



Washing Effect on the Synthesis of Silica-Pillared Clays

A. SAMPIERI

Benemérita Universidad Autónoma de Puebla, Facultad de Ciencias Químicas. Blvd. 14 Sur y Av. San Claudio, C.P. 72570, Puebla, PUE, Mexico; Instituto Nacional de Investigaciones Nucleares, Area de Química, A.P. 18-1027, Col. Escandón, C.P. 11801, México, D.F., Mexico

G. FETTER*

Benemérita Universidad Autónoma de Puebla, Facultad de Ciencias Químicas. Blvd. 14 Sur y Av. San Claudio, C.P. 72570, Puebla, PUE, Mexico
geolarfetter@yahoo.com.mx

P. BOSCH

Universidad Nacional Autónoma de México, Instituto de Investigaciones en Materiales, A.P. 70360, Ciudad Universitaria, C.P. 04510, México, D.F., Mexico

S. BULBULIAN

Instituto Nacional de Investigaciones Nucleares, Area de Química, A.P. 18-1027, Col. Escandón, C.P. 11801, México, D.F., Mexico

Received January 30, 2003; Revised January 30, 2004

Abstract. Silica-pillared clays were prepared by two methods: conventional and microwave irradiated. Preparation time of the conventional intercalating solution took about two days but only 15 minutes when it was microwave irradiated. Washing extent determined the size and the amount of intercalated silica pillars.

The surface areas of the compounds obtained by these two different methods are comparable within error range, but the pillaring mechanism must be different as in the conventionally intercalated samples calcium is preferentially exchanged, instead in the microwave irradiated samples sodium is preferred.

Keywords: clays, montmorillonite, silica pillars, microwave irradiation, microporous materials

1. Introduction

Catalysis and adsorption applications require materials with a high porosity and a large surface area. Among aluminosilicates, zeolites or clays are often chosen. Although zeolites are molecular sieves, they present the disadvantage of their small pore size. Clays have a

layered structure and therefore they may be expanded, the size of the molecules entering this materials can be larger. Furthermore, the texture of clays can be improved by substantially introducing pillars between the layers. These pillars are obtained by intercalating large inorganic metal polyoxocations between the aluminosilicate layers. The polyoxocations are, then, converted into stable metal oxide pillars through a calcination step, holding the layers permanently apart and thus creating microporosity.

*To whom correspondence should be addressed.

The porosity of the obtained pillared interlayered clays can be tailored by changing the size, shape and concentration of the intercalating species [1–3]. Among the often used metal polyoxocations (Al, Zr, Cr, . . .) silica presents the following advantages: silica pillars are hydrophobic and they present a high thermal stability.

Endo et al. [4] and Pinnavaia et al. [5] used silicon acetylacetonate to obtain silica-pillared clays (montmorillonite and hectorite). These pillared clays showed a 001 spacing of 12.6 Å after calcination at 500°C, corresponding to a single SiO₂ pillar. A different approach was followed by Farfan-Torres et al. [6]. They used positively charged silica sol obtained by acid hydrolysis of Si(OEt)₄ to intercalate into a montmorillonite clay. After intercalation at room temperature, they obtained 001 spacings of 14.9 Å which decreased to 10 Å upon calcination at 600°C. Moreover, Lewis et al. [7] focused mainly on the preparation of silica–intercalated montmorillonite using oligosilsesquioxane species, resulting from controlled hydrolysis of alkylchlorosilane precursors, such as the trichlorosilylethylpyridine. Once calcined at 600°C in air, the pillared clay presented a 001 spacing of about 19.2 Å and a good stability in steam up to 750°C.

Fetter et al. [8] synthesized silicon polyoxocations by means of partial hydrolysis of trichlorosilylethylpyridine (TCSEP) and 3-aminopropyltrimethoxysilane (APTMS) that diffused slowly into the clay particles. The distribution of pillars for both TCSEP and APTMS was heterogeneous. Using TCSEP, the 001 spacing was 26.4 Å after intercalation and 18.3 Å after calcining at 600°C. The surface area was found to be close to 240 m²/g. Instead, using APTMS, the 001 spacing was 20.0 Å after intercalation at room temperature and 16.0 Å upon calcination at 600°C. The surface area reached 360 m²/g.

