



Novel synthesis of active metal oxide surface from a self-organising system of inorganic solids

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Abstract

Self-organising aqueous suspension of layers of cationic montmorillonite and anionic mixed metal layered hydroxides (MMLH) after thermal treatment at about 500°C gives active and well-dispersed layers of metal oxides over montmorillonite matrix exhibiting enhanced reactivity with gaseous reactants. Increased absorption of H₂S by ZnO supported on montmorillonite matrix is given as an example. © 2000 Elsevier Science B.V. All rights reserved.

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Negatively charged layers of montmorillonite clay when contacted with positively charged layers of mixed metal layered hydroxides (MMLH) of hydro-talcite type in aqueous medium gives a highly thixotropic suspension. This remarkable thixotropy arising out of the gel formed by self-organised [1] bridges of positive MMLH layers between two negatively charged montmorillonite layers (Fig. 1) provides a homogeneous distribution of the former over the latter. Such an interaction of montmorillonite with other inorganic solids like γ -alumina, silica gel, zeolite, etc. cannot be expected as they do not have positive surface charge.

The positive layer charge of MMLH is higher than (2.4 to 4.1 meq/g anion exchange capacity [2])

the negative layer charge of montmorillonite (0.7 to 1.5 meq/g cation exchange capacity), therefore 1 g of the former can electrostatically neutralize more than 1 g of the latter. Presently, the thixotropic property of MMLH–montmorillonite interaction is advantageously utilized to formulate novel drilling fluid for petroleum exploration [3,4]. However, apart from this, no report has been made so far about the application of MMLH–montmorillonite interaction to design advanced materials for application in other fields.

MMLH on thermal decomposition at about 500°C gives a bivalent oxide having the layered morphology of the precursor [5] but at higher temperatures, a spinel is formed. Due to their layered nature, these oxides are expected to show high surface area and hence, could be highly reactive for different gas solid reactions than granular oxide particles [6]. One of the industrially important reactions reported for such a system is the reaction of H₂S gas with highly dis-

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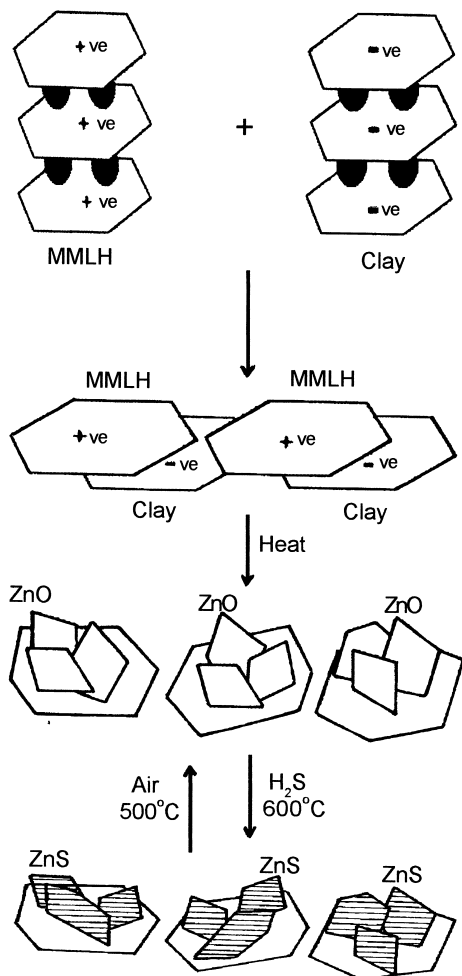


Fig. 1. Schematic diagram of formation of active metal oxide (ZnO) over montmorillonite matrix from MMLH and their reactivity with H₂S.

persed ZnO particles derived from thermal decomposition of Zn–Al type MMLH [7–9]. In the present

work, the synthesis of highly dispersed and active ZnO over montmorillonite matrix and its interaction with H₂S gas at high temperature (about 600°C) has been studied.

Ca-montmorillonite (M/s LOBA Chemie, India), and [Zn₂Cr(OH)₆]Cl · H₂O synthesised by following a reported method [10], were mixed thoroughly in 1:1 weight ratio. The mixture was then dispersed in water under a very high shearing (14,000 rpm) and was set aside for hydration. After about 7 days, the hydrated slurry was carefully dried at 60°C and subsequently calcined at different temperatures viz. 500°C, 750°C, 950°C at a heating rate of approximately 3°C/min in an electric muffle furnace under oxygen atmosphere.

