

**Synthesis of aluminosilicates under high pressure and using sulfur as directing agent:
study of hydrogen and water adsorption.**

Sandra Loera^{1,*}, Jorge Flores¹, Enrique Lima², Heriberto Pfeiffer², Miguel A. Olivier³, and
Victor H. Lara⁴

¹Universidad Autónoma Metropolitana Azcapotzalco, Av. San Pablo 180, Col. Reynosa Tamaulipas
Azcapotzalco, 02200, México D.F. Mexico.

²Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito exterior s/n,
Cd. Universitaria CP 04510, México. D. F. Mexico.

³ESIQUIE-IPN, Departamento de Ingeniería Química - Laboratorio de Investigación en Materiales Porosos,
Catálisis Ambiental y Química Fina. UPALM Edif.7 P.B., 07738, México D.F. Mexico.

⁴Universidad Autónoma Metropolitana Iztapalapa, Av. San Rafael Atlixco 186, Col. Vicentina, 09340,
México D. F. Mexico.

E-mail: sls@correo.azc.uam.mx

ABSTRACT

In the present work we have investigated the use of aluminosilicates with sulphur as potential hydrogen storage materials. Two aluminosilicates were prepared under hydrothermal conditions. Silica, sodium aluminate, sodium sulfide and sulfur were used as raw materials. Starting with similar reacting mixtures, analcime (zeolite, $\text{Na}(\text{Si}_2\text{Al})\text{O}_6 \cdot \text{H}_2\text{O}$) and beidellite (clay, $\text{Na}_{0.3}\text{Al}_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$) were synthesized varying pressure, 2 kbar and 1 kbar, respectively. Sulphur was present in both aluminosilicates's surfaces, which confer to them particular adsorption properties. Additionally, water adsorption isotherms, under dynamic conditions, were obtained. Fractal dimension values and SEM micrographs reveal very different textural and morphological properties of two prepared aluminosilicates. Hydrogen adsorption capacities were measured at 77 K and low pressure (until 1 bar). The results showed that hydrogen uptake in aluminosilicates are strongly dependent on framework and sulphur content.

KEYWORDS

Beidellite; Aluminosilicate; Catalysts; Sulphur; Analcime.

1. Introduction

Zeolites occur naturally, they are formed where volcanic rocks and ash layers react with alkaline groundwater. Generally, the crystallization of minerals in volcanic rocks occur through interactions between fluids with pre-existing crystal phases and with glass,



the latter representing the most abundant fraction in pyroclastic materials [1]. The chemical composition of the glass plays a crucial role in the resulting mineral and the kinetics reaction. Actually, silica-rich glasses are not very reactive. Temperature, fluid composition, and pH are also important factors driving reaction kinetics [2]. Thus, geological conditions are determinant to crystallize sediments as chabazite, analcime and phillipsite, among others zeolites. Even, zeolites occur naturally, the synthetic ones are the most widely used as sorbents, catalysts, support catalysts and ion-exchange materials. The most common synthetic way of zeolites is the hydrothermal treatment at moderate temperatures ($\sim 200^\circ\text{C}$) and elevated pressure in presence of water excess [3].

Physicochemical parameters are, of course, determinant for synthesis. Temperature and pressure effects have been largely studied on hydrothermal synthesis of zeolites [4-6]. It is possible to drive the synthesis for obtaining different aluminosilicates starting from same reactants, for example, in the four component system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 1013 bars, and excess of water, synthetic phase of albite, analcime, mordenite, hydroxycancrinite, natrolite, nepheline hydrate, hydroxysodalite, and montmorillonite are formed varying the temperature between 290 and 700°C [7-9].

Zeolites have a great capacity to host many chemical species, mainly water, cations and hydrogen. Structure determines the capacity as adsorbents and their selectivity of shape. In this sense Line and coworkers [4] have studied the dehydration kinetics on two analcime structures. The first one was X-analcime (formed by ion exchange from leucite) whose surface area of $20\text{ m}^2/\text{g}$ and the second one was H-analcime (synthesized by hydrothermal conditions) with $2\text{ m}^2/\text{g}$ of surface area. Porous network, which is determined by parameters of synthesis, is the main responsible of the adsorption capacity.

