Hydrothermal Synthesis and Characterization of an Akaganeite-type Iron Oxide Octahedral Molecular Sieves

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Iron oxide octahedral molecular sieve with 2x2 tunnel, designated as FeOx-OMS (2x2) was successfully synthesized by hydrothermal method. FeOx-OMS (2x2) has high degree of purity and higher thermal stability than those of previously reported akaganeite-type materials. The X-ray powder diffraction (XRD) pattern shows peaks that are characteristic of pure akaganeite-system. Based on its TGA profile, its thermal stability is reported up to 255 °C, and beyond 402 °C, new phases are formed which is a mixture of hematite and magnetite based on its XRD pattern. The SEM result shows needle-like morphology that is typical of a tunnel structure.[1]

INTRODUCTION

The widespread applications of octahedral molecular sieves (OMS) and octahedral layer have led to fruitful interdisciplinary interaction in material science, environmental chemistry and industrial chemical technology. Octahedral molecular sieves have three-dimensional open framework structures that consist of octahedra linked by corner-, edge- or face-sharing which form tunnels of varying sizes[2] while octahedral layer forms layer structures. Due to the promising catalytic activity exhibited by manganese nodules abundant in the ocean floor[3], numerous studies have been focused on preparing the synthetic counterparts of tunnel and layered materials present in the nodules. A series of manganese oxide OMS and OL materials that have been prepared include the following: (a) synthetic todorokite which has a (3x3) octahedra manganese oxide tunnel structure designated as OMS-1[4]; (b) cryptomelane, which is a related (2x2) structure of the mineral hollandite, referred to as OMS-2[5-7]; and (c) birnessite-type layered material labeled as (OL-1)[6-8]. These OMS materials are synthesized via reduction-oxidation reactions between Mn^{2+} and MnO_4^- or other oxidants under different conditions[9]. The existence of iron in the nodules as α-FeOOH (goethite) and mixture of γ-FeOOH and β-FeOOH (akaganeite) proven by Mossbauer studies on the Pacific Ocean nodules[3] has further expanded the interest of researchers on these metal oxides having tunnel structures. This was not surprising since iron and manganese are abundant metallic elements in the earth's crust (Fe 5.1 wt%, Mn 0.12 wt%) with similarities chemically and

geometrically.[10] The iron oxides found in the nodules are isostructural with manganese oxides with tunnel structures. Goethite has similar structure with MnO_2, ramsdellite that has a (1x2) tunnel, while akaganeite has the hollandite-type structure (α-MnO_2) with a 2x2 tunnel. Iron and manganese also often occur within close concurrence in separate mineral phases or substitute for another. Hydrothermally deposited hollandite (Mn oxide) samples also appear to contain up to 8% by weight Fe^{3+}.

Iron oxide has been profusely used as coloring agent and pigment. As technology progressed and developed, the utilization of iron oxides has been extended. Numerous applications of iron oxides include raw material for iron and steel industry, adsorbents for water and gas purification, in mineral separations and as catalyst.[11] Iron oxide catalyst has been extensively used in various industrial syntheses. However during the reaction, the oxide may be reduced to some intermediate product that may lead to loss of catalytic activity, particularly a reaction involving H_2 and high temperature.[11] The catalytic limitations of nonporous iron oxide particularly magnetite and hematite, could be addressed by developing iron oxide catalyst with superior catalytic activity such as iron oxide OMS. In fact, the manganese oxide OMS and OL systems have been previously reported to demonstrate excellent catalytic activity both in total and selective oxidations.[3,5] Mixed-valent metal oxides, in general, are effective catalysts for partial or total oxidation because of the tendency of the relevant metal cations to cycle between different valence states, and availability and mobility of lattice oxygen ions.[12] Although there have been reports on goethite (1x2) tunnel to catalyze the hydrolysis of carboxylate[13], little is known in utilizing β-FeOOH. Akaganeite or β-FeOOH, has larger tunnel structure of 2x2 tunnel, making it more porous. This is of great importance in the field of catalysis because the presence of tunnel structure inherent with these OMS system may influence, if not dictate selectivity and specificity of catalytic reactions as achieved in the zeolitic pores and cavities.

Moreover, Fe (II)/Fe (III) mixed-valent system could provide a material that is highly conductive thermally and electrically since the presence of these ions in adjacent octahedra may enable electron hopping to occur. Thus, the synthesis of iron oxide OMS would tap the utilization of these materials for varied and versatile applications.

