

USE OF CLAY AS CATALYST: A REVIEW

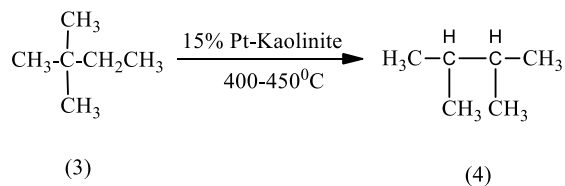
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Abstract

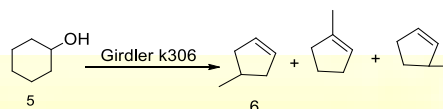
Clays can be used in many organic reactions as catalyst. The catalytic isomerisations, oxidations, hydrogenation and anionic-cationic reactions are well established. These naturally occurring materials provide us cheaper and greener ways of doing various chemical reactions eliminating many hazardous chemicals which are not environmentally benign. Clays have been widely used as catalyst as such or in modified forms such as acid treated or pillared etc. The increased use of such catalyst in organic reactions stems from their being efficient, non-polluting, non-corrosive, sufficiently selective, high yielding and offering clean work-up.

Key words: catalyst, acid activated, isomerisation, non-polluting

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2.2. Isomerisation of alkene



n-alkane undergo skeletal isomerisation giving branched olefins at high temp (300-500⁰C) in clay catalysed gas phase reactions[8-10]. In several cases n-alkanes were generated from n-alkanols by dehydration, carried out simultaneously with isomerisation on the same catalyst [8-12].

In the presence of kaolin-clay aluminium mixture only double bond migration took place subsequent to dehydration of n-hexene in a similar temperature range (250-450⁰C) affording 2-hexene and 3-hexene in 80-85% yield [17].

Galwey[11] has demonstrated that n-hexanol chemisorbs on lewis acidic sites of natural montmorillonite on equilibrium mixture of n-hexene at 90-180⁰C by dehydration and subsequent double bond migration. When the removal of these primary product and water was not rapid, isoalkanes were formed due to Bronsted acidity of the clay particles. Extrapolated kinetic data showed that such reactions at mineral surfaces provided a route for petroleum genesis.

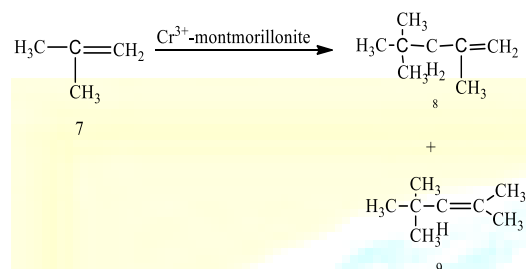
Monmorillonite clays catalyse isomerisation of unsaturated fatty acids (such as oleic acid and its esters) [12-15] and jojoba oil. Changes of conditions (e.g. addition of cocatalyst) can affect the effect the nature of isomerisation products (cis-trans isomerisation, double bond migration or skeletal isomerisation).

Cyclohexene is readily isomerised over montmorillonite or kaolinite to methylcyclopentenes by ring contraction [13, 16, 18]. Starting from cyclohexenol (5) dehydration (in 100% conversion) and isomerisation (91% conversion) take place in a tabular reactor at 500⁰C over Girdler k3.06 catalyst. 4-methyl cyclopentene (6) is the prevalent isomer [18].

Layered clays activated with 10% HCl [19], monmorillonite treated with hydrogen at 360⁰C [19], montmorillonite activated with 5% HCl [20] serve as catalyst.

