

# HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION OF VANADIUM SILICATE MOLECULAR SIEVES WITH ANALCIME, MAGEDITE AND ZSM-11 STRUCTURE

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## Abstract

Vanadium silicates such as V-Al-analcime, V-analcime, V-magediite and V-ZSM-11 were synthesized using vanadium pentoxide or vanadyl sulfates. Vanadium silicates with analcime structure with and without aluminum (V-Al-analcime, V-analcime) were prepared as pure phase by hydrothermal crystallization from a gel with molar composition of (1 SiO<sub>2</sub>; 0.2 V<sub>2</sub>O<sub>5</sub>; 1 Na<sub>2</sub>O; 0.034 Al<sub>2</sub>O<sub>3</sub>; 35.7 H<sub>2</sub>O) and (1 SiO<sub>2</sub>; 1 Na<sub>2</sub>O; 5.3×10<sup>-3</sup> V<sub>2</sub>O<sub>5</sub>; 34.7 H<sub>2</sub>O) at 130°C in 72 h respectively. XRD and SEM results showed that, although these two have similar XRD patterns, their morphologies were completely different. The new magediite with and without aluminum was also prepared as pure phase by hydrothermal crystallization. Vanadium silicate with ZSM-11 structure was synthesized by sodium silicate, tetrabutylammonium hydroxide (TBAOH) and V<sub>2</sub>O<sub>5</sub> or VOSO<sub>4</sub>.nH<sub>2</sub>O. The structures obtained are stable up to 700°C. The role of tetrabutylammonium hydroxide (TBAOH), tetrabutylammonium bromide (TBABr), tetraethylammonium chloride (TEACl) and triethanolamine (TENA) were studied. The results showed that although TBAOH and TBABr had essential role on V-ZSM-11 formation, TEACl led to the formation of a mixture of V-ZSM-11 and V-magediite. Effect of time and temperature were also studied.

**Keywords:** Vanadium silicalite; Vanadium magediite; Vanadium analcime

## Introduction

In the last two decades, zeolites have played an important role in the petrochemical and chemical industries. The regular structure of pores and cages

cause them to act as good catalysts for a variety of processes such as conversion of methanol to gasoline (MTG), cyclooligomerization conversion of low molecular weight olefins and alkanes to aromatics and photocatalyzed oxidation of hydrocarbons [1-3].

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Today's, molecular sieves, containing redox active metals like Ti, V, Cr and Fe are increasingly used as heterogeneous catalysts for oxidation of organic compounds [4-9]. Studies on incorporated vanadium in microporous lattice which started around 1980, have showed increasing attention regarding these remarkable catalytic behaviours [10-15]. Several types of vanadium silicates such as V-ZSM-5, V-ZSM-11, V-ZSM-48, V-ZSM-12, V-NCL, V-Beta, VAPO and VSAPO have been so far reported in literature [16-22]. Incorporation of vanadium on mesoporous lattice such as MCM-41 [23,24] was also studied and was claimed to be active in the oxidation of cyclodecane and cyclic ether with  $H_2O_2$  or TBHP [25,26].

The aim of present study was the synthesis of several vanadium silicate molecular sieves with and without aluminum with analcime, magediite and ZSM-11 structures.

## Experimental Section

### Materials

Tetraethylorthosilicate (TEOS), sodium silicate solution (25.5-28.2%  $SiO_2$ , 7.5-8.5%  $Na_2O$ ), sulfuric acid 98%, triethanolamine (TENA), tetrabutylammonium hydroxide (TBAOH), triethylamine (TEA), tetrabutylammonium chloride (TEACl), tetrabutylammonium bromide, vanadyl sulfate 5 hydrate, and vanadium pentoxide 5 hydrate all were obtained from Merck Company. Silicagel (60G) was purchased from Sigma.

### Synthesis

In a typical procedure, appropriate amount of vanadium pentoxide 5 hydrate or vanadyl sulfate 5 hydrate was added to sodium silicate solution. After formation of a clear solution, template was slowly added. In the case of incorporation of aluminum in lattice, sodium aluminate solution was slowly added to the above mixture. The resulting solution was stirred to form a hydrogel and the reaction mixture was then aged for 2 to 6 days. The gel composition (as molar ratios) for each experiment is shown in Tables 1-7.

The synthetic gel was transferred into a stainless steel autoclave and kept at 140-180°C for 2 to 3 days. The product was washed with distilled water and dried at 100°C for several hours.

