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K10 Montmorillonite clays as environmentally benign catalysts for organic reactions

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Abstract

Montmorillonite is one of the most intensively explored catalytic materials in heterogeneous catalysis due to its low cost and eco-friendliness. Also, it possesses some unique properties like cation exchange capacity and swelling ability, thereby accommodating various guest species in its interlayers. In this *perspective*, we describe the catalytic utility of K10-montmorillonite as solid acids, support for complex or metal nanoparticles in unimolecular as well as bimolecular reactions reported mainly from our group. A very brief introduction is presented to highlight the structural properties of K10 clay and the merits of it in heterogeneous catalysis. The main part of this review is organized according to the role of clay in various organic reactions. An emphasis is given in highlighting the greenness of the processes and a fair comparison is also provided between clay catalysts with respect to other homogeneous or heterogeneous catalysts. Finally, we summarize the current status and provide our views in future trends and developments.

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1. Introduction

Recent progresses in heterogeneous catalysis demonstrate that the field is promising in industrial applications, especially in fine chemical synthesis. The newly developed catalysts and methods make it possible to prepare robust heterogeneous catalysts while still maintaining the selectivity and activity. To overcome the difficulties and waste arising from homogeneous reactions, mineral solids such as clays, zeolites, heteropoly acids, oxides, *etc.*, are used as catalysts for organic reactions.[1-12] Clays, a group of aluminosilicates, is widely used in many applications as they exhibit specific features like acidity, swelling, ion-exchange properties, high versatility, wide range of preparation variables, use in catalytic amounts, ease of work-up, milder experimental conditions, gain in yield and /or selectivity, low cost *etc.*,[3,6] They are layered materials which can be used as a solid support for expensive or not-easily available reagents, organometallic complexes, nanoparticles (NPs) and provide the possibility for easy recovery and reuse of the reagents. These supports act like small molecular containers as well as reactors and modify the characteristics of free catalysts by increasing the steric constraints and enhancing the local concentration of reagents near the surface where the reaction takes place. Thus, investigation into their fundamental structure as well as characteristic properties in particular their confining influence mimicking of biological systems can reveal great potential in the development of new processes and systems composed of functionalized organic and inorganic compounds.

Clays are broadly classified into two classes namely cationic and anionic clays.[7] The cationic clays have negatively charged aluminosilicate layers, with small cations in the interlayer space to balance the charge, while the anionic clays have positively charged brucite-type metal hydroxide layers with balancing anions and water molecules located interstitially.

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Clay minerals are hydrous silicates of the phyllosilicate family[1] (*i.e.*, layered silicates or silicates based on a two-dimensional structure), in which the basic building blocks are the Si(O,OH)$_4$ tetrahedra and the M(O,OH)$_6$ octahedra (where M = Al^{3+}, Mg^{2+}, Fe^{3+} or Fe^{2+}). The combination of a sheet of tetrahedra with a sheet of octahedra gives rise to the layer (thickness 0.7 nm *ca.*) of the 1:1 minerals (kaolinites or serpentinites for M = Al^{3+} or Mg^{2+}, respectively), while in the layer of the 2:1 type clays (thickness 1.0 nm *ca*.) a sheet of octahedra is sandwiched between two sheets of Si-tetrahedra (Figure 1). Clay minerals can be dioctahedral or trioctahedral, based on the number of octahedral sites per unit cell occupied, which in turn depends essentially on the cation present (for example, Al^{3+} or Mg^{2+}) in the octahedral sheets. Montmorillonite is a dioctahedral layer type which has the molecular formula $M_x(Al_{2-x}Mg_x)(Si_4)O_{10}(OH)_2.nH_2O$. Montmorillonite is classified to the family of 2:1 smectite type of clay minerals. It is composed of aluminosilicate layers, where one octahedral alumina sheet is sandwiched between two tetrahedral silica sheets. The distance between the two layers is known as interlayer distance or gallery height, while the interlayer distance plus thickness of a single aluminosilicate layer constitutes the basal spacing (Figure 1). In the layers of aluminosilicate, partial isomorphous substitution of Si^{4+} ions by trivalent metal cations and Al^{3+} ions by divalent metal cations causes a charge deficiency. In order to balance this charge deficiency, hydrated alkali and alkaline earth metal cations occupy the interlayer space of montmorillonite. These cations in the interlayer are highly exchangeable, thereby making montmorillonite able to accommodate various guest molecules (metal complexes, metal NPs and organocatalysts) in its interlayer space.

Various types of metal cations can be introduced readily into the expandable interlayer spaces, thus making it possible to alter the acidic nature of the material by simple ion-exchange.[13-17] The concentration of exchangeable cations is called cation-exchange capacity

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(CEC) usually measured in milliequivalents per 100 g of dried clay. Smectites have the highest CEC of interlayer cations (typically 70 – 120 mequiv./100 g). Structural defects at layer edges give rise to additional CEC and a small amount of anion exchange capacity too.[6]

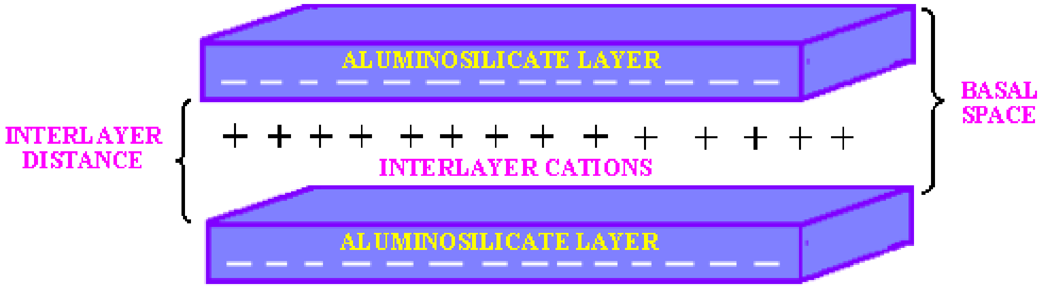

Figure. 1 *Interlayer distance and basal spacing in K10 montmorillonite clay*

In recent years, synthesis of nanomaterials is one of the thrust areas in materials research due to their distinct properties like optical, electronic, magnetic, and catalytic than those of individual atoms or their bulk counterparts due to quantum size and surface effects. Metal NPs is emerging as a new type of important functional materials[18a] as they possess a large surface to volume ratio compared to their bulk materials, which makes them particularly attractive for many applications. Therefore, synthesis of metal NPs and to retain them in small size is a challenging task since in most of the cases they tend to form bigger NPs through the process called agglomeration. Therefore, immobilization of metal NPs on suitable supports has triggered substantial interest over past few decades due to the potential control of NPs size and shape which ultimately determine their activity.[18b] In addition, immobilization of metal NPs on a suitable solid support also prevents agglomeration by maintaining them in smaller sizes.[18c] Recently, a review has been reported on the various methodologies adopted for the syntheses of montmorillonite supported metal NPs and their applications.[18d]

Kaneda *et al.*,[19] have reported that metal-cation exchanged montmorillonite catalysts possess three types of metal ion species with unique structures within the interlayer of the

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montmorillonite. The interlayer space of montmorillonite can be widely used to accommodate a variety of metal complexes to isolate the active species from the formation of μ-oxo species. In addition, it can also be used to introduce many organic surfactant species and robust metal oxides as pillars to produce pillared clays, thereby increasing the surface area. This process will also enhance the possibility of organic molecules diffusion in order to reach the active sites but however a care has to be taken to differentiate immobilization of any guest molecule from mere adsorption over the clay minerals. Figure 2 shows the possible modification of clay minerals by metal cations, anchoring of amino groups and metal NPs.

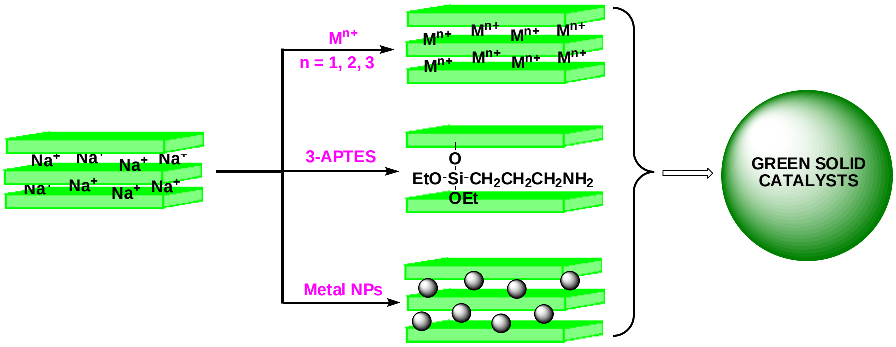

Figure 2. *Schematic representation of clay modification with metal cations, anchoring amino groups and metal NPs.*

Many clay minerals absorb water between their layers, which move apart and the clay swells. For efficient swelling, the energy released by cations and/or layer solvation must be sufficient to overcome the attractive forces (such as hydrogen bonding) between the adjacent layers. In 1:1 clay minerals (kaolinite), water forms strong hydrogen bonds with hydroxyl groups on hydrophilic octahedral layers, allowing swelling to occurs. With 2:1 clay minerals, the ability to swell depends on the solvation of interlayer cations and layer charge.

The interlayer cation also contributes to the acidity of clay minerals. Some of these cations may be protons or polarizing cations (*eg*., Al^{3+}) which give rise to strong Brönsted/Lewis

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acidity.[20] The higher the electronegativity of M^+, the stronger are the acidic sites generated. Brönsted acidity also stems from the terminal hydroxyl groups and from the bridging oxygen atoms. In addition, clay minerals have layer surface and edge defects, which would result in weaker Brönsted and/or Lewis acidity, generally at low concentrations. The acid strength is usually expressed by the Hammett scale. On this scale, the acidity of clay minerals can be comparable to that of concentrated sulfuric acid. The surface acidity of natural clays with Na^+ or NH_4^+ as interstitial cations ranges from +1.5 to -3. Washing of the clay with mineral acids such as HCl, brings down the Hammett (H_o) function from -6 to -8, which is between conc. HNO_3 (-5) and H_2SO_4 (-12).

As a general remark in the catalytic applications of clay based catalysts, it is highly important to measure the surface area before the catalytic reactions. It is also advisable to remove the unwanted or excess cations present in the clay minerals in order to gain maximum surface area for the reactants to diffuse in between the interlayers of clay minerals. This is very important from the fact that clay possesses already low surface area (220-270 m^2/g) compared to other solid catalysts like zeolites. Catalyst stability, maintenance of its layered structure under the reaction conditions have to be continuously surveyed and firmly proved, particularly when using high polar solvents and corrosive reagents. Comparison of powder XRD patterns of the fresh catalyst and after its repeated use should be reported to ascertain its stability. In addition, surface area measurements of the spent catalyst after careful evacuation of solvents and adsorbed products should provide surface area values similar to the fresh catalyst.