In this work, we present the pressure and time effect on aluminosilicate synthesis by hydrothermal conditions using sulfur as directing agent at 280°C . The aluminosilicates were prepared using silica, sodium aluminate, sulfur and sodium sulfide as precursors. We also determined hydration and dehydration behavior of synthesized samples.



2. Experimental

Synthesis: Sodium aluminate (Fisher Scientific), silica and sulfur and sodium sulfides (Aldrich) were ground together with a molar ratio 1.0:1.0:0.94:0.23, respectively. Teflon containers, were filled with 12.8 cm³ of the mixture, then 3.2 ml of water were added and the containers were sealed and placed in an autoclave. All hydrothermal experiment were performed using high pressure autoclaves (type AE 0010AS22 1517, Autoclave Engineers, USA) with Bridgeman sealing technique at a static water pressure [10]. Temperature imposed for all synthesis was 280 °C. Two different samples were synthesized, SiAl_Z and SiAl_C. The SiAl_Z sample was synthesized at 2 kbar of pressure during 23 days. The SiAl_C sample was obtained at 1 kbar of pressure for 46 days. All samples were filtered and washed several times with deionized water to eliminate soluble residues, then dried to 80°C and characterized.

Characterization: The energy dispersive X-ray spectroscopy was performed with an EDS, EDAX DX4 SUTW-USA, coupled to a Cambridge S90B scanning electron microscope, Great Britain system. Focus of beam assures covering an area of 6 μm² and a depth of 4 μm. A powder diffractometer (Siemens D500) coupled to a copper anode X-ray tube was used to identify compounds present in each sample. The Kα₁ radiation was selected with a diffracted beam monochromator. Scanning electron microscopy (SEM with field emission cathode, Philips XLS 30 ESEM) gave morphological information such as particle size and shape, dispersion of the powders and other microstructural properties of the samples.

High resolution thermogravimetric analyses (TGA Q500HR, TA Instruments) were used to determine the thermal stability of the samples. Each dynamic thermogram was carried out at 5 °C/min, into an air atmosphere. Additionally, a Q5000SA thermobalance equipped with a humidity-controlled chamber, from TA Instruments, was used to performed a water sorption analysis, where the experiments were performed using N₂ (Praxair, grade 4.8) as carrier gas and distilled water as the vapor precursor, using in all the



cases a total gas flow of 100 ml/min. The relative humidity percentages were controlled automatically with the Q5000SA equipment. Samples were tested as produced (native) and thermally activated at 600 °C for 4 hours.

3. Results

X-Ray diffraction patterns of SiAl_Z and SiAl_C samples are compared in Figure 1. Both XRD patterns showed the formation of pure but different phases, at least at the XRD detection limit. While, the SiAl_Z diffraction pattern fitted with the analcime structure (a zeolite, $\text{Na}(\text{Si}_2\text{Al})\text{O}_6 \cdot \text{H}_2\text{O}$, with JCPDS 19-1180), the SiAl_C sample fitted with the beidellite, a clay ($\text{Na}_{0.3}\text{Al}_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, with JCPDS 43-0688). Peaks labeled as Pt correspond to (111), (200) and (220) planes of the platinum sample holder. The SiAl_Z XRD pattern corresponds to fully crystalline analcime, which possesses an orthorhombic crystalline system. The cell parameters were calculated: 13.67, 14.26 and 13.67 Å (± 0.06 Å).

