentration. The metakaolinite activated with 4M HNO_3 has the highest surface area and surface acidity. The effect of impregnating $ZnCl_2$, $FeCl_3$, $MnCl_2$, $SnCl_2$ and $AlCl_3$ on the catalytic activity of a natural kaolinite for Friedel-Crafts alkylation of benzene with benzyl chloride and its activated form is examined.[37] The most effective catalyst was clay with $FeCl_3$. Catalysts supported with $AlCl_3$ proved to be the least effective for the alkylation studied.

2. Diels-Alder Reaction

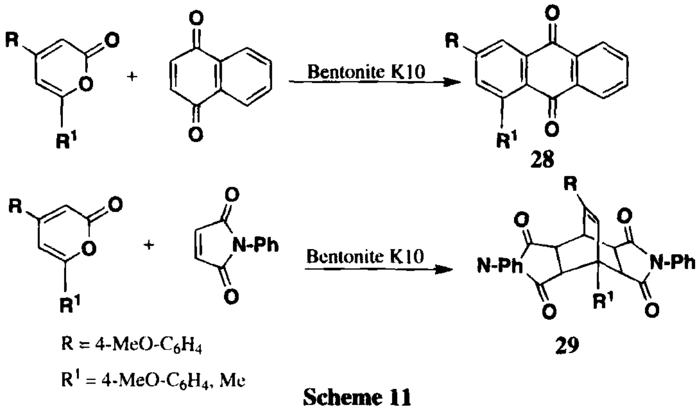
A wide range of transition metal-exchanged Tonsil (a German montmorillonite) clays were used for Diels-Alder reactions which involves the use of α,β-unsaturated carbonyl compounds, such as methyl vinyl ketone and methyl acrylate as dienophiles (*Scheme 10*).[38]



Scheme 10

A number of simple cyclic and acyclic dienes such as cyclopentadiene, 1,3-cyclohexadiene, isoprene and heterocyclic dienes, (furan, pyrrole) successfully undergo Diels-Alder reaction in presence of clay catalyst, but thiophene fails to give Diels-Alder adduct. The proportion of the kinetically less favored but less bulky, *exo*-isomer may be improved by choosing a clay catalyst which has higher layer charge and thus narrower interlamellar space. The ratio of the formation of the stereoselective *endo*/*exo* products (**25** and **26**) can be altered by manipulation of the inter-layer spaces of the clay catalyst. The non-transition and lanthanide cation-exchanged clays were found to be ineffective catalyst for the above reaction.

The Diels-Alder reaction of 4,6-*bis*-(4-methoxyphenyl) and 4-(4-methoxyphenyl)-6-methyl-2H-pyran-2-one with 1,4-napthoquinone and N-phenylmaleimide have been carried out by adsorbing the reactant on silica gel, n-silica or bentonite K10 clay in the absence of solvent (*Scheme 11*).[39] The

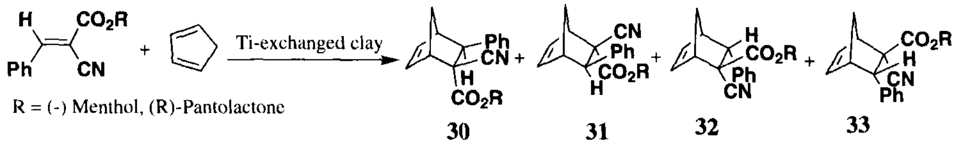


$R = 4\text{-MeO-}C_6H_4$
$R^1 = 4\text{-MeO-}C_6H_4$, Me

Scheme 11

Diels-Alder product formation was studied with respect to the temperature of the reaction. It is found that in the case of the bentonite K10 clay, the product formation is maximum at 160° and thereafter the product formation decreases with further increase of the temperature.

The Diels-Alder reaction of the non chiral menthyl (E)-2-cyanocinnamate and the chiral (E)-2-cyanocinnamate of (-)-menthol and (R)-pantolactone with cyclopentadiene is carried out in the presence of cation-exchanged clay and silica catalyst (*Scheme 12*).[40] With the three dienophiles, it is possible to reach high percent of conversion with good *endo/exo* selectivities for compounds (**30-33**).



Scheme 12

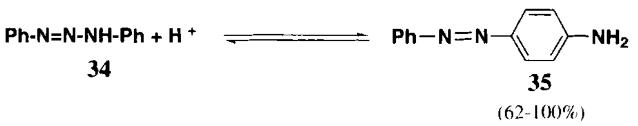
(E)-2-Cyanocinnamate of (-)-menthol leads to higher asymmetric induction than (E)-2-cyanocinnamate of (R)-pantolactone. Ti^{4+},Cu^{2+}, Ag^{+} and Ba^{2+}-exchanged montmotrillonite K10 clays were used for Diels-Alder reaction among which Ti-exchanged clay gave maximum yield (83.5%) and *endolexo* selectivity (*endolexo* ratio 3:1).

The reaction of furan with α,β-unsaturated carbonyl dienophiles catalyzed by montmorillonite K10 under solvent-free condition was reported to produce the corresponding Diels-Alder adducts.[41] In the case of methyl vinyl ketone, Michael-type products was obtained under much milder conditions than the conventional protocols. The results are consistent with acid catalysis on the clay surface. Acrylates gave lower yields and/or decomposition products. The reaction can be extended to alkynic substrates such as dimethyl acetylene dicarboxylate (DMAD) to afford cycloadducts in good yields.

Cation-exchanged montmorillonite K10 displays a high Lewis/Bronsted acidity ratio and efficiently promotes the reaction of (-)-menthyl acrylate with cyclopentadiene.[42] Clays promotes Diels-Alder reaction in three different ways. The most efficient and most selective reaction is due to the Lewis acidic sites than Bronsted acidic sites. The reaction can take place through a radical cation mechanism, which is favored by the addition of promoters such as anisole. In this case, the *endo/exo* and diastereofacial selectivities are noticeably reduced. Another interesting result is that calcination of the cation-exchanged montmorillonite clays increases the Lewis/Bronsted acidity ratio whereas this ratio is reduced after silylation and calcination of the clay.

3. Rearrangements

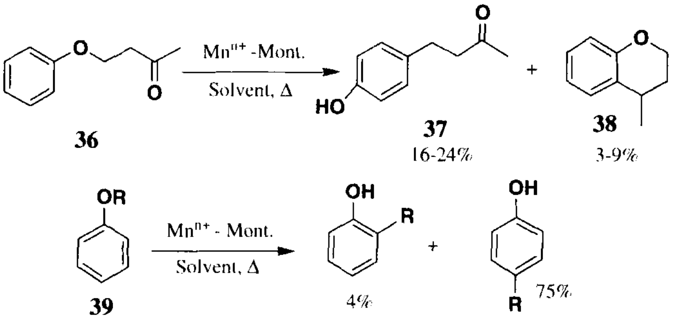
Rearrangement of diphenyltriazene (**34**) to *p*-aminoazobenzene (**35**) is achieved by acidic cation (M^{+n})-exchanged montmorillonite K10 clays (where, M^{+n} = H^{+}, Al^{3+}, Fe^{3+}, Cr^{3+}, Cu^{2+} and Ni^{2+}) at room temperature within 3h (*Scheme 13*).[43]



Scheme 13

The rearrangement of the alkyl phenyl ethers such as 4-phenoxybutan-2-one (**36**), 1-phenoxybutane (**39a**), 2-phenoxybutane (**39b**), 2-methyl-2-phenoxypropane (**39c**) and phenoxycylohexane (**39d**) have been investigated in the presence of cation (M^{n+})-exchanged montmorrilonite (where, $M^{n+} = Zr^{4+}$, Al^{3+}, Fe^{3+} and Zn^{2+}).[44] The ether (**36**) was rearranged to 4-(4-hydroxyphenyl)butane-2-one (**37**) (raspberry ketone) in 16-34% GLC yield; in this transformation, Zn^{2+}-montmorillonite was the most effective catalyst.

Similarly, other ethers (**39a-d**) were rearranged to the corresponding alkylphenols in up to 75% yield with excellent product selectivity, Al^{3+}-montmorillonite being the catalyst of choice. Al^{3+}-montmorillonite catalyst is recovered and reused, thus making the reaction truly a heterogeneous one (*Scheme 14*).