After exchanging the appropriate metal cations with the native clay minerals, it is recommended to determine the weight percentage of metal ions and subsequently their acidity must be calculated by any one of the standard adsorption techniques. This will be highly useful to calculate turnover number or turnover frequency for any given reaction. One of the main problems associated with the heterogeneous catalysts is the leaching of active sites. This issue must be addressed by hot filtration test and also analyzing the aqueous part by atomic absorption spectroscopic technique to identify the concentration of active sites (metal ions or NPs), if they should have leached from the solid catalyst to the solution during the course of reaction. This particular experiment will throw significant insights on the catalyst durability so that it can be reused successfully without any decay in its activity.

Due to the versatile nature of K10 montmorillonite, it can be easily modified and employed for many applications.[10, 21a,b] In the last two decades, we have extensively used either K10 clay or its modified catalysts by intercalating with metal complexes or metal NPs and reported their catalytic applications in a variety of organic reactions. The present *Perspective* summarizes various catalytic systems reported in our group using clays and clay supported catalysts for organic reactions are discussed in the following order based on the type of catalysts. They are

a) natural clay/acid treated clays as solid acid catalysts
b) cation exchanged clays
c) support for metal complexes/reagents and
d) support for metal NPs

2. K10 clay as solid acid catalyst

2.1 Unimolecular reactions

Acid clays have been used as versatile catalysts for many functional group transformations and skeletal rearrangements. For example, K10 Montmorillonite clay treated with heteropoly acid like dodecatungstophosphoric acid has been found to be an effective

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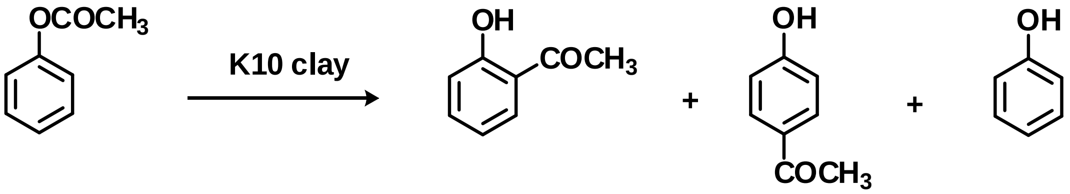
catalyst in the ring opening reaction of 1,2-epoxyoctane to octanal, octenol and other products.[22a] Different natural as well as modified palygorskite clays and zeolite 4Å have been used as catalysts for rearrangement of epoxides.[22b] Alumina and zirconia pillared clays modified with Ce^{3+} and La^{3+} montmorillonite clays have been reported for the conversion of longifolene to isolongifolene.[22c] Isomerization of 1-butene to *trans*-2-butene and *cis*-2-butene has been studied with Al^{3+} and Fe^{3+} ion-exchanged with natural smectite clay.[22d] Isomerization of two highly branched 25-carbon isoprenoid olefins have been studied using K10 montmorillonite clay as catalyst.[22e] Isomerization of *R*(+)-limonene to dioxatricyclodecane has been reported using solid acid catalysts such as clays, zeolites and solid superacids.[22f] Isomerization of allylic alcohols of the pinene series and their epoxides has been reported using K10 montmorillonite clay as catalyst.[22g] Migration of isoprenyl group in phenyl isoprenyl ether to *o*-hydroxy isoprenylbenzene and *p*-hydroxy isoprenylbenzene has been investigated using K10 montmorillonite clays and KSF montmorillonite clay as catalyst.[22h] Stereoregulated substitutive migration of a phenyl group from *tert*-butyldiphenylsilane ether has been reported using K10 montmorillonite clay as catalyst.[22i] K10 montmorillonite clay has been used successfully in enriching the *cis* isomer in an isomeric mixture of *cis*- and *trans*-lauthisan from an isomeric ratio of *cis:trans*=1:1.7 to 17:1.[22j] This section describes the catalytic activity of solid acid K10 clays as catalysts for unimolecular (Fries and Fischer Hepp rearrangement) or bimolecular reactions.

Fries rearrangement of phenyl and naphthyl esters has been reported using K10 clay with framework aluminium acting as a Lewis acid catalyst (Scheme 1).[23] In general, the percentage conversions and related yields of these isomers are mainly based on the size of the substrates. In the case of phenyl acetate, the rearrangement was highly facile with K10-clay and Na^+ exchanged K10-clay resulting in *p*-isomer (≈80 %) exclusively with 88 and 81 %

conversion, respectively. However, when the catalyst amount was increased to two-fold excess, an increase in the amount of the *o*-isomer was observed. For example, K10 clay exhibited 100 % conversion with 18 % of *o*-isomer and 82 % of *p*-isomer as products. A similar activity and selectivity was observed for Al^{3+}/K10 as catalyst. On the other hand, phenyl benzoate gave *p*-isomer as the major product, along with the formation of the *o*-isomer as well as phenol. K10 clay showed 90 % conversion of phenyl benzoate with 10 % of *o*-isomer, 62 % of *p*-isomer and 18 % of phenol as rearranged products. When the *p*-position was blocked with substituents, the benzoyl group goes to *o*-position. For instance, 100 % conversion of phenyl *p*-toluenesulfonate was achieved with 88 % of *o*-isomer and 12 % of *p*-isomer clearly demonstrating the effect of substituent over the selectivity to *o*-isomer. These experiments clearly illustrated the solid acid nature of K10 clay in promoting Fries rearrangement under mild reaction conditions. The salient features of this protocol from the viewpoints of green chemistry are solvent-free reaction conditions and achieving high conversion and selectivity. Also, it is believed that the reaction takes place mostly on the external surface. Although the comparison of K10 clay activity with other solid acid catalysts is lacking, it would be ideal to have a comparison with other solid catalysts in the future works.



Scheme 1. *Fries rearrangement of phenyl acetate catalyzed by K10 clay.*

Fischer-Hepp rearrangement of *N*-methyl-*N*-nitrosoaniline has been reported using K10, KSF, bentonite clays and cation-exchanged K10 clays as catalysts (Scheme 2).[24] The possible products in the rearrangement were, *N*-methyl-4-nitrosoaniline, *N*-methylaniline and aniline.

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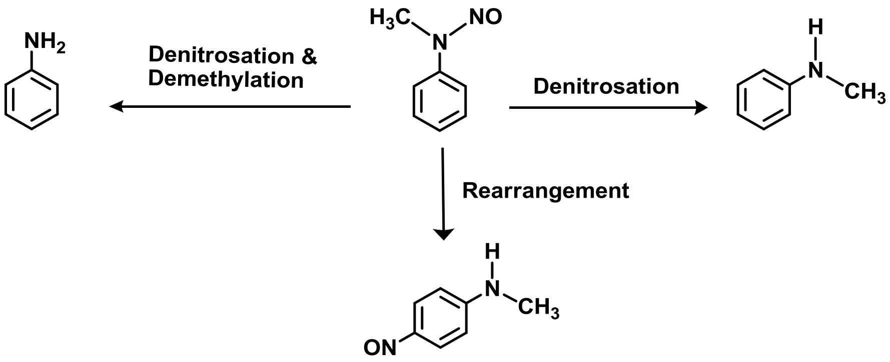
Although complete conversion of *N*-methyl-*N*-nitrosoaniline was observed with K10 or cation exchanged K10 clays as catalysts in solid state but however, mixture of three products was observed with high mass balances. Under identical conditions, KSF showed 64 % conversion with no enhancement in the product selectivity. In contrast, a rearrangement with a conventional homogeneous catalyst like HCl after 24 h resulted in 89 % conversion yielding 69 % of *p*-nitroso-*N*-methylaniline and 20 % of *N*-methylaniline. However, when the reaction was studied in various solvents with K10 clay as catalyst, *p*-nitroso-*N*-methylaniline is predominant in polar protic solvents, such as methanol, ethanol, 2-propanol and iso-butanol. On the other hand, the same reaction in dichloromethane and benzene as solvents gave 100 and 68 % yield of the product but these results are not encouraging from the green chemistry perspectives. The better activity of clay based catalysts compared with HCl in terms of conversion and selectivity is compensated by the use of benzene and dichloromethane, which are not environmentally benign solvents. Hence, the future studies must be performed with environmentally benign and green solvents to develop a sustainable process. The enhanced activity in protic polar solvent may be due to the formation of the corresponding alkyl nitrite in polar solvents which will favor nitrosation. This was further confirmed by performing the reaction with nitrite traps such as hydrazine, sulfamic acid or sodium nitrite observing a complete arrest of rearrangement product.



Scheme 2. *Fischer-Hepp rearrangement of N-methyl-N-nitrosoaniline catalyzed by clays.*

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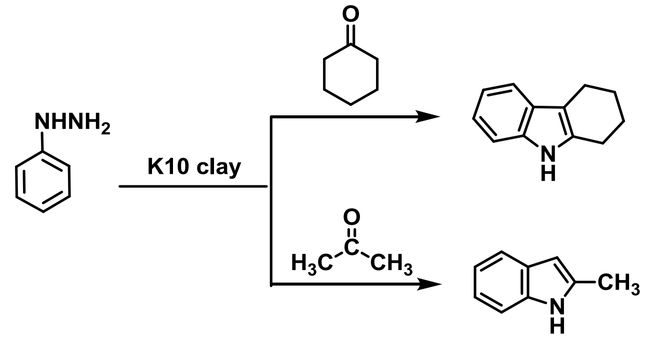
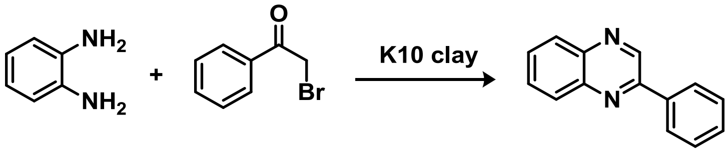
2.2 Bimolecular reactions

Fischer indole,[25] synthesis has been one of the few heterocyclic syntheses studied in great detail, due to its versatility and broad applicability in the synthesis of a number of biologically active products.[26,27] One-pot synthesis of substituted indoles has been reported in very high yields from the reaction between ketone and phenylhydrazine in the presence of mordenite and zeolite-Y as catalysts.[28] In our group, the synthesis of 1,2,3,4-tetrahydrocarbazole and substituted indoles have been reported using a solid acid catalyst, namely K10 clay *via* Fischer indole synthesis in methanol medium (Scheme 3).[29] K10 clay showed 96 and 94 % of 1,2,3,4-tetrahydrocarbazole using thermal and microwave irradiation method under mild reaction conditions in methanol. Using this catalytic system, a serious of substituted indole derivatives were synthesized using thermal as well as microwave irradiation method. The products were obtained in high yield, good purity and no further purification is required. The clay catalyst was reused two times with almost equal efficiency. Other advantages of these solid acid catalysts are atom economy, one-pot reaction, absence of side reactions and formation of a wide range of substituted indoles, even in cases where the reaction fails in solution media. Also, the present clay mediated Fischer indole synthesis conditions are quite milder and efficient and will be highly useful in the design and synthesis of naturally occurring indole skeletons. It is interesting that K10 clay showed higher activity in the synthesis of 1,2,3,4-tetrahydrocarbazole but its activity must be compared with commercial solid catalysts.