2.3. Dimerisation of alkenes

Nodding and Cleary [21] at Dow Chemical Co. devised a Cr^{3+} -montmorillonite promoted vapour phase process for the selective dimerisation of isobutene (7) (11-68% yield, 55-100% selectivity)

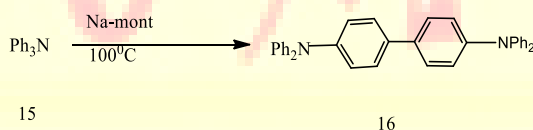


Dimerisation of ethene and isomerisation of the initial product (1-butene to 2-butene) are both catalysed by Ni^{2+} -exchanged montmorillonite or antigorite. The acid sites are responsible for catalytic activity[22]. Trans-stilbene (10) thermally dimerise at 200°C in a mass spectrometer in presence of Cu^{2+} exchanged montmorillonite.

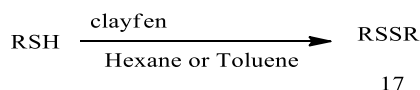
Cu^{2+} -exchanged montmorillonite functions as efficient catalyst for the preparation of dimer (13) and trimer(14) from indene (12) in good yield.

2.4 Oxidative coupling

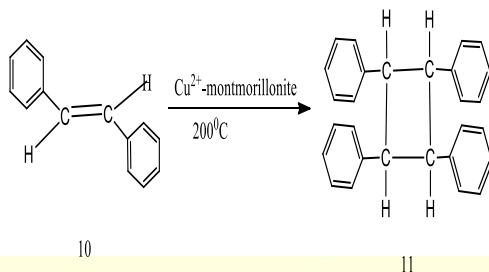
Dimerisation of triphenylamine (15) was accomplished by the use of montmorillonite at 100°C to yield N, N, N', N'-tetraphenylbenzidine (16) as the sole product [23].



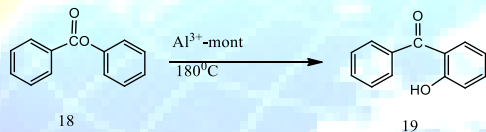
Thiol can be converted into symmetrical disulphides (17) under mild conditions with fair to excellent yields using k-10 clay supported ferric nitrate (clayfen) [24].



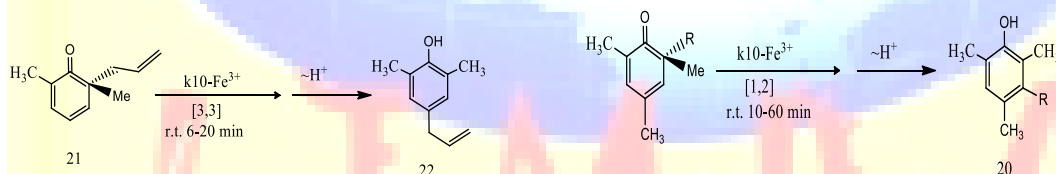
2.5. Rearrangements



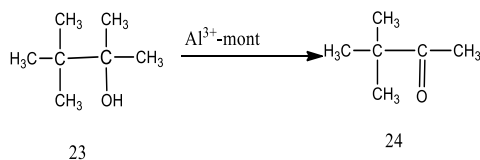
Al^{3+} ion-exchanged synthetic mild or montmorillonite are effective in the Fries rearrangement. Phenylbenzoate (17) for instance, is converted into 2-hydroxybenzophenone (18) (180°C , 4h, 45% conversion, 99% selectivity)[25].



Laszlo et al [29] have devised a very efficient Lewis-acidic clay system (Fe^{3+} -doped k 10 montmorillonite) for catalysis of the cyclohexadien-olphenol rearrangement.



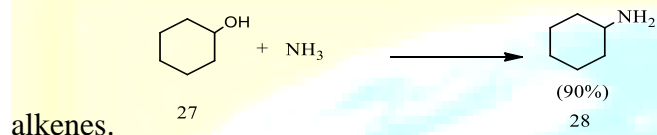
According to recent studies pinacol (23) adsorbed in the interlayer space of Al^{3+} -montmorillonite rearrange quantitatively to pinacolone (24) by thermal treatment. Similarly 23-diphenyl-2, 3-butanediol gives two ketones, the selectivity is correlated with the surface characteristics (e.g., the nature of active sites and the acidity of the interlayer cation[26]).