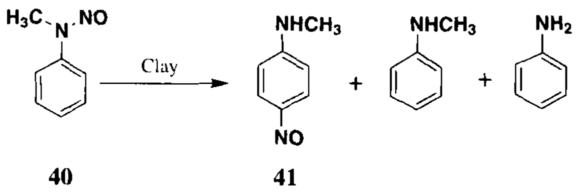


Solvent : PhOH, PhCl, PhMe

R= (a) Bu, (b) Bu^s, (c) Bu^t (d)Cyclohexyl

Scheme 14

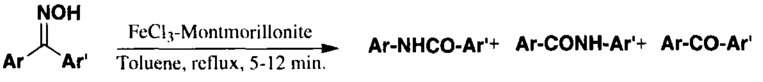
N-Nitroso-N-methylaniline (**40**) undergoes the Fischer-Hepp rearrangement in clay micro-environment (*Scheme 15*).[45] Three different types of clays, such as montmorillonite K10, KSF and



Scheme 15

bentonite clays as well as cation (M^{n+})-exchanged montmorillonite K10 (where, $M^{n+} = H^+$, Fe^{3+}, Al^{3+}, Cr^{3+}, Co^{2+}, Mn^{2+} *etc.*) were employed for this transformation. The rearranged product, N-nitroso-N-methylaniline (**41**) was found to be the major product along with N-methylaniline and aniline being formed in the solid state reaction. The reaction shows that the rearranged product predominates under polar protic solvents.

$FeCl_3$-impregnated montmorillonite K10 was employed to catalyze the Beckmann rearrangement of diaryl ketoximes (**42**) in toluene under reflux to produce the rearranged products (**43**) and (**44**) along with the deoxymated product (*Scheme 16*).[46] Formation of the products was



42 **43** **44**

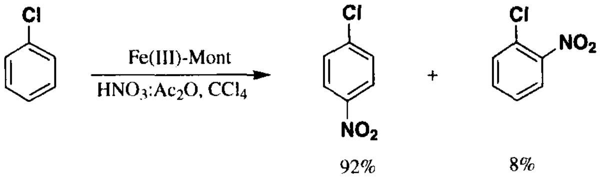
Scheme 16

observed within 5-12 min and the yields are ~98-100%. Rearrangement of the phenyloxiranes in presence of clay to produce aldehydes, ketones and cyclic ethers has been reported.[47] Benzyl phenyl ether can undergo rearrangement regiospecifically to produce *o*-benzylphenol as the exclusive product in presence of montmorillonite K10 as catalyst.[48]

4. Nitration

Aromatic substrates (*e. g.* benzene, toluene, anisole *etc.*) are nitrated by an activated mixture of a silicate (*e. g.* montmorillonite clay, aluminosilicates *etc.*) optionally modified with metal nitrates (*e. g.* $Al(NO_3)_3$, $Bi(NO_3)_3$, $Cd(NO_3)_2$, *etc.*) and acid anhydride (*e. g.* Ac_2O, propionic anhydride, trifluoroacetic anhydride *etc.*) and an organic solvent (*e. g.* $CHCl_3$, CCl_4, DCM *etc.*). Thus, addition of HNO_3 to the above reaction mixture results in the formation of the nitrated product (*e. g.* 1,3-dinitrobenzene, 2,4-dinitrotoluene *etc.*).[49] This process can produce either mono or polynitrated aromatic compounds depending upon the condition selected and with respect to the aromatic substrate. Thus, it is an industrially advantageous process due to high yield, cost effectiveness and greater safety than previously used nitration methods.

The Fe(III)-exchanged montmorillonite clay was employed to achieve the high *para*-selective nitration of chlorobenzene.[50] The nitration is carried out using fuming nitric acid and acetic anhydride in CCl_4 in the presence of Fe(III)-exchanged montmorillonite as the catalyst. It is possible to achieve the *para*-selectivity up to 92% and the yield of the product is about 90% (*Scheme 17*). The porous nature of the montmorillonite results in the shape selective nitration. Similar report of nitration of toluene and chlorobenzene with *para*-selectivity has been reported by Peng *et al.*[51]



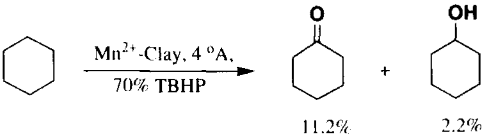
Scheme 17

A facile solvent-free synthesis of β-nitrostyrenes from styrene and its substituted derivatives used inexpensive "doped" clay reagents, clayfen and clayan.[52] A one-pot nitration of aromatic compounds by clay-cop, a reagent consisting of an acidic montmorillonite clay impregnated with anhydrous cupric nitrate has been reported.[53] By simple variation of the conditions, it is possible to drive the reaction towards mononitration or polynitration. Both the yield and selectivities are superior to those obtained under homogeneous conditions. The successful mononitration of a variety of electron-rich aromatic substrates has been described, employing claycop as the nitrating agent.[54] Nitration of phenol was carried out using ferric nitrate and fluoridated clay (tonsil) and also using cupric nitrate and fluoridated clay.[55] Solvents of different polarity were employed as reaction media. The study shows that in solvents of low polarity the formation of the *para*-isomer is favored, while in solvents of high polarity the reaction is inhibited. The highest yields (of the order of 92%), were obtained using chloroform and carbon tetrachloride.

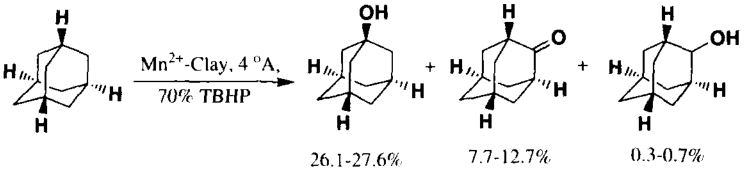
A study to examine the best clay-based catalyst to achieve high degree of the *para*-selective nitration of the chlorobenzene and to improve the yield of the product formation of the nitration reaction has been carried out.[56] The use of transition metals [Fe(III), Mn(III) and Cr(III)]-pillared clay has resulted in 94% *para*-selectivity of the nitration. The acid washed pillared clay calcined at 300° shows still higher activity than unactivated one. The activity of the cation-exchanged pillared clays both activated and unactivated towards *para*-selective product formation follows the order Cr(III)-acid activated pillared clay >Mn(III)-acid activated pillared clay >Fe(III)-acid activated pillared clay and the yield of the product formation follows the order Fe-AAPILC (Fe-acid activated pillared clay) > Cr-AAPILC > Mn-AAPILC.

5. Oxidation

Oxidation of alkanes such as cyclohexane, cyclooctane, adamantane and octane with 70% *tert*-butyl hydroperoxide (TBHP) in benzene in the presence of Mn^{2+}-exchanged clay as catalyst and 4Å molecular sieves produced the corresponding ketones and alcohols with high turn over number (*Scheme 18a and 18b*).[57]

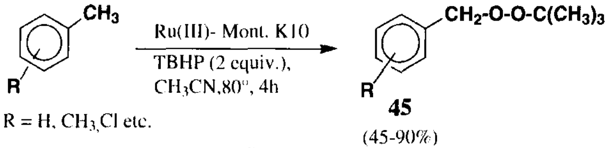


Scheme 18a



Scheme 18b

We recently reported the selective oxidation of alkyl arenes to aryl *tert*-butyl peroxides (**45**) with TBHP (*tert*-butyl hydroperoxides) catalyzed by Ru(III)-exchanged montmorillonite K10 clay (*Scheme 19*).[58]

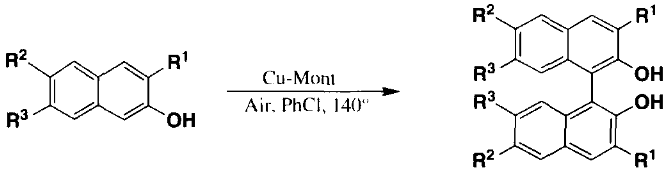


Scheme 19

The oxidation of aromatic alkenes with TBHP in the presence of Ru(II)-bipyridine anchored montmorillonite clay as catalyst and triethylamine produces mainly *vic-bis*(*tert*-butyldioxy)alkanes.[59] Bipyridylsilylated montmorillonite (bpy-mont.) prepared from H-montmorillonite and 6-(ethoxydimethylsilyl)-2,2'-bipyridine. Treatment of the bpy-mont. with $[RuCl_2(CO)_2]_n$ affords a novel clay catalyst Ru(II)-bpy. A similar oxidation of 2,3-dimethyl-1,3-butadiene affords 1,4- and 1,2-*bis*(*tert*-butyldioxy)alkenes. In the absence of triethylamine, the oxidation of 1,1-diphenylethylene gives 2-(*tert*-butyldioxy)-1-hydrodioxy-1,1-diphenylethane as a major product.