Although the synthetic OMS counterparts of natural manganese oxides have been thoroughly explored, little is known in synthesizing tunnel and layered iron oxides using hydrothermal method. Previous synthesis of akaganeite involves direct precipitation from soluble Fe^{III} species that are supplied by dissolution. Akaganeite produced with this method containing copper ions in the structure has a thermal stability of 360 °C.[14] Akaganeite produced from hydrothermal method has not been reported and characterized so far. Hydrothermal method has been found to be an effective way of preparing OMS materials in the laboratory. This method duplicates the conditions by which many minerals naturally crystallize from hot water-rich solutions. An autoclave or a "bomb" which is a heavy-walled steel cylinder closed at one end designed to withstand high temperature and high pressure is used to achieve hydrothermal growth. Thermal and phase stability analyses show that many hydrothermally prepared materials have definite composition and significantly higher thermal stability exceeding that of naturally occurring minerals.[9]

This study reports the successful hydrothermal synthesis of iron oxide octahedral molecular sieve, designated as FeOx-OMS (2x2). The route employed direct dissolution and autoclaving iron oxide at different controlled parameters such as pH, aging temperature, incubation period and counter-ion effects. The iron oxide OMS may be as promising, if not surpass the mixed-valent Mn system with better thermal stability, effective catalytic and adsorptive capacities, with high degree of crystallinity and purity for commending area of industrial application.

EXPERIMENTAL DESIGN AND METHODOLOGY

Synthesis

Factors that can influence the crystal growth and crystallinity of OMS materials such as varying concentration, pH, templates, ageing time, temperature and pressure conditions were investigated.

A solution that contains 0.06 moles of $FeCl_3 \cdot H_2O$ and 10.2 g of urea was diluted to 100 ml distilled deionized water (DDW). The solution was transferred to 100-mL bomb and autoclaved at 100°C for various aging period (24, 40 and 48 hours). The precipitated polycrystalline materials were filtered and washed with approximately 250 mL DDW and 30 mL of 2.2 M HCl. The final washing gave a solution with pH 2.5-3.0. The crystalline precipitates obtained were dried at 100 °C for two hours and stored in sealed glass bottle for XRD and characterization analyses. The series of products obtained were labeled u-FeOx-O, u-FeOx-P, u-FeOx-Q, u-FeOx-R, and u-FeOx-S.

Characterization

(a) ***X-ray Diffraction (XRD) Studies.*** Powder X-ray diffraction analysis was done using X-ray diffractometry model XD-610 with a Cu Kα radiation source. The ground sample was spread on a glass slide and was scanned from 1 to 60 2θ, at a rate of 4° 2θ/ min.

(b) ***Thermal Analyses.*** Thermogravimetric analysis (TGA) was carried out using DuPont 951 TGA instrument. About 4-10 mg of sample powder was loaded into platinum sample holder for TGA. TGA measurements were done under nitrogen atmosphere to check oxygen loss during heating. Samples were heated from room temperature to 700 °C at a heating rate of 20 °C/ min.

(c) ***Scanning Electron Microscopy (SEM) Studies.*** Sample powders were spread uniformly on carbon paste on an aluminum sample holder and then gold coated before SEM photographs were taken in an Amray 1645 scanning electron microscope.

(d) ***Energy Dispersive X-ray Analysis (EDX).*** A JEOL energy dispersive X-ray analyzer Model JSM-5300, WD 13-48 mm was used for EDX analysis.

(e) ***Heating and XRD Analyses for Identification of Phases at Varying Temperatures.*** A sample of about 1.5 g was placed in the crucible and heated in the furnace at the temperature that corresponds to its thermal stability obtained from TGA result. The furnace used was equipped with a temperature-controlled program. The heating rate was 20 °C/min with holding time of 5 minutes for the removal of crucible from the furnace. The sample obtained after heating was subjected to XRD analyses to determine the structural integrity and phase changes at that temperature.

RESULTS AND DISCUSSION

Synthesis

Synthesis by hydrothermal method via direct dissolution of iron chloride with urea additive obtained a series of products with lab codes given as: u-FeOx-O; u-FeOx-P; u-FeOx-Q; u-FeOx-R; and u-FeOx-S. These were synthesized at various temperatures and aging periods as presented in Table 1.

