MICROWAVE-ASSISTED SYNTHESIS OF LOW-SILICA/ALUMINA-RATIO ZEOLITES FROM GEOTHERMAL SILICA

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ABSTRACT

Zeolites A, X, hydroxysodalite and hydroxycancrinite (ZA, ZX, ZS, and ZC, respectively) were obtained using geothermal silica (GS) as a raw material and microwaves (MW) as an energy source. GS is an industrial byproduct from the Cerro Prieto geothermal plant in Baja California, México. It is a potential raw material for zeolite manufacturing because of its chemical composition and its high reactivity given by its small particle size. First, GS was treated with NaOH to generate zeolite precursors; the resulting products were crystallized by MW using sodium aluminate to adjust the SiO₂/Al₂O₃ ratio in the reaction mixture. An experimental design based on an orthogonal array was employed to study the effects of the main factors involved in the zeolitization process of GS. The obtained yields of zeolites ZC, ZA and ZS were 95, 97, and 76.6% respectively. These zeolites were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray fluorescence (XRF), and their calcium binding capacity (CBC) was determined. The obtained results were similar to those of commercial zeolites.

Keywords: microwaves, geothermal silica, zeolite, Taguchi orthogonal array.

1. INTRODUCTION

The interaction of geothermal fluids with reservoir rock releases a siliceous material referred to as geothermal silica (GS). GS accumulates during the transit of steam through heat exchangers during the electricity production process in geothermal fields, or it precipitates from geothermal brine before being re-injected into the earth. Purified GS may contain more than 95 % silica¹ and may include alkali, transition and rare earth elements². Cerro Prieto is one of the most important geothermal fields in Mexico. It is located in Baja California³, where approximately 50,000 tons of GS⁴ is generated annually. GS has been shown to exhibit a pozzolanic behavior in Portland cement⁵. Wairakei GS has been used as a raw material in the synthesis of zeolites^{6,7}. Because of the expansive use of zeolites in the chemical industry as adsorbents, cationic exchangers, and catalysts, among other important applications⁸, the development of low-cost methods for their manufacture is important. Zeolites have traditionally been prepared using long reaction times and high temperatures⁹⁻¹². Cancrinite, for example, has been obtained at temperatures and crystallization times of approximately 200°C and 48 h⁹. Additionally, chemical additives such as NaHCO₃⁹, Na₂CO₃¹⁰ or NaNO₃¹¹ are incorporated into the starting gel. Zeolite A has been prepared from chemical reagents by a hydrothermal process at 60–100°C for 3–24 h¹³. The replacement of chemical reagents by cheaper silica and alumina sources, such as industrial byproducts with no commercial value, has proven to be an attractive alternative for producing zeolites¹⁴⁻¹⁹. Our research group has previously reported the use of other byproducts generated by carbo-electric plants (fly ash) as a raw material for zeolite production²⁰⁻²².

Microwaves are electromagnetic energy in the frequency interval between 300 and 300,000 MHz. The energy of microwave photons (0.037 kcal/mol) is low in comparison to the energy required for the breaking of molecular bonds (80-120 kcal/mol). Consequently, microwaves do not affect the structures of molecules²³.

Microwaves interact with materials by two different mechanisms: bipolar rotation and ionic conduction. In the case of bipolar rotation, molecules with permanent or induced dipoles align with the electric field. At 2450 MHz, the field oscillates such that the bipolar molecules do not align themselves completely, and heat is produced as a consequence. In the ionic conduction mechanism, the energy transference is attributed to the movement of ionic species in the solution as they try to follow the oscillating electric-field component of the microwaves. Highly polar compounds tend to warm quickly when irradiated with microwaves, whereas substances with low polarities or highly ordered

crystalline structures absorb microwaves poorly. The increased kinetic energy and generated heat promote chemical reactions. Because the energy transferred from the microwaves is directly applied to the reactant species, reactions that take place in days with conventional heating are performed in minutes when irradiated with microwaves²³. Therefore, an additional alternative to reduce the costs of the GS zeolitization process is the replacement of expensive common heating systems with more efficient sources of energy, such as microwave generators.

The first patent to claim the use of microwaves in the synthesis of zeolites was issued in 1988 to Mobil for the synthesis of zeolites NaA and ZSM-5²⁴. Currently, the microwave syntheses of several zeolites have been disclosed and studied, but only at the laboratory level²⁵. Studies have shown that microwave energy increases the heating rate of the synthesis mixture and thereby increases the reaction rate²⁶. Additional investigations aimed at explaining the effects of microwave energy have led to devices that heat the reaction mixture more uniformly²⁷. Nonetheless, some studies have concluded that hot spots are created within the mixture^{28,29}. Other studies have shown that microwaves change the association between species within the reaction mixture^{30,31} or that microwave energy enhances the dissolution of the precursor gel^{32,33}.