### Characterization

X-ray powder diffraction (XRD) patterns of synthesized vanadium containing zeolites were obtained

by XRD (Philips, PW 1840, with Cu tube). The micrograph of prepared compound was taken with Scanning Electron Microscope (NIOC, SEM 360). FTIR (KBr) spectra were recorded using a Philips Pu-9800 FTIR Spectrophotometer.

## Results and Discussion

### Synthesis of V-Al-analcime

According to the results shown in Table 1, the hydrothermal transformation of gels with molar composition of runs 1,2,3 with TMACl (runs 1,2) and TEA (run 3) were amorphous (Fig. 1a). By decreasing  $SiO_2/Na_2O$  ratio from 2.8 to 0.99, a crystalline phase was obtained (Fig. 1b). The XRD pattern was similar to that of Al-analcime [27]. The FTIR spectra of products of run (1,2,3) and product of run 4, *i.e.* V-Al-analcime are shown in Figure 2a,b. The IR spectrum of V-Al-analcime (run 4) showed a strong vibration at  $\sim 1000\text{ cm}^{-1}$  which is due to internal tetrahedral vibration of T-O stretching and the peak at  $400\text{ cm}^{-1}$  is assigned to T-O bending. Two bands in the region of  $\sim 756\text{-}760\text{ cm}^{-1}$  are related to the presence of double ( $D_4R$ ) rings in the framework structures of an external linkage due to the symmetrical stretching of tetrahedral atoms [28]. The appearance of a peak at  $960\text{ cm}^{-1}$  should be due to the V-O band stretching mode in  $V(O_3Si-OM)$  ion in the  $[SiO_4]$  structure [21]. The chemical analysis of V-Al-analcime (run 4) is given in Table 8.

Scanning Electron Micrograph (SEM) of V-Al-analcime (run 4) is shown in Figure 3. The diameter of particles was  $14\text{ }\mu\text{m}$  and is similar to Al-analcime which was prepared with TENA in our groups [25].

According to the results of Table 2, by keeping  $SiO_2/V_2O_5$  constant and changing  $SiO_2/Na_2O$  ratio from 4 to 2.8 with TEACl as template, products of run 6,7 were amorphous. In reaction run 9 with special condition and without using template, a crystalline phase was formed. It was consistent to the magediite type structure (Fig. 4). Since by adding TBAOH (run 10), the XRD pattern of product (run 10) was similar to ZSM-11 type structure, we named it V-ZSM-11 (Fig. 5).

By increasing  $SiO_2/V_2O_5$  ratio to 19,32 and finally 94 (runs 11,12,13), the crystalline phases were similar to the run 10.

Table 3 shows the investigation results regarding to the effect of the template's type on formation of vanadium silicates (runs 14-20). It is obvious that, the most important reaction variables in the synthesis of high silica zeolites are the ratios of  $SiO_2/MO$ ,  $OH/SiO_2$  and  $organic/SiO_2$ . Therefore in these cases, all ratios

**Table 1.** Starting gel composition, synthesis conditions and products obtained

Reaction run no. & sample code	$\frac{\text{SiO}_2}{\text{V}_2\text{O}_5}$	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{Na}_2\text{O}}$	$\frac{\text{SiO}_2}{\text{H}_2\text{O}}$	$\frac{\text{SiO}_2}{\text{T}}$	Products
1	5	28.6	2.8	0.028	1.02	Amorphous
2	5	28.6	2.8	0.028	1.02	Amorphous
3	5	28.6	2.8	0.028	1.02*	Amorphous
4	5	28.6	0.99	0.028	—	Analcime
5	5	104	0.99	0.028	—	Analcime

T: means template; TEACL: tetrabutylammonium chloride

\* T in this case was triethanolamine (TEA)

Reaction aging time = 2 days; Reaction time = 2 days

**Table 2.** Starting gel composition, synthesis conditions and products obtained\*

Reaction run no. & sample code	$\frac{\text{SiO}_2}{\text{V}_2\text{O}_5}$	$\frac{\text{SiO}_2}{\text{Na}_2\text{O}}$	$\frac{\text{SiO}_2}{\text{H}_2\text{O}}$	$\frac{\text{SiO}_2}{\text{T}}$	Type of T	Products
6	5	4	0.028	1.02	TEACL	Amorphous
7	5	2.8	0.028	1.02	TEACL	Amorphous
8	5	3.6	0.039	—	—	Amorphous
9	15	3.6	0.039	—	—	Magediite
10	15	3.6	0.039	50	TBAOH	V-ZSM-11
11	19	3.6	0.039	50	TBAOH	V-ZSM-11
12	32	3.6	0.039	50	TBAOH	V-ZSM-11
13	94	3.6	0.039	50	TBAOH	V-ZSM-11

