ABSTRACT

Recent advances in the intercalation and intersalation (accommodation of ion-pair salt into the interlamellar region) reactions of metal complexes or other organic compounds with layered clay minerals particularly montmorillonite (Mnt hereafter) clay have paved the way for the development of new classes of supported (heterogeneous) catalysts, bioactive agents, chemical sensors, slow release materials, adsorbents etc. The versatility of the clay structure is the main reason for ever-growing interest in this area.

The results of the present work are embodied in the thesis which consists of four major chapters.

First chapter:-

It is an introductory one which contains a critical review of the background of clay based materials, its chemistry and applications. Mnt a member of smectite group of clay is a 2:1 phyllosilicate. Such clay possesses exchangeable cations {expressed as Cation Exchange Capacity (CEC) i.e milli equivalent / 100gm of the clay} in the interlamellar space. Mnt is unique in the way that they may intercalate suitable metal complexes more than CEC to form double or pseudo-trilayer composites. Intecalated Mnt composite like Pillared Interlayered Clays ( PILC ), metal ion – exchanged clays or metal complex – intercalated clay composites can act as selective catalyst in Fluidized cracking of heavy hydrocarbon, Friedel - Crafts reaction, hydrogenation etc. they can be used as supports for slow release pesticides and medicinal drugs, effective adsorbent for radioactive and toxic industrial wastes, separator for
enantiomeric compounds etc. Thus Mnt composites may be tailor made for many industrially important processes. X-ray diffraction, Thermal analysis, UV visible and IR spectroscopic analyses, SEM-EDX and Surface area analyses etc are utilized for the characterization of the composites.

Chapter 2:-

It contains all the experimental details of the work. The clay used were from M/S Neelkanth Chemicals, Jodhpur and Wyoming bentonite. The crude clay contained various impurities like quartz, sand etc. which could be removed by sedimentation technique by applying Stoke’s law and -2 μm fraction of clay rich in Mnt was collected. The -2μm fraction of Mnt was then converted to Na-Mnt form which was glycolated to give a basal spacing of 16.5 – 17 Å characteristic of Mnt clay. Besides XRD, thermogravimetric curves and IR spectra were also studied which showed characteristic patterns for Mnt clay.

Metal complexes of $[M(L-L)_3]X_2$ type were prepared by known methods where $M = \text{Ni, Fe}$ and $L - L = 1,10$-phenanthroline (phen), 2,2′-bipyridine (bpy) etc., $X = \text{Cl}^-, \text{SO}_4^{2-}, \text{CH}_3\text{COO}^-$ etc.

Hydration behaviour of Mnt was studied under several relative humidities (11, 32, 42, 68, 84 and 100%) at room temperature. The exchangeable cations were varied as $\text{Na}^+, \text{Ca}^{2+}$ and $\frac{1}{2}\text{Na}^+\frac{1}{2}\text{Ca}^{2+}$- Mnt. The basal spacings were recorded for samples hydrated from 24 to 240 hrs.

Intercalation (excess adsorption over CEC) and intercalation reactions of $[M(L-L)_3]X_2$ type metal complexes with Mnt – clay have been studied under different experimental conditions, such as, (i) Stirring at room temperature (ii) Autoclaving (iii) Refluxing and (iv)
Ultrasonication. Effect on adsorption of such metal complexes by different fractions of Mnt, -0.5, -1 + 0.5, -1.5 + 1 and -2.0 + 1.5 μm under microwave and ultrasonic radiations were studied.

Intersalation reaction of \([\text{Fe}(1,10\text{-phen})_3]SO_4\) with Mnt were studied in different states of aggregation of the clay-aggregated, dispersed and delaminated state. Intersalation in presence of different salts also has been studied.

Intercalation of \([\text{Ni}\{\text{di}(2\text{-aminoethyl})\text{amine}\}_2]\) and \([\text{Ni}(2,2',6',2''\text{-terpyridine})_2]\) onto Na-Mnt was carried on by stirring an aqueous solution of the respective metal complexes with a suspension of the clay.