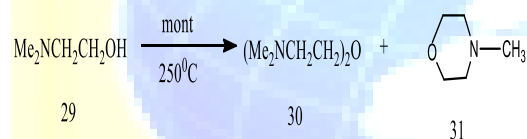
Silica gel or montmorillonite containing 1% TiO₂ are effective catalyst for gas phase dehydration and subsequent rearrangement of formyl allylamines (25) (600°C / 0.8 mbar). Crotononitrile (R=H) (26) was formed in 91.2% yield as a cis-trans isomer mixture.

2.6 Condensation reactions

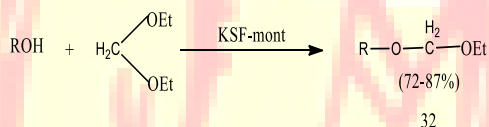
Acid activated montmorillonite catalyse the amination of primary alcohols (C₁-C₆); amines are produced in moderate yields, influenced somewhat by the volume addition rate (0.05-0.06 h⁻¹, 300-400°C, 20-46%) [27]. The amination reaction was also accompanied by dehydration into



N, N-dimethylethanolamine (29) in contact with montmorillonite at 250°C gave linear ether (30) together with some 4-methylmorpholine (31) [28].



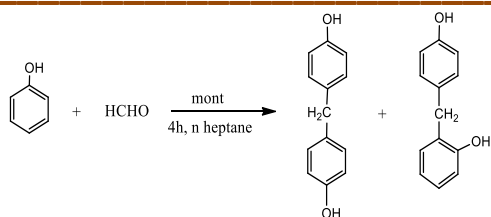
Clay mineral also serves as catalyst for the etherification of phenols by aliphatic alcohols [30].



Alcohols and phenols can be converted into ethers (32) by treatment of KSF montmorillonite catalyst [31]. The O-ethoxy methyl protective group can be removed without loss of configuration with 10% HCl.

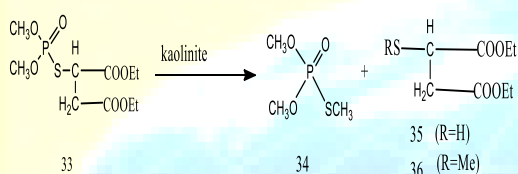
2.7. Coupling reaction involving aromatic compounds

Phenol condenses with formaldehyde to give dehydroxydiphenylmethane in 90% yield (k10 montmorillonite catalyst, 4h reflux in heptanes) [32].

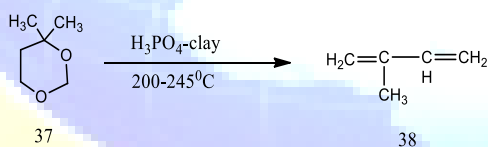


2.8. Thermal and hydrolytic decomposition

Isomalathion (36) decomposes to an extent of 40-50% on kaolinite after 12 days of incubation at 55°C, O, S, S-trimethylphosphorodithionate (34), diethylmercaptosuccinate (35) were identified as major degradation products [33].



Clays like kaolinite, montmorillonite treated with 5.30% H₃PO₄ are effective for ring cleavage of 4, 4-dimethyl-m-dioxane (36) (83.9%) conversion, 78.8-82 selectively [34-35].



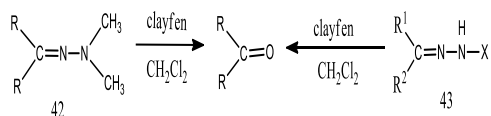
2.9. Condensation reaction with amines and anilines

Schiff bases are easily prepared from aliphatic ketones (C₆₋₁₃) and primary amines [36] or diamines [37] in the presence of acid activated clays such as kaolinite, bentonite, fuller's earth, montmorillonite.