Conversely, the XRD pattern of SiAl_C sample fitted with a beidellite laminar structure, with an hexagonal crystalline cell: $a_0 = 5.11$ Å and $c_0 = 12.55$ Å. The material was characterized by $d_{(001)}$ -spacing equal to 12.55 Å which is closed to reported value, 12.6 Å, [7]. Hence, pressure induces the formation of different structures, where a higher pressure produced a denser material (zeolite), as it could be expected. Additionally, the crystal size, of both samples, was obtained from profile fitting of the 100 % intensity diffraction peak according to the Scherrer equation, being 102.9 Å and 614.9 Å for SiAl_C and SiAl_Z , respectively. The crystal size was larger rising synthesis pressure, being this result consistent with pressure. Some papers suggest a hydrothermal synthesis mechanism, which consists in precursor dissolution, supersaturation of the hydrothermal fluid and the consequent recrystallization from the supersaturated solution [8, 11].

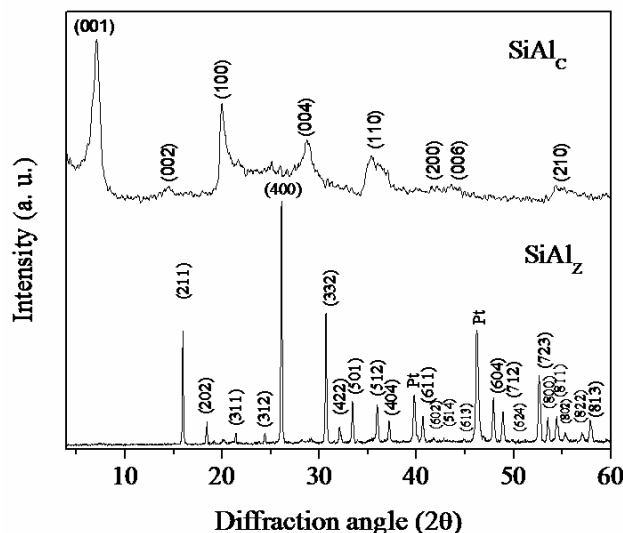


Figure 1. X-ray diffraction patterns of SiAl_Z and SiAl_C . Each diffraction pattern was indexed with the corresponding JCPDS card; 19-1180 for SiAl_Z and 43-0688 for SiAl_C . Peaks labeled as Pt correspond to platinum support (4-0802 JCPDS card).

The chemical composition of SiAl_Z and SiAl_C was determined by EDX, [Table 1](#). Note that sulfur found, on the SiAl_C surface, was higher than that observed on the SiAl_Z sample. This difference does not correspond to the expected sulfur composition of the surfaces, because the same amount of sulfur was used during material synthesis. The sulfur difference (2.54 wt %) may be attributed to occlusion of sulfur molecules into the aluminosilicate network. It seems that more sulfur reached the bulk of the clay, in comparison to the zeolite. It must be noticed that sodium contents was rather low compared to other similar materials [12]. Nevertheless, it is assumed that sulfur is present as S^{2-} , the overall charge on zeolite is more negative which means that protons must be as compensating cations.



Table 1. Chemical analysis of aluminosilicates as determined by EDX.

Element	Composition (wt%)	
	SiAl _Z	SiAl _C
O	48.23	42.06
Na	9.07	3.01
Al	16.27	16.16
Si	21.45	31.24
S	4.99	7.53

A SEM image of the SiAl_Z sample is presented in Figure 2, where polyhedral particles as large as 150 μm are observed. At higher magnifications, it can be seen that polycrystalline particles are the consequence of self-assemble oriented platelets in the [111] plane [5]. Single grains, smaller than 15 μm , were formed and then the second particles generation as layer (*c.a.* 10 μm) formed on the primary single grain indicates that the supersaturation limit was reached at least a second time during the synthesis process, leading to a oriented growth. Figure 3 presents SEM images of sample SiAl_C. SEM picture showed an irregular morphology of particles smaller than 1 μm which agglomerate. The morphology of this sample differs significantly if compared with SiAl_Z sample. These differences can be attributed to combined action of the pressure and synthesis time.