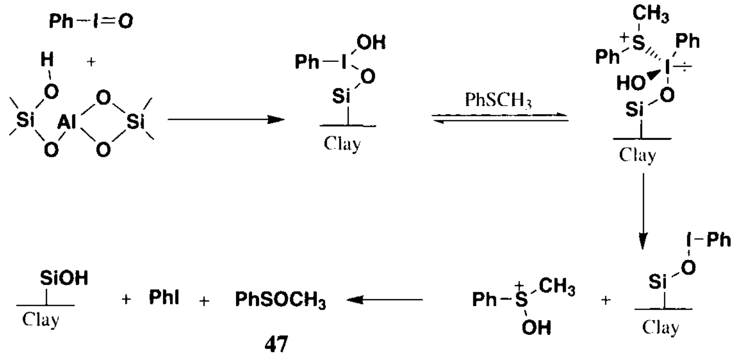
Oxidative cleavage of ketoximes with heterogeneous bentonitic clay supported Cu(II)-nitrates as a catalyst in hexane-acetone solvent system gave the parent ketone in 60-97% yield within 25 to 90 min.[60] Benzylic oxidation of substituted benzyl alcohol such as $XC_6H_4CH(OH)R$ (where R = H, Me and X = 2-, 3-, 4-MeO, 2-, 3-, 4-NO_2, 4-Br) are achieved using optimally water loaded montmorillonite K10 dopped with Fe(III)-nitrate (clayfen) yielding corresponding ketones.[61, 62] Alkyl, aryl and cyclic sulfides were rapidly oxidized to the corresponding sulfoxides in high yields upon microwave irradiation with Fe(III)-nitrate impregnated on clayfen clay under solvent-free conditions.[63] The conversion also occurs in refluxing DCM but requires much longer reaction time. The role of the support in acid-treated montmorillonite Cu(II)-nitrate oxidation reagents has been examined in an attempt to identify which structural features within the support are important in conferring reactivity to the supported nitrate.[64] Reactivity has been measured in the oxidation of benzyl alcohol to benzaldehyde using a series of progressively acid-treated clay supports, with a range of salt loading and following thermal activation at up to 180°. Optimum reactivity has been achieved with a salt loading of 2.7mmol/g support and following thermal activation at 130°. The most effective support was montmorillonite clay, which received only very brief acid treatment. It is proposed that the oxidation by supported nitrate operates most effectively by a mechanism, which involves acid sites on the support and the optimum support combines a high surface area and a high concentration of acid sites.

Copper-exchanged montmorillonite catalyzes the oxidative coupling of 2-naphthols under aerated conditions to give binaphthols (**46**) in 40–95% yields (*Scheme 20*).[65]



Scheme 20 **46**

An efficient oxidative coupling of thiols leading to the formation of S-S bond at pH 7.2 using Fe^{+3}-exchanged montmorillonite clay as heterogeneous catalyst in 80 to 90% yield has been described.[66] Clay-supported tetrabutylammonium periodate oxidizes benzylic alcohols to aldehydes efficiently without over-oxidation to acids. It also oxidizes aryl sulfides to sulfoxides selectively.[67] Dihydroxylation of styrene has been studied using iodosylbenzene as the oxidant in the presence of various modified bentonite clays (proton-exchanged clay, Fe(III)-exchanged clay, and Mn(III)-salen-exchanged clay) as catalyst.[68] Catalytic activity was higher for Fe(III)-exchanged clay in intermediate epoxide formation. Free Fe(III) species present in the interlayer space are responsible for its reactivity. The intermediate epoxide is converted to the corresponding diol at Bronsted acidic sites of the clay and the water present in the reaction media. Oxidation of alkyl, aryl and diaryl sulfides to sulfoxides (**47**) using iodosylbenzene supported on neutral montmorillonite K10, KSF and bentonite clay has been achieved in acetonitrile under heterogeneous conditions.[69] In this reaction, iodosylbenzene acts as an oxidizing agent in presence of montmorillonite or bentonite or some cation-exchanged such as Na^+, H^+, Al^{+3}, Cr^{+3} and Cu^{+2} clay (*Scheme 21*).

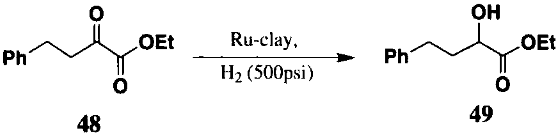


Scheme 21

A natural saponite was pillared with hydroxy-aluminum, hydroxy-chromium and hydroxy-chromium-aluminum solutions and the catalytic activity of these materials in the oxidation of acetone has been investigated.[70] Clay-supported non-chiral Mn(III)-salen catalyst were prepared by two methods, direct exchange of the complex or treatment of the Mn(III)-exchanged clay with the salen ligand;[71] the first method leads to more homogeneously distributed catalysts. The clays used are laponite, bentonite, and montmorillonite K10. All the solids promote epoxidation reactions with iodosylbenzene. However, the supported chiral catalyst leads to a slightly lower enantioselectivity. The recovery of the catalysts leads to a reduction of activity and mainly of enantioselectivity as in the case of the chiral catalyst, which cannot be related with leaching of complex. Spectroscopic studies indicate that the decomposition of the ligand is the main reason for this behavior.

6. Reduction

Ruthenium clay, prepared by the reaction of $RuCl_3.xH_2O$ with 3-phosphinopropyl- functionalized Fluka K10 montmorillonite, is an effective catalyst for the reduction of the α-ketocarbonyl group of α-ketoesters and α-ketoamides (50-89% yield). *e. g.* α-ketoester (**48**) is reduced by hydrogen at 500*psi* in the presence of Ru(III)-clay to give (**49**) in 87% yield (*Scheme 22*).[72]



Scheme 22

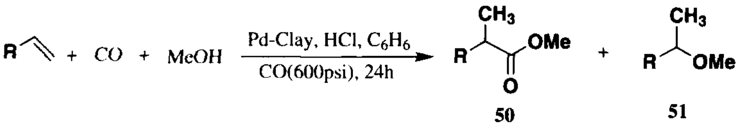
The same group has also reported the Ru(III)-clay catalyzed chemoselective hydrogenation of unsaturated esters, epoxides, sulfones and phosphonates.[73] In this case, the Ru(III)-clays were prepared by the reaction of $RuCl_3.xH_2O$ with montmorillonite-PPh_2 or montmorillonite-bpy and montmorillonite clays. The hydrogenation of organic substrates under 40atm. pressure at 70° has been described using ruthenium isopropoxide intercalated in the interlamellar layers of bentonite clay.[74] Thus hydrogenation of benzene gave cyclohexane selectively with a high turnover frequency (TOF) 0.98mol product per gram catalyst per hour. Similarly, toluene, *p*-xylene, nitrobenzene were also converted to their reduced products and hydrogenation of allylic alcohol gave propanol (TOF = 0.76). Hydrogenation of phenol at 120° and 45atm. pressure gave cyclohexanol (95%) and cyclohexane (5%) respectively with a TOF = 0.312. A novel bentonite clay catalyst containing a heterogenized Rh(I)-triphenylphosphine complex (Rh-bentonite) has been prepared *via* ion-exchange of a Hungarian Na^+-bentonite with Wilkinson complex $[RhCl(PPh_3)_3]$.[75] This clay catalyst was found to be efficient in the liq-phase hydrogenation of 1-octene, cyclohexene, norbornadiene, 1,5-cyclo- octadiene, phenylacetylene and cyclohexene-3-one. The catalytic activity for hydrogenation of benzene was also studied using lanthanum and nickel systems either supported on an Al-pillared montmorillonite clay or incorporated in a montmorillonite clay at 70-170° and atmospheric pressure in a differential bench scale reactor.[76] The liquid phase hydrogenation of styrene and 1-octene using Pd(II)-hexadecylammonium montmorillonite (Pd(II)-HDAM) catalysts was studied by Mastalir *et al.* [77] The reaction of styrene was found to be less dependent on the dispersion of palladium than that of 1-octene. The highest activities were observed for samples of low and medium palladium content. Use of nickel containing anionic clay minerals as precursors of catalysts for the hydrogenation of nitriles has been reported by Tichit *et al.*[78] Hydrogenations of acetonitrile and valeronitrile in the gas and liquid phases respectively were carried out on catalysts obtained from Ni/Mg/Al layered double hydroxides (LDHs) precursors of various Mg/Ni molar ratios. Selectivity to primary amine is higher than 90% obtained on catalysts with Mg/Ni molar ratios in the range 0.3-1.

Vanadium-doped titania-pillared montmorillonite clay was found to be a good catalyst for selective catalytic reduction of NO by ammonia.[79] The catalytic performance of these systems depends on its vanadium content. Our group also examined the catalytic efficiency of Ru and Rh-exchanged montmorillonite K10 clay for transfer hydrogenation using 2-propanol as hydrogen doner.[80] Although the reaction proceeds in good yields, the rate of the reaction is found to be rather slow.

7. Esterification

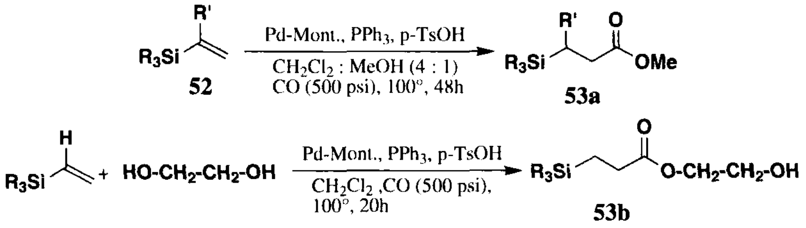
A process has been developed for preparation of methyl acetate by reacting methanol with acetic acid in the presence of a solid catalyst in gas phase.[81] The solid acid comprises Ru(II), Sn(II)-cluster complexes such as $[(Ph_3P)_2N][Ru(SnCl_3)]$ supported on activated charcoal, silica, clay mineral, copper oxide, alumina, titania and zirconia.