Scheme 3. *Synthesis of 1,2,3,4-tetrahydrocarbazole and 2-methylindole catalyzed by K10 clay.*

Syntheses of quinoxalines and their derivatives are receiving considerable interest due to their biological activities and pharmaceutical applications.[30] Recently, one-pot synthesis of 2-substituted quinoxalines has been reported from 1,2-diamines and phenacyl bromides using K10 clay as a catalyst (Scheme 4).[31] Among the various reaction conditions tested, 92 % yield of 2-phenylquinoxaline was achieved with K10 clay as catalyst at 50 °C in acetonitrile. It is also interesting to note that the same reaction resulted in 77 % yield under solvent-free conditions in 6 h at 50 °C with higher mass balances. This result is encouraging from the view points of green and sustainable process since it does not require any solvent in the reaction process. The optimized reaction conditions were successfully utilized to syntheses a series of 2-substituted quinoxalines under mild reaction temperature in acetonitrile in high yields. The catalyst was reused six times with a slight decrease in the yield. In any case, this method offers an easy and facile approach for the syntheses of substituted quinoxalines in high yields.



Scheme 4*. Synthesis of 2-phenylquinoxaline from 1,2-diaminobenzene and phenacyl bromide using K10 clay as catalyst.*

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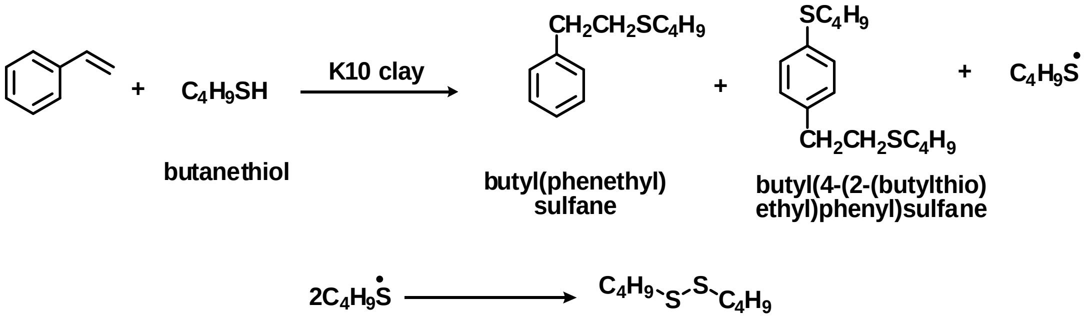
The catalytic activity of K10 and cation exchanged montmorillonite clays to act as radical initiators as well as achieving high selectivity using cetyltrimethylammonium chloride (CTAC)-pillared clays has been reported in the addition of butanethiol to styrene. (Scheme 5).[32] The reaction between styrene and butanethiol in the presence of K10 clay resulted in 95 % conversion of butanethiol with 55 % selectivity of product butyl(phenethyl)sulfane and 26 % of butyl(4-(2-(butylthio)ethyl)phenyl)sulfane, and 14 % of the 1,2-dibutyldisulfide. Generally, the butyl(phenethyl)sulfane formed by the anti-Markovnikov addition was the major product. The Markovnikov product (addition involving an ionic mechanism) is not formed with any of the thiols. The operation of radical route was evidenced by the observation of a very slow reaction in the case of H^+ exchanged clays, which are more suited for ionic additions. The significant decrease in reaction (45 % conversion) with H^+ exchanged clay is attributed to the more efficient protonation of styrene by generating a carbonium ion of the type $C_6H_5C^+HCH_3$. This decreases the effective concentration of free styrene available for radical addition. A blank experiment, in which a mixture of butanethiol and styrene was heated at 95 ^oC but no addition product is observed. Hence, the present work demonstrates the ability of the clay microenvironment to act as radical initiator. When a hydrophobically modified clay such as CTAC-pillared clay was employed, the formation of 1,2-dibutyldisulfide and butyl(4-(2-(butylthio)ethyl)phenyl)sulfane totally suppressed and butyl(phenethyl)sulfane formed by anti-Markovnikov addition as the exclusive product. This remarkable selectivity towards the formation of butyl(phenethyl)sulfane by the addition of thiol to olefin may be rationalized by visualizing both the hydrocarbon chain of thiol and the aryl ring of styrene embedded in the hydrophobic pillar, namely CTAC and the functional groups are oriented towards the ionic interface of the pillaring agent and the clay surface. It is also likely that the hydrocarbon pillars may have impeded the movement of radical intermediates. A closer look at the data reveals that, on increasing the chain length of thiol, the percentage conversion decreases and also the side products 1,2-dibutyldisulfide and butyl(4-(2-(butylthio)ethyl)phenyl)sulfane are formed in lesser amounts. This may be attributed to the restricted diffusion of the radical fragments upon increasing the chain length.



Scheme 5. *Radical addition of butanethiol to styrene catalyzed by K10 clay.*

The catalytic activity of K10, cation exchanged K10 and surfactant-pillared K10 clays have been tested in the cleavage of carbon–sulfur bond in methyl phenyl sulfide, substituted phenyl methyl sulfides and *n*-butyl phenyl sulfide and observing the corresponding disulfide as the major product (Scheme 6).[33] K10 clay showed 84 % conversion of methyl phenyl sulfide with 77 % selectivity towards diphenyldisulfide in solid state at 95 ^{o}C. On the other hand Cr^{3+}, Al^{3+}, Mn^{2+}, Ni^{2+} and Na^{+} exchanged K10 clays exhibited 91, 93, 89, 91 and 82 % conversion of methyl phenyl sulfide respectively under identical conditions. In contrast, CTAC-pillared K10 clay exhibited 7 % conversion with only detectable yield (0.2 %) of disulfide. This was believed to be due to the decrease of clay surface area by the introduction of surfactants. This factor, coupled with its low-surface acidity, may be responsible for the low catalytic activity of a CTAC-pillared clay. It is interesting to observe that substituted phenyl methyl sulfides (i.e., *p*-methoxy, *p*-nitro and *p*-carboxylic groups), gave negligible reaction with K10, cation-exchanged and pillared clays. This was attributed to the decreased mobilities of substituted phenyl methyl

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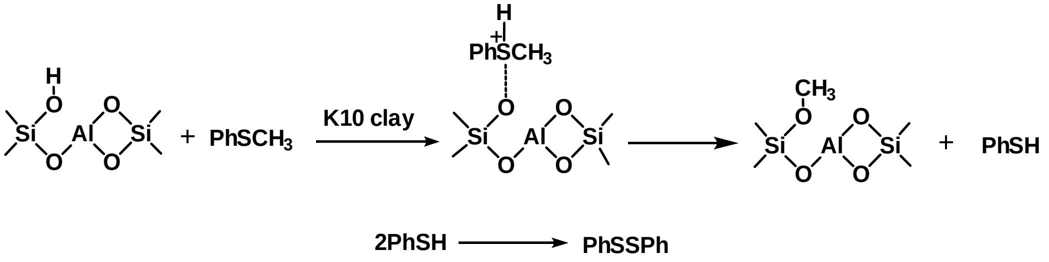
sulfides (in comparison with phenyl methyl sulfide) when placed in a solid environment. Though smaller benzenoid derivatives were fairly mobile in the clay microenvironment,[34] in the dealkylation of anisole using clays based on their MAS-^{13}C-NMR experiments, it is believed that the presence of an additional substituent makes the mobility more difficult leading to a significant size effect in this reaction. Further, CTAC-K10 showed 0 % conversion of n-butyl phenyl sulfide at 95 ^{o}C in 11 h under solid state. Increasing the reaction time further to 41 h under the same temperature slightly increased the conversion to 11 %. However, a considerable increase in the conversion to 97 % was noticed at 145 ^{o}C after 41 h with 85 % selectivity of the corresponding disulfide. The recovery of products by extracting with solvents from these clay catalysts were always high.



Scheme 6. *Dealkylation of organic sulfide in sheet silicate.*

Bromination of toluene to benzyl bromide (Scheme 7) has been reported with bromine in carbon tetrachloride at room temperature.[35] Selective bromination of alkylbenzenes has been reported using K10 clay as catalyst.[36a] Bromination of toluene (Scheme 7) using Br_2/CCl_4 at room temperature gave benzyl bromide as the sole product. However, bromination in the presence of Kl0-clay under similar conditions yielded 33 % of *o*-bromotoluene and 67 % of *p*-bromotoluene. On the other hand, unlike toluene, *p*-bromo derivative (69 %) was obtained as the major product in clay mediated bromination of ethylbenzene. In contrast, cumene resulted in 84 % conversion with 74 % of *p*-isomer and 10 % of polybromination. The suppression of *o*-isomer

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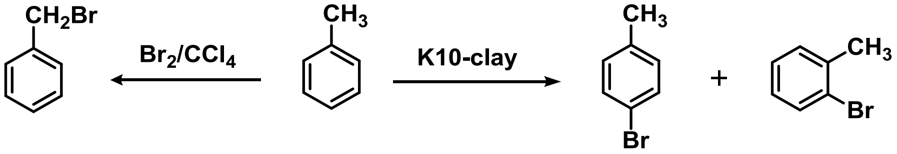
formation may be explained due to steric crowding in the transition state. Extending this protocol to other substrates like *o*-, *m*-, *p*-xylene yielded exclusively side chain brominated products in the absence of clay. However, clay-mediated bromination of these substrates showed ring brominated products. Bromination in clay microenvironment results exclusively in aromatic substitution through an ionic mechanism, while bromination in the absence of clay yields mainly the side chain brominated product involving a radical route. This difference in selectivity may be attributed due to the polar environment in clays which favours electrophilic aromatic substitution and also due to the steric restrictions imposed by the constrained clay microenvironment on the larger transition states in side-chain brominations. Additional experiments are required with bulkier substrates to delineate whether the reaction occurs on the external surface or in between the interlayer sheets of K10 clay. It has also been shown that bromination of aromatic compounds into their corresponding ring brominated products can be conveniently performed using Fe_2O_3/Zeolite[36b] and NaY zeolite[36c] as catalysts.



