

Importance of Clays in Organic Reactions

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Abstract: *Clays and modified or supported clays have become some of the widely used catalysts for a variety of organic reactions, due to their easy structural modifications and activation, low - cost, eco - friendly nature, ready availability, ability to act as acidic or basic catalyst without being corrosive. The present article is on 'Importance of clays in organic reactions'. In 1983 Adams used neutron diffraction study for kaolinite. The use of aluminosilicates in heterogeneous catalysis is almost as old as the catalytic concept itself. In 1865 von Liebig has observed the catalytic activity of powdered porcelain. He showed that reaction between hydrogen and oxygen to form water and the conversion of sulphurous acid to sulphuric acid can be catalysed with powdered porcelain or ordinary pumice. An early example from organic chemistry is that by Montaland who in 1911 used Palygorskite as catalyst for the isomerisation of Pinene to camphene. In the next year Gurwitsch reported the use of the same catalyst to polymerise pentenes and hexenes to di and trimers and higher polymers.*

Keywords: Kaolinite, Palygorskite

1. Introduction

The term clay is a generic term and may include almost any earthy material. The name China clay or Kaolin is a more exactly defined material. Kaolinite is a mineral predominantly present in kaolin. Kaolinite is formed from the decomposition by weathering of certain aluminium bearing rocks. Kaolinite is a crystalline material and its internal structure is made up of sheets of alumina and silica. Cleavage planes are existing between the sheets. The mineral occurs in the form of flakes or plates and stacks composed of a number of plates in a book like assembly. Chemical composition of kaolinite is closely approximating the formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Because of the complex chemical composition of silicates, a satisfactory systematic classification was not formulated until the special arrangement of the atom was revealed by X - ray diffraction studies. It is now known that physical chemical properties of clay are greatly influenced by a very small change in its chemical composition.

The confusion regarding the nature of interlayer hydrogen bonding in kaolinite and dickite has been removed by the location of the H^+ protons of the OH group in these minerals. From electron density and difference electron density maps, Adams and Hewat located the H^+ protons in dickite for the first time. Rozhdestvenskaya, *et al.* in the next year and Sen Gupta, *et al.* in 1984 [3] also located the proton positions on electron density maps. All these electron density studies show that the OH vector of the inner hydroxyl points away from the octahedral sheets and is inclined $14^\circ - 20^\circ$ to the (001) plane. The OH vectors of the three surface hydroxyl form bent hydrogen bonds to the adjacent basal oxygens.

Clays in organic synthesis

The use of aluminosilicates in heterogeneous catalysis is almost as old as the catalytic concept itself. In 1865 von Liebig has observed the catalytic activity of powdered porcelain. He showed that reaction between hydrogen and oxygen to form water and the conversion of sulphurous acid to sulphuric acid can be catalysed with powdered porcelain or ordinary pumice. An early example from organic chemistry is that by Montaland who in 1911 used Palygorskite as catalyst for the isomerisation of Pinene to camphene. In the next year Gurwitsch reported the use of the same catalyst to polymerise

pentenes and hexenes to di and trimers and higher polymers. In an industrially important example, Gurwitsch used Palygorskite as a catalyst in 1923 for the oxidation of alcohols to aldehyde and for the cleavage of hydrazobenzene to azobenzene and aniline. Around the same time Thomas had studied the catalytic activity of Florida, somerset bleaching earth for the decomposition of hydrogen peroxide. It is found that Florida earth (Palygorskite) was the best catalyst. Clays are used as cracking catalyst for gasoline production. In 1938 Houdry solved the problem of catalyst regeneration and made catalytic cracking commercially feasible. In the subsequent decades, several organic reactions have found to be effectively catalysed by clays.