TMACl: Tetraethylammonium chloride; TBAOH: tetrabutylammonium hydroxide

\*Reaction aging time=2 days; Reaction time=2 days

Source of Vanadium= $\text{V}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$

**Table 3.** Effect of template on products formation

Reaction run no. & sample code	Type of template	Products
14	TENA	Magediite
15	TEA	Magediite
16	TMACl	Magediite
17	—	Magediite
18	TEACL	Magediite, ZSM-11
19	TBABr	ZSM-11
20	TBAOH	ZSM-11

TENA: Triethanolamine; TEA: Triethylamine

Reaction mixture=94  $\text{SiO}_2$ ; 1  $\text{V}_2\text{O}_5$ ; 26  $\text{Na}_2\text{O}$ ; 2410  $\text{H}_2\text{O}$ ; 1.88 Template  
aging time=2 days; reaction time=2 days

**Table 4.** Effect of aging time on formation of products (V-magediite and V-ZSM-11)

Reaction run no. & sample code	Template	Aging time	Products
21	TBAOH	2	Amorphous+V-ZSM-11
22	TBAOH	6	V-ZSM-11
23	—	2	Magediite +amorphous
24	—	6	Magediite
25	TMACl	2	Magediite is forming
26	TMACl	6	Magediite

Reaction mixture=94 SiO<sub>2</sub>; 1 V<sub>2</sub>O<sub>5</sub>; 26 Na<sub>2</sub>O; 2410 H<sub>2</sub>O; 1.88 Template  
 Reaction time=2 days; Temp. 140°C

**Table 5.** Effect of Vanadyl Sulfate on formation of products

Reaction run no. & sample code	$\frac{\text{SiO}_2}{\text{V}_2\text{O}_5}$	$\frac{\text{SiO}_2}{\text{Na}_2\text{O}}$	$\frac{\text{SiO}_2}{\text{H}_2\text{O}}$	$\frac{\text{SiO}_2}{\text{T}}$	Products
27	25	3.6	0.039	50	Amorphous
28	50	3.6	0.039	50	V-ZSM-11, magediite
29	94	3.6	0.039	50	V-ZSM-11, magediite
30	188	3.6	0.039	50	V-analcime

Reaction time = 2 days

**Table 6.** The effect of template on crystalline phase formation by using VOSO<sub>4</sub>.5H<sub>2</sub>O

Reaction run no. & sample code	Type of template	Products
31	TBAOH	V-ZSM-11, V-magediite
32	TBABr	V-ZSM-11, V-magediite
33	TEACl	V-ZSM-11, V-magediite
34	TMACl	V-magediite
35	TENA	V-magediite
36	—	V-magediite

Reaction mixture is similar to reaction no. 21

**Table 7.** The effect of time (aging & crystallization) on product formation

Reaction run no. & sample code	Aging time	Crystallization time (days)	Products
37	1	2	V-ZSM-11 is forming
38	2	2	V-ZSM-11 is forming
39	2	3	V-ZSM-11 is forming
40	3	1	Amorphous
41	3	3	V-ZSM-11
42	5	3	V-ZSM-11
43	6	3	V-ZSM-11

Reaction mixture = 94 SiO<sub>2</sub>; 1 V<sub>2</sub>O<sub>5</sub>; 26 Na<sub>2</sub>O; 2410 H<sub>2</sub>O; 1.88 template (TBAOH)

**Table 8.** Chemical analysis\* of V-Al analcime, V analcime, V-magediite and V-ZSM-11

Type of Sample	SiO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	H <sub>2</sub> O
V-Al-analcime	57.04	0.08	20.22	13.11	9.55
V-analcime	94.1	0.06	—	14.10	1.74
V-magediite	93.8	0.07	—	5.17	1.68
V-ZSM-11	90.66	0.06	—	3.85	5.43