After the synthesis the products were subjected to X-ray powder diffraction analysis. Their XRD patterns have peaks that are characteristic of pure akaganeite material. Table 2 gives the X-ray diffraction data for synthesized materials and comparing the indexed peaks for akaganeite. The d-values (Å) with shifted values are enclosed in parenthesis. From the table, it is noticeable that products of u-FeOx-series have values closest to the computed d-values for akaganeite. Almost all akaganeite lines are present in their X-ray diffractograms.

Among the synthesized materials, u-FeOx-O, hydrothermally synthesized for 40 hours at 100 °C, was found to be the most crystalline and relatively pure based on XRD result. One of the many applications of powder X-ray diffraction

is the determination of phase purity.[15] The absence of other reflections that are not characteristic of the material under investigation establishes the relative purity of the material. This is true, however, assuming that the impurity is crystalline. In cases where the impurity is amorphous, this will not give detectable peaks but will increase the background of the powder pattern. The XRD pattern of the synthesized akaganeite-type material did not show peaks other than those that can be indexed as characteristic of the material and analysis of the background profile did not suggest the presence of amorphous impurities. The strong tunnel diagnostic akaganeite peaks are apparent at 7.4443 Å (110), 5.2527 Å (200) and 3.3191 Å (310). XRD pattern of u-FeOx-O is similar with that of the XRD pattern of pure akaganeite. Those materials prepared at lower aging period of 24 hours are less pure and less crystalline as suggested by the appearance of other reflections and broadening of the peaks, respectively. The XRD patterns showed the diagnostic peaks but additional peaks appearing at 4.0085 Å and at 3.1820 Å for u-FeOx-P and u-FeOx-Q, as indicated in Table 2 account for the appearance other phases or impurities namely goethite and unconverted $FeCl_3$, respectively. Absence of peaks at higher 2q is noted, particularly peaks at 2.07 Å (510) and 1.86 Å (440). The absence of these peaks at higher 2q angles may account for the relatively low degree of crystallinity for these materials. Product u-FeOx-R which was synthesized at longer aging period of 48 hours, has a shifted peak at 2.7646 Å (310) against the strongest akaganeite peak of 3.11 Å (310). This suggests a significant change in the lattice parameter of the material or signals the onset of another phase when the material is aged more than 48 hours. Synthesis of u-FeOx-S, prepared with higher urea to iron chloride ratio and was autoclaved for 48 hours was unsuccessful because the maximum acidity/ pressure tolerance of the bomb was exceeded.

Table 1. Summary of Conditions and Results for the Hydrothermally ***Synthesized FeOx-OMS(2x2) via Direct Dissolution Method.***

Code	Reactants	Hydrothermal Conditions		Product
u-FeOx-O	0.06 Mol $FeCl_3.6H_2O$ & 10g urea	100 °C	40h	Akaganeite-type (purest), Dark brown
u-FeOx-P	0.06 Mol $FeCl_3.6H_2O$ & 10g urea	100 °C	24h	Akaganeite-type, dark brown
u-FeOx-Q	0.06 Mol $FeCl_3.6H_2O$; 10 g urea and 2 ml 2.2 M HCl	100 °C	24h	Akaganeite-type, brown
u-FeOx-R	0.03 Mol $FeCl_3.6H_2O$; 7.2g urea and 2 ml 2.2 M HCl	100 °C	48h	Akaganeite-type, dark yellow brown
u-FeOx-S	0.03 Mol $FeCl_3.6H_2O$ & mol 7.2g urea	100 °C	48h	100 - ml bomb leaked during the autoclaving period. Teflon cover expanded due to pressure