Sulphurisation experiments were carried out by passing H₂S gas at a flow-rate of 40 cm³/min through a 2.5-cm length plug of 5.0 g powder (< 150 μm size) of MMLH–clay composite calcined at 500°C. This plug was placed in a 1.5-cm diameter silica tube at 600°C for 60 min in a cylindrical furnace. The flow of hydrogen sulphide gas was maintained during cooling and was continued till the temperature of the reactor came down to 200°C.

In order to compare the efficacy of the supported system with a non-supported one, a neat sample of Zn–Cr MMLH was also calcined at 500°C in a similar way as that of calcined MMLH–clay composite. 5.0 g of the calcined product (particle size < 150 μm) was subjected to sulphidisation reaction with H₂S similar to that of the supported system as described above. Quantitative estimation of sulphur adsorbed in the calcined products of Zn–Cr MMLH (neat) and Zn–Cr MMLH–montmorillonite were done gravimetrically by converting S²⁻ to BaSO₄ [11]. The active ZnO surface can be regenerated

Table 1

Main crystalline phases formed at different temperatures (the corresponding powder diffraction files or literature reference numbers are given in brackets)

Sample: (Zn–Cr MMLH: montmorillonite 50:50 wt.%)	Crystalline phases
Dried at 60°C	Ca-montmorillonite (PDF 13-135), [Zn ₂ Cr(OH) ₆]Cl · H ₂ O [10]
Calcined at 500°C	Degraded Ca-montmorillonite (PDF 13-135) and poorly crystalline ZnO (PDF 36-1451)
Sulphurised at 600°C	Cr ₂ ZnS ₄ (PDF 16-507), degraded Ca-montmorillonite (PDF 13-135), ZnS (PDF 39-1363)
Regenerated at 500°C	Degraded Ca-montmorillonite (PDF 13-135), ZnO (PDF 36-1451)
Calcined at 750°C	Degraded Ca-montmorillonite (PDF 13-135), ZnO (PDF 36-1451), ZnCr ₂ O ₄ (PDF 22-1107)
Calcined at 950°C	Degraded Ca-montmorillonite (PDF 13-135), Zn ₂ SiO ₄ (PDF 24-1469), ZnCr ₂ O ₄ (PDF 22-1107)

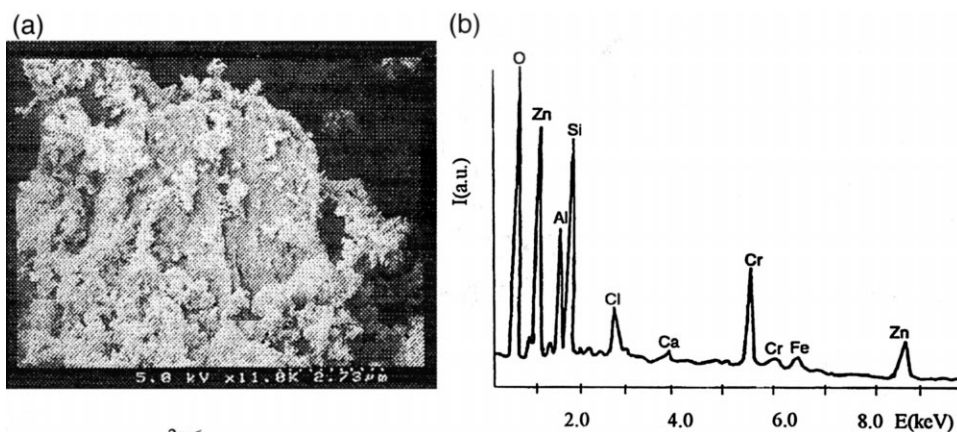


Fig. 2. (a) SEM pattern of calcined MMLH-clay composite and (b) total EDXA pattern of the sample.

from the sulphurised product by heating the latter at 500°C for 1 h in air (Table 1).

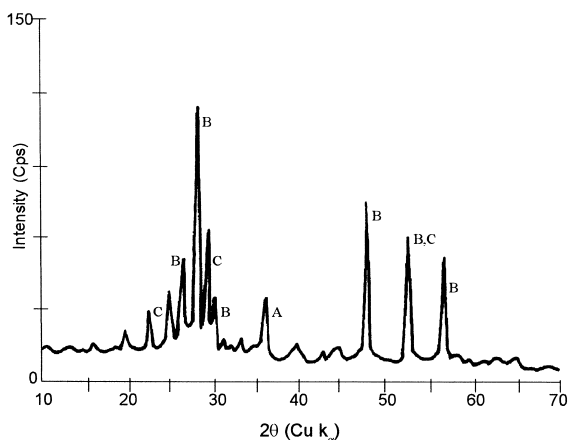


Fig. 3. XRD pattern of sulphurised product, A = ZnO, B = ZnS, C = Cr_2ZnS_4 .