Palladium acetate immobilized on montmorillonite acts as an efficient catalyst for the alkoxyformylation of olefins with CO and methanol in the presence of PPh_3 and an acid promoter affording branched chain esters (**50**).[82] The reaction is regiospecific for aryl olefins as well as for vinyl benzoate and aliphatic olefins (*Scheme 23*).



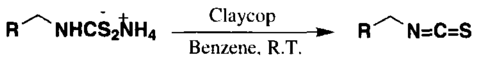
Scheme 23

The regiospecific alkoxyformylation of vinylsilanes (**52**) catalyzed by Pd-complex intercalated into montmorillonite in the presence of PPh_3 and *p*-toluenesulphonic acid (PTSA) afforded β-silylesters (**53a**) in high yield (22-95%) (*Scheme 24*).[83] The alkoxyformylation reaction of trimethylvinylsilane in the presence of a diol gives the monoesterification product (**53b**) in a regioselective manner.



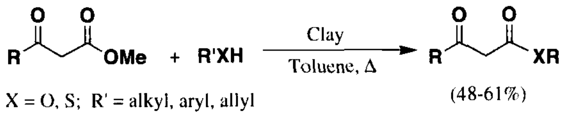
Scheme 24

A convenient and simple synthesis of alkyl, amino acid and peptides isothiocyanates by decomposition of corresponding ammonium dithiocarbamates using claycop under milder conditions has been reported by Yadhav *et al.*[84] The aryl dithiocarbamates well rapidly converted to aryl isothiocyanates but reaction rates are slow for alkyl dithiocarbamates (*Scheme 25*).



Scheme 25

We have reported that natural kaolinite clay catalyze the transesterification and transthioesterification of β-ketoesters with variety of alcohols and thiols very efficiently.[85] The clay has been found to be an efficient catalyst in transesterification of long chain alcohols, unsaturated alcohols and phenols to give the corresponding β-ketoesters in high yields. For the first time, transthioesterification of β-ketoesters with variety of thiols has been achieved under catalytic conditions (*Scheme 26*).

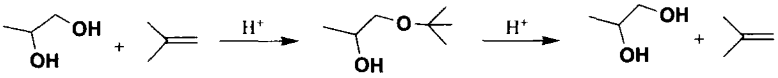


Scheme 26

Montmorillonite K-10 and KSF are highly efficient catalysts for the acetylation of a variety of alcohols, thiols, phenols and amines with acetic anhydride. Amino groups can be selectively acetylated in the presence of hydroxy groups, while the hydroxy groups can be preferentially acetylated in the presence of thiol groups.[86] But selectivity is not observed for primary and secondary hydroxy groups. The catalysts were inefficient for the acetylation of tertiary alcohols. These catalysts were also effective for acylations with acetyl chloride and benzoyl chloride. Cyclic anhydrides such as succinic anhydride, maleic anhydride, phthalic anhydride and acid chloride such as *p*-toluenesulfonyl chloride are less reactive than acetic anhydride and acyl chlorides.

8. Etherification

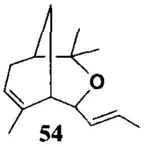
A two-step procedure for the separation of isobutene from mixed C_4 hydrocarbon streams such as Raffinate-1, has been demonstrated using solid acid catalysts.[87] The procedure involves initial etherification of the C_4 mixture with a suitable aliphatic diol such as ethylene glycol or 1,2-propylene glycol to give the corresponding glycol mono-*tert*-butyl ethers; de-etherification of these monoethers was achieved at higher temperature to yield pure isobutene and the glycol. Suitable classes of solid acid catalysts include acidified montmorillonite clays and heteropoly acids dispersed on Gr IV oxides, such as 12-tungstophosphoric acid on titania (*Scheme 27*).



Scheme 27

The allyl glycidyl ethers were prepared by reaction of C_{1-5} unsaturated alcohols with epichlorohydrin in the presence of activated clay without formation of by-product dichlorophenol. The alkali-mediated cyclization neither left nor produced chlorine-containing compounds.[88] The yields of the ether obtained are nearly 88%.

The use of askanite-bentonite clay in the cycloaddition of carbonyl compounds to olefin results in the formation of the cyclic ethers.[89] For example, cycloaddition of alloocimene to α,β-unsaturated carbonyl compounds produces cyclic ether such as (**54**).

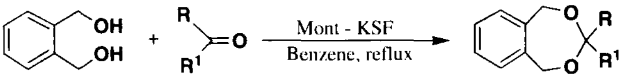


54

KSF catalyses the selective O-alkylation of various primary allylic and benzylic alcohol when reacted with different orthoester at room temperature to yield ethers in moderate to high yields.[90] The preparation of cholesteryl ethers from alcohols and phenols with cholesterol was carried out at 50-70° using montmorillonite K-10 catalyst in chloroform or cyclohexane.[91]

9. Acetal formation

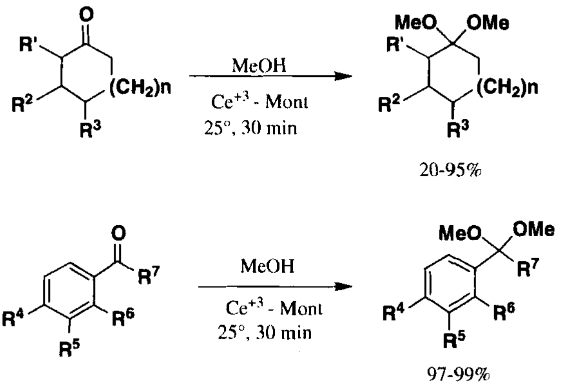
A mild and efficient procedure for the protection of carbonyl compounds with diol such as (**55**) to yield 1,5-dihydro-3H-2,4-benzodioxepines (**56**) in high yields has been described by using KSF catalyst (*Scheme 28*).[92]



55 **56**
(33-99%)

Scheme 28

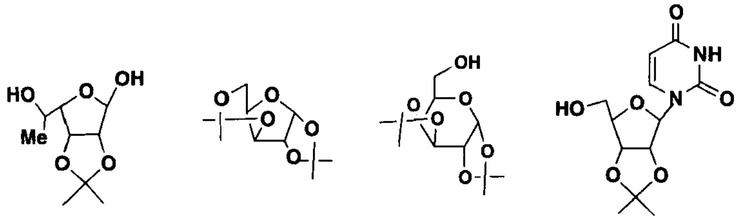
The protection of alcoholic and phenolic hydroxy groups can be accomplished with 3,4-dihydro-2H-pyran in the presence of a readily available and inexpensive Spanish sepiolite as a heterogeneous acidic clay catalyst.[93] The acetalization of carbonyl compounds with methanol was investigated in the presence of cation (M^{n+})-exchanged montmorillonite clays (where, $M^{n+} = Ce^{3+}, Zr^{4+}, Fe^{3+}, Al^{3+}, Zn^{2+}, H^+$ and Na^+) (*Scheme 29*).[94]



Scheme 29

Ce^{3+}-montmorillonite was found to be the most effective catalyst for substrate selective acetalization. Cyclohexanones, benzaldehydes and acid-sensitive 2-furancarboxaldehyde were also converted nearly quantitatively to the corresponding acetals in methanol at 25° in the presence of Ce^{3+}-montmorillonite The substrates were activated by a Lewis acidic Ce^{3+}-cation present in the interlayer space.

The protection of the diol in sugars under milder reaction condition using acetone in presence of clay catalyst has been reported by Yashihar *et al.*[95] Thus, treatment of various monosaccharides and/or ribonucleosides with acetone in the presence of montmorillonite K10 clay results in the formation of isopropylidene protection of the diol in good yield, (**57–60**) (*Fig 2*).

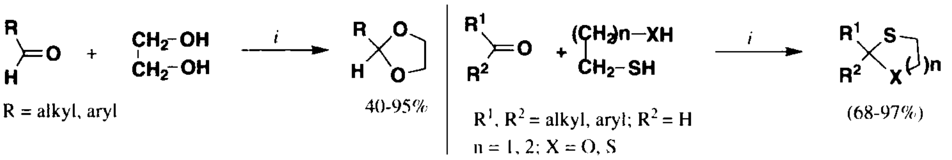


57 **58** **59** **60**

Fig. 2

The preparation of diacetals from 2,2-*bis*(hydroxymethyl)-1,3-propanediol with aldehydes and ketones catalyzed by montmorillonite clays was reported by Zhang *et al.* [96] The reaction was carried out using benzene or toluene as solvent. However, the use of microwave for these reactions may help in carrying out the reaction without solvent. Thus, protection of aldehydes or ketones as acetals or ketals catalyzed by KSF clay was readily achieved from orthoformates or 1,2-ethanediol under microwave irradiation without solvent within short times.[97] The use of microwave irradiation reduces the reaction time. Sandhu *et al.* reported the use of montmorillonite K10 clay for the synthesis of acetals in dry media under microwave activation.[98] For example, the treatment of 4-chlorobenzaldehyde with acetic anhydride in the presence of montmorillonite K10 gave 4-chlorobenzylidene diacetate [i.e.,(4-chlorophenyl)methanediol diacetate].