2.10. Carbonyl group deprotection

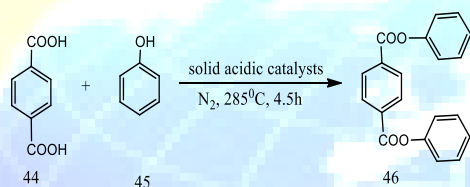
Use of clayfen (k10 clay supported ferric nitrate) offers an efficient mild easy to run method for unmasking the carbonyl groups from imino derivatives such as N, N-dimethylhydrazones (42) [38], tosylhydrazones (43, X=SO₂C₆H₄CH₃), phenylhydrazones (43, X=C₆H₅), 2,4-dinitrophenylhydrazone (43, X=CONH₂) [39]. The reactions are generally fast (30 min-5 h), but

2, 4-dinitrophenylhydrazone require 15-20 h at reflux temperature to drive the reaction to completion.

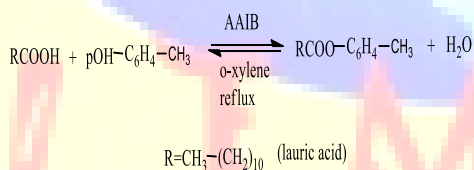


2.11. Esterification reactions

Terephthalic acid (44) reacts with phenol (945) in the presence of a solid acidic catalyst (E.g. SiO₂-Al₂O₃, bentonite, kaolinite) to form diphenylterephthalate 9460 (285⁰C, 4.5h, N₂, 96% yield) [40].



Esterification of long chain fatty acids (e.g. lauric acid) by p-cresol can be done by refluxing in o-xylene with bentonite (acid-activated) for 3 hrs.

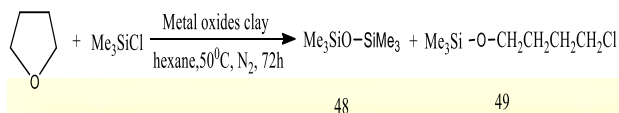


2.12. Decarboxylation reactions

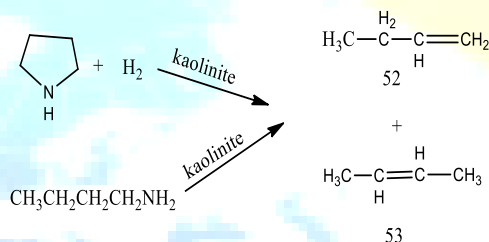
Wilson and Galwey [41] have examined the reaction of stearic acid on the surface of kaolinite, montmorillonite and illite 125-275⁰C. The formation of 2-methyl and 3-methylalkanes is favoured while n-alkanes are obtained only in small amounts.

2.13. Cleavage of C-O bond

Tetrahydrofuran was cleaved by trimethylsilyl chloride in the presence of metal oxides (hexane, 50°C, N₂, 72h) [42]. Clays such as kaolinite and bentonite give selectively (48) but in moderate yields (49) only (10-18%).



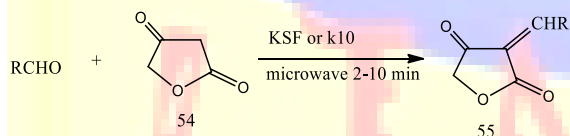
Hydrodinitrogenation of pyrrolidine (50) and butylamine (51) have been catalysed by clays



(450°C, 2.4 bar pulse reactor).

2.14. Use of microwave in clay catalysis

K10 montmorillonite catalysed dry condensation of aromatic aldehydes with tetronic acid has been accomplished under microwave irradiation [43].



3. Acknowledgement

I am grateful to my institution, Digboi College, for providing me the opportunity to study this topic.

4. Conclusion

The present study shows that clays can effectively be used as catalyst in many organic reactions. It is a very inexpensive catalyst and thus a very cost effective catalyst. The catalyst can be easily

recovered in many cases by simple filtration. The method is environmental-friendly as clays replace hazardous metal catalyst. Thus clay can contribute towards green chemistry.

5. References:

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