Scheme 7. *Bromination of toluene with or without K10 clay.*

Dimerization of *trans*-stilbene in the presence of concentrated mineral acids and metal halides results in the formation of tetralin and indane derivatives under very rigorous conditions.[37] Cation-exchanged K10 clays have been reported to catalyze efficiently the dimerization of *trans*-stilbene, 1,1-diphenylethylene and α-methylstyrene, through the formation of carbocationic intermediates (Scheme 8).[38] Dimerization of stilbene, 1,1-diphenylethylene and α-methylstyrene proceeds efficiently in the presence of acidic clays catalyzed by their Brönsted

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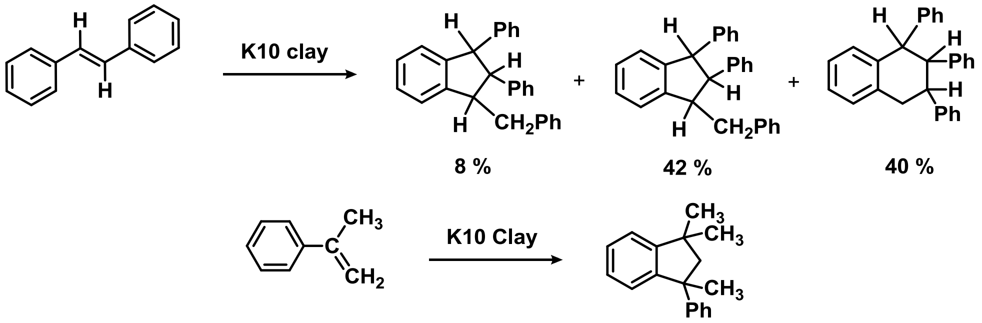
acidity. Fe^{3+} and Al^{3+}-exchanged K10 clays exhibited 100 % conversion of *trans*-stilbene in 10 min and H^{+}-K10 clay required 60 min to achieve 100 % conversion. Although these catalysts showed different activity in dimerization, the product distribution remains almost identical. In contrast, Cu^{2+}, Mg^{2+}, Ca^{2+} and Na^{+}-K10 clays showed much lower activity even after 180 min clearly demonstrating the different acidic nature of these catalysts. Using α-methylstyrene as substrate, Fe^{3+} and Al^{3+}-K10 clays resulted in 100 % conversion in 10 min but however the yields were 75 and 68 % respectively. Further, H^{+}-K10 exhibited 100 % conversion in 10 min with 69 % yield. In general, H^{+} as well as M^{3+} exchanged clays found to be very efficient and the reaction took a longer time with M^{2+}exchanged clays. The present protocol does not require stringent conditions such as high vacuum, very high temperature and other advantages include simpler work-up, selectivity, milder conditions and eco-friendliness. In addition, no organic solvent was used to perform dimerization of olefins and hence it reduces much waste to the environment. Further studies are required to explain the different products obtained with *trans*-stilbene using cation exchanged K10 clays. In addition, the diffusion of these substrates to reach the active sites either at internal/external sites remains unclear.



Scheme 8. *Dimerization of trans-stilbene and α-methylstyrene catalyzed by K10 clays.*

3. Cation exchanged clays as catalysts

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Catalysis of organic reactions by inorganic solids is an important new dimension in organic chemistry.[3,5,6] The use of clay as catalyst or catalyst support has received considerable attention due to their high chemical and thermal stability. In addition, the naturally occurring K10 clay can be exchanged with mono-, di-, tri- and tetra-valent metal ions from their corresponding nitrates or chloride salts to obtain cation exchanged K10 clays.[13] Laszlo and coworkers in their pioneering works have extensively used K10 clay as a solid support for incorporating many inorganic reagents. For instance, cupric nitrate exchanged K10 clay has been reported as catalyst for regioselective nitration of aromatic hydrocarbons in the presence of acetic anhydride.[39a] In another study, nitration of estrones has been studied using K10 montmorillonite clay modified with ferric nitrate as catalyst.[39b] Rapid and stereoselective Diels-Alder reaction has been investigated using Fe^{3+}-doped K10 montmorillonite clay as catalyst.[39c] The efficient conversion of hydrazines to azides has been performed in the presence of ferric nitrate supported K10 montmorillonite clay as catalyst.[39d] Cation exchanged montmorillonites have also been used as catalysts for Friedel-Crafts reaction particularly in benzylation of arenes.[39e,f] $InCl_3$ and $GaCl_3$ supported on K10 montmorillonite clay has been shown to be active in benzylation of benzene.[39g] Oxidation of primary and secondary alcohols has been reported using Fe^{3+} exchanged on K10 montmorillonite clay as catalyst with H_2O_2 as oxidant.[39h] Vanadium containing K10 montmorillonite clay has been used as catalyst in the liquid phase oxidation of sulfides.[39i] $ZrOCl_2.8H_2O$ on K10 montmorillonite clay has been shown to be as an efficient catalyst for conjugated addition of variety of conjugated alkenes such as α,β-unsaturated carbonyl compounds, carboxylic esters, nitriles and amides under solvent-free conditions.[39j] Recently, Fe^{3+} supported on K10 montmorillonite clay has been reported as an efficient catalyst for solvent-free aza-Michael addition of amines to α,β -unsaturated carbonyl compounds.[10]

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Fe^{3+}exchanged K10 montmorillonite clay has been reported as a catalyst for the reaction between 1,4-dihydropyridines and 1,2,4,5-tetrazines to give 2-oxo-1,2-dihydropyridines.[39k] Fe^{3+}-exchanged K10 montmorillonite clay has been used as catalyst for cyclohexadienone-phenol rearrangement at room temperature in few minutes.[39l] Fe^{3+} exchanged K10 montmorillonite clay has been reported as catalyst for the cycloaddition reaction between *N*-benzylidine aniline and ethyl vinyl ethers.[39m] The same catalyst was also used as catalyst for the cycloaddition reaction of furan with α,β-unsaturated aldehydes and ketones.[39n] $ZnCl_2$ impregnated over K10 montmorillonite clay has been found to be an efficient catalyst for Friedel-Crafts alkylation reactions in benzene.[39o]

This section describes on the catalytic activity of various metal cation exchanged K10 clay as catalysts for a variety of reactions either as solid acid catalysts or to achieve regioselectivity, either in unimolecular (Fries rearrangement) or in bimolecular reactions.

3.1 Unimolecular reactions

Fries rearrangement of phenyl benzoate catalyzed by Lewis acids in homogeneous solution produced a mixture of 2- and 4-hydroxybenzophenones (*ortho*/*para* ratio ≈ 1).[40] Cation exchanged montmorillonite clays have been reported as heterogeneous catalysts for the Fries rearrangement of phenyl toluene-*p*-sulphonate to give selectively *o*- and *p*-hydroxyphenyl *p*-tolyl sulphones as major and minor products respectively (Scheme 9).[41] K10 clay as well as other cation-exchanged montmorillonite clays (Al^{+}, Fe^{3+}, Co^{2+}, Cu^{2+}, Cr^{3+} and H^{+}) showed 100 % conversion of the substrate with higher selectivity towards the *o*-isomer as the major product than *p*-isomer indicating the superiority of cation exchanged K10 clay over anhydrous aluminium chloride as Lewis acid catalyst which showed only 40 % conversion under identical conditions. Among the various cations exchanged K10 clays, Co^{2+}, Cu^{2+} and Al^{3+} showed 96, 93

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and 92 % of *o*-isomer, respectively. Although, H^+-exchanged K10 clay exhibited 100 % conversion, 65 and 35 % of *o*- and *p*-isomer were obtained, respectively. This clearly shows that the *o*/*p*-isomer ratio is mainly depends on the acidity of the clay as well as the nature of metal cations. This study clearly illustrates that the role of metal cation in the interlamellar space in controlling the formation of one isomer over the other by confining the movement of reactive intermediates within the interlayer. It would have been interesting if the activity of metal ion exchanged K10 clay is compared with metal ion exchanged zeolites.

Scheme 9. *Fries rearrangement of phenyl toluene-p-sulphonate catalyzed by K10 clay.*

The rearrangement of *N*-phenylhydroxylamine to *p*-aminophenol is known as Bamberger rearrangement.[42-46] K10 and its cation-exchanged clays have been used as catalysts to transform *N*-phenylhydroxylamine to *p*-nitrosodiphenylamine, an unexpected product rather than the conventional Bamberger product, namely *p*-aminophenol (Scheme 10).[47] K10 clay resulted in 100 % conversion of *N*-phenylhydroxylamine with 88 and 12 % of *p*-nitrosodiphenylamine and unidentified products, respectively in 30 min in water at room temperature. A quantitative yield of *p*-nitrosodiphenylamine was achieved in solvent-free conditions in 30 min using K10 clay as catalyst. On the other hand, Fe^{3+}, Cr^{3+}, Mn^{2+}, and Ti^{4+} exchanged K10 clays gave quantitative yields of the desired product in 15 min in water at room temperature. Further, > 90 % yield of *p*-nitrosodiphenylamine was observed with Co^{2+}, Ni^{2+}, Cu^{2+} and Zr^{4+} K10 clays as catalysts under identical conditions. Further, it was noticed that the reaction was relatively faster with cation-exchanged (Al^{3+}, Fe^{3+}, Cr^{3+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Zr^{4+} and Ti^{4+}) clays when compared

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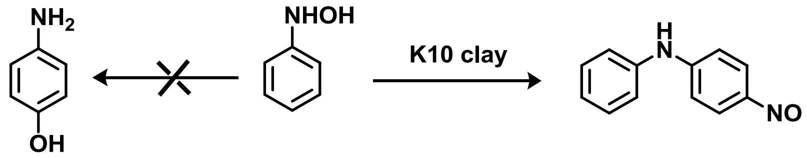
to native K10 clay. The formation of an unexpected product with the present experimental reaction conditions employing solid acids as catalysts compared to a conventional acid-catalyzed Bamberger rearrangement of *N*-phenylhydroxyl amine clearly demonstrates the uniqueness of the clay microenvironment acting as an efficient "nanoscopic microreactor". It is yet another example to illustrate the greenness of the process in where the reaction was performed either in water or in solid state and achieving high selectivity towards *p*-nitrosodiphenylamine without any loss in the mass balance. Here again, it would be interesting to compare the catalytic activity of cation exchanged K10 clays with other cation exchanged solid acids like zeolites in terms of conversion and selectivity.



Scheme 10. *Conversion of N-phenylhydroxylamine to p-nitrosodiphenylamine.*

In an another report, Orton rearrangement of *N*-chloroacetanilide has been reported using K10 clay or cation exchanged K10-montmorrilonite clays as catalysts to achieve *p*-chloroacetanilide as a major product (Scheme 11).[48] K10 clay resulted in complete conversion at with 12 and 88 % of *o*- and *p*-isomer, respectively at 60 ^{o}C in 1 h. Under similar reaction conditions, both H^+ and Al^{3+}/K10 clays exhibited 100 % conversion with 7 and 93 % *o*- and *p*-isomers respectively. Surprisingly, Cd^{2+} and Ag^+ exchanged K10 clays showed 100 % conversion with 100 % selectivity towards *p*-isomer, indicating the efficiency of these catalysts in promoting highly selective reaction. Although Cd^{2+}/K10 clay showed high conversion and selectivity, the toxic nature of Cd^{2+} does not contribute to the development of green and sustainable process. On the other hand, a conventional catalyst, namely HCl exhibited 80 %

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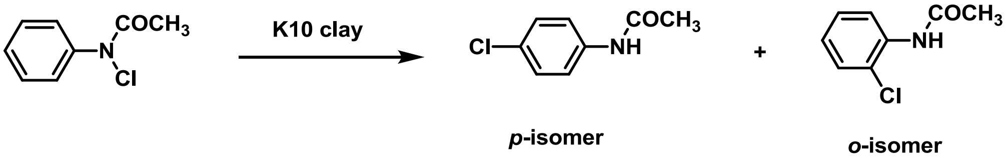
conversion in 2 h at 80 °C with 22 and 51 % of *o*- and *p*-isomer along with 27 % of aniline as rearranged products. These experiments clearly explains the microenvironment of K10 clay as a green reaction medium in promoting the reaction with high conversion and selectivity compared to homogeneous conventional catalyst like HCl.