\*(W%)

were kept constant and only the type of template was changed. It was found that, when TENA, TEA or TMACl used as template, the products were vanadium magediite (run 14-16) (Fig. 6a). It was observed that without using any template, V-magediite was formed (run 17). By using TEACl, the product was a mixture of V-magediite and V-ZSM-11 (run 18) (Fig. 6b). Finally by using TBOAH and TBABr, V-ZSM-11 was formed (run 19,20) (Fig. 6c). It seems that the type of template has effective role on product formation. Although the effect of TMACl, TENA, or TEA was similar, by increasing the template size to TBABr and TBAOH, ZSM-11 was formed. In Table 4, the effect of aging time with templates TBAOH and TMACl and without template (runs 21-26) is shown. It was observed that when TBAOH was used (run 21) a mixture of amorphous phase and crystalline phase V-ZSM-11 was formed. By increasing aging time to 6 days, pure ZSM-11 phase is obtained. Using TMACl as template, a mixture of V-magediite and amorphous were formed after two days. The same result was obtained without using any template.

Another set of experiments was designed to investigate the effect of vanadyl sulfate instead of vanadium pentoxide in zeolite formation. We found that at SiO<sub>2</sub>/V<sub>2</sub>O<sub>5</sub> ratio of 25 with TBAOH (run 27), product was amorphous (Table 5). By increasing the ratio to 50 and then 94, a mixture of two phases of V-ZSM-11 and V-magediite was formed (Fig. 7). At ratio of ~188, a crystalline phase was formed which its XRD pattern was similar to the analcime (run 30).

In Table 6, the effect of template on the formation of crystalline phase of V-ZSM-11 and V-magediite is shown. By using TBAOH, TBABr and also TEACl, two mixture phases of V-ZSM-11 and magediite were formed. By decreasing the size of template to TMACl, V-magediite was formed. With TENA and without any template, the product was V-magediite. In those cases, the reaction gel composition was similar to reaction run 20. Finally, after investigation on reaction aging and crystallization time, we found that increasing of aging to

three days led to crystallization time (run 41) and pure phase of V-ZSM-11 were formed.

In general, by changing the reaction conditions and gel composition, four crystalline compounds of vanadium silicate with analcime, magediite, and ZSM-11 were obtained [29,30]. The chemical analysis of prepared compounds is given in Table 8.

SEMs of V-Al analcime and vanadium are shown in Figure 8. Comparing SEMs of V-Al analcime and V-analcime shows that, their morphologies are completely different, in spite of similar XRD pattern. As shown in Figure 8, the morphology of the first one is spherical with 14 μm diameter whereas the last one looks like a leaf.

Two other compounds of vanadium silicate with and without template were prepared with magediite structure. The crystallinity of magediite with template TENA was much better than the one prepared without using template.

The SEMs of synthesized V-magediite and magediite [29] are shown in Figure 9. It was found that hydrogen peroxide is decomposed by V-magediite. The FTIR spectra before and after addition of H<sub>2</sub>O<sub>2</sub> are shown in Figure 10. The existence of a peak at 960 cm<sup>-1</sup> is due to the presence of V-O bond in lattice. After calcination of V-magediite, its crystallinity changes to the opal and crystoballite.

The third pure phase was V-ZSM-11. Its SEM is shown in Figure 11.

## Conclusion

1. V-Al-analcime and V-analcime were prepared for the first time by V<sub>2</sub>O<sub>5</sub>.5H<sub>2</sub>O or VOSO<sub>4</sub>.5H<sub>2</sub>O respectively.

2. These two compounds with similar XRD pattern have two different morphologies. The first one is spherical and the latter looks like a leaf.

3. V-magediite was prepared. Its SEM was similar to Al-magediite.

4. By changing the type of template at fixed gel compositions, two compounds were formed. In the case of TBAOH, the product was V-ZSM-11, by using TEABr, a mixture of V-magediite and V-ZSM-11 was formed. Finally with TENA or TMACl as template in which the first one is not cationic and the second one is much smaller than TBAOH, pure phase of V-magediite was formed.

5. It was also found that aging and crystallization time both show essential effect on formation of mentioned products.

6. Reaching to pure phase of V-ZSM-11 is much easier by using V<sub>2</sub>O<sub>5</sub>.5H<sub>2</sub>O instead of VOSO<sub>4</sub>.5H<sub>2</sub>O.