Although the silica-pillared clays with a high surface area can be obtained by conventional methods using different silicon precursors, the procedure takes a lot of time and requires a large amount of water because of low clay concentrations. Furthermore, it is difficult to determine whether the samples are free of precursor residues or not. Ahenach et al. [9] have shown the correlation of surface area values with water concentration and precursor ions.

Recently alumina-pillared clays have been synthesized using microwave irradiation during the intercalation step [10] or instead, on the final thermal treatment [11]. The preparation time of pillared clays was

considerably reduced from hours to minutes. The alumina pillaring of montmorillonite from highly concentrated aluminum solution and highly concentrated clay suspensions (up to 50 wt%) has been reported [12]. For alumina intercalated samples the washing degree is easily determined with the chloride test [13]. Hence, this method may be adequate to prepare silica-pillared clays, with the advantage of a short preparation time.

In this paper we compared the properties of silica-intercalated montmorillonites synthesized by the conventional and microwave irradiation methods. The silica intercalating species were obtained using 3-aminopropyltrimethoxysilane as a precursor. We also studied the influence of the water amount in washing processes on the properties of the solids.

2. Experimental

2.1. Materials

Na⁺-Ca²⁺-montmorillonite from Sigma, with a cation exchange capacity of 90 meq/100 g of clay was used to prepare the pillared clays (PILC's). The chemical composition (wt % on humid basis) was: SiO₂: 59.6; Al₂O₃: 18.5; Fe₂O₃: 2.70; MgO: 2.07; Na₂O: 2.78; K₂O: 0.32; CaO: 1.54.

The silane precursor was 3-aminopropyltrimethoxysilane (APTMS) from Fluka Chemika and the solvents used were methanol and acetone, both from Baker.

2.2. Preparation of the Pillaring Solution Following the Conventional Method

The procedures for the hydrolysis of the silane were similar to those reported by Fetter et al. [8]. APTMS (1 g) was mixed with 3 mL of methanol at room temperature, and then, 0.3 mL of an aqueous solution of HCl (16%) was added to the mixture. The solution was stirred for 27 h and then 7 mL of acetone were added to it. Finally, the solution was heated to reflux for 1 h, then cooled at room temperature while stirring for 3 h. The solution was stored in the dark for 24 h, known as aging stage.

2.3. Preparation of the Pillaring Solution Using Microwave Irradiation Method

For the preparation of the pillaring solution we used the same reagent ratios as for the conventional method [8].

The methanol/APTMS/HCl mixture was microwave irradiated in a domestic oven (Philco) operating at 2.45 GHz and at 180 W of power. In this method the aging stage was eliminated. Two irradiation treatments were given to the pillaring solution which was first irradiated for 10 minutes. Then acetone was added to the methanol/APTMS/HCl solution and the resulting mixed solution was again microwave irradiated for 5 minutes.

2.4. Preparation of the Pillaring Clays

2.4.1. Intercalation by the Conventional Method.

The clay was dispersed in deionized water (2.5 g/L) and the mixture was stirred for 1 h. The pillaring solution was, then, added dropwise to the clay slurry and maintained under stirring for 36 h at room temperature. The final pH was 9.7. Two samples were prepared, the first was washed with 2 liters of water per gram of clay (CW2 sample) and the second, with 0.5 liter of water per gram of clay (CW0.5 sample) using in both cases deionized water. The samples were washed redispersing the clay in water under stirring for 5 minutes and recovered by decantation. The molar ratio was 2.0 mmol of silica per gram of clay. The samples were filtered and dried at 60°C.

2.4.2. Intercalation by the Microwave Irradiation Method.

In this case, the clay was not dispersed in water, it was added in powder form to the pillaring solution obtained previously by the microwave irradiation method. The slurries were stirred continuously until disaggregation and, then, they were microwave irradiated for 10 minutes. The washing step was similar to the one previously described for conventional samples, hence two samples resulted (MW2 and MW0.5). Finally, they were filtered and dried at 60°C.

2.5. Thermal Treatments

The intercalated clays were calcined in air at 600 and 700°C to anchor the pillars to the clay sheets and remove the organic moiety of the pillars. A bed of clay was set in a horizontal furnace swept by an air flow of about 100 mL/min. The heating rate was 60°/h and the desired temperature was maintained for 5 h. A fresh sample was used for each calcining temperature.

2.6. Characterization Techniques

Powder X-ray diffraction patterns were obtained using a Siemens D500 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The powder samples were non-oriented.

