CHAPTER 5
SYNTHESIS OF ACTIVE OXIDE FROM MMLH-MONTMORILLONITE COMPOSITE

5.1 Introduction:

MMLH possess positive charge over the layers; this characteristic is opposite in nature to clay minerals like montmorillonite, vermiculite, etc. where the layers bear negative charge. Very high thixotropic, and stable viscous gel is obtained when negatively charged layers of montmorillonite clay are contacted with positively charged layers of MMLH in aqueous medium. Such an interaction provide a homogenous distribution of one type of layered material over the other type. Simple inorganic salts like metal carbonates, nitrates, etc. do not give such a stable dispersed thixotropic gel with montmorillonite in aqueous medium. Likewise, a similar interaction of MMLH with inorganic solids like γ-alumina, silica gel, zeolite etc. cannot be expected as they are not charged layered material with hydrational properties similar to montmorillonite.

In the present work, highly dispersed metal oxides have been synthesised over an aluminosilicate matrix formed by thermal decomposition of an aqueous gel of cationic montmorillonite with anionic MMLH. The novelty of the work lies in the point that it may provide a cheap and easy method to prepare well dispersed active oxide adsorbents or catalysts over a ceramic matrix having very high surface area.
5.2 Results and discussions:

The magnitude of negative charge in montmorillonite layers (0.7 to 1.5 meq g\(^{-1}\) C.E.C.) is lower than that of positive charge in MMLH layers (2.4 to 4.1 meq g\(^{-1}\) A.E.C.). Such high charge density prevents MMLH to form gels as they cannot swell like montmorillonite. Viscous suspensions, as obtained from MMLH and montmorillonite, are extremely thixotropic. The thixotropy here arises out of the gel formed by bridges of positive MMLH layers between two negatively charged montmorillonite layers in aqueous medium. As the force of interaction between two oppositely charged layered materials is electrical in nature, the bridging of particles is a self-organising low energy process. Such an interaction provides a homogeneous distribution of one layered material over the other. Since the gels are stable, therefore free water release on standing from the gels is minimum. Apart from MMLH, other simple inorganic salts like metal carbonates, nitrates, etc. do not give such a stable dispersed thixotropic gel with montmorillonite in aqueous medium with low free water releasing property. Inorganic solids like \(\gamma\)-alumina, silica gel, zeolite etc. which do not hydrate like negatively charged montmorillonite layers, also cannot form similar composites with MMLH.

Report has so far been made about suitability of supporting of MMLH over several oxides like freshly prepared hydrated alumina, \(\gamma\)-alumina, \(\alpha\)-alumina, \(\text{ZrO}_2\), silicates, \(\text{TiO}_2\), etc. to prepare advanced
catalysts. However no report is found about supporting MMLH over montmorillonite to design advanced materials for application in the fields of catalysis, adsorbents, etc. Supporting of positively charged MMLH over negatively charged montmorillonite is expected to be useful in designing improved materials for the following factors:

(1) MMLH on thermal decomposition at about 500°C gives some bivalent oxides having the layered morphology of the precursor\textsuperscript{238}. Due to their layered nature, these oxides are expected to exhibit very high surface area and hence could be highly reactive for different gas solid reactions than granular oxide particles\textsuperscript{189}. Thus synthesis of supported layered oxides over montmorillonite matrix from MMLH precursors is likely to increase the reactivity of these layered oxides further;

(2) Due to formation of bridges of positively charged MMLH layers between negatively charged montmorillonite layers in aqueous medium by an electrostatic interaction, the MMLH particles will be evenly distributed which in turn pave the way for deriving well dispersed oxides on thermal decomposition; and

(3) The alumino-silicate supported material obtained by thermal decomposition of montmorillonite precursors is a relatively inert ceramic matrix for certain reactions\textsuperscript{187,188} e.g. desulfurization of coal gases.

One of the industrially important reactions reported is the interaction of \( \text{H}_2\text{S} \) gas with highly dispersed and active ZnO particles derived
from thermal decomposition of Zn-Al type MMLH\textsuperscript{1,5}. Thermodynamically ZnO is one of the most suitable oxides for adsorption of H\textsubscript{2}S from gaseous state\textsuperscript{239}. This oxide is used mainly during desulphurisation of fuel gases for fuel cells\textsuperscript{240-242}, where purity of feed gas required is very important. The efficiency of the reaction is however decreased by various contaminants like H\textsubscript{2}O, CO, CO\textsubscript{2}, etc.\textsuperscript{243}. Supporting of ZnO over other matrix like silica, alumina, titania and chromia etc. to increase the efficiency of the process has also been reported\textsuperscript{244}. Development of porous ceramic filters in moulded form from suspensions of kaolinite and ZnO have also been reported\textsuperscript{245,246}. Preparation of ceramic membranes from hydroxy-aluminium chloride pillared montmorillonite on $\gamma$-alumina support has also been reported\textsuperscript{247}.