Scheme 11. *Orton rearrangement of N-chloroacetanilide catalyzed by K10 clay.*

O-Benzylphenol was obtained as the exclusive product in the rearrangement of benzyl phenyl ether in the presence of K10 or cation exchanged K10 clays as catalysts under solvent-free conditions. (Scheme 12).[49] Generally, rearrangement of benzyl phenyl ether gives rise to *o*-benzylphenol, *p*-benzylphenol and phenol as the products. K10 clay showed 91 % conversion with 55 and 36 % of *o*- and *p*-isomer as products in 3 h. Increasing the reaction time further to 12 h resulted in complete conversion of benzyl phenyl ether with complete selectivity towards *o*-isomer. On the other hand, H^+, Al^{3+} and Fe^{3+} exchanged K10 clays exhibited 100 % conversion at 3 h with the exclusive formation of *o*-isomer. In contrast, Co^{2+}, Mn^{2+} and Ni^{2+} exchanged K10 clays showed moderate activity under identical reaction conditions. Notably, Cu^{2+}-exchanged K10 clay resulted in 90 % conversion with 67 and 13 % of *o*- and *p*-isomer along with the formation of 10 % phenol. This study clearly shows the utility of acidic or cation exchanged clays as solid acid catalysts in the conversion of benzyl phenyl ether to *o*-benzylphenol with high regiospecificity. The greenness of this protocol is solvent-free reaction conditions and achieving high selectivity of *o*-isomer. Although the present result is quite interesting considering the

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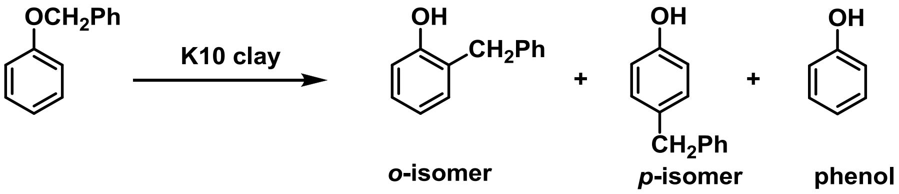
higher selectivity, of *o*-isomer but however, the comparison of K10 clay activity with other solid catalysts to gain the merits of K10 clay is lacking.



Scheme 12. *Rearrangement of benzyl phenyl ether catalyzed by K10 clay.*

Rearrangement of diazoaminobenzene has been reported in the presence of either acidic or cation-exchanged K10 clays towards the formation of *p*-aminoazobenzene at room temperature (Scheme 13).[50] K10 clay exhibited 100 % conversion of diazoaminobenzene in 3 and 6 h with 62 and 86 % yield of *p*-aminoazobenzene respectively, in solid state. In contrast, H^+, Al^{3+}, Fe^{3+} and Cr^{3+} exchanged K10 clays exhibited 100 % conversion and selectivity towards *p*-aminoazobenzene in 3 h under solid state reaction conditions. On the other hand, Cu^{2+} and Ni^{2+} exchanged clays exhibited 88 and 81 % selectivity in 6 h along with the proportionate percentage of byproduct formation. Greater acidity of cation exchanged clays led to the protonation of diazoaminobenzene which then dissociates into diazonium ion and aniline. The diazonium ion attacks aniline at the *para* position to give *p*-aminoazobenzene. Achieving high selectivity at higher conversion at room temperature and absence of solvent are the appreciable merit of this protocol. Further, this method reduces the use of organic solvent and no chromatographic purification is required as the reaction conditions allowed to obtain a single isomer/product. It is interesting to state that the mass balances in all these cases were almost high. The comparative studies on the catalytic activity of K10 with other solid catalysts are to be performed in the future works. Further studies are required to have some insight whether the catalytic reaction occur on the external/internal active sites.

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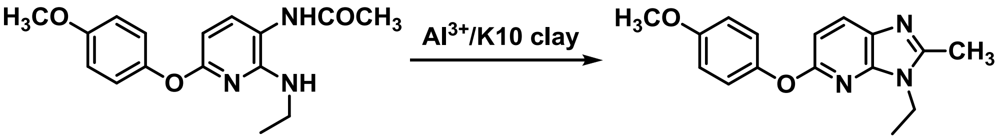
Scheme 13. *Rearrangement of diazoaminobenzene to p-aminoazobenzene catalyzed by K10 clay.*

Imidazopyridines are biologically very important compounds because of their widespread applicability in medicinal chemistry such as antiproliferative activity and DNA binding,[51] FLT3/aurora kinase inhibitor,[52] hypoglycemic activity,[53]and many other noteworthy biological activities like anticonvulsants, anticancer *etc*.[54-57] Recently, we have reported an efficient method for the synthesis of a series of imidazopyridine derivatives *via* intramolecular cyclization of amides using Al^{3+} exchanged on K10 montmorillonite clay (Al^{3+}/K10 clay) as a catalyst (Scheme 14).[58] Among the various catalysts investigated for the synthesis of imidazopyridine from the corresponding amide, Al^{3+}/K10 exhibited higher activity (93 %) than $AlCl_3$, Al_2O_3, Cu^{2+}/K10, Zn^{2+}/K10 and Ti^{4+}/K10 clays as catalysts. Xylene was found to be a choice of solvent for this reaction at 140 ^oC. A series of imidazopyridines were synthesized in higher yields using Al^{3+}/K10 clay as catalyst. This protocol offers practically an easy and facile methodology for the intramolecular cyclization of amides to imidazopyridines. The catalyst was readily recovered and reused five times without a slight decrease in its activity. Although, this report compares the catalytic activity of Al^{3+}/K10 with other metal ion exchanged K10 clays, it fails to compare with other solid acid catalysts under identical reaction conditions. Considering the molecular dimerization of the amide, it can be assumed that the cyclization occurs mostly on the external surface of K10 clay.



Scheme 14. *Synthesis of imidazopyridine using Al^{3+}/K10 clay as catalyst.*

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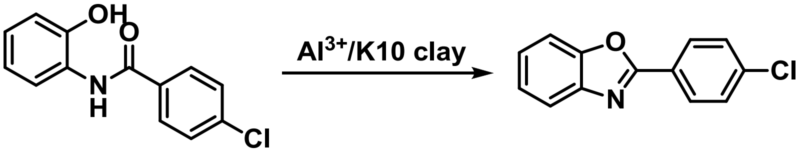
Heterocyclic compounds are privileged organic compounds and especially compounds with N, O-hetero atoms such as oxazole and benzoxazole derivatives are found to be medicinally active and pharmaceutically interesting analogues.[59-61] In another precedent, a new route for the synthesis of 2-substituted benzoxazole derivatives from the corresponding amide through N-C-O bond formation using Al^{3+}/K10 clay has been reported in high yield under mild reaction conditions (Scheme 15).[62] A yield of 97 % was achieved for the synthesis of 2-substituted benzoxazole from the corresponding amide using Al^{3+}/K10 as catalyst in xylene at 140 ^{o}C. Under identical reaction conditions, $AlCl_3$, Al_2O_3, Cu^{2+}/K10, Zn^{2+}/K10, Tl^{4+}/K10 gave lower yields suggesting the superior nature of Al^{3+}/K10 clay in promoting this cyclization. A series of 2-substituted benzoxazoles were synthesized in very high yields under mild reaction conditions and practically no difficulties were encountered suggesting the wide scope of this catalyst. This catalyst was readily recovered and reused five times. These examples clearly establish the superior performance of cation exchanged clays in synthesizing a series of heterocycles, thus contributing for the development of new green protocols.



Scheme 15. *Synthesis of 2-substituted benzoxazole using* Al^{3+}*/K10 clay as catalyst.*

3.2 Bimolecular reactions

Benzimidazoles are very useful intermediates for the development of molecules of pharmaceutical and biological interest. Substituted benzimidazole derivatives have found applications in diverse therapeutic areas including antiulcers, antihypertensives, antivirals, antifungals, anticancers, and antihistaminics.[63-65] A series of benzimidazole derivatives have been synthesized from 1,2-diaminobenzene and aromatic aldehydes using modified Scolecite catalyst in good yields at 70 °C in ethanol medium.[66a] A simple, green and efficient protocol has been reported using zinc chloride exchanged over K10 montmorillonite clay (clayzic) as a Lewis acid catalyst for the synthesis of benzimidazoles and quinoxalines from carbonyl compounds and *o*-phenylenediamine in aqueous media at room temperature (Scheme 16).[66b] Among the various catalysts (including claycop and $Zn^{2+}Y$) studied, clayzic produced benzimidazoles and quinoxalines in higher yields, and with a flexible diamine such as ethylenediamine resulted in the formation of a bis-Schiff base. For example, the reaction between benzaldehyde and *o*-phenylenediamine using clayzic as catalyst afforded 94 % yield of 2-phenylbenzimidazole at room temperature in 24 h in water methanol mixture. Under identical reaction conditions, $Zn^{2+}Y$ zeolite resulted in 26 % yield of 2-phenylbenzimidazole. These results clearly demonstrate the enhanced activity of clayzic compared with $Zn^{2+}Y$ zeolite catalyst. The same protocol was further extended to the synthesis of quinoxaline from *o*-phenylenediamine and benzil to obtain 89 % yield of 2,3-diphenylquinoxaline at room temperature in 2.5 h. Reusability experiments were performed for the synthesis of 2-phenylbenzimidazole and found that it can be reused for four consecutive cycles with no appreciable change in its activity. An attempt to synthesize imidazoline from benzaldehyde and a flexible diamine such as ethylenediamine using clayzic as a catalyst resulted in the formation of bis-Schiff base in which both the amino groups condensed with benzaldehyde to give N^1,N^2-dibenzylideneethane-1,2-diamine rather than the anticipated imidazoline. It is interesting to note that clayzic mediated synthesis of benzimidazoles is a better protocol than the Scolecite based synthesis since, the former catalytic system requires room temperature and water methanol-mixture as solvent, while the later catalyst needed 70 °C.