The nitrogen adsorption isotherms at -196°C were recorded on a Micromeritics Gemini 2360 automated gas adsorption system. The samples were degassed at 300°C during 3 h prior to analysis. Surface areas were calculated according to BET equation.

The elemental analysis (Si, Al, Na and Ca) of the initial clay and the intercalated samples was determined by atomic absorption using a Perkin-Elmer 2280 spectrophotometer. The sample (0.1 g) was decomposed by alkaline fusion (boric acid and lithium carbonate) and then dissolved in a 5 N HCl solution.

3. Results and Discussion

3.1. Conventional Synthesis

The samples CW2 and CW0.5 had the same Si/clay nominal ratio, but only the amount of water used during the washing process was different in these two samples. The corresponding X-ray diffraction patterns were similar (Fig. 1) but the c-dimension (001 peak) was 16.0 \AA when 2 L of water per gram of clay were used. For 0.5 L of water per gram of clay, the distance was 17.8 \AA . These values have to be compared with the 001 distance of the initial clay, 12.6 \AA . On the one hand, these differences may be due to the decomposition and/or fractionation of pillaring species, hence the larger the water amount the easier to destroy these species. On the other hand, the larger species may diffuse out with water. With larger washing water amount, more large species are expelled from the layers. It has to be emphasized that the pH of the mixture is basic ($\text{pH} = 9.7$), hence the positive charge of silica species is screened by OH groups and the interaction with clay is weak.

Table 1 presents the elemental composition of these samples compared to the composition of the initial clay. The silicon amounts in the CW2 and CW0.5 samples were much larger ($\text{Si/Al} = 3.26, 3.33$ respectively) than that in the non intercalated clay ($\text{Si/Al} = 2.68$). The Si/Al values for CW2 and CW0.5 were similar within error range, thus, this observation is in agreement with large silica species diffusing out of the clay. Therefore, to explain the difference in the interplanar 001

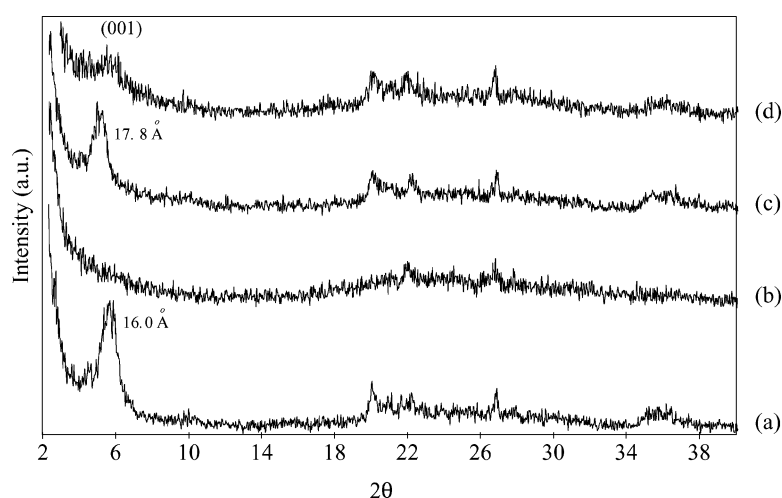


Figure 1. X-ray diffractograms of the samples: CW2 not calcined (a); CW2 calcined at 600°C (b); CW0.5 not calcined (c) and CW0.5 calcined at 600°C (d).

distance, larger intercalated silica species have to be assumed in the CW0.5 sample. Furthermore, to evaluate the amount of pillars introduced the ratios Na/Si and Ca/Si are most illustrative as they refer to the number of cations to the total number of silicon atoms, i.e. from montmorillonite and pillars. These ratios clearly diminish from 0.050 to 0.037 and 0.041 to 0.018 respectively showing that silica species have been exchanged with those cations. It seems that calcium is more easily exchanged than sodium, such is not the case with other polyoxocations as aluminum or zirconium polyoxocations [14, 15]. Hence, in this system the exchange is determined by the cation charge.

The presence of larger silica intercalates in the CW0.5 is confirmed by the calcined samples results. Table 2 compares the surface areas of the samples CW2 and CW0.5 which were intercalated, and also calcined at 600 or 700°C. In the intercalated samples,

the surface area decreased from 112 to 60 m²/g as the amount of washing water decreased. The intercalated silica species are larger in CW0.5 and, as the organic radicals are still present, they occupy a larger inter-lamellar space, then, they block the nitrogen adsorption. However, when these materials were thermally treated at 600°C, the specific surface areas were 60 and 198 m²/g for CW2 and CW0.5, respectively. At this temperature all organic moieties are burnt and only the siloxane skeletons remain. As in CW0.5 the initial species were larger, the corresponding pillars result in a

Table 1. Elemental analysis of the initial clay, the conventionally (CW) and microwave irradiated (MW) samples, expressed in molar ratios.