Electrophilic Substitution Reactions

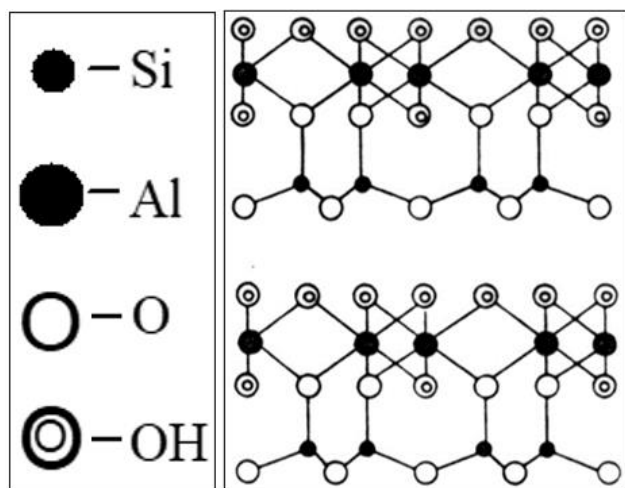
Electrophilic aromatic substitution reactions are bimolecular reactions. In a usual reaction vessel reactions take place in a three - dimensional reaction space. The most significant advantage of clay - supported reactions are reduction of dimensionality of reaction space. Here reaction is constrained to the surface of the clay sheets. Because of this reduction from 3D to 2D, there is a large increase in frequency of collision. Thus rate of reaction increased by several orders of magnitude when reactions are conducted on clay surface.

Benzene can be alkylated with alkyl halide in presence of AlCl_3 as catalyst. The transition state in this case would be $\text{C}_6\text{H}_5 - (\text{H}; \text{R})^+ \text{AlCl}_4^-$ complex. Clay surfaces stabilize these polar transition states and intermediates. The clay interface bears an electric double layer. The positive charge ions are attributed towards the negatively charged tetrahedral layer of montmorillonite clay. This atmospheric condensation increases the ionic strength at clay interface. The concentration of counter ions near negatively charged tetrahedral layer of montmorillonite clay is greater by 3 or 4 orders of magnitude than their average concentration of the medium. The electric field near the clay surface can reach the value of $\text{ca. } 10 \text{ V nm}^{-1}$.

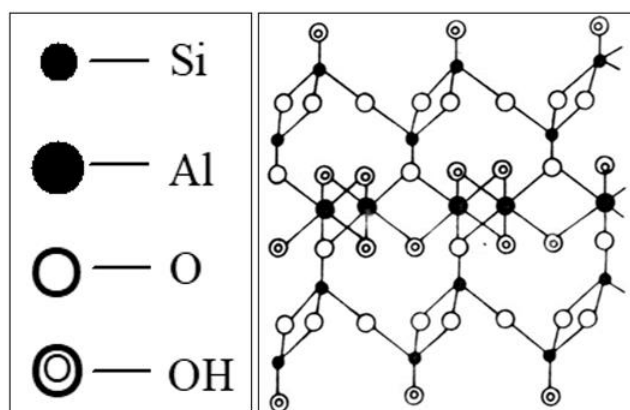
It has been suggested that this value is sufficient to overcome totally the energy barrier for an $\text{S}_\text{N}2$ reaction.

Surface acidity of clay

The most prominent and remarkable feature of clays is their surface acidity. The surface acidity of clay makes its acidity equal to that of some of the strongest inorganic acids. The Hammet acidity function H_0 for a number of clays has been measured. The acidity of montmorillonite clays, after washing with 0.1 mol l^{-1} hydrochloric acid or other mineral acids, can reach the range of -6 to -8. Kaolinite (1: 1 clays) and montmorillonite (2: 1 clays) have surface acidities that place them between concentrated nitric acid and sulphuric acid.



Kaolinite (1: 1 clay)



Montmorillonite (2: 1 clay)

In the case of montmorillonite, the exceptionally high surface acidities are due to isomorphous substitution in the framework of the clay. In the tetrahedral layer silicon (IV) is occasionally replaced with aluminium (III). Now the valences of four oxygen's coordinated to aluminum are not saturated and an excess of negative charge remains on these oxygens. This change can be delocalized over the whole clay surface equivalent to conjugate base of a strong inorganic acid. A second reason for high Bronsted Acidity of clay is the presence of interlamellar cations. A layer of water molecule is found in between the negatively charged oxygen and the positively charged counter ions (scheme - 3). These water molecules are strongly polarized and thus favour proton loss.