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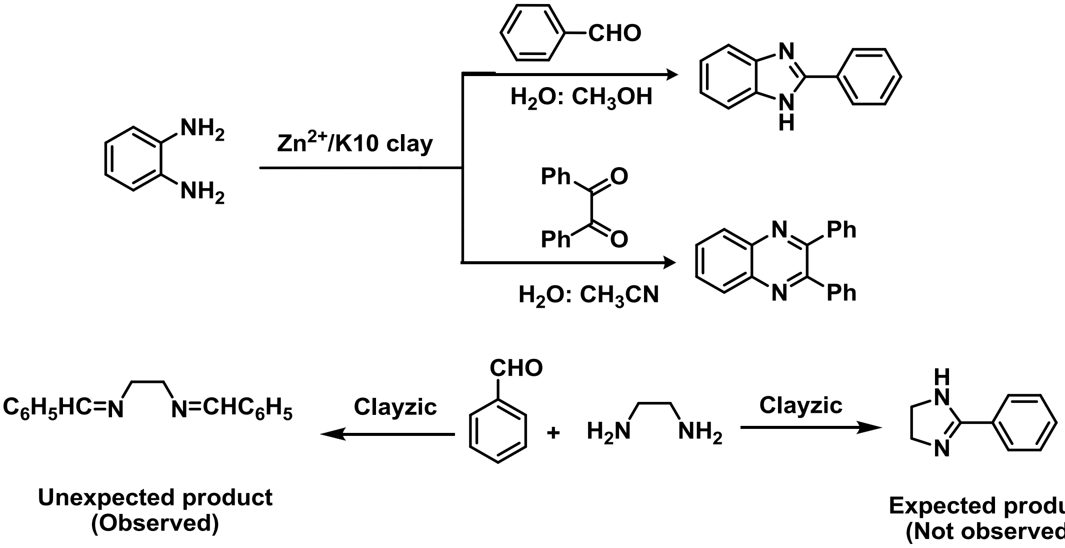

Scheme 16. *Synthesis of benzimidazole, quinoxaline and* N^1,N^2*-dibenzylideneethane-1,2-diamine using clayzic as catalyst.*

In recent years an increasing interest has been devoted in the use of green reaction media to perform organic reactions in eco-friendly manner.[67-69] Use of microwave in a reaction as an alternative source of energy is one of the powerful techniques in green chemistry, especially when a reaction is carried out without solvent. This tends to bring significant advantages such as less solvent consumption and easy reaction setup. Oxadiazoles are utilized as pharmacophores due to their metabolic stability, ability to bind with target peptides and can engaged in hydrogen bond formation and have broad range of applications in medicinal chemistry aspects.[70] The reaction between acid hydrazides and orthoesters has resulted in the formation of 1,3,4-oxadiazoles under harsh reaction conditions with the use of excess orthoformate and longer reaction time.[71, 72] Considering these points in mind, a facile one-pot synthesis of 1,3,4-oxadiazole and 1,2,4-oxadiazole derivatives have been investigated from the corresponding acid hydrazide and amidoxime upon treatment with trimethyl/triethylorthoesters using Al^{3+}-K10 clay as a heterogeneous catalyst under solvent-free microwave conditions with complete recovery of

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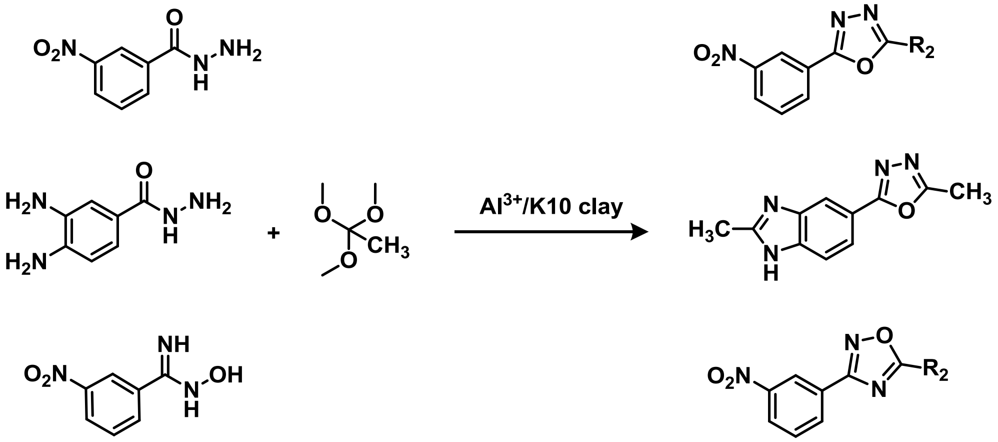
products by extraction with solvents with high mass balances (Scheme 17).[73] Among the various clay catalysts tested for these reactions, Al^{3+}/K10 clay exhibited higher activity. This optimized protocol was further expanded to synthesize a series of 1,2,4 and 1,3,4-oxadiazoles in high yields under mild reaction conditions. The practical applicability of the present protocol is that the products are obtained exclusively without any side product and the catalyst was easily separated by simple filtration. The present catalytic system enjoys many advantages such as reusability, environmental compatibility, low cost, nontoxic and operational/experimental simplicity and green catalyst and provides excellent yield of the products.



Scheme 17. *Al^{3+}/K10 clay catalyzed synthesis of 2-substituted 1,2,4 and 1,3,4-oxadiazoles.*

Benzoxazole, benzothiazole, oxazolopyridine and imidazopyridines are considered to be privileged organic compounds and often used in medicinal chemistry research due to their significant therapeutic activities and have served as pharmacological agents.[74] Benzoxazole, benzothiazole, oxazolopyridine and imidazopyridine derivatives are prepared from 2-aminophenol, 2-aminothiophenol, *o*-hydroxyaminopyridine, and 2,3-diaminopyridine as the respective starting precursor. These amines can be coupled with carboxylic acid or carboxylic acid derivatives and followed by dehydration, generally catalyzed by strong acids such as polyphosphoric acid,[75] sulfuric acid,[76] phosphorous oxychloride[77] and Lewis acids.[78]

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2-Aminophenol or diamine treated with trimethylorthoesters in the presence of acid catalyst such as sulfuric acid, $BF_3.EtO_2$ and hydrochloric acid gave the corresponding benzoxazoles and benzimdazoles.[79]

Benzoxazoles have been synthesized from salicylaldoximes using a series of acid catalysts.[80a] For example, K10 montmorillonite clay resulted in 77.4 % conversion with 50.4 % benzoxazole selectivity at 225 ^{o}C in benzene-acetonitrile mixture at 3 h. Under identical reaction conditions, H-Y, H-ZSM-Y, H-β zeolites exhibited 100 % conversion with the selectivity of benzoxazole being 71.9, 70.1 and 79.6 %, respectively. Although these solid acid catalysts showed high conversion with moderate selectivity towards benzoxazole, the use of benzene acetonitrile solvent mixture is not encouraging from the viewpoints of green chemistry. Recently, we have developed a sustainable protocol for the synthesis of benzoxazoles and benzothiazoles with an aim of achieving high yields and purity of products using Al^{3+}/K10 clay as solid acid catalyst (Scheme 18).[80b] One-pot synthesis of a series of 2-substituted benzoxazoles, benzothiazoles, oxazolopyridines and imidazopyridines have been prepared by reacting the corresponding 2-amino-3-hydroxy and 2,3-diamine derivatives with trimethylorthoesters in presence of a heterogeneous Al^{3+}/K10 clay as catalyst under microwave in a solvent-free reaction and achieving the desired product in high yields with high mass balances. This protocol ensures the development of an alternative and safer chemical route than the existing one towards the synthesis of these heterocyclic compounds with high yields using Al^{3+}/K10 as heterogeneous catalyst. The present methodology has advantages such as use of solid acid catalyst, non-toxic, simple workup procedure, short reaction time and achieving high yield without any side reaction. However, the comparison of the activity of Al^{3+}/K10 with other solid commercial catalysts is still need to be performed in order to understand the scope of Al^{3+}/K10 catalyst.

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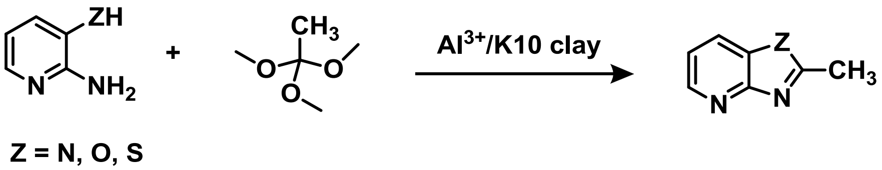

Scheme 18. *One-pot synthesis of 2-substituted benzoxazole, benzothiazole, oxazolo and imidazopyridine compounds catalyzed by Al*$^{3+}$*-K10 clay*.

3.3 A^{3} *Coupling*

Propargylamines are frequently used as synthetically adaptable key intermediates[81,82] for the production of many nitrogen-containing biologically active compounds such as conformationally restricted peptides, oxotremorine analogues, β-lactams, isosteres, therapeutic drug molecules and natural products.[83] Recently, Ag^{I}-exchanged K10-montmorillonite clay (Ag^{I}/K10) has been reported as an efficient heterogeneous catalyst for the one-pot three component coupling of terminal alkynes, amines and aqueous formaldehyde (A^{3} coupling) to yield the corresponding propargylamines in water (Scheme 19).[84a] The reaction between phenylacetylene, aqueous formaldehyde and diisopropylamine gave 86 % yield of the corresponding propargylamine in the presence of Ag^{I}/K10 clay in water at room temperature in 8 h. In contrast, AgY resulted in 69 % yield of propargylamine under identical reaction conditions. These results clearly indicate the superiority of Ag^{I}/K10 clay compared to AgY zeolite catalyst. The catalyst was reused for six times with no significant changes in its yield. This optimized reaction conditions was further extended to synthesize a series of propargylamines in high yields. Further, Ag^{I}/K10 clay catalyzed coupling between phenylacetylene, benzaldehyde and pyrrolidine resulted in 85 % yield of the corresponding propargylamine under solvent-free conditions at 100 ^{o}C in 20 h. On the other hand, 75 % yield of the corresponding propargylamine was achived with AgY zeolite as catalyst. Substituted benzaldehyde/phenylacetylene reacted smoothly with pyrrolidine in the presence of Ag^{I}/K10 clay to afford high yields of their

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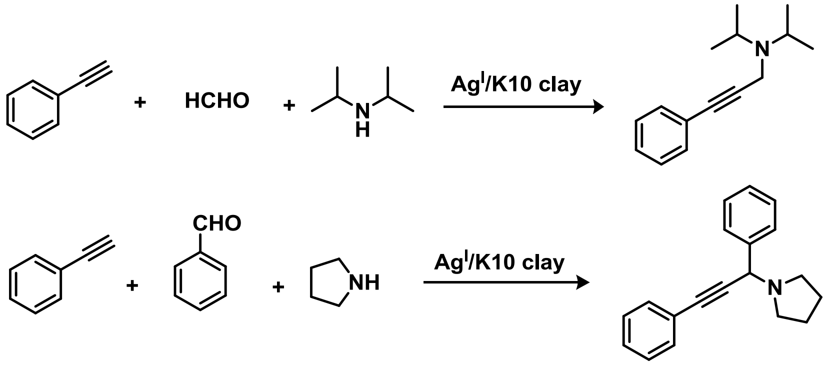
respective propargylamines. Quantitative yields of the desired products were obtained in all the tested examples using Ag^I/K10 clay as catalyst. On the other hand, Cu(I) modified USY zeolite has been reported for the synthesis of propargylamines from benzaldehyde, phenylacetylene and piperidine as substrates under solvent-free conditions at 80 °C resulting in 95 % yield.[84b] Although clay based catalysts exhibited higher activity than zeolites, the diffusion of these reactants in between the interlayer sheets of K10 clay and the interaction of reactants with the active sites need further investigations. This atom economical methodology does not require an additional co-catalyst or activator, and water is the only byproduct. Interestingly, the reaction can also be performed under solvent-free conditions in the case of aromatic and aliphatic aldehydes too, besides formaldehyde, affording the propargylamine derivatives in higher yields with satisfactorily high mass balances.