Sample	Si/Al	Na/Si	Ca/Si
Initial clay	2.68	0.050	0.041
CW2	3.26	0.041	0.020
CW0.5	3.33	0.037	0.018
MW2	3.50	0.017	0.038
MW0.5	3.47	0.013	0.023

Table 2. Surface areas of the initial, intercalated and calcined samples.

Sample	Calcining temperature (°C)	Surface area (m ² /g)
Initial clay	n.c.	37
CW2	n.c.	112
	600	60
	700	21
CW0.5	n.c.	60
	600	198
	700	64
MW2	n.c.	148
	600	17
	700	15
MW0.5	n.c.	56
	600	155
	700	60

n.c.: not calcined.

more expanded clay. This remark was confirmed by the X-ray diffraction patterns; in Fig. 1 the sample CW0.5 treated at 600°C still gave the main clay peaks whereas the 600°C treated CW2 sample was already a micro-crystalline compound.

The samples calcined at 700°C exhibit surface areas of 21 and 64 m²/g. Both values are approximately one third the surface areas obtained at 600°C, showing that the thermal effect is the same in both samples. This indicates that thermal stability is not dependent on the pillar size or the amount of exchanged cations. In the CW2 sample this process was started at a lower calcining temperature (600°C) due to a non uniform distribution of the pillars in the clay particles.

3.2. Synthesis in Presence of Microwave Irradiation

The samples MW2 and MW0.5 were prepared with a solution irradiated for 10 minutes and this is a much shorter treatment time compared with the CW2 and the CW0.5 samples which were equilibrated for 36 hours. The X-ray diffractograms of the intercalated samples are shown in Fig. 2. The samples maintained their crystallinity and the silica species were intercalated as the (001) distance increased, in the sample MW2 up to 16.9 Å and in the sample MW0.5 up to 18.0 Å. As discussed above, the smaller washing water amount favors larger intercalated species which are apparently more uniformly distributed. The irradiation time (10 minutes)

is enough to provide the intercalating silica species, while the conventional method required more than 50 hours. Still, the structure of the species present in conventional and microwaved solutions are not necessarily the same. Furthermore, the Si/Al molar ratios for these samples were 3.47 and 3.50 (Table 1) which are higher than the values obtained for the conventionally prepared samples and the surface areas were 148 and 56 m²/g (Table 2). The Na/Si molar ratio values for the MW samples are smaller and are about half the values of the CW samples. The Ca/Si values for the microwaved preparations were higher than the values obtained for the CW samples. Hence, with this procedure the sodium ions are preferentially exchanged. It seems, therefore, that microwave irradiation which has a well defined wavelength, probably excites more the sodium-montmorillonite as in the case of zeolites [16] and thus Na is able to be replaced faster.

With calcination (600°C), the diffraction patterns (Fig. 2) were similar to those found for conventional preparations. The MW2 did not give the characteristic peaks of the clays, but the MW0.5 was still crystalline. The corresponding surface areas were 17 and 155 m²/g (Table 2), reproducing the tendency found for the CW samples. At 700°C the MW samples gave similar surface area values as those that were obtained for conventional samples (CW2 and CW0.5).

If our results are compared to those reported by Fetter et al. [8] the obtained surface areas are ca. 55%