Table 2. X-Ray Diffraction Data for Iron Oxides

Data for Akaganeite[10]		Inteplanar spacings in Angstrom units (Å) observed in different samples						
hkl	D (Å)	u-FeOx-0	u-FeOx-P	u-FeOx-Q	u-FeOx-R	u-FeOx-L2	u-FeOx-L3	u-FeOx-A1
								(13.081) (10.267)
110	7.40	7.443	7.3921	7.5250	7.4585	7.4565		7.5250
200	5.25	5.2527	5.5494	5.2919	5.2581	5.2581	(4.1482)	5.2919
220	3.70	(3.9479)	(4.0085) 3.7211	3.7542	3.3207	(4.2115)	3.7884 (3.4870)	3.3473
)310	3.311	3.3191	3.3344 (3.1820)	3.3473	(2.7646)	3.3334	3.3880	
400	2.616	2.6189	2.6362	2.6359	2.6277	(2.6943) (2.6359)	(2.9273) 2.7290	2.6441
211	2.543	2.5409	2.5493	2.3662	2.5418	2.5492 (2.4541)	2.4898	2.5568
420	2.343	2.3527	2.3534	2.2969		2.3469		2.2969
301	2.285	2.2903	2.2370	2.0775	2.2908	2.2908		
321	2.097	2.0321	2.0677		2.0924			
510	2.064	2.0577			2.0532	1.9927		
411	1.944	1.9488	1.9532	1.9571	1.9488	1.9531		1.9618
440	1.851	1.8552		1.8709	1.8554			
600	1.7646	1.7852	1.7578	1.7610	1.7508	1.7542	1.7440	1.7542
501,431	1.719	1.7473	1.7374		1.7307	1.7144		1.7048
521	1.635	1.6407	1.6437	1.6466	1.6408	1.6437		1.6437

Note: those in ( ) have d values that deviate from calculated d .
[10] Cornell, R.M. and Schwertmann, U. *The Iron Oxides.*, 1st Ed., VCH Publishers, NY, USA, 1996.

It was revealed by powder X-ray diffraction analysis that u-FeOx-O is the most crystalline having sharp diffraction lines identical to that of pure akaganeite and with all the reflections characteristic of the mineral present in the XRD pattern. For reproducibility of the procedure, u-FeOx-O was prepared again employing the same conditions. Figure 1 shows its XRD pattern and the peaks are being clearly identical to those of pure akaganeite-type material. This confirms that the procedure for u-FeOx-O is a successful route in producing pure akaganeite-type material by hydrothermal method. The sample code u-FeOx-O is changed to FeOx-OMS (2x2) and this will be used in the succeeding discussion.

Characterization of Successfully Prepared Akaganeite-type FeOx-OMS (2x2)

The TGA profile of FeOx-OMS (2x2) is given in Figure 2. The thermal stability of akaganeite that was previously reported[16] was up to 150°C. FeOx-OMS (2x2), however, exhibited higher thermal stability, with the first weight loss observed at 255 °C and another stable phase starts to form at 402 °C. To investigate the structure integrity at 255 °C, the temperature, which corresponds to the first weight loss, XRD measurements were done on the heated powder. The XRD pattern of FeOx-OMS (2x2) obtained after heating at 255 °C at the rate of 20 °C/min and holding time of 5 minutes is shown in Figure 3. The weight loss at this temperature is due to the loss of water physically sorbed at