Microwave heating enhances the reaction rate and improves the selectivity toward desirable products during inorganic synthesis, the modification of zeolites and various catalytic processes³⁴⁻³⁶. The dissolution of the starting raw materials in alkalis is enhanced during MW exposure, which is essential to induce the nucleation and further crystallization of zeolites^{34,37,38}. The synthesis of zeolite A has been performed by using a continuous MW process, reagent-grade chemicals³⁹ and kaolin⁴⁰. The dissolution of the starting raw materials in alkalis is essential for inducing the nucleation and further crystallization of zeolites⁴¹⁻⁴³.

No reports appear in the literature regarding the synthesis of high-added-value zeolites using GS as a starting material and MW as the heating source. Therefore, the present work is aimed at determining the best conditions for the low-cost synthesis of zeolites using GS as a material with no other commercial value and MW as a heating source. An orthogonal array proposed by Taguchi (OAT) was used to study the effects of the SiO₂/Al₂O₃ molar ratio, NaOH concentration, time (tTT) and temperature (TTT) of the initial thermal treatment as well as the time (tc) and temperature of crystallization (Tc). The type and content of zeolite in the product served as the response parameters. The analysis of variance (ANOVA) and the study of the effect of each variable were performed to define the best conditions for the zeolite synthesis. The optimal conditions were calculated statistically and used to synthesize zeolites A,

hydroxysodalite, hydroxycancrinite and X. The morphological, mineralogical and chemical properties of these zeolites are discussed.

2. EXPERIMENTAL

2.1. Reagents and materials

The GS used in this study was obtained from the Cerro Prieto power plant (Baja California Norte, Mexico). Because of its origin, GS may contain NaCl, KCl, MgCl_2 and CaCl_2 . The initial total chlorides content in the sample of GS was approximately 15%; this sample was cribbed at 88 μm and washed with deionized water using a water/GS ratio of 3:1 at 80°C under stirring for 20 min to eliminate the salts. This procedure was repeated until the total chlorides content in the GS sample was 0.05%. Sodium aluminate ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and sodium hydroxide (NaOH) used were reagent grade (Spectrum) and deionized water was used. Calcium chloride 99% (JT Baker) was used for determining the calcium binding capacity (CBC), Ca concentration was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Commercial zeolites A and X in sodium from Chemical industries of the Ebro (Spain) were used for comparison.

2.2. Equipment and geothermal nanosilica zeolitization process

A mixture of GS and NaOH was homogenized for 15 min in a PM200 planetary mill (Retsch) at 350 rpm using agate vessels and balls. The resultant mixture was thermally treated in a microwave furnace (Phoenix Airwave, model 905400) using an output power of 1400 W at a frequency of 2.45 GHz. The product obtained was placed in a 300 mL TeflonTM reaction vessel. Zeolitization was performed in a microwave oven (CEM, MARSH) operated at 2.45 GHz with an output power ranging from 30 to 1800 W. To determine the zeolitic phases, the crystallization products were analyzed by XRD using a Phillips X'Pert 3040 equipped with Cu-K α radiation source operated at 45 kV and 40 mA with a scan rate of 2° θ min⁻¹. The morphology of the products was characterized by scanning electron microscopy (SEM, Phillips XL30) at 20 kV. Particle size was observed by transmission electronic microscopy (TEM, Jeol JEM 201) at an accelerating voltage of 200 kV. Chemical composition was determined by X-ray fluorescence (XRF, Bruker S4 Pioneer) by the standardless method with a relative deviation of 0.1%. Loss on ignition (LOI) was determined at 950°C for 1 h using a furnace (Thermolyne F6200-60-80).

The OAT was used to define the main factors involved in the GS zeolitization process. Among the different options for optimizing the time and resources required for different experimental designs, the OAT method has proved to be a useful tool⁴³ because it allows the collection of reliable information with the smallest number of experiments. OAT is a simplified and standardized fractional factorial experiment design that enables the study of the effects of the main parameters and their contribution to the process. The experimental design was established in accordance with an experimental matrix L_{18} (2¹, 3⁷) proposed by Taguchi⁴⁴. The method involves 18 experiments (L_{18}), with one of the factors at two levels (2¹), and seven factors at three levels (3⁷), of which five were investigated. The factor studied at two experimental levels (3 and 4) was the SiO₂/Al₂O₃ molar ratio (S/A). The five additional factors (T_c , t_c , t_{TT} , TTT, and NaOH concentration) and their experimental levels are listed in Table 1.