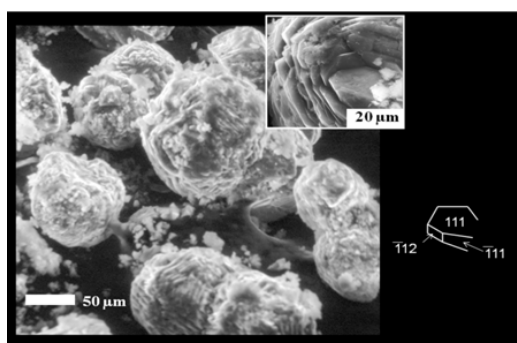


Figure 2. SEM image of SiAl_Z sample. Grains of around 150 μm of size are observed, which are mostly agglomerates of smaller particles (15 μm). These particles presented a layered morphology.

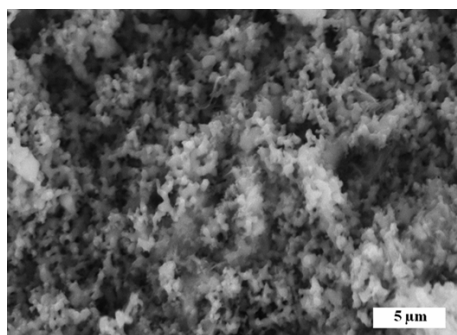


Figure 3. SEM micrograph of beidellite particles of about 1 μm of diameter obtained after 46 days at 280 $^{\circ}\text{C}$ (1 kbar of pressure).

Figure 4 shows the SiAl_Z and SiAl_C thermograms. As it could be expected, according to the structural and morphological characterizations, samples presented different thermal behaviors. SiAl_Z sample, which possesses an analcime zeolitic structure, did not loss weight between room temperature and 160 $^{\circ}\text{C}$. Then, between 160 and 390 $^{\circ}\text{C}$, this sample lost 7.1 wt%, attributed to water evaporation of molecules located into the zeolitic channels. Finally, between 445 and 552 $^{\circ}\text{C}$ the sample lost 0.4 wt%. In this temperature range it is not expected a loss weight in pure analcime. Then, it may then be attributed to sulfur species decomposition. On the other hand, the SiAl_C sample presented a different thermal behavior, as it could be expected. Initially, from room temperature to 360 $^{\circ}\text{C}$ the sample lost weight exponentially (4.3 wt%), attributed to the water evaporation of superficial and interlayered molecules. After the dehydration process, sample presented a second lost of weight, equal to 2.7 wt% (370-540 $^{\circ}\text{C}$), which corresponded to the dehydroxylation process, and consequently, to the layered structure destruction. Finally, the sample lost 0.8 wt%, between 560 and 650 $^{\circ}\text{C}$, which may be attributed to loss of sulfur as in case of analcime sample. Note that the amount of sulfur lost in zeolite and clay agrees, roughly, with the relative amount of sulfur detected by EDX analysis at the particle surfaces.



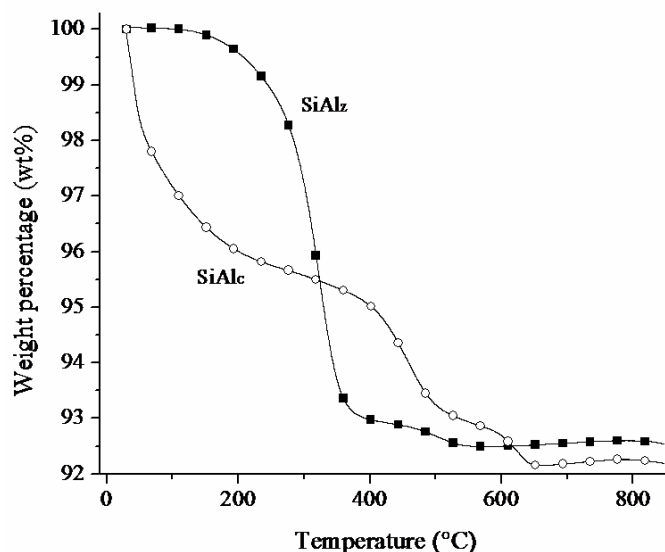


Figure 4. Dynamic thermograms of the SiAl_Z and SiAl_C samples.