Our group has also recently reported that natural kaolinite clay can very efficiently catalyze the acetalization and thioacetalization of carbonyl compounds with ethane-1,2-diol and ethane-1,2-dithiol respectively[99,85] (*Scheme 30*). This catalyst is found to be superior to the montmorillonite K10 or KSF clay for acetalization.



i) Clay (10 wt%), benzene, reflux, 2h

Scheme 30

The use of microwave irradiation increases the rate of reaction of carbonyl compounds with 1,2-ethylenedithiol in the presence of montmorillonite K10 clay to give the products in high yield under solvent-free conditions.[100]

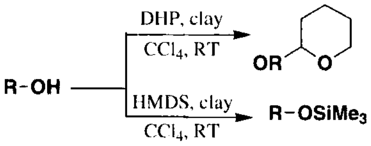
Aldehydes were cleanly and selectively converted to the corresponding dithioacetals nearly quantitatively (70-98%) with catalytic amounts of Fe(III)-exchanged montmorillonite even in presence of ketone.[101] Al-Fe-pillared montmorillonite clay was used for the preparation of acetals from various aldehydes at room temperature in DCM in quantitative yield. Conversion of short linear aldehyde is higher than long chain as well as that of C2- and C3-alkyl substituted ones.[102] However, good conversion can be achieved for the latter substrates by increasing the temperature to 60°. Although this method uses metal exchanged or pillared clays for acetalization of aldehydes and ketones, this reaction also can be catalyzed by montmorillonite K10 in absence any metal on it. [103] However, under similar condition benzophenone do not undergo ketal formation.

A facile preparation of 1,1-diacetates from aldehydes with montmorillonite clay as catalyst at room temperature has been carried out in excellent yield (<98%).[104] Montmorillonite K10 and KSF give similar results (0-2% variation) in terms of reaction time and yield. It is observed that 2-hydroxy and 3-methoxy-4-hydroxybenzaldehyde undergo triacetate formation, while 4-hydroxybenzaldehyde and *p*-(N,N-dimethylamino)benzaldehyde fails to react. This is possibly due to the selective adsorption of the substrate over clay from the side of the OH group and amino group. (*Scheme 31*).

$$\mathrm{RCHO} \xrightarrow[\mathrm{Ac_2O,\ R.\ T.\ 0.2\text{-}6h}]{\mathrm{Mont.\ K\ 10\ or\ KSF}} \underset{<98\%}{\mathrm{RCH(OAc)_2}}$$

Scheme 31

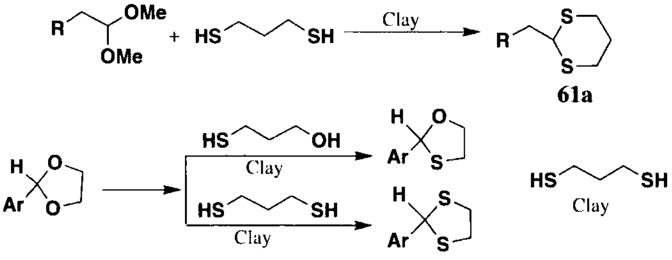
Kaloinite clay can also be a very effective catalyst for the protection of alcohols. We have reported that alcohols can be very conveniently protected as its OTHP or trimethylsilyloxy derivatives by reacting alcohols with 3,4-dihydropyrane (DHP) or hexamethyldisilazane (HMDS) in presence of kaolinite clay (*Scheme 32*).[105]



Scheme 32

A facile preparation of trimethylsilyl ethers of alcohols and phenols with 1,1,1,3,3,3-hexamethyldisilazane, catalyzed by montmorillonite K10 at room temperature has been reported.[106] Desilylation of the trimethylsilyl ethers was also carried out by montmorillonite K10 catalyst in methanol at ambient temperature in high yields.

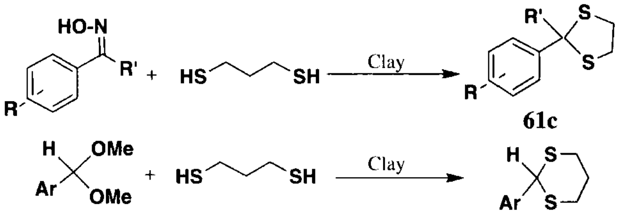
We have recently described the transdithioacetalization of acetals, ketals, oximes, enamines and tosylhydrazones using 1,2-ethanedithiol and 1,3-propanedithiol in presence of naturally occurring kaolinite clay as an efficient catalyst to give high yields of transdithiacetalyzed products (**61a-b**) (*Scheme 33a*) and (**61c-d**) (*Scheme 33b*).[107]



61a

61b

Scheme 33a

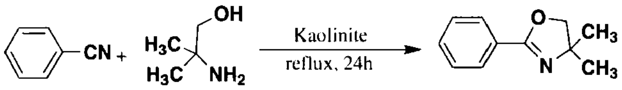


61c

61d

Scheme 33b

Naturally occurring kaolinite clay has been found to be an effective catalyst for transformation of aromatic and aliphatic nitriles with 1,2-aminoalcohols to their corresponding 2-oxazolines (**62**),[108] thus providing an effective method for the protection of nitrile functionality (*Scheme 34*).

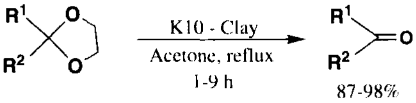


62 (56-96%)

Scheme 34

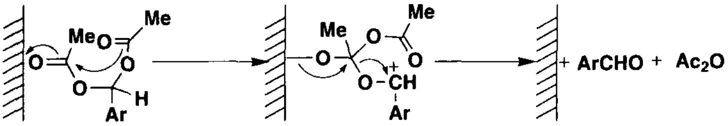
10. Acetal Cleavage

A facile cleavage of acetals has been carried out in excellent yield in wet acetone at reflux in presence of montmorillonite K10 clay as the catalyst (*Scheme 35*).[109] The product is isolated by simple filtration of the catalyst and evaporation of the acetone under vacuum.



Scheme 35

Carbonyl groups can be regenerated from their oximes, phenylhydrazones and tosylhydrazones derivatives using clay supported ammonium nitrate (clayan) under microwave irradiation.[110] Li *et al.* reported the deprotection of variety of 1,1-diacetates in 86-98% yields under milder reaction conditions using montmorillonite K10 or KSF clays in refluxing DCM or benzene as the solvent.[111] The propose mechanism of the deprotection reaction is depicted in the scheme (*Scheme-36*).



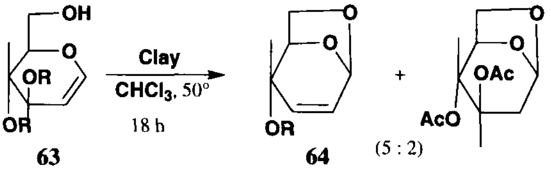
Scheme 36

Thioacetals and ketals derived from aldehydes and ketones are readily deprotected by clayfen under solvent-free reaction condition.[112] Most of the time the reaction takes place by simple mixing of clayfen and the thioacetals; in some cases, slight warming may be required and may be performed using microwave irradiation. A variety of thioacetals and dithianes are deprotected to the carbonyl compounds under mild conditions using clayan.[113] This procedure of deprotection of thioacetals, dithiolanes and dithianes was later simplified by carrying out the reaction under microwave irradiation in presence of clayan as catalyst under solvent-free condition.[114] Natural kaolinitic clay can be used for selective regeneration of carboxylic acids from their corresponding allyl or cinnamyl esters.[115]

Another interesting use of deprotection chemistry in presence of clayan is the preparation of pyrrolo[2,1-c][1,4]benzodiazepine (PBD) imines *via* ethanethiol deprotective cyclization.[116] A significant improvement in yield over the customary $HgCl_2/HgO$ deprotective cyclization method was observed and the reaction proceeded without racemization.