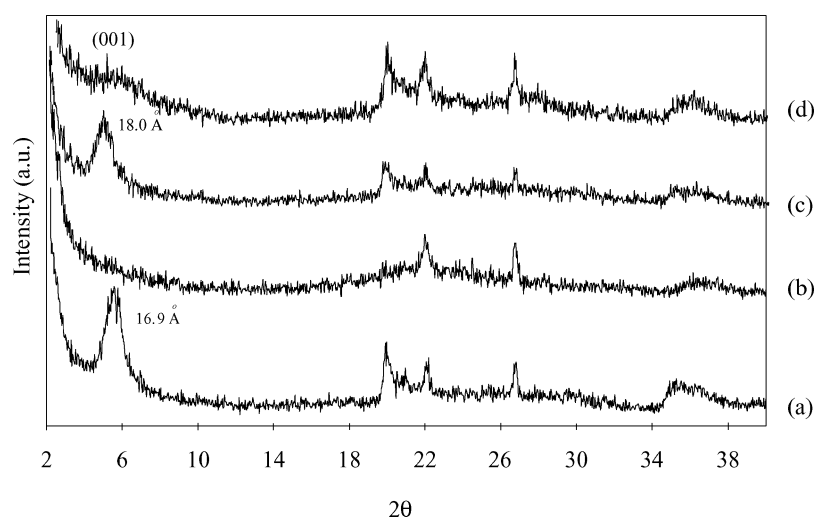


Figure 2. X-ray diffractograms of the samples: MW2 not calcined (a); MW2 calcined at 600°C (b); MW0.5 not calcined (c) and MW0.5 calcined at 600°C (d).

lower. As in the conventional preparation, the solution was similar, this difference has to be attributed on the one hand to the used clays. In the referenced work, the Volclay was a montmorillonite whose iron content, Si/Al ratio and particle size were different from those of the Sigma clay. Another difference from the previous study [8] is probably the degree of washing. Unfortunately in reference [8] the amount of washing water was not given. It is shown in this work that the amount and size of pillars which depend on the washing procedure determine in turn the surface area and the thermal stability of silica-pillared montmorillonite.

4. Conclusion

The use of microwave irradiation speeds up the pillaring process. Microwave irradiation provides adequate intercalating silica species in less than 15 minutes, while the conventional procedure requires about two days.

The cations which are present in the clay may be selectively exchanged depending on the preparation method. Microwave irradiated solution exchanged preferentially sodium ions whereas stirred solution led to the exchange of calcium ions. For samples washed with larger water content (2 L of water per gram of clay), the larger silica species were expelled irrespective of the preparation method. Washing step is crucial in both conventional or microwave-assisted preparation methods, as it determines the interlayer space and the porosity. The pillared structures were stable up to 600°C, but at 700°C they collapsed.

Acknowledgments

The authors gratefully acknowledge the CONACYT for financial support.

References

1. A. Gil, L.M. Gandia, and M.A. Vicente, *Cat. Rev.-Sci. Eng.* **42**, 145 (2000).
2. J.T. Kloprogge, *J. Porous Mater.* **5**, 5 (1998).
3. F. Figueras, *Cat. Rev.-Sci. Eng.* **30**, 457 (1988).
4. T. Endo, M.M. Mortland, and T.J. Pinnavaia, *Clays Clay Miner.* **28**, 105 (1980).
5. T.J. Pinnavaia, M.M. Mortland, and T. Endo, *U.S. Pat.* 4,367,163,9 (1983).
6. E.M. Farfan-Torres, P. Grange, and B. Delmon, *XI Simposio Iberoamericano de Catálisis Proceedings* (Guanajuato, México, 1988), p. 271.
7. R.M. Lewis, K.C. Ott, and R.A. van Santen, *U.S. Pat.* 4,510,257 (1985).
8. G. Fetter, D. Tichit, P. Massiani, R. Dutartre, and F. Figueras, *Clays Clay Miner.* **42**, 161 (1994).
9. J. Ahenach, P. Cool, E. Vansant, O. Lebedev, and J. van Landuyt, *Phys. Chem. Chem. Phys.* **1**, 3703 (1999).
10. G. Fetter, G. Heredia, A.M. Maubert, and P. Bosch, *J. Mater. Chem.* **6**, 1857 (1996).
11. A.M. de Andres, J. Merino, J.C. Galvan, and E. Ruiz-Hitzky, *Mater. Res. Bull.* **34**, 641 (1999).
12. G. Fetter, G. Heredia, L.A. Velázquez, A.M. Maubert, and P. Bosch, *Appl. Catal. A* **162**, 41 (1997).
13. G. Fetter, D. Tichit, L.C. de Menorval, and F. Figueras, *Appl. Catal. A* **126**, 165 (1995).
14. F. Figueras, Z. Klapyta, P. Massiani, Z. Mountassir, D. Tichit, and F. Fajula, *Clays Clay Miner.* **38**, 257 (1990).
15. F. Figueras, A. Mattrod-Bashi, G. Fetter, A. Thrierr, and J.V. Zanchetta, *J. Catal.* **119**, 91 (1989).
16. S. Komarneni and R. Roy, *Mat. Lett.* **4**, 109 (1986).