Na-Mnt was converted to phosphate linked (P0-Mnt) clay by treatment with phosphoric acid under suitable condition.

Na-Mnt was partially intercalated with \([\text{Ni}(\text{phen})_3]^{2+}\) or \([\text{Ni}(\text{bpy})_3]^{2+}\) complex and remaining exchange sites were occupied by Al\(^{3+}\) or Cu\(^{2+}\) or Cd\(^{2+}\). These were used as catalysts in benzylolation reaction or as adsorbent for H\(_2\)S or NH\(_3\).

The equipment used for characterization of different clay based products were TGA-DTA instruments, X-ray diffractometer, IR and UV-visible spectrophotometers, Elemental analysers, Gas chromatogram, Surface area analyser, SEM-EDX etc. Different instruments used for carrying the experiments were ultrasonic bath and ultrasonic probe, microwave oven, autoclave, ultra-centrifuge etc.

Chapter 3:-

It contains the results and discussion of the entire experiments shown in chapter 2.
Section 3.a:-

It contains about the hydration of Mnt under restricted conditions of relative humidity. The change in basal spacings were plotted against time which showed steady increase for crystalline swelling. It was observed that Na-Mnt is unlike Ca-Mnt and ½Na-½Ca-Mnt in hydration behaviour. In a ½Na-½Ca clay, Na ions are supposed to reside on the external surface while Ca ions occupy the internal surface.

Section 3.b:-

It contains about intersalation of [M(L-L)3]X2 type metal complexes with Mnt. The results showed that the order of intersalation is stirring < autoclaving < refluxing < ultrasonication. Moreover, it was found that higher temperature favours intersalaton. Phen complexes are adsorbed in greater amount than bpy complexes. Similarly, sulphate containing complexes are found to be adsorbed in greater amount than chloride containing ones.

Section 3.c:-

It contains the results for intersalation of [Fe(1,10-phen)3]SO4 with Mnt. Intersalation reaction occurred with the dispersed / delaminated clay to yield a double layer while dried clay exhibited intersalated complex as a stable single layer. Intersalation has been observed to increase in presence of sulphate salts.

Section 3.d:-

It contains the thermal and spectroscopic studies on the decomposition of [Ni{di(2-aminoethyl)amine}2] and [Ni(2,2′,6′,2″-terpyridine)2]-Mnt intercalated composites. The
thermal analysis, IR spectroscopic and XRD studies showed that the clay composites gained an extra thermal stability of 50° and 150°C respectively for [Ni\{di(2-aminooethyl)amine\}$_2$] and [Ni(2,2',6',2''-terpyridine)$_2$]-Mnt compared to their corresponding metal complexes. Thus it reveals that the metal complexes having ligands with aromatic backbone got higher thermal stability than aliphatic one upon intercalation into layered clays.

Section 3.e:-

It contains about phosphate bridged films of Mnt and their intercalation/intersalation behaviour. It is stable in aqueous environment even at 90°C for a couple of hours. The CEC was slightly affected and the layer structure of the original clay was maintained. The intercalation and intersalation behaviour of this modified clay was been studied in comparison with Na-Mnt.

Section 3.f:-

It contains applications of such clay intercalated composites:

(i) As catalyst: These composites with partially exchanged Al$^{3+}$ ions were converted to Lewis acid sites by heating around 300°C and were found to be effective in benzylation reactions (Friedel-crafts reaction) as catalysts.

(ii) As adsorbents for odorous indoor air. These composites contain metal complexes and metal ions like Cu$^{2+}$ or Cd$^{2+}$ in the interlamellar spacing and were found to adsorb indoor pollutant gases like H$_2$S or NH$_3$. 
Chapter 4:-

The last chapter, comprises general comments and conclusions of the research work. The work can be extended in several directions in near future. Especially the application part (i.e., catalysis and adsorption) has a good scope. Further study is proposed in the field of separation of optical isomers.

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