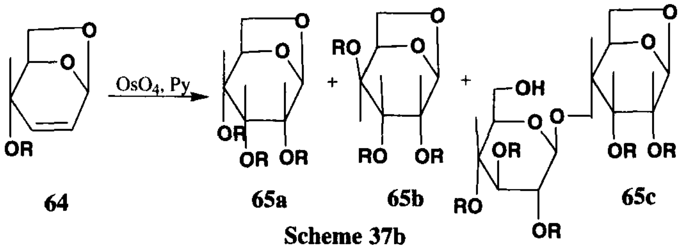
11. Asymmetric Synthesis

Montmorillonite clay supported silver agent (claysil) has been used in the intramolecular Ferrier reaction of 6-hydroxy glycals, (**63**) to unsaturated sugars (**64**) (*Scheme 37a*).



Scheme 37a

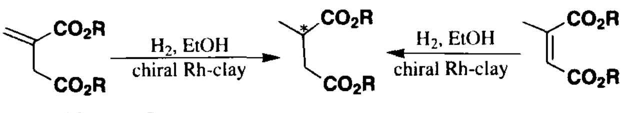
The unsaturated sugars (**64**) obtained were stereoselectively dihydroxylated leading to the rare 1,6-anhydrosaccharides (**65**) (*Scheme 37b*).[117] The formation of disaccharide is an important process otherwise made by lengthy sequence of reaction in poor yield. In presence of Hg over clay, the reaction time gets reduced to eight hours whereas in presence of claysil reaction found to complete within two hours. The (**65a**) is only the product formed in both the cases. Synthesis of (D)-allosan and (D)-gulosan were also achieved in a similar manner.



Scheme 37b

Several clays, exchanged with cationic Cu(II)-*bis*(oxazoline)complexes have been developed for heterogeneous asymmetric catalysis. In the presence of these catalysts, asymmetric cyclopropanation of styrene has been achieved with ethyl diazoacetate.[118] This study demonstrated that the enantioselectivity of this catalyst is comparable to that of homogeneous ones and predominant formation of *cis*-cyclopropane was observed. These heterogeneous asymmetric catalysts can be reused several times without loosing their activity.

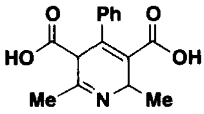
The synthesis of chiral rhodium complex intercalated into modified smectite and its use for asymmetric hydrogenation have been reported by Sento *et al.*[119] Asymmetric hydrogenation of α,β-unsaturated carboxylic acid esters containing ester group of various chain lengths was studied on modified hectorite (a type of smectite).[120] Hectorite (HT)-supported rhodium complex catalysts were prepared by the intercalation of $[Rh(P^*\text{-}P^*)(COD)]^+$($P^*\text{-}P^*$=(S)-2,2'-*bis*(diphenylphospino)-1,1'-binaphtyl (BINAP) and (S) or (R)-N,N'-Dimethyl-1-[(S)-1,2-*bis*(diphenylphospino)-ferrocenyl]ethylamine (BPPFA), (COD = cyclooctadiene) into sodium hectorites in MeCN/H_2O. The dependence of selectivity on employed solvents and bulkiness of the ester groups suggested that the interaction between substrate and the active sites increased in the interlayer space, thus enhancing the asymmetric selectivity. The enantioselectivity achieved in the order of 4-88% ee. Significant enantioselectivity was observed only in the case of (*n*)-butyl ester (<88%) using ethanol as solvent (*Scheme 38*).



Scheme 38

12. Synthesis of Heterocycles

Azabenzenes derived from aromatic aldehydes [*i. e.* benzaldehyde(phenylmethylene)hydrazone] undergo montmorillonite K10 clay catalyzed cyclization with 3-aminocrotonate to afford 1,4-dihydro-2,6-dimethyl-4-phenyl-3,5-pyridinedicarboxylates (**66**) as major product and 6-[(methoxycarboxyl)-methylene]-3-methyl-4-phenyl-3-pyridinecarboxylates (**67**) and 3-(methoxy- caboxyl)-2-methyl-6-phenyl-4-pyridineacetates as minor products (**68**).[121]



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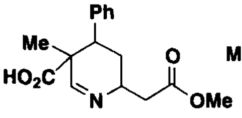

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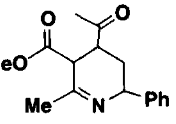
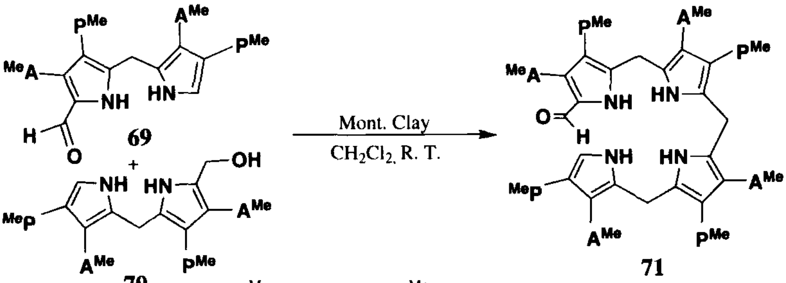


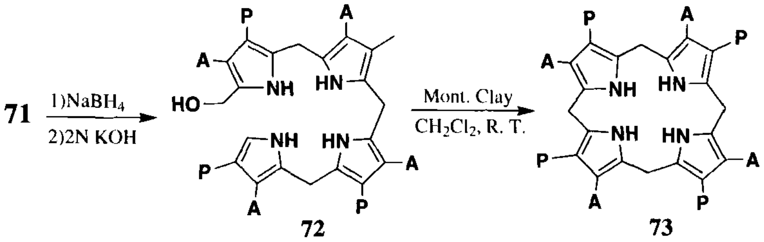
68

N-Substituted 2,5-dimethylpyrroles were prepared using IR energy in presence of a clay catalyst, in dry medium.[122] Thus, cyclocondensation of 2,5-hexanedione with aniline gave 2,5-dimethyl-1-phenylpyrrole. Linear tetrapyrroles, *e. g.* (**71**), were obtained by condensation of hydroxymethyldipyrrolmethanes (**70**) with free dipyrrolmethanes (**69**) using montmorillonite clay as acid catalyst (*Scheme 39a*).[123] After reduction of the formyl group in (**71**) resulted hydroxymethylbilanes (**72**), were cyclized to uroporphyrinogens (**73**) in presence of clay (*Scheme 39b*).



$A^{Me} = CH_2CO_2Me$; $P^{Me} = CH_2CH_2CO_2H$

Scheme 39a

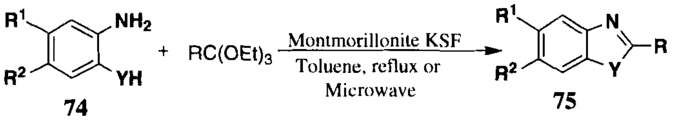


A = CH_2CO_2H; P = $CH_2CH_2CO_2H$

Scheme 39b

Bentonite K10 clay has been used to catalyze the formation of enamino carbonyl derivatives, 2-methyl-1H-benzimidazoles. Hantzch 1,4-dihydro pyridines, Hantzch pyridines 2-substituted 1,3-diphenylimidazolidines and tetrahydropyranylbenzoxazoles.[124] Thus, bentonite K10 clay catalyzed the nucleophilic addition of EtO_2CCH_2COMe with benzylamine forms $EtO_2CCH{=}CMeNHPh$ in 90% yield.

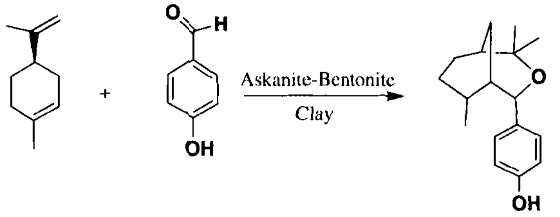
Condensations of ortho esters with *o*-substituted aromatic amines (**74a-d**) into a variety of heterocycles (**75**) have been reported over KSF clay as a catalyst in toluene under reflux or without solvent under microwave irradiation (*Scheme 40*).[125]



74 a) R^1 = H, Y = NH; b) R^1 = CH_3, Y = NH; c) R^1 = H, Y = O; d) R^1 = H, Y = S, R^2 = H, CH_3

Scheme 40

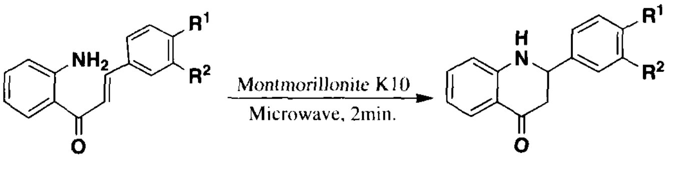
A modified procedure to the Hantzch method to obtain pyridines in a one pot reaction using ammonium nitrate and bentonite clay as catalyst under microwave irradiation has been described.[126] The reaction of salicylaldehyde with some dienes with hydroxyolefin of natural origin on the askanite-bentonite clay under milder condition was shown to undergo double heterocyclization forming compound with xanthene framework, condensed with tetrahydropyran or tetrahydrofuran rings.[127,128] For example, condensation of *p*-hydroxybenzaldehyde with R(+)-limonene gives formation of 2,2,6-trimethyl-4-(4-hydroxyphenyl)-3-oxabicyclo[3,3,1]non-6-ene (**76**) (*Scheme 41*).