In the present work highly dispersed metal oxides viz. ZnO, MgO and NiO have been synthesised, as described in the sections \textit{2.3-14-a} and \textit{2.3-14-b}, over an aluminosilicate matrix formed by thermal decomposition of an aqueous gel of cationic montmorillonite with anionic MMLH like Zn-Cr MMLH, Ni-Al MMLH and Mg-Al MMLH respectively. In Fig. 5.1 a schematic representation is given about formation of ZnO layers over montmorillonite matrix obtained from Zn-Cr-Cl MMLH. The reactivity of supported and unsupported ZnO obtained from Zn-Cr-Cl-MMLH-clay composite and Zn-Cr-Cl-MMLH respectively towards H\textsubscript{2}S at 500°C are described in detail in section \textit{2.3-15}. 

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The $\zeta$-potential measurements (Table 5.1) of samples carried out at various pH have shown that there is a gradual increase of -ve $\zeta$-potential of Ca-montmorillonite on rise of pH. MMLH in general show increase of +ve $\zeta$-potential and then a decreasing trend with increase of pH. In general MMLH Ca-montmorillonite (1:1 Wt. ratio) show an initial trend of increase of -ve $\zeta$-potential upto a certain value and then it decreases (with the exception of Mg-Al-MMLH:Ca-montmorillonite composite).

The Zn-Cr-CI MMLH-clay composite after calcination at different temperatures converts to different crystalline products and XRD patterns of them are shown in Fig. 5.2. While at room temperature the dried composite shows XRD peaks typically of Zn-Cr MMLH only, the calcined (500°C) product gives wide peaks of ZnO corresponding to degradation of Zn-Cr-CI MMLH. XRD patterns of composites calcined at 750°C shows segregation of Zn-Cr MMLH to ZnO and ZnCr$_2$O$_4$. ZnO thus produced over the aluminosilicate matrix of calcined montmorillonite attacks the silica layer of montmorillonite at 950°C producing Zn$_2$SiO$_4$ as shown in the Fig 5.2.

Fig. 5.3 shows the scanning electron micrographs of neat Zn-Cr MMLH (5.3a) and calcined (at 500°C) Zn-Cr MMLH-clay composite (5.3b). SEM pictures show the formation of layered ZnO surfaces projected like displayboards over ceramic matrix of calcined montmorillonite. The Energy Dispersive X-ray (EDX) analysis of these area show that the
relative amount of Cr is higher, which can be ascribed as originating from ZnCr$_2$O$_4$ crystals. The corresponding total EDX analysis of the composite material calcined at 500°C is shown in Fig. 5.4. The EDX analysis of dark area seen in SEM of the grains exhibit essentially peaks associated to O, Al and Si and corresponds to the montmorillonite clay.

The XRD pattern of different crystalline products obtained after calcination of Ni-Al-MMLH-clay composite are shown in the Fig. 5.5. At room temperature, the dried composite shows XRD peaks typically of Ni-Al MMLH only, while the 500°C calcined product gives wide peaks of NiO corresponding to degradation of Ni-Al MMLH. XRD patterns of composites calcined at 950°C shows segregation of Ni-Al MMLH to NiO and NiAl$_2$O$_4$. NiO thus produced over the aluminosilicate matrix of calcined montmorillonite attacks the silica layer$^{245}$ of montmorillonite at only 1200°C producing Ni$_2$SiO$_4$ as shown in the Fig. 5.5. The total EDX analysis of samples calcined at 500°C gives the composition of the material as consisting of O, Al, Si and Ni mainly (Fig. 5.6).

Similarly, the Mg-Al-MMLH-clay composite after calcination at different temperatures converts to different crystalline products; the XRD patterns of them are shown in Fig. 5.7. The dried composite at room temperature shows XRD peaks typically of Mg-Al MMLH only while the calcined product gives wide peaks of MgO corresponding to degradation of Mg-Al MMLH even upto 950°C. XRD patterns of composites calcined
at 1050°C shows formation of MgSiO₃. MgO thus produced over the alumino-silicate matrix of calcined montmorillonite attacks the silica layer of montmorillonite at only 1050°C. The XRD pattern of the product calcined at 1200°C shows formation of Mg₂Al₄SiO₁₀ and MgAl₂O₄ as shown in the Fig. 5.7.