Scheme 19. *Ag^I/K10 clay catalyzed synthesis of propargylamines.*

4. K10 clay as support for metal complexes/reagents

Immobilization of transition metal complexes and reagents on K10 montmorillonite clay appears to be an ideal way of heterogenizing homogeneous catalysts onto a solid matrix. These heterogenized–homogeneous catalytic systems not only offer the combined advantages of homogeneous (mild conditions) and heterogeneous (easy separation) media, but also impose shape selectivity in catalytic process. In this regard, several studies have been reported using

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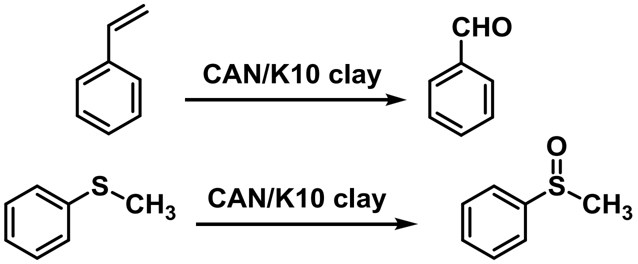
immobilized transition metal complexes and reagents on K10 montmorillonite clays as catalysts for many organic transformations. Molybdenum acetylacetonate complex immobilized on K10 montmorillonite clay has been used as catalyst for the epoxidation of vegetable oils.[85a] Copper(II) complexes with 12- and 13-membered diaza dioxa Schiff-base macrocyclic ligands were entrapped onto K10 montmorillonite clay and its activity was studied in epoxidation of cyclohexene.[85b] Coupling of thiols into their corresponding disulfides has been reported using K10 montmorillonite clay supported nitrosation reagent as catalyst under mild reaction conditions.[85c] K10 Montmorillonite clay supported ferric nitrate has been used as catalyst in the oxidation of alcohols.[85d] A simple and inexpensive procedure has been investigated for the conversion of thiocarbonyls to carbonyl compounds with good yields using K10 montmorillonite clay supported ferric nitrate as catalyst.[85e] Epoxidation of geraniol has been reported using vanadyl acetylacetonate anchored onto amine-functionalized K10 montmorillonite clays as catalyst.[85f] Recently, isomerization of allylic alcohols has been reported using [$RuCl_2(\eta^6$-arene)(PTA-Me)] supported on K10 montmorillonite clay as catalyst.[85g] Tetraazamacrocycle complexes of Cu(II) and VO(IV) exchanged in the interlayers of K10 montmorillonite clay has been used as catalyst for the aerobic oxidation of styrene.[85h] K10 montmorillonite clay supported ferric or cupric nitrates has been used as catalysts for selenoacetals cleavage reaction.[85i] Cupric nitrate supported on K10 montmorillonite clay has been reported as catalyst for the nitration of halobenzenes with improved *para* selectivity.[85j] K10 clay supported metal nitrates have been used as catalysts for the conversion of thiobenzophenones into benzophenones.[85k]

Preparation of aldehydes by oxidative cleavage of carbon-carbon double bonds is a useful reaction, but is often difficult to achieve in good yields as the products are susceptible to further oxidation under the reaction conditions.[86a] We have reported an efficient and selective method for the oxidation of carbon-carbon double bond in olefins and chalcones to carbonyl compounds and oxidation of sulfides to sulfoxides using molecular oxygen as an oxidant using K10 clay supported ceric ammonium nitrate (CAN/K10) in methanol medium (Scheme 20).[86b] Styrene was selected as a model substrate to optimize the reaction conditions and the substrate to CAN ratio was 6:1. Oxidation of styrene resulted in 11 % benzaldehyde using CAN as homogeneous catalyst in methanol while CAN/K10 clay gave 95 % yield of benzaldehyde at room temperature, thus, clearly suggesting the enhanced catalytic activity of CAN/K10 with CAN. A similar trend was observed for all the olefins and chalcones leading to higher yields of the respective carbonyl compounds. CAN/K10 clay was also used as catalyst for the selective oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide with 100 % yield at room temperature while using CAN catalyst resulted in 35 % yield. As it has been observed in oxidation of styrene, here again CAN/K10 clay exhibited higher activity compared to CAN as homogeneous catalyst. Thus, the enhanced activity of CAN/K10 clay in the oxidation of olefin, chalcone and sulfide was attributed to localizing/confining the oxidant and substrate within the layered space of clay. Further, it provides ‘‘high local concentration” of reactants which is normally not observed in homogeneous media. The catalyst was reused for two cycles with no significant drop in the activity suggesting the catalyst stability under the present experimental conditions.



Scheme 20. *Oxidation of styrene and methyl phenyl sulfide using CAN/K10 clay as catalyst.*

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The oxidation of alcohols to carbonyl compounds is an important oxidation reaction in organic chemistry.[87,88] Clay-supported tetrabutylammonium periodate (TBAPI) has been prepared and its activity was tested for the oxidation of benzylic alcohols to the corresponding carbonyl compounds in good yields (Scheme 21) with substrate TBAPI ratio of 2:1.[89] Benzyl alcohol was oxidized to benzaldehyde in 98 % yield using clay supported TBAPI as catalyst in 1.5 h. Substituted benzyl alcohols showed moderate to high yields of the corresponding carbonyl compounds at longer reaction time and a poor correlation between availability of electron density and reactivity was observed. 3-Nitrobenzyl alcohol showed no activity under identical reaction conditions. Similarly, bulkier alcohols like piperonyl alcohol and adamantanol exhibited no reaction. On the other hand, bulkier alcohols having planar geometry and are able to retain it in the transition state undergo efficient oxidation. For example, diphenylmethanol was smoothly oxidized to benzophenone in 98 % yield in 4 h. Similarly, hydroquinol, benzoin and cyclohexanol were oxidized to their corresponding carbonyl product in 70, 99 and 70 % yields respectively. This observation prompted us to propose that the presence of a hydroxyl group in the substrate leads to partial swelling of the clay interlayer, between which the substrate penetrates and can be oxidized by the active form of the oxidant.

This catalytic system was further tested in the oxidation of sulfides to sulfoxides. Methyl phenyl sulfide and its substituted analogues were oxidized to their corresponding sulfoxides in high yields at short reaction time. This catalyst required 15 min to oxidize methyl phenyl sulfide to its corresponding sulfoxide in 98 % yield. On the other hand, a physical mixture of TBAPI and $AlCl_3$ showed only 70 % yield in 240 min. These experiments clearly establish the superior nature of this catalytic system in the oxidation reactions.

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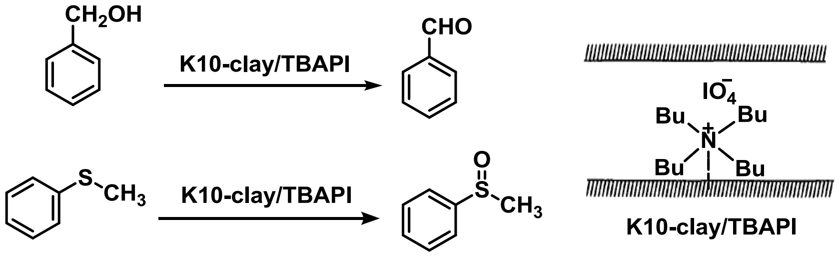
The present catalytic system does not require a polar medium and protic acid catalysis needed for periodate oxidation which puts severe restrictions on its use with acid-sensitive and easily hydrolysable molecules. TBAPI alone is not able to transform hydroxyl groups to the corresponding carbonyl compounds in aprotic solvents. However, in the presence of Kl0-montmorillonite clay, TBAPI can act as a strong oxidizing agent. Though oxidation is observed with TBAPI in the presence of Lewis acid in aprotic polar solvents, the clay-TBAPI composite is superior due to a much simpler work-up, a hydrocarbon solvent is sufficient for the oxidation of alcohol.



Scheme 21. *Oxidation of benzyl alcohol and methyl phenyl sulfide by clay-supported TBAPI.*

Syntheses of sulfoxides have been the subject of considerable research, partly due to their importance of sulfoxides as useful intermediates in organic chemistry.[90-93] Though several oxidants have been employed for the oxidation of sulfides, it is desirable to have a simple and convenient method for the exclusive preparation of sulfoxides without further oxidation.[94-99] In this aspect, the oxidation of sulfides to the corresponding sulfoxides has been reported in the solid state using iodosylbenzene (PhIO) in clays as well as in the suspension of acetonitrile (Scheme 22).[100] The oxidation of sulfides were performed with a 1:l and 1:2 ratio of clay and PhIO. In the case of alkyl aryl sulfide, the presence of electron releasing substituent on benzene ring favors a significant increase in the oxidation in the solid state as well as in solution. An increase in the yield of sulfoxide was obtained with an increase in the

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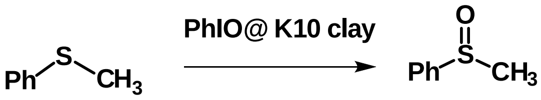
concentration of PhIO. Using 1:1 ratio of clay and PhIO, 45 and 89 % of yields were achieved for methyl phenyl sulfide and 4-methoxyphenyl methyl sulfide respectively in 5 h. On the other hand, 1:2 weight ratio of clay and PhIO, 100 % yield was observed for methyl phenyl sulfide in 5 h while 4-methoxyphenyl methyl sulfide gave 100 % yield in 3 h.

A series of sulfoxides were prepared in quantitative yields using 1:2 ratio of clay and PhIO in short reaction time. The oxidation was facile using K10 clay as well as with other natural clays namely KSF and bentonite. On the other hand, same reaction failed to show any activity with cetyltrimethylammonium chloride (CTAC) and 3-aminopropyltriethoxysilane pillared clays. In these clays, after intimate mixing of reactants the sulfide prefers to stay in the hydrophobic (lipophilie) region while PhIO stays in the hydrophilic region. This limits the contact between these two reagents and consequently, no reaction was observed. Although, the clay can be reused in the successive runs, the use of PhIO is not preferred as it generates iodobenzene as the by-product. Further work-up is necessary to isolate the product from the reaction mixture. In this context, it is always desirable to use molecular oxygen or hydrogen peroxide as environmentally benign oxidants.