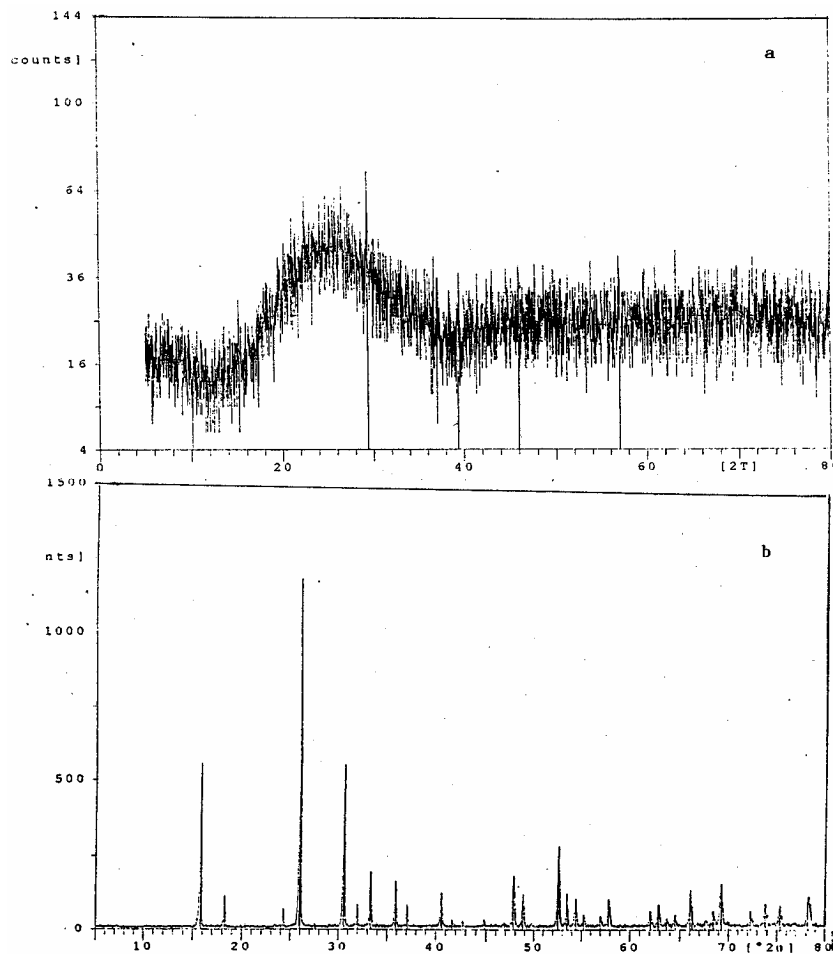


Figure 1. XRD Pattern of (a) amorphous phase (sample code 1,2,3); (b) V-Al analcime (sample code 4).

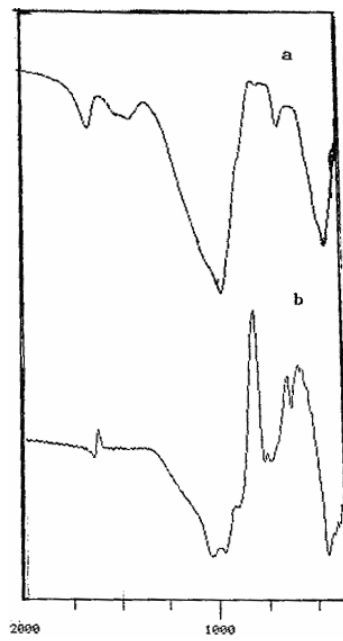


Figure 2. FTIR spectra of (a) amorphous phase (sample code 1,2,3); (b) V-Al analcime (sample code 4).

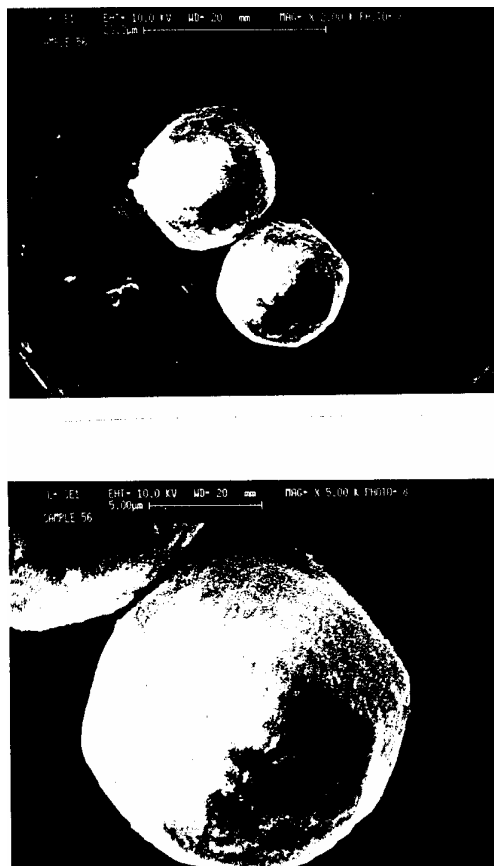


Figure 3. SEM micrograph of V-Al analcime (sample code 4).