Table 1. Factors evaluated and the established levels for the zeolitization of GS.

		Parameters		
Factors		1	2	3
A	SiO ₂ /Al ₂ O ₃ ratio	4	3	-
B	T_c (°C)	120	150	180
C	t_c (min)	60	120	240
D	T_{TT} (°C)	200	400	600
E	t_{TT} (min)	30	60	120
F	NaOH conc (eq)	0.35	0.45	0.55

The parameters were ordered according to the OAT. Table 2 shows, in columns 2-7, the experimental conditions of the trials established according to the AOT. These experiments were performed by mixing 12.3 g of GS with the corresponding amount of NaOH, and the mixture was thermally treated at temperatures TTT for times tTT, as shown in Table 2. The thermally treated material was slowly added under stirring to a sodium aluminate solution prepared with 191 mL of water at the corresponding SiO₂/Al₂O₃ molar ratio. The water content of the sodium aluminate reagent was subtracted from the

total water for zeolite synthesis. After an aging period of 17 h, the mixture was crystallized at the selected temperature, $T_c \pm 3^\circ\text{C}$, for time t_c . After cooling, the product was filtered and washed with 1.5 L of deionized water until the effluent exhibited a pH of 10.5. The product was then dried at 105°C for 24 h.

2.3. Calcium binding capacity

The CBC was determined by exchanging the sodium on the zeolite surfaces with calcium ions. Approximately 10 mL of 0.01 M CaCl_2 solution was mixed with 0.1 g of zeolite at room temperature. The suspension was stirred for 30 min; it was then separated from the liquid by centrifugation for 30 min at 850 rpm.

3. RESULTS AND DISCUSSION

3.1. Geothermal silica conditioning and characterization

The XRD pattern of GS before washing is shown in Fig. 1(a), and the pattern after washing is shown in Fig. 1(b). As evident in Fig. 1, the reflections of NaCl and KCl in the GS disappeared after the sample was washed (Fig. 1(b)). The particle size was observed using TEM (Fig. 1(c)). The GS was composed of particles with an average size of approximately 20 nm, and the particles exhibited a tendency to agglomerate. After the GS was washed, its chemical composition, as determined by XRF, was 91.07% SiO₂, 0.31% Al₂O₃, 0.01% TiO₂, 0.27% Fe₂O₃, 0.03% SO₃, 0.05% Cl, 0.09% MgO, 0.29% K₂O, 0.31% Na₂O, 0.47% ZnO, and 0.59% CaO; 6.45% of the weight was lost on ignition.

Fig.1. XRD patterns of GS (a) before and (b) after the washing treatment; (c) micrograph of GS by TEM at 200,000 $\times$.

3.2. Mineralogical composition of products

The zeolite content of the product served as the OAT response parameter for optimizing the synthesis. The percentage of the zeolites was estimated semi-quantitatively by computing the area under the reflection peaks of the XRD pattern in the 2θ range of $11-40^\circ$. After elimination of the background, the total area was assumed to be 100%. The sum of the areas under the diffraction peaks that correspond to each phase was calculated. The amorphous phase was obtained by subtracting the area under the peaks from the total area. Small unidentified peaks were attributed to an amorphous phase. Table 2 shows the experimental conditions and the zeolite content of each trial, as determined from the area under the reflection peaks in the XRD pattern.

Table 2. Experimental conditions according to the OAT and the percentages of zeolites obtained in each trial.