Scheme 41

76 (39%)

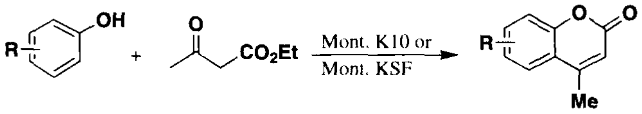
The microwave irradiation of 2-aminochalcone (**77**) under solvent-free dry condition on montmorillonite K10 clay provides easy and efficient procedure for the formation of 2-aryl-1,2,3,4-tetrahydro-4-quinolones (**78**) in pure form and good yields.[129] This tetrahydro-4-quinolones serves as valuable precursors to medicinally important 2-aryl-4-quinolones bearing substituent in either of the aromatic rings (*Scheme 42*).



77 **Scheme 42** **78** (70-80%)

The microwave assisted synthesis of heterocyclic fused quinones in dry media has been achieved using montmorillonite K10, quartz and feldspar clays *via* cyclization of substituted 2-thienobenzoic acids. Microwave irradiation accelerates the rate provides higher yield than conventional heating (21-92%).[130]

A simple and rapid method for the synthesis of flavones was described *via* a solid-state dehydrative cyclization of *o*-hydroxydibenzoylmethanes on a clay surface using microwave.[131] Montmorillonite clay is used to synthesize coumarins (**79**) *via* Pechmann condensation of phenol and ethyl acetoacetate (*Scheme 43*).[132]



79

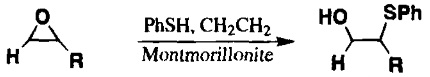
Scheme 43

13. Miscellaneous

The synthesis of diaryl carbonates from the reaction of phenols with phosgene or phenyl chloroformate in presence of montmorillonite clay catalyst has been patented.[133] A new method or production of 2-phenylbenzoxazole *via* cyclocondensation of 2-aminophenol with benzoic acid in the presence of montmorillonite clay has been reported.[134] Condensation of indoles with carbonyl compounds in the presence of montmorillonite clay produces *bis*(indol-3-yl)methanes in good yield; an extension of this procedure, involving nucleophilic ring opening of oxiranes, produces 1,2-*bis*(indol-3-yl)ethanes.[135]

The partial dehydration of glucose to hydroxymethylfurfural (HMF) and the subsequent rehydration of HMF to formic acid and 4-oxopentanoic acid in aq. solution was promoted by acidic pillared clay catalyst, including Al, Cr, Fe-pillared montmorillonite provided the highest glucose conversion rate with 100% in 12h at 150°.[136] A simple and highly efficient synthesis of α-azidoketones from readily accessible α-tosyloxyketones and sodium azide using recyclable phase-transfer catalysts such as surfactant pillared clays was reported by Varma *et al.*[137] Michael addition of imidazole and benzimidazole to alkyl propiolates can be promoted by montmorillonite K10 clay affording alkyl 3-(imidazol-1-yl)acrylates and alkyl 3-(benzimidazol-1-yl)acrylates, respectively.[138] The Michael adduct of 2-mercaptobenzimidazole undergoes cyclization in the presence of a clay catalyst to give 4-oxo-4H-[1,3]thiazino[3,2-a]benzimidazole. Bolourtchian and coworkers reported the reductive coupling of carbonyl compounds with trimethylchlorosilane on montmorillonite K10 clay in a microwave oven with quantitative yields of *bis*(trimethylsilyl)pinacols.[139] Recently a patent described a method for preparing arylaminoalkylidenemalonate derivatives in a single step, by reacting an aromatic amine with an alkyl malonate and an ester or an orthoester in the presence of clay catalyst.[140] The invention also concerns a method for obtaining 4-hydroxyquinoline-3-carboxylic acid derivatives or corresponding esters from arylaminoalkylidenemalonates prepared by said method. Thus, methyl (3-benzyloxy-4-butylanilino)methylenemalonate was prepared in 76% yield by montmorillonite clay catalyzed condensation of methyl malonate with 3-benzyloxy-4-butylaniline.

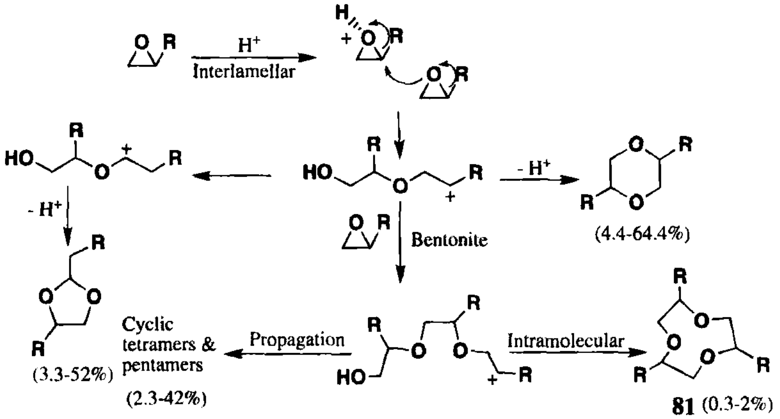
Montmorillonite clay catalysed regioselective ring opening of oxiranes by thiophenols was achieved under heterogeneous conditions to produce *β*-hydroxy sulfides (**80**) in 55 to 75% yields in 25 to 60min (*Scheme 44*).[141]



Scheme 44

The nucleophilic ring opening of oxiranes with trimethylsilyl azide, trimethylsilyl cyanide and aniline was also achieved by using Mn-salen immobilized on montmorillonite clay.[142] Bentonite clay mediated cylooligomerization of epoxides lead to a new route in a one-pot synthesis of crown ethers (**81**), thus making possible the synthesis of substituted 1,3-dioxolane, 1,4-dioxanes, 9-crown-3,12-crown-4 and 15-crown-5 (*Scheme 45*).[143]

A recent patent described the preparation of 1-alkoxy-1-methylthiomethyl phenyl ketones from (2-oxo-4-phenyl)butylmethyl sulfoxides in presence of clay catalysts.[144] For example, treatment of p-$MeOC_6H_4COCH_2SOMe$ with ethanol in the presence of KSF at 73° for 7h to give 88% p-$MeOC_6H_4COCH(OEt)SMe$.

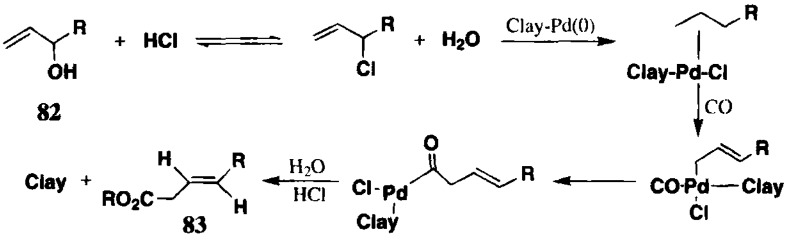


Scheme 45

A process has been developed for the synthesis of low molecular weight glycol ether from oxiranes, water and α-olefins in presence of acid catalyst such as 1,2-ditungstophosphoric acid and montmorillonite clay.[145] This is a useful substitute for carcinogenic ethylene glycol monomethyl and monoethyl ether as paint solvents. Cyclic and linear oligomerization of 3,4,5-trimethoxybenzyl alcohol with a bentonite clay as catalyst has been reported.[146]

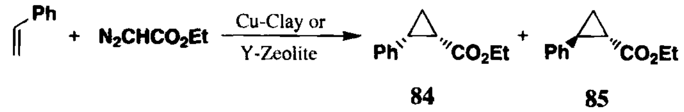
A simple and highly selective non-phosgene route has been developed for the preparation of alicyclic and/or aromatic, mono, di and triurethanes from the corresponding amine by montmorillonite bipyridinyl palladium(II) acetate as a catalyst *via* oxidative addition of carbonmonoxide in presence of sodium iodide as a promoter.[147]

Palladium(II) acetate immobilized on montmorillonite clay is an effective catalyst for carbonylation of secondary allylic alcohols (**82**) with carbon monoxide in presence of triphenylphosphines and acid promoter, affording β,γ-unsaturated acid (**83**) in 39-56% isolated yield.[148] The reaction occurs without isomerisation of C-C double bond and the reaction is regio and stereospecific with the E-isomer formed as the only product. A small amount of lactone was observed as secondary product (*Scheme 46*).



Scheme 46

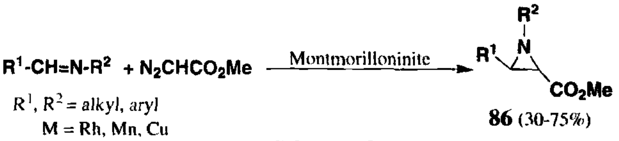
Cyclopropanation of styrene was carried out using ethyl diazoester in presence of heterogeneous catalyst such as Cu(II)-exchanged clays *e.g.* bentonite, laponite, montmorillonite K10 and 'Y'-zeolite.[149] In the case of Cu(II)-exchanged montmorillonite K10, the *cis*-isomer (**84**) is the major product, where as other catalysts lead preferentially to the *trans*-isomer (**85**) (*Scheme 47*).