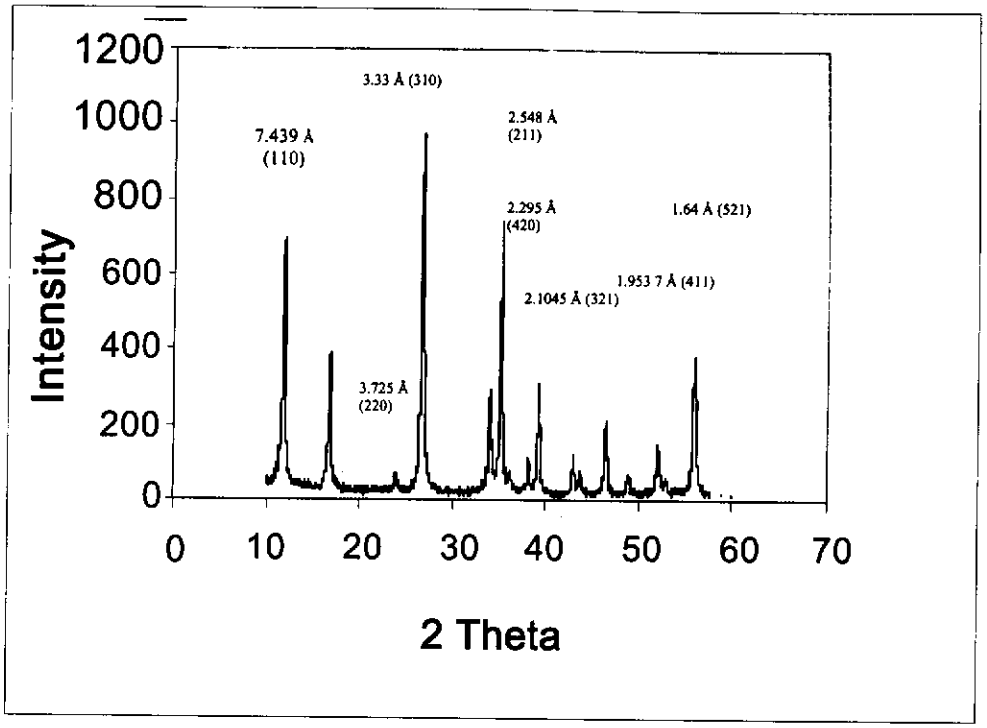


Figure 1. XRD Pattern of FeOx-OMS (2x2)

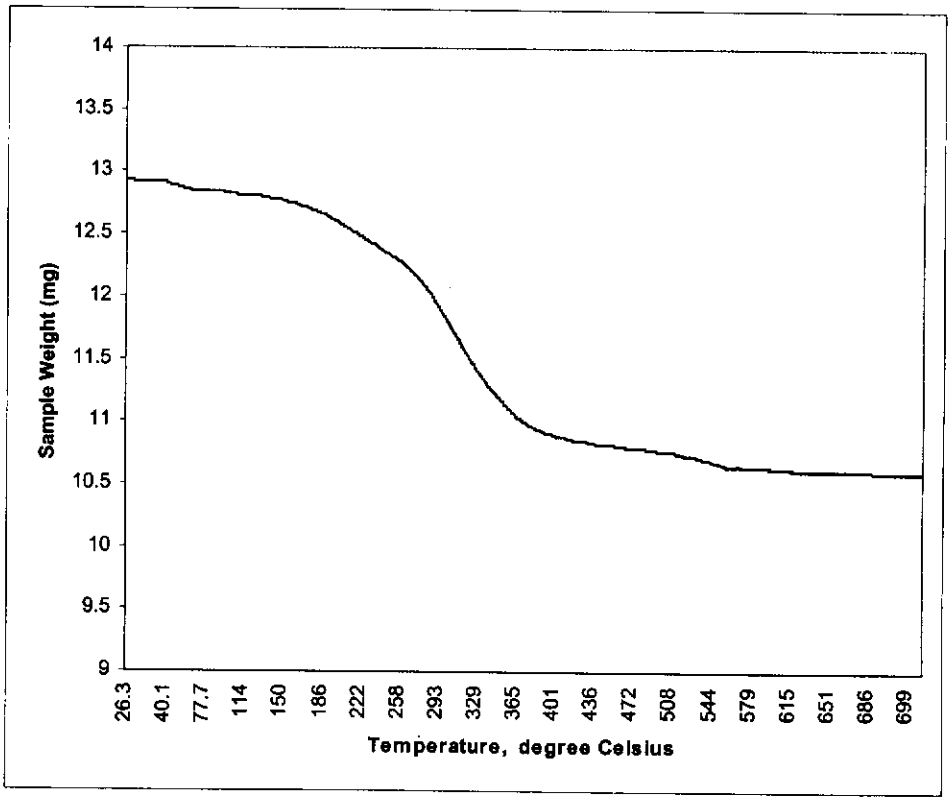


Figure 2. TGA Profile of FeOx-OMS (2x2) from temperature to 700 °C under N_2 atmosphere.