Based on the thermally stability results, part of both samples was heat treated at 650 °C for 6 hours, in order to eliminate all the water, hydroxyl and other species of the samples and then to analyze the water sorption phenomena. Figure 5 shows different water adsorption-desorption isotherms of the SiAl_Z sample, original and thermally treated at 650 °C. As it can be seen during the adsorption process, all the curves presented isotherms type III which, according to the IUPAC, correspond to weak attractive adsorbate-adsorbent interactions, and the adsorbate-adsorbate interactions plays an important role. After that, desorption or dehydration process varied as a function of the thermal treatment. Initially, SiAl_Z sample previously treated at 650 °C adsorbed more water as a function of temperature. Water adsorbed increased from 0.91, 1.05 and 1.11 wt% if the adsorption process was produced at 50, 60 or 70 °C, respectively. Of course, the quantities of water adsorbed are very low, in comparison to the water desorption produced during the thermal activation (see Figure 4). Additionally, in these cases the desorption processes were not completed, as 0.2-0.3 wt% of the total adsorbed water remained at the end of the desorption process. Therefore, these water molecules must have been adsorbed over the zeolite surface and only a very small quantity of water diffused into the zeolitic channels, inhibiting their



desorption at these thermal conditions. However, the SiAl_Z original sample, which was only tested at 70 °C, was the sample that adsorbed less water (0.71 wt%), and in this case all the water was desorbed. Hence, the previous thermal treatment cleaned surface and the zeolitic channels. However, it has to be mentioned that water adsorption was, in fact, low and most of it was only superficially adsorbed.

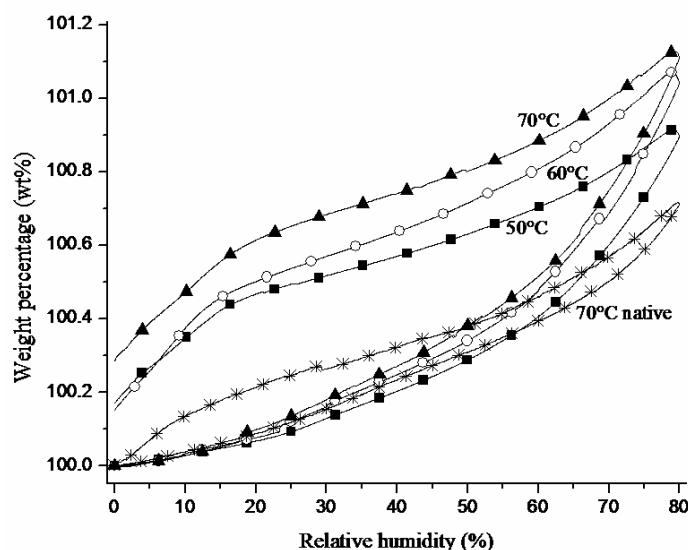


Figure 5. Water adsorption-desorption isotherms of the SiAl_Z native sample and after a thermal treatment at 650 °C. The isotherms were performed at 70 (native and thermally treated samples) and 60 and 50 °C (sample thermally treated).

Although SiAl_C presented the same kind of isothermal behavior than SiAl_Z , water adsorbed was much higher in this case, Figure 6. Samples thermally treated at 650 °C adsorbed up to 8 wt% and the residual water in all the cases was similar, around 1 wt%. Nevertheless, in this case, the original sample was the sample which adsorbed more water 10.2 wt%, but this sample practically desorbed all water at the end of the desorption process. In this case, thermal activation did not improve water adsorption, although in all the cases it was always higher than that obtained in the zeolite structure. It may be explained in terms of external surface area, which must be higher in the SiAl_C sample.