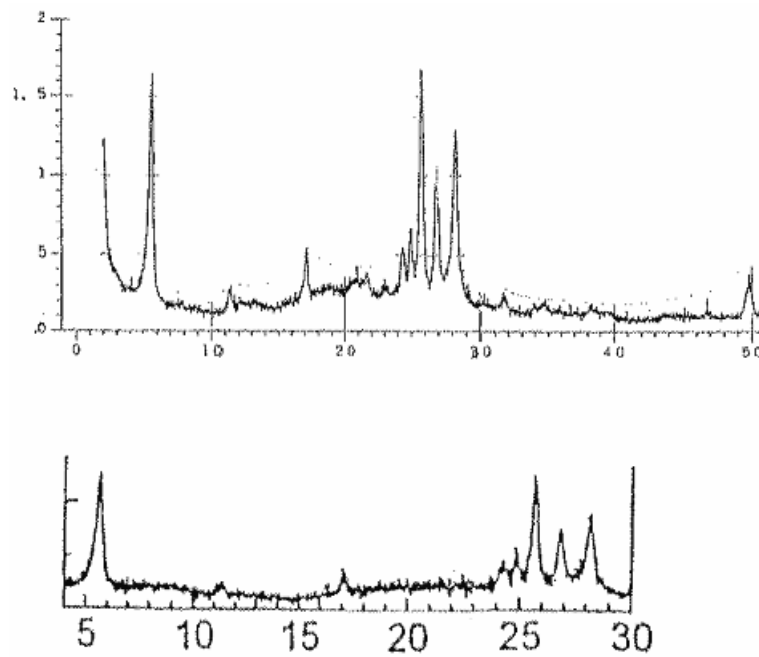
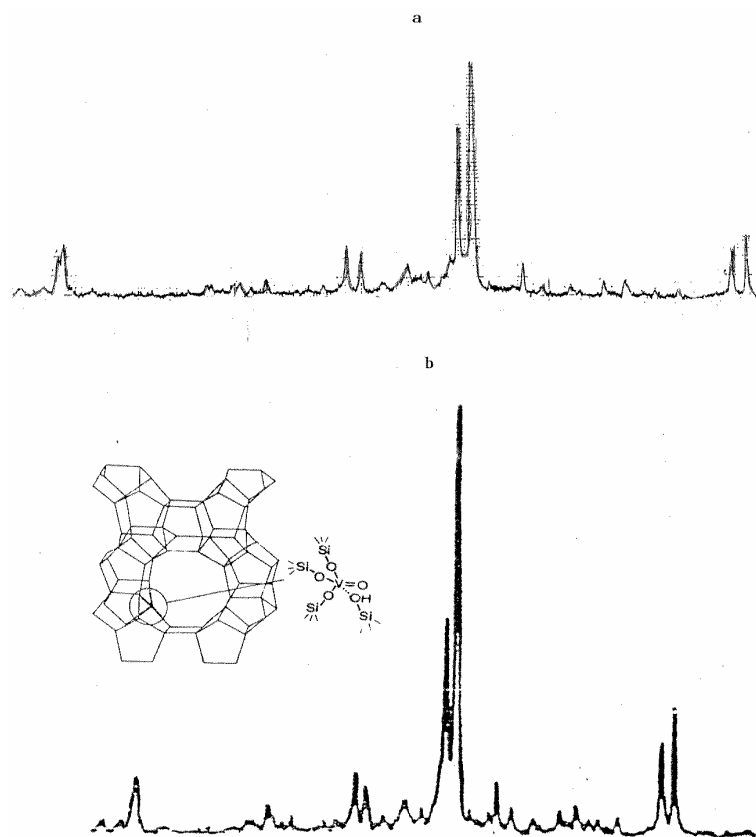
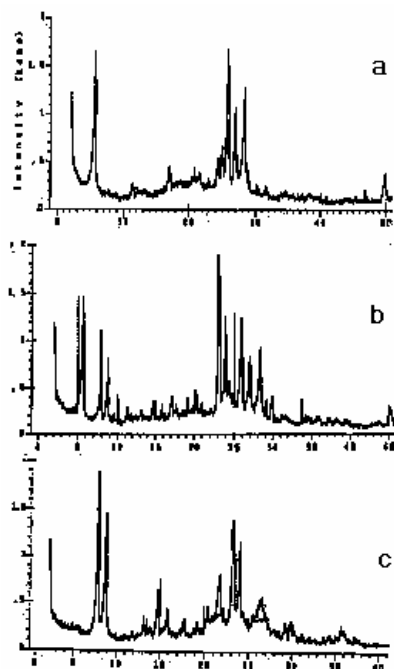