Trial	S/A ^a	T _c (°C)	t _c (min)	T _{TT} (°C)	t _{TT} (min)	NaOH conc (eq)	% Ap ^b	% ZX	% ZA	% ZS	% ZC	% Other zeolites	
1	4	120	60	200	30	0.35	12.36	60.34	27.30	-----	-----	-----	-----
2	4	120	120	400	120	0.45	31.00	17.34	12.00	39.57	-----	-----	-----
3	4	120	240	600	60	0.55	28.36	46.31	4.65	20.67	-----	-----	-----
4	4	150	60	200	30	0.35	26.15	8.52	29.10	32.75	-----	3.48 ^c	-----
5	4	150	120	400	120	0.45	37.21	1.08	0.93	53.68	-----	7.10 ^c	-----
6	4	150	240	600	60	0.55	21.03	2.42	6.85	45.24	-----	24.45 ^c	-----
7	4	180	60	400	30	0.35	39.27	-----	-----	-----	27.42	33.30 ^f	-----
8	4	180	120	600	120	0.55	10.98	-----	-----	24.53	24.82	38.47 ^c	-----
9	4	180	240	200	60	0.45	1.50	-----	-----	33.88	51.12	13.51 ^c	1.20 ^e
10	3	120	60	600	30	0.35	34.71	11.72	40.69	12.88	-----	-----	-----
11	3	120	120	200	120	0.45	18.97	9.54	41.21	30.28	-----	-----	-----
12	3	120	240	400	60	0.55	26.88	-----	34.01	39.11	-----	-----	-----
13	3	150	60	400	30	0.35	23.10	-----	44.30	20.58	-----	12.01 ^d	-----
14	3	150	120	600	120	0.45	34.06	-----	3.34	46.11	11.20	5.28 ^d	-----
15	3	150	240	200	60	0.55	18.80	-----	-----	76.68	-----	4.52 ^e	-----
16	3	180	60	600	30	0.35	26.20	-----	-----	6.07	25.24	6.13 ^d	36.36 ^f
17	3	180	120	200	120	0.55	26.76	-----	-----	24.17	16.05	6.23 ^d	26.78 ^f
18	3	180	240	400	60	0.45	10.60	-----	-----	37.45	42.38	9.57 ^e	-----

^a SiO₂/Al₂O₃ molar ratio, ^b amorphous phase, ^c Analcime, ^d Na₃(AlSi₃O₄)3H₂O,

^e Na₈(Al₆Si₆O₂₄)(OH)_{2.04}(H₂O)_{2.66}, ^f Nepheline.

Zeolitic phases were obtained for all of the trials. The minimum conversion of GS was 60.3% (trial 7). ZS was obtained at the studied conditions in 16 trials, and ZA was obtained in 11 trials. Therefore, the selected conditions favored the crystallization of both ZS and ZA. In contrast, ZC was obtained in only seven experiments, high percentages were obtained at T_c = 180°C. ZX mixed with other products was detected at T_c = 120°C and a SiO₂/Al₂O₃ ratio of 4. The optimal conditions to obtain a highest content of ZA, ZS, ZC and ZX were determined. The ANOVA and the study of the main effects of factors in the synthesis of these zeolites are presented in the following section.

3.3. ANOVA for zeolites: A, hydroxysodalite, hydroxycancrinite and X.

The purpose of the ANOVA was to identify the factors that were statistically significant with respect to the zeolitization process. Percentages of the zeolites obtained in the 18 experimental trials (Table 2) were statistically treated. The ANOVA shows the variability of the different factors. The contribution of each factor was measured by eliminating the effects of the other factors. The F values obtained using the ANOVA study helped to confirm the statistical significance. If the F test value is greater than the F theoretical value, then this variance is statistically significant for each of the factors. The F theoretical value was 5.14 for a confidence level of 95%. The residue was obtained by subtracting the degrees of freedom of the factors from the total freedom degrees (Table 3). The percentage of the contribution of each factor and the F values for each response are shown in Table 3.

According to the ANOVA results, the crystallization temperature is statistically significant (F > 5.14) in the synthesis of ZA, ZC and ZX. For ZS, both the crystallization temperature and time were statistically significant (F > 5.14). The contribution percentages of the crystallization temperature for obtaining zeolite were 68.44%, 66.54%, 42.08% and 27.74% for ZC, ZA, ZS, and ZX, respectively. Crystallization time exhibited a contribution of 47.94%, 16.45%, 7.88% and 5.97% for ZS, ZX, ZC and ZA, respectively. The NaOH concentration exhibited a contribution of 2.48%, 3.61%, 12.34% and 6.31% for ZA, ZS, ZC and ZX, respectively. The factors with the least influence on GS transformation were the temperature and time of the initial thermal treatment prior to crystallization. This finding indicates that GS could react with NaOH at a lower temperature than that used in this study. Further studies are required to define the lowest temperature and time needed to perform the GS alkaline pretreatment.

Table 3. Analysis of variance for zeolite A (ZA), hydroxysodalite (ZS), hydroxycancrinite (ZC) and zeolite X (ZX).