In the present study, the bivalent, microfine, layered metal oxide (ZnO) formed is situated over the ceramic matrix of calcined clay and consequently, their reactivity to gaseous reactant is highly enhanced by the exposed surfaces. The temperature involved in thermal decomposition of MMLH is extremely important because at higher temperature (around 950°C), active metal oxide begins to attack silica layer of the clay forming Zn_2SiO_4 (Table 1) which is an inactive species. MMLH calcined at 750°C gives segregated phases of ZnO and ZnCr_2O_4 (Table 1), and further lowering the temperature to about 500°C, a broad XRD peak at around $36^\circ(2\theta \text{ CuK}\alpha)$ of ZnO is obtained (Table 1). The broadness of ZnO peak is attributed to the small size of the ZnO crystallites and also to the presence of Cr_2O_3 in the lattice of ZnO. A similar observation was also indicated when Al_2O_3 -MgO solid solution was obtained on thermal decomposition of Mg-Al type MMLH [12,13].

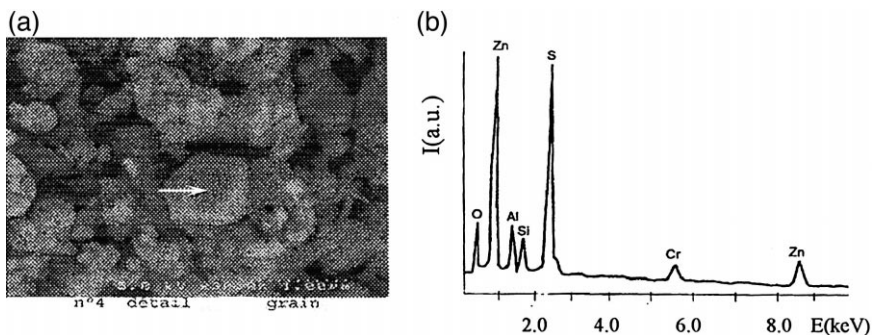


Fig. 4. (a) SEM of calcined Zn-Cr MMLH-clay composite after sulphurisation showing well-grown crystals of ZnS over montmorillonite matrix and (b) EDXA of selected area of sulphurised product.

Table 2
Sulphur retention ability of MMLH–clay composite and neat MMLH

Sample no.	Sulphurisation condition		Amount of sulphur in the product (wt.%/wt.)
	Temperature (°C)	Time (h)	
1 ^a	600	2	13.9%
2 ^a	600	2	13.6%

^aInitial composition of samples No. 1: Clay:MMLH (0:100 wt.%); No. 2: Clay:MMLH (50:50 wt.%).

The layered metal oxides formed at 500°C is seen from scanning electron microscope (SEM) in Fig. 2a and are projected like small display boards from the surfaces of montmorillonite layers. Corresponding energy-dispersive X-ray analysis (EDXA) patterns (Fig. 2b) confirm their chemical composition. Due to their layered projections, these oxides are highly reactive. Reaction of H₂S at 600°C, with such active oxides derived from Zn–Cr MMLH produces ZnS as indicated by the characteristic XRD pattern of the same (Fig. 3). SEM (Fig. 4a) shows well-grown crystals of ZnS over the ceramic matrix of montmorillonite. EDXA confirms the composition of these particles as ZnS (Fig. 4b). Amount of sulphur chemically adsorbed in calcined products of Zn–Cr MMLH (neat) and Zn–Cr MMLH–montmorillonite (MMLH:clay 50:50 wt.%) were found to be 13.9% and 13.6% (wt.%), respectively (Table 2) which indicates clearly that the latter showed almost twice the amount of sulphur adsorption than the former.

The self-organised aqueous thixotropic suspension of cationic montmorillonite and anionic MMLH after thermal treatment gives exfoliated layers of metal oxides over montmorillonite matrix which are very reactive to gaseous reactants. The technique has been utilized to enhance by almost two times the absorp-

tion of H₂S over ZnO layers derived from Zn–Cr MMLH.

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