Figure 4. XRD pattern of (a) V-magediite; (b)magediite [29].



**Figure 5.** XRD pattern of (a) as synthesized V-ZSM-11; (b) V-ZSM-11 [30].



**Figure 6.** XRD pattern of (a) V-magediite (run 15); (b) V-ZSM-11 and V-magediite (run 18), (c) V-ZSM-11 with some impurities.



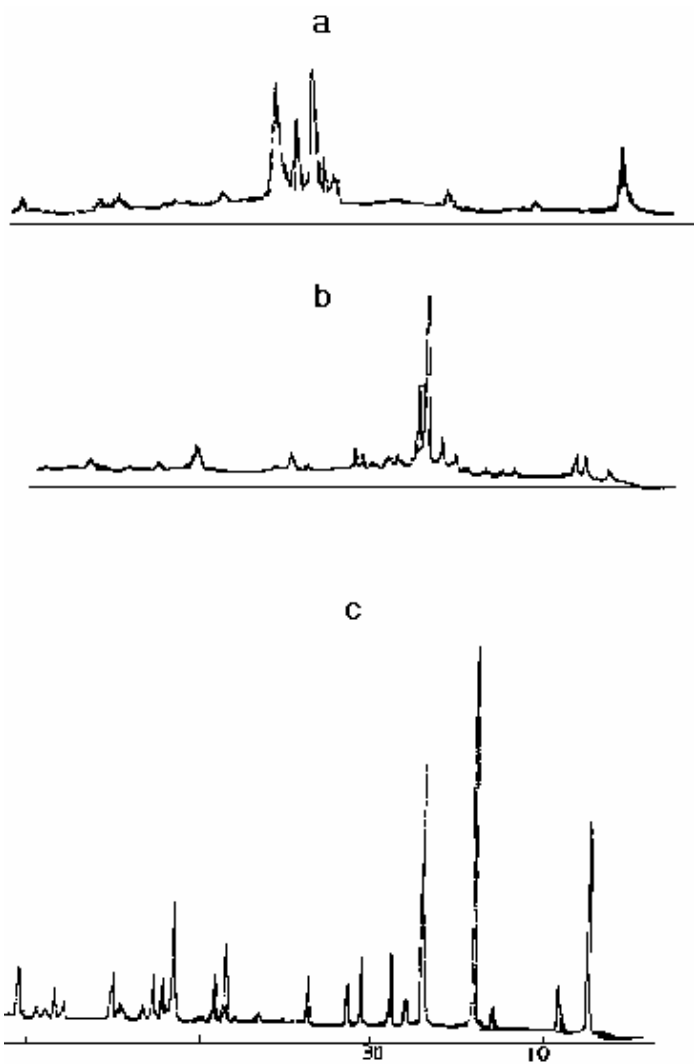


Figure 7. XRD pattern of (a) V-magediite; (b) V-ZSM-11 and V-magediite; (c) V-analcime.