Evaluation of activity of ZnO surface derived from thermal decomposition of Zn-Cr-MMLH-clay composite was carried out by some sulphurization experiments with H₂S gas at a constant flow-rate. Due to the layered projections, ZnO and ZnCr₂O₄ are highly reactive. Reaction of H₂S with such layered oxides produces ZnS and ZnCr₂S₄ as indicated by the XRD pattern shown in Fig. 5.8. SEM (Fig. 5.9a) shows well grown crystals of ZnS over the ceramic matrix of montmorillonite. EDX analysis confirms the composition of these particles as ZnS (Fig. 5.9b). The amount of sulphur chemically adsorbed in the calcined products of Zn-Cr MMLH-montmorillonite were measured by gravimetric method as indicated in section 2.3-15. The amount of sulphur adsorbed by the calcined composite (1:1 wt ratio Zn-Cr-MMLH: montmorillonite) and calcined neat Zn-Cr MMLH is found to be 13.6% and 13.9% (wt./wt.) respectively. This clearly indicates that the amount of sulphur adsorption in supported material is higher than in the unsupported one. Though the starting Zn-Cr MMLH content in the neat material is nearly twice than in the composite material. Thus, there is an almost two fold increase in
sulphur adsorption ability of ZnO due to supporting of it on ceramic matrix of montmorillonite clay. The increased reactivity of ZnO derived from Zn-Cr MMLH can be linked up with the self-exfoliation of the layers of both the materials and distribution of MMLH particles uniformly in the whole gel, which on thermal decomposition gives uniformly distributed upwardly projected metal oxide layers over the clay particles as shown in the Fig. 5.1. The regenerability of ZnO layers from the sulphurised product has been observed by XRD also, when the latter is heated at 500°C for one hour in air.

5.3 Summary:

1. Highly reactive metal oxide particles projected like display boards over a ceramic matrix can be prepared easily by a process of self-exfoliation of MMLH to discrete layers by montmorillonite through intimate contact, hydration and subsequent drying and calcination of hydrated mixture.

2. Surface active ZnO particles obtained from Zn-Cr MMLH-montmorillonite composite show very high adsorption of sulphur from H₂S gas at 500°C and the active surface may be regenerated easily by thermal treatment.

3. Apart from ZnO, any suitable MMLH from a combination of transition/non-transition metals like Ni, Co, Mn, Ca, Mg, Li etc. may be utilized in order to prepare other active metal oxide surface-clay composite.
Table 5.1 The ζ-potential values of samples of Ca-montmorillonite, different MMLH and MMLH-clay composites.

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<th>pH of the suspensions</th>
<th>Ca-montmorillonite</th>
<th>Zn-Cr MMLH + Ca-montmorillonite (1:1 wt ratio)</th>
<th>Mg-Al MMLH + Ca-montmorillonite (1:1 wt ratio)</th>
<th>Ni-Al MMLH + Ca-montmorillonite (1:1 wt ratio)</th>
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*Experimental condition: Neutral electrolyte concentration (NaCl) 10^-2 mol l^-1, cell temperature 25°C, ζ potential = +5mV.*
Fig 5.1 - Scheme of synthesis of active metal oxide (ZnO) surfaces over montmorillonite (clay) matrix from MMLH and their reactivity with gas (H₂S).
Fig 5.2: XRD patterns of Zn-Cr MMLH clay composite after calcination to different temperatures 1. 25°C, 2. 500°C, 3. 750°C, 4. 950°C; phases A - ZnCr₂O₄, B - ZnSiO₄, C - ZnO.
Fig 5.3: SEM of Zn-Cr MML,1 (3a), Zn-Cr MML,1 clay composite (3b)
Fig. 5.4 E DX total analysis of Zn-Cr-MMLH-montmorillonite composite.
Fig 5.7: XRD patterns of Mg-Al MMLH-clay composite after calcination to different temperatures 1. 25°C, 2. 500°C, 3. 1050°C, 4. 1200°C; phases A - Mg$_2$Al$_4$SiO$_{10}$, B - MgAl$_2$O$_4$, C - MgSiO$_3$, D - MgO.
Fig 5.6. EDX total analysis of Ni-Al MMLH-clay composite calcined to 500°C.
Fig 5.5: XRD patterns of Ni-Al MMLH-clay composite after calcination to different temperatures 1. 500°C, 2. 750°C, 3. 950°C, 4. 1200°C; phases A - Ni$_2$SiO$_4$, B - NiAl$_2$O$_4$, C - NiO.
Fig. 5.8: XRD pattern of sulphurised product, $\Lambda = \text{ZnO}$, $B = \text{ZnS}$, $C = \text{Cr}_2\text{ZnS}_4$
Fig 5.9: (9a) SEM of calcined Zn-Cr MMLH-clay composite after sulphurisation showing well grown crystals of ZnS over montmorillonite matrix, (9b) EDXA of selected area of sulphurised product.