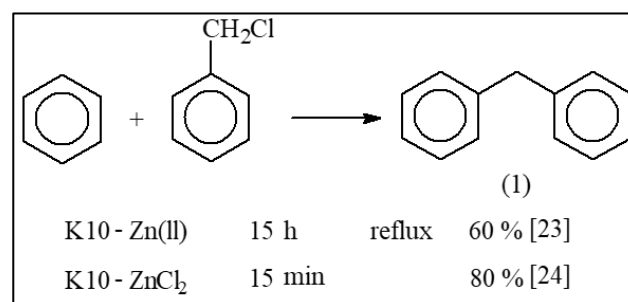
This explains the decrease in the surface acidity as the moisture increase in the clay sample. The monomolecular layer of water between clay and metal cation was confirmed by detailed examination using multinuclear magnetic resonance method of D_2O molecules interacting with clay particles. The high surface acidity of clay is useful for generating carbocations from a variety of compounds like halides, acid halides, alcohols and olefins. Thus in the presence of clay, Friedel Crafts reactions can be carried out effectively. The following points make clay catalysts quite outstanding for Friedel Crafts reactions.

- 1) High yield
- 2) Reduced reaction time
- 3) High conversion
- 4) Lack of rearrangement
- 5) Elimination of toxic waste.

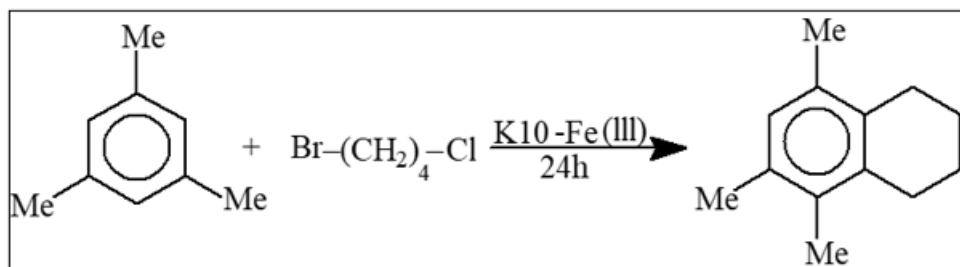
Clay promoted organic reaction with halides

Alkylation of aromatic compounds with halides is best carried out at the mildest conditions. Hectorite and saponite exchanged with metal gave similar result with aliphatic chlorides or bromides in alkylation with olefins. Reactivity of different alkyl bromides in alkylation of benzene and toluene at reflux temperature was studied by Gosselck and Lotz. The order of reactivity was found as tertiary > secondary >> primary alkyl bromide.

Benzene on benzylation with benzoyl chloride in presence of K10 montmorillonite doped with transition metal cations were studied by Laszlo and Mathy. The best selectivity was shown by K10 - Ti (IV) - 66% of monoalkylated and 20 % of dialkylated products. The most active catalysts were K10 Fe (III), K10 Zn (II), K10 Cu (II) and K10 Zn (IV). The most important advantage of clay catalyst is that they can be re-utilized. The K10 Fe (III) sample was reutilized up to 5 times with no loss in activity.



K.10 supported ZnCl_2 ("clay zic") shows greater reactivity and selectivity compared to previous mentioned ion exchanged K10. The unsupported zinc chloride can be considered as one of the weakest Friedel - Craft catalyst. Thus, the greater reactivity and selectivity is a remarkable feature of "clay zic". The activity of the catalyst mainly depends on the activation temperature, the reagent loading and on the anion. Alkylation of mesitylene with 1 - bromo - 4 - chlorobutane gave 1, 2, 3, 4 - tetrahydro - 5, 6, 8 - trimethylnapthalene. Here alkylation is followed by 1, 2, migration of the methyl group.



Alkylation of benzene with tert - butyl bromide in presence of dry Cu^{2+} - bentonite catalyst gives tert - butylbenzene. The yield is about 79 %. When the water content in the bentonite increases, the formation of dialkylated products with para predominance increases. When Ca - bentonite is used as heterogeneous catalyst, a considerable amount of 1, 4 - dialkylated products are also formed.

2. Conclusion

Natural as well as commercially available clays and their diverse modified forms are good catalysts for accomplishing a large variety of organic reactions. Since the procedures employed for their modification are usually simple chemical operations, there is great scope to prepare newer clay - supported catalysts that are capable of steering organic reactions in any desired direction to achieve higher yields and greater selectivity including diastereo - and enantioselectivity. The studies carried out so far indicated that many reactions can be carried out using clays. The degradation observed by “clay cop” presently could therefore in part be due to the high acidity and surface activity of the clay itself. However, substrates which are more robust could be more easily reacted especially they can be nitrated. These include naphthols and its methyl ether.

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