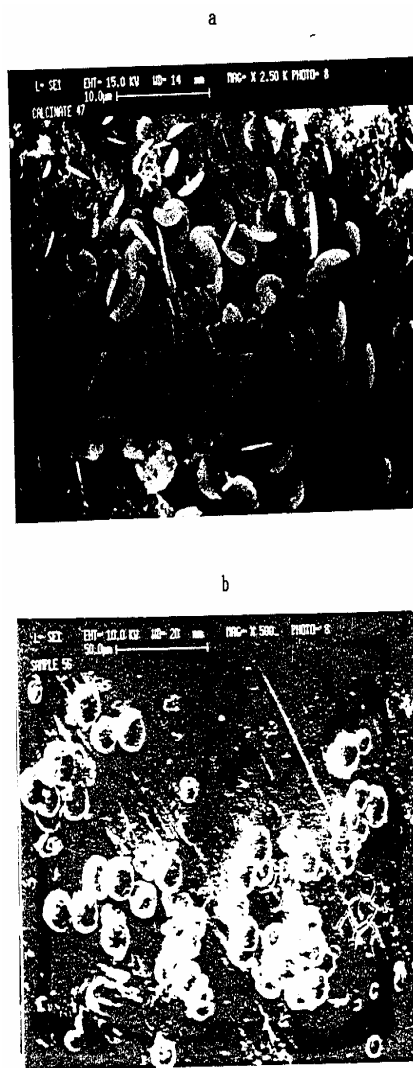


Figure 8. SEM micrograph of (a) V-analcime; (b) V-Al-analcime.



Figure 9. SEM micrograph of (a) as synthesized V-magediite; (b) magediite.

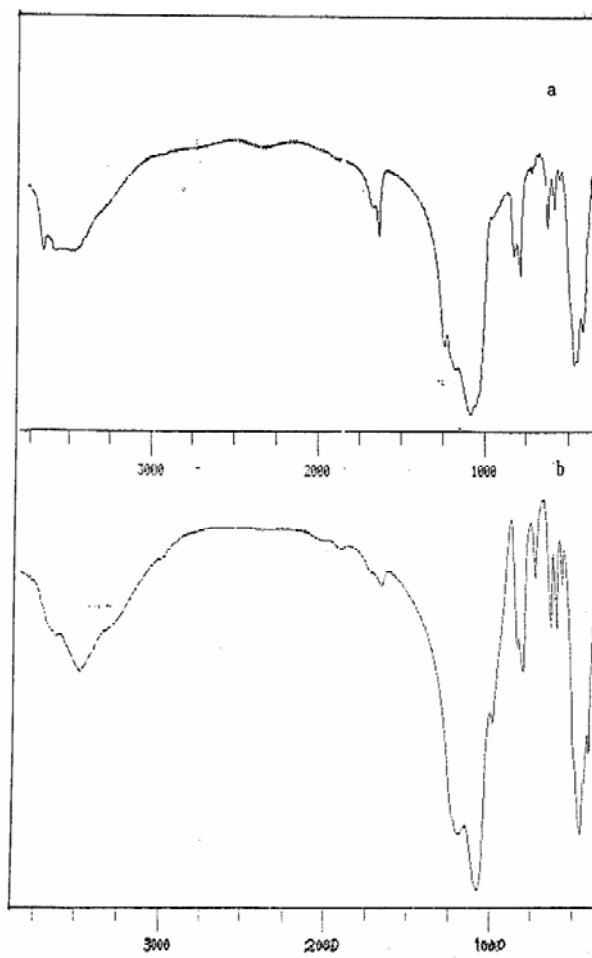


Figure 10. FTIR spectra of (a) V-magediite; (b) V-magediite after addition H<sub>2</sub>O<sub>2</sub>.

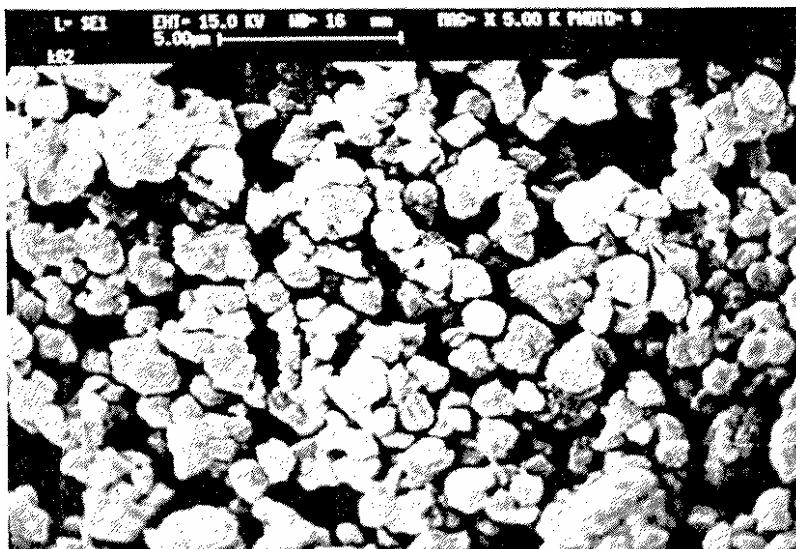


Figure 11. SEM micrograph of V-ZSM-11.

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