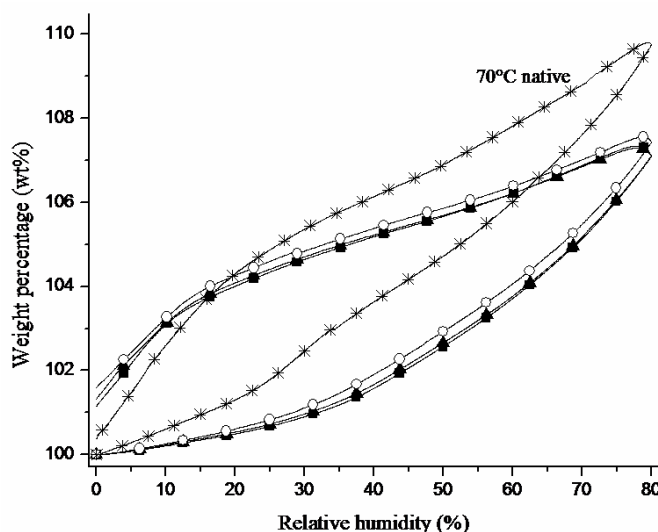


Figure 6. Water adsorption-desorption isotherms of the SiAl_C native sample and after a thermal treatment at 650 °C. The isotherms were performed at 70 (native and thermally treated samples) and 60 and 50 °C (sample thermally treated).

4. Discussion

Contrary to conventional materials synthesis, in this work sulfur was used as a directing agent during the hydrothermal synthesis. When the synthesis pressure was 1 kbar the resulting material was a clay (SiAl_C , beidellite). Upon the pressure increases up to 2 kbar the resulting material was a zeolite (SiAl_Z , analcime). Clearly, the pressure is a key parameter to drive the synthesis of aluminosilicate and the driving is directly related with changes observed on sulfur with pressure.

Actually, the analysis of low-pressure phase diagram of sulfur [14] under isobaric conditions (1 kbar), illustrate that at room temperature sulfur possesses an orthorhombic crystal structure. At around 170-190 °C the sulfur liquid phase appears. In fact, 190 °C was precisely the synthesis temperature of synthesis of the aluminosilicates. During the standard hydrothermal synthesis under isobar conditions without agitation, the experiment begins with a water fluid with solid precursor materials. Then, it gets more and more concentrated as time goes on, until the supersaturation is produced. At a certain level of supersaturation a



spontaneous crystallization will finally occur, leading to a decrease of the concentration in the hydrothermal fluid [11]. Therefore, changes in sulfur structure are the determinant factor to lead the clay structure. Furthermore, the high amount of sulfur in this sample, as determined by EDX analysis, can be explained because of the presence of sulfur which is easily incorporated to clay structure either adsorbed at surface of clay or as interlayered stable species.

If pressure is increased up to 2 kbar, sulfur is at the frontier where solid orthorhombic remains i.e. S_8 species are the main molecules present. Actually, under this pressure the S_8 adopts a crown configuration [15]. It could be possible that at 2 kbar and 190 °C S_8 rings might have collapsed and liquid sulfur appeared, so material crystallized mainly as analcime and formation of big agglomerated is favored because of ordered sulfur species drives a stacking of small particles. At end of growing step, big globular roughed particles are obtained which are interesting because their surface presents strong water adsorption sites. In contrast, the clay structure allows the water interlayer deposition more easily than zeolite. Nevertheless, thermal activation decreased the water adsorption capacity, perhaps as part of superficial sulphur was lost.

5. Conclusion

Hydrothermal synthesis of aluminosilicates can be tuned to obtain either beidellite clay or analcime zeolite. By using sulfur as a directing agent a functionalization with sulfur centers of surface of both aluminosilicates is induced. These sulfur centers, together with aluminum cations, can play the role of strong adsorption sites to adsorb polar molecules such water. Polyhedral particles of analcime presented a roughed surface because of the defects such as edges of stacked smaller particles. On the contrary, the particles of clay agglomerate leading to surfaces almost smoothed.

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