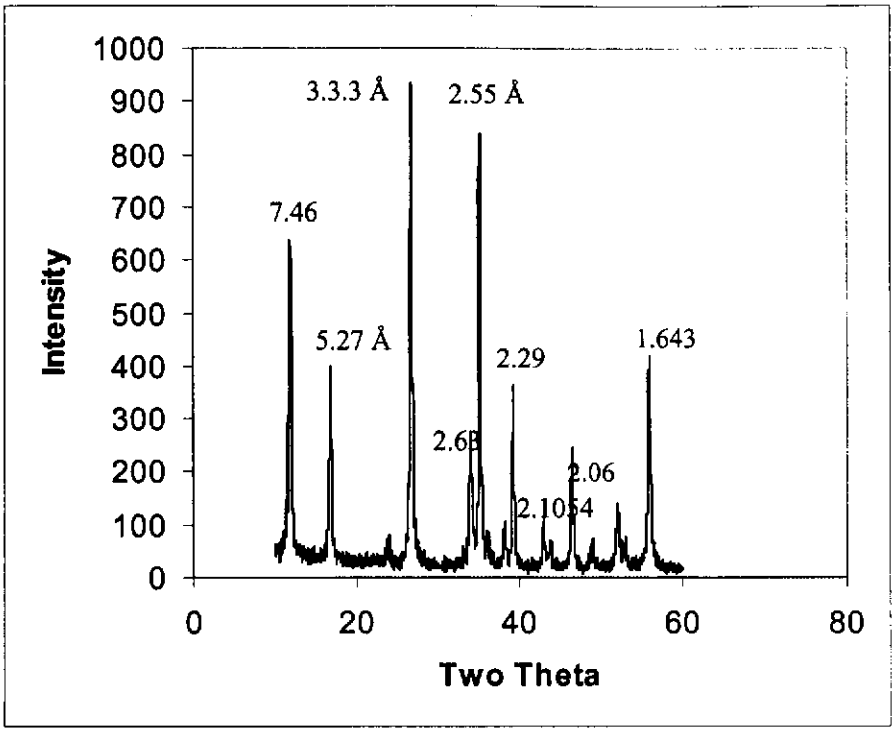


Figure 3. XRD Pattern of FeOx-OMS (2x2) obtained after heating at 255 °C.

the surface. The presence of akaganeite peaks is still evident with slight or minor deviations in the d-values. The XRD pattern of the material heated at 402 °C in Figure 4 shows the presence of hematite peaks at 2.708 Å (104) and 1.699 Å (116) as well as the diagnostic magnetite peak at 2.525 Å (313). The strong akaganeite peaks at 7.40 Å and 5.27 Å also disappeared suggesting that new phases existed upon loss of lattice oxygen. This indicates that hematite is not only the sole reaction product but intermediate phases are included such as quasi amorphous phase. The weight loss at this temperature was found to be 15.71%, which is higher than the theoretical value of 10% corresponding to the change:

$$2\,FeOOH \rightarrow Fe_2O_3 + H_2O$$

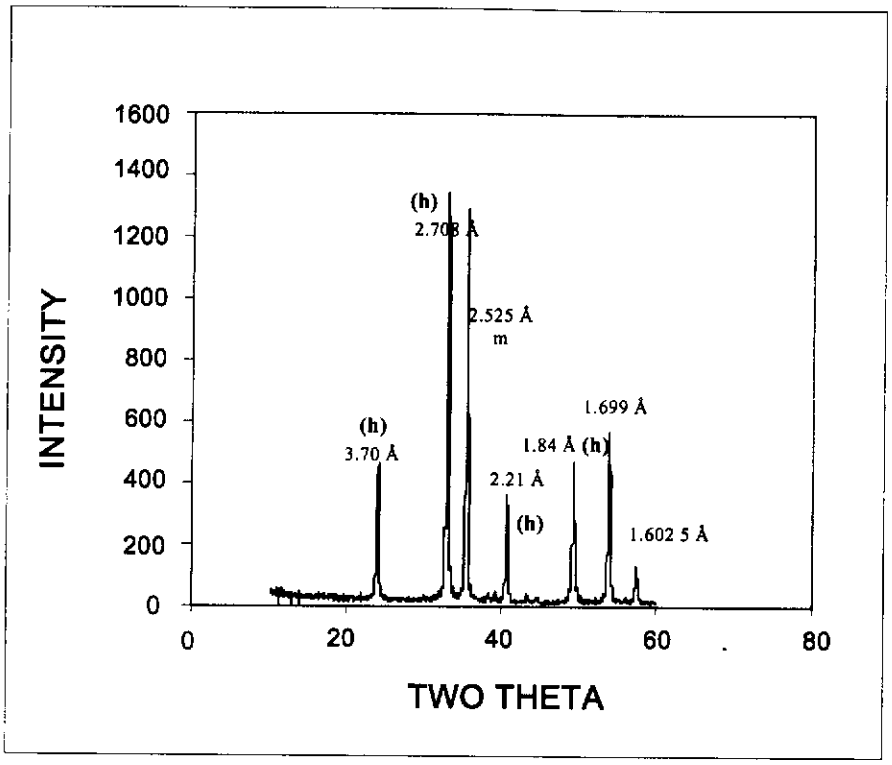
The result supports previous report[17] that above 250 °C, akaganeite releases water and the chloride content starts to decrease and HCl (under N_2) or Cl_2 (under O_2) is evolved.[15] Above 400°C, some $FeCl_3$ sublimes. The dehydration of crystal water in the structure also occurs. The weight loss at this peak is mainly due to lattice oxygen evolution.