Scheme 22. *Oxidation of methyl phenyl sulfide catalyzed by K10 clay.*

Oxidative cleavage of olefins is one of the often used reactions in organic chemistry. The various reagents used for the cleavage of C=C bond are cobalt(II)–Schiff base complexes,[101, 102] $KMnO_4$ under acidic conditions,[103, 104] thiyl radical,[105] OsO_4–Oxone,[106] OsO_4–$NaIO_4$,[107] Ru(II),[108] and Au(I).[109] Although good results are obtained, the high cost of these catalysts posses many drawbacks. In this aspect clay-anchored iron[*N,N''*-

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ethylenebis(salicylideneaminato)] complex was synthesized by direct exchange and its activity was studied in the oxidation of various olefins and chalcones in aqueous acetonitrile using hydrogen peroxide as terminal oxidant. Aldehyde and its derivatives were obtained as oxidation products by the cleavage of C=C double bonds (Scheme 23).[110a] Styrene was oxidized selectively to benzaldehyde using clay-anchored iron salen complex in 30 % yield in acetonitrile. The yield of benzaldehyde was decreased to 10 % when the reaction was performed in water/acetonitrile mixture. Although, the later method showed lower yield, the catalyst is still able to promote the oxidation reaction in aqueous medium. A serious of benzaldehyde derivatives was prepared from their respective olefins in moderate yields using this catalytic system. This protocol was also extended further to the oxidation of chalcone derivatives to their respective aldehydes in moderate to good yields. When comparing the activity of iron–salen complex in solution, the clay catalyzed pathway not only increases the rate of reaction, but also provides selective oxidation towards the formation of aldehyde. Some chalcones gave very good yield in water using clay anchored iron-salen complex compared to the solution. This method allowed oxidizing olefins and chalcones to the corresponding ketones/aldehydes in aqueous medium using hydrogen peroxide as an oxidant within the microenvironment of clay interlayer where the local concentration of active oxygenating species and substrate are more localized. As the polarity of the reaction medium is increased by water–acetonitrile mixture, more substrates may be intercalated into the layers of clay to increase their local concentration in a heterogeneous medium with faster reaction rate. The catalyst can also be reused without any loss in the selectivity and activity. Selective catalytic oxidations of olefin have been carried out with second- or third-row transition metal complexes based on Ru(II),[111] and Au(I).[109] On the other hand, Mn(III) salen complexes have been encapsulated within the cages of NaX, NaY zeolites

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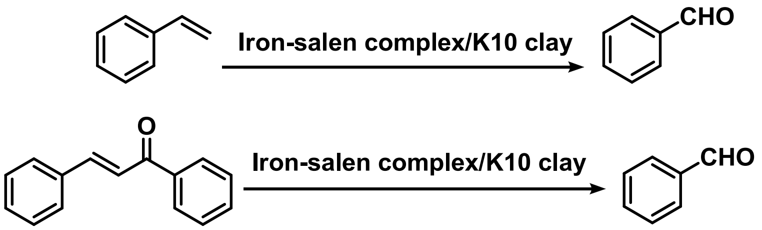
and their catalytic activity was reported on the oxidation of styrene using *tert*-butylhydroperoxide as oxidant.[110b] This catalytic system resulted in the formation of benzaldehyde, styrene oxide and phenylacetaldehyde in dichloromethane as solvent at 60 °C. Although, benzaldehyde was the major product, this method affords a mixture of products in the oxidation of styrene. This result clearly demonstrates that the clay catalyzed oxidation of styrene is superior then zeolite based catalyst in terms of product selectivity.



Scheme 23. *Oxidation of styrene and chalcone catalyzed by clay anchored iron-salen complex using H_2O_2 as an oxidant.*

Clays have been modified by introducing 3-aminopropyltriethoxysilane and also by surfactants onto the clay interlayer and used in organic transformations.[112, 113] The efficiency of surfactant-pillared clays to act as a dispersed solid phase in a triphasic catalyst system prompted us to study other practically useful reactions using organo-clay assemblies.[114] Benzyl halides were cyanated, thiocyanated and hydroxylated using triphasic catalyst (Scheme 24). The utility of a variety of surfactants, namely cetyltrimethyl-, tetrabutyl-, tetraethyl- and tetramethylammonium chlorides and 18-crown-6 intercalated clay has been demonstrated in this nucleophilic substitution reaction.[115] This simple procedure could be used to prepare benzyl cyanides, thiocyanides and alcohols from the corresponding benzyl halides from sodium cyanide, thiocyanide and hydroxide respectively. This method provides a relatively benign approach for the preparation of a variety of benzyl derivatives using a triphasic catalyst. The utility of an

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18-crown-6 intercalated clay assembly in these nucleophilic substitution reactions provides relatively improved yields.

Scheme 24. *Cyanation of benzyl chloride catalyzed by organo clay assembly.*

5. Clays as supports for metal NPs

Nanomaterials have attracted considerable interest in recent years because of their unique properties which are different from those of their corresponding bulk materials. The utility of metal and metal oxide NPs is intensively pursued because of their importance in both fundamental science and advanced technology. Exploring the potential of nanoparticle-based materials as catalysts for green organic synthesis is a challenge for researchers.[116]

In recent years, metal and metal oxide NPs such as Au, Ag and Pd as catalysts have gained much attention in synthetic organic chemistry.[117-119] However, Au NPs are highly expensive and Ag NPs are moisture and light sensitive. On the other hand, Ni NPs are found to be more specific and are complementary to their Pd analogues due to their air stability, ease of preparation and separation of the catalyst mixture from the products at the end of the reaction sequence and ease of recyclability. K10 clay entrapped nickel NPs (Ni/K10) have been prepared, characterized and their activity tested in hydrogenation of olefins using hydrazine hydrate as the reducing agent (Scheme 25).[120] The Ni NPs were highly dispersed on the clay matrix mostly on the outer surface with the average diameter of 15-20 nm. The reaction was optimized using styrene as substrate and 82 % of ethylbenzene was obtained with Ni/K10 as catalyst in 8 h at 70 ^oC. A series of olefins were hydrogenated with high yields and selectivities. A chemoselective

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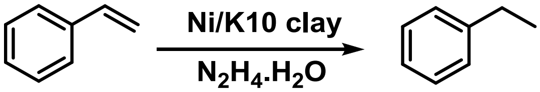
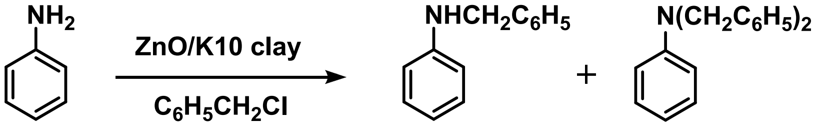
hydrogenation of chalcone was observed with 74 % yield. Allyl phenyl sulfide was selectively reduced to phenyl profile sulfide with 79 % yield. The catalyst was reused three times with no significant drop in its activity for the hydrogenation of styrene. Catalyst poisoning a common problem with heterogeneous catalysts is significantly reduced as the catalytic efficiency remained unaltered even after the third run. This catalytic system is economic and ecofriendly as it requires neither high temperature nor harsh acids and bases, and produces and high yields with excellent chemoselectivity. The workup and product isolation from the catalyst is easy.



Scheme 25. *Hydrogenation of styrene to ethylbenzene catalyzed by Ni/K10 clay as catalyst.*

N-benzylation of amines with alkyl halides is an important synthetic method to obtain mono- and di-N-benzylated products.[121-123] ZnO encapsulated in K10-clay was synthesized and characterized by UV-DRS, emission spectra, powder XRD, SEM and HRTEM analyses. The constrained space and also the polar active sites offered by the clay support stabilize zinc oxide NPs by preventing their aggregation and consequently no extra-capping agent is required. The synthesized ZnO/K10 catalyst was used for the efficient *N*-benzylation of anilines and the reusability of the catalyst also studied[124] (Scheme 26). A serious of amines were subjected for benzylation and observed mono and dibenzylated products. An aliphatic amine afforded exclusively in dibenzylated products in 89 % yield. The catalyst was reused for five times with no significant change in the yield.



Scheme 26. *N-Benzylation of aniline catalyzed by ZnO/K10 clay.*

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6. Conclusions and future prospects

In this *Perspective*, we have emphasized the utility of K10 clay as well as its modified forms as solid acid catalysts or supports to metal complexes, oxidants and metal NPs in several representative organic reactions which are quite important for the synthesis of fine chemicals. Their confined interlayer space as a negatively charged layer and swelling nature in polar solvents plays a vital role in achieving high selectivities. Consequently in most cases, the reported catalytic system resulted in a very high reactivity and selectivity of the desired products in a facile manner using solvent-free conditions or using water as a green solvent. In addition, it is demonstrated that metal ion (Al^{3+}) exchanged K10 clay can be used to synthesize a series of heterocyclic compounds under mild reaction conditions with very high yields. In a similar view, a multicomponent reaction namely, A^3 coupling can be conveniently performed using Ag^1-exchanged K10 clay either in water as solvent at room temperature or under solvent-free conditions with high yields of the desired products. Further, K10 clay was used as a robust support for the deposition and stabilization of metal NPs and its catalytic activity was tested in the hydrogenation of olefins.

The above examples presented in this review demonstrate the utility of K10 clay as a suitable solid acid catalyst or support for simple organic transformations. Although the one-pot methodology has highly promising aspects for the synthesis of complex molecules, in principle this methodology is still poorly exploited mainly because there are no definite rules for anticipating interactions and incompatibilities arising between the reactants involved in each reaction step. Therefore, it would be highly desirable to develop one-pot multicomponent reactions using K10 clay or its modified forms to enhance the existing protocols towards the synthesis of simple or complex molecules which are in demand for mankind in the context of the

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principles of green chemistry. Hence, despite the significant developments recently achieved in this field, the direct implementation of a one-pot process for synthesizing a desired molecule is still in the early stages and so the future developments will require not only a more systematic design, characterization and deep knowledge on catalyst but also a thorough understanding of the physic-chemical features of the catalyst and reaction mechanisms to design more efficient processes for the synthesis of various molecules, particularly pharmacologically relevant heterocycles.

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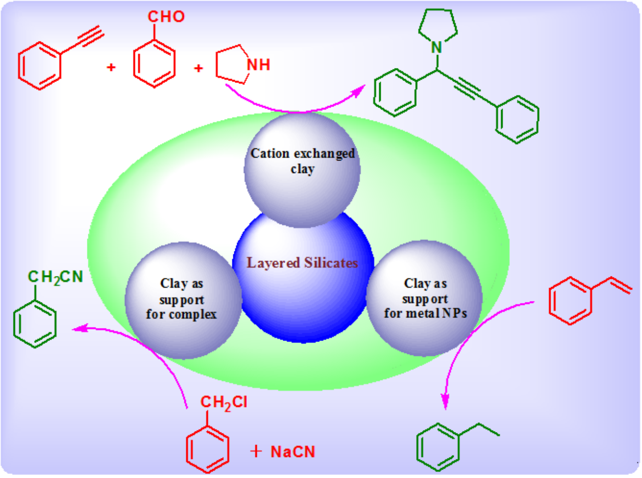

This perspective summarizes the catalytic activity of K10 Montmorillonite as multifunctional catalyst for organic reactions

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