Scheme 47

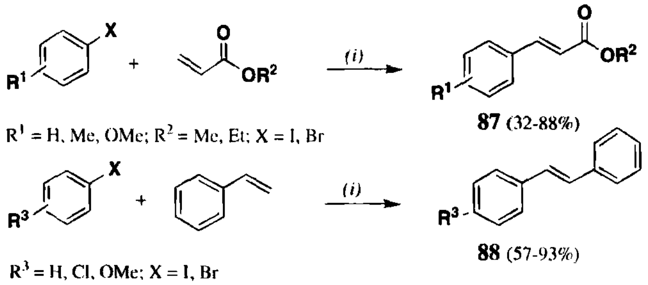
Several chiral Cu(II)-*bis*(oxazoline) complexes were supported by cation-exchange in laponite, bentonite and montmorillonite K10 and their catalytic performances were compared in the benchmark cyclopropanation reaction of styrene with ethyl diazoacetate.[150] The results depended on the nature of the support, the chiral auxiliary, the precursor and solvent used to carry out the cation-exchange. The best results are obtained when laponite is used as the support. The interaction with the support led to a modification of the stereochemical course of the reaction, leading to an increase of the *cis*-cyclopropanes compared to that observed in the homogeneous phase. Some of the catalysts can be recovered and reused, without affecting the catalytic activity and enantioselectivity. We have also carried out the same reaction of cyclopropanation over Cu(II)-exchanged clays.[151] Cyclopropane carboxylates were prepared from alkenes and methyl diazoacetate using Cu(II) and Rh(III)-exchanged montmorillonite K10 clays as catalysts in good yields. The *trans*-isomers were the major products in most of the cases. Rh-clay gave better *trans*-selectivity than Cu-clay.

We have developed a catalytic method for the preparation of *trans*-aziridines (**86**) from imine and methyl diazoacetate using Rh(III) and Mn(II)-montmorillonite K10 clay (*Scheme 48*).[152]



Scheme 48

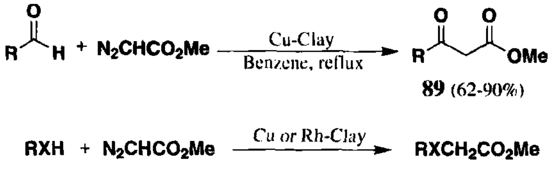
Vinylation of aryl halides (Heck reaction) catalyzed very efficiently by Pd(II) and Cu(II)-exchanged montmorillonite clays to provide unsaturated compounds (**87**) and (**88**).[153] We have examined various Cu-exchanged as well as Pd-exchanged montmorillonite and both Pd(II), Cu(II)-exchanged montmorillonite K10 clay for the Heck reaction and found that best result was obtained if both palladium and copper are present in the same catalyst system (*Scheme 49*).



(*i*) Pd-Cu-Mont. K 10, K_2CO_3, DMF, reflux

Scheme 49

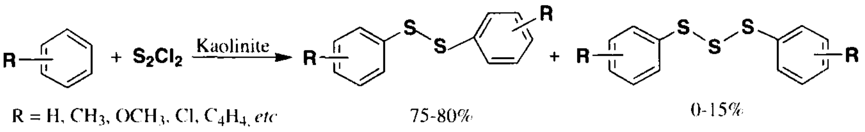
We have reported the Cu(II)-exchanged montmorillonite K10 clay efficiently catalyzes the reaction between aldehydes and diazoester for the formation of *β*-keto esters (**89**) in high yields.[154] This catalyst can also promote the insertion reaction of carbenes into NH and SH bond of amines and thiols respectively. However, it cannot catalyze the insertion reaction of carbene into OH bonds which may be accomplished in the presence of Rh(III)-exchanged clay; the reaction proceeds well when the alcohol itself is used as solvent (*Scheme 50*).



Scheme 50

The reactions of terpenoids of the *p*-menthane and carene with aromatic aldehydes over askanite-bentonite clay resulted in the formation of various heterocyclic compounds.[155] The reactions of terpene olefin derivatives with aldehydes in the presence of the same clay provide polyheterocyclic compounds.[156] For example, camphene reacted with formaldehyde in toluene at 100° to give the cyclised product. The reaction of methyl benzoate with NH_3 was studied over montmorillonite K10 clay at temperature 280-340°C.[157] Benzonitrile, benzoic acid, benzamide, N-methylbenzamide, and methanol were formed as products in varying amounts. The clay catalyst was equally active for other aromatic and aliphatic esters. The actual pathways leading to formation of products was studied in detail. The adsorption study of ammonia and pyridine over clay catalyst shows that, the ammonia adsorbed on the acidic Al-OH sites forms ammonium ions and participate in the reaction. The Lewis acidic sites are likely to be involved in the formation of benzonitrile.

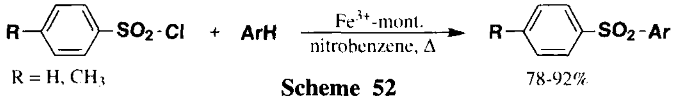
We have reported the method for the synthesis of symmetrical 4,4'-arene disulfides in the presence of kaolinite clay catalyst with sulfur monochloride.[158] An interesting feature of this method is the completely regiospecific formation of 4,4'-arene disulfides over sterically congested 2,2'-arene disulfides (*Scheme 51*).



Scheme 51

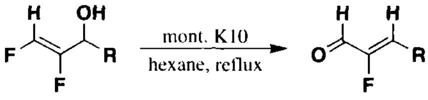
Both the montmorillonite K10 and modified-montmorillonite clays such as cation-exchanged and surfactant-pillared clays catalyzes the cleavage of carbon-sulfur single bond resulting in desufurization of organic sulfides in high yields.[159] Metal-exchanged pillared clays (PILCs) were studied as catalysts for selective catalytic reduction (SCR) of NO by ethylene.[160] Cu, Zr, Fe, Co, Ti, Ga, Al and Ce-metal is used for the pillaring study. Cu-Ti-PILC was found to be the most effective catalyst. The catalytic activity can be increased by doping 0.5% of Ce_2O_3 on Cu-Ti-PILC.

Fe(III)-exchanged montmorillonite clay catalyzed the Friedel-Crafts sulfonylation of arenes with aryl sulfonyl chloride to the corresponding sulfones in excellent yield (*Scheme 52*).[161]



Scheme 52

Aryl substituted α,β-difluoroallyl alcohols (**90**) were readily hydrolyzed in the presence of a catalytic amount of montmorillonite K10 in hexane at reflux temperature for 1h to give the corresponding (Z)-α-fluoro-β-aryl substituted acrylaldehydes (**91**) in good yields (*Scheme 53*).[162]



90 **Scheme 53** **91** (64-78%)

II. CONCLUSION

Clays are widely available in nature and find wide applications as solid catalysts. They can be modified easily by exchanging or pillaring with various transition metal-cations. Their properties can be suitably molded for a specific catalytic activity. A large number of organic reactions catalyzed by clays are being reported every year. These clays both in the natural as well as modified forms exhibit high regioselectivity, enhanced rate, excellent yields and unusual reactivity pattern in various organic reactions. Clays being inexpensive, readily available and reusable solid catalyst, show tremendous potential for many industrial reactions such as nitrations, alkylations, acylations, oxidations, reductions, *etc* asymmetric catalysis using clays as catalysts holds promise in the future work.

III. ABBREVIATIONS

Ac	Acetyl
Ar	Aryl
BET	Braunner-Emmette-Teller
BINAP	2,2'-*bis*(diphenylphophino)-1,1'-binaphthyl
CO	Carbon monooxide
COD	Cyclooctadiene
Clayfen	Ferric-nitrate dopped clay
Claysil	Silver supported clay
DMAD	Dimethyl acetylenedicarboxylate
DCM	Dichloromethane
DHP	Dihydropyran
DMF	Dimethyl formamide
Et	Ethyl
Ee	Enantiomeric excess
FePILCs	Iron-pillared-clays
FeAAPILC	Iron-acid activated-pillared-clay
HMDS	Hexamethyldisilazane
HMF	Hydroxymethyl furfural
IR	Infra-red
LDHS	Layer double hydroxides
LAB	Linear alkyl benzene
M^+	Metal cation
Min	Minutes
NO	Nitric oxide
PLS	Pillared layer structure
Pd-HDAM	Palladium-hexadecylammonium-montmorillonite
PTSA	*p*-Toluene sulfonic acid
TBHP	*tert*- Butylhydrogen peroxide
TOF	Turn over frequency

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