$$\underset{\text{Hematite}}{6\,Fe_2O_3} \rightarrow \underset{\text{Magnetite}}{4\,Fe_3O_4} + O_2$$

The gradual loss of around 17% wt. at above 400 °C is due to the collapse of the structure.

The structure of synthetic akaganeite crystal is dependent on the synthetic methods being employed. Previously synthesized akaganeite materials have displayed basic morphologies of somatoids (spindle), rods or capsule-shaped. As shown in the SEM micrograph in Figure 5, synthetic akaganeite formed by hydrothermal method revealed needle-like morphology that is typical of the tunnel-structured hollandite. The fibers have an average dimension of 1,800 nm length and 300 nm in thickness.

The samples are subjected to energy-



Note: Haematite peaks and magnetite peaks are designated as (h) and (m), respectively.

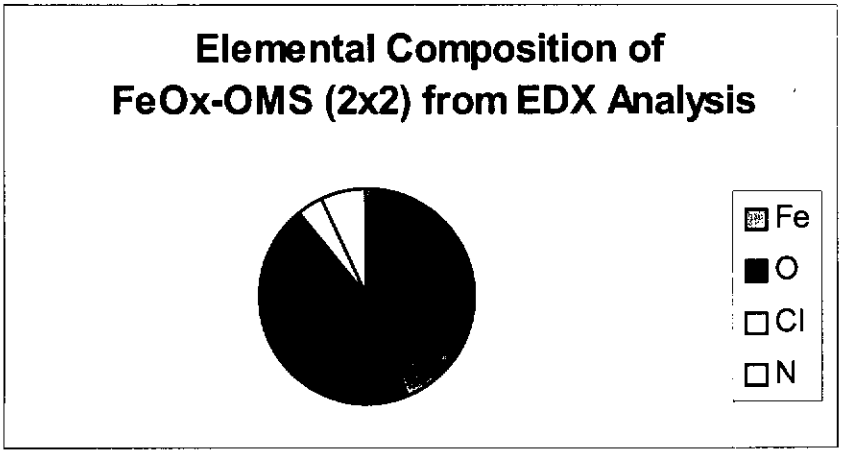
Figure 4. XRD Pattern of FeOx-OMS (2x2) obtained after heating at 402 °C.

Figure 5. SEM of FeOx-OMS (2x2)

1μm

Table 3. Elemental Composition from Energy Dispersive X-ray Analysis (EDX)

Element (%)	FeOx-OMS(2x2)
Fe	43.74
O	45.35
Cl	4.11
N	6.80



dispersive X-ray spectrometry which chemically identifies elements using characteristic X-ray photons produced by bombarding the sample with electrons. Table 3 shows the elemental percentages of FeOx-OMS (2x2). Small amount of chloride is present as counter-anion to balance the charge of the framework. The presence of nitrogen is due to the incorporation of urea.

CONCLUSION AND RECOMMENDATION

Hydrothermally synthesized FeOx-OMS with 2x2 tunnel structure, designated as FeOx-OMS (2x2), is found to have high degree of purity and has a higher thermal stability than those of previously reported[13,14,16] akaganeite-type materials. The XRD pattern shows peaks that are characteristic of pure akaganeite system.[11] Based on its TGA profile coupled with XRD analysis, its thermal stability is reported at 255 °C and the material forms hematite-magnetite phases beyond 400 °C. The scanning electron micrograph of FeOx-OMS (2x2) shows needle-like morphology.

Other preparative routes such as incorporation of counter-anions, pH adjustment and use of different reactants such as oxidizing agent and anhydrous source were explored in this research. These preparations gave mostly low recovery of less than a gram and did not give an akaganeite-type material based on the XRD results.

Catalytic studies of the material are also a potential field for future research. Evaluation of the catalytic performance of iron oxide OMS for partial and total oxidation to explore its laboratory and industrial applications would be a challenging endeavor.

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