Source	DF ^a	SS ^b	MS ^c	F ^d	% ^e	SS ^b	MS ^c	F ^d	% ^e
					ZA				
S/A ^f	1	225.19	225.19	1.31	3.55	4.26	4.26	0.10	0.06
T _c (°C)	2	4223.91	2111.96	12.27	66.54	2929.20	1464.60	33.40	42.08
t _c (min)	2	378.72	189.36	1.10	5.97	3336.62	1668.31	38.04	47.94
T _{TT} (°C)	2	232.01	116.00	0.67	3.65	135.08	67.54	1.54	1.94
t _{TT} (min)	2	98.45	49.22	0.29	1.55	40.62	20.31	0.46	0.58
NaOH ^g	2	157.53	78.76	0.46	2.48	251.58	125.79	2.87	3.61
Residue	6	1032.57	172.09	-----	16.27	263.12	43.85	-----	3.78
Total	17	6348.37	373.43	-----	100.00	6960.48	409.44	-----	100.00
					ZC				
S/A ^f	1	0.02	0.02	0.00	0.00	321.54	321.54	2.14	8.98
T _c (°C)	2	2439.64	1219.82	42.06	68.44	992.95	496.47	3.30	27.74
t _c (min)	2	281.05	140.53	4.85	7.88	589.06	294.53	1.96	16.45
T _{TT} (°C)	2	74.18	37.09	1.28	2.08	340.60	170.30	1.13	9.51
t _{TT} (min)	2	155.96	77.98	2.69	4.38	207.05	103.52	0.69	5.78
NaOH ^g	2	439.79	219.89	7.58	12.34	225.82	112.91	0.75	6.31
Residue	6	174.00	29.00	-----	4.88	902.96	150.49	-----	25.22
Total	17	3564.63	209.68	-----	100.00	3579.97	210.59	-----	100.00
					ZX				
S/A ^f	1	0.02	0.02	0.00	0.00	321.54	321.54	2.14	8.98
T _c (°C)	2	2439.64	1219.82	42.06	68.44	992.95	496.47	3.30	27.74
t _c (min)	2	281.05	140.53	4.85	7.88	589.06	294.53	1.96	16.45
T _{TT} (°C)	2	74.18	37.09	1.28	2.08	340.60	170.30	1.13	9.51
t _{TT} (min)	2	155.96	77.98	2.69	4.38	207.05	103.52	0.69	5.78
NaOH ^g	2	439.79	219.89	7.58	12.34	225.82	112.91	0.75	6.31
Residue	6	174.00	29.00	-----	4.88	902.96	150.49	-----	25.22
Total	17	3564.63	209.68	-----	100.00	3579.97	210.59	-----	100.00

^a Degree of freedom, ^b sum of squares, ^c mean of squares, ^d F test, ^e contribution percentage, ^f SiO₂/Al₂O₃ ratio, ^g concentration (eq).

3.4. Effect of the synthesis parameters on zeolite content

The statistical treatment of the experimental data was performed following the procedure of Taguchi ⁴⁴. The effect of the different parameters was taken into account to define the level of each factor that enabled the highest zeolite content to be obtained. Fig. 2 shows the effect of the main factors on the zeolite content; the plots present the effect of each parameter (x-axis) on the percentages of hydroxycancrinite, zeolite X, zeolite A, and hydroxysodalite (y-axis) according to the zeolite content results for the trials. Fig. 2(a) shows that the percentage of ZC is highest for the reaction conditions T_c = 180°C, t_c = 240 min and NaOH = 0.45 eq. Fig. 2(b) indicates that the highest ZX content is obtained under the conditions for trial 1 (Table 2). The conditions for a high content of ZA are shown in Fig. 2(c): T_c = 120°C, SiO₂/Al₂O₃ ratio = 3 and NaOH = 0.35 eq. The content of zeolite ZS is highest when T_c = 150°C and t_c = 240 min, as shown in Fig. 2(d). The best conditions for the synthesis of ZC, ZX, ZA and ZS are listed in Table 4.

3.5. Synthesis of zeolites at statistically calculated conditions

ZC was prepared from a starting mixture of GS with NaOH = 0.45 eq and SiO₂/Al₂O₃ ratio = 4. The crystallization process was performed using MW to reach and maintain 180°C for 240 min. After the product was washed and dried, 24.1 g of white powder was obtained. The XRD pattern (Fig. 3(a)) shows ZC as the predominant phase (95%) and the presence of an amorphous material. Cancrinite synthesis has also been reported using a conventional hydrothermal process with the addition of chemical reagents ⁹⁻¹¹. When kaolin was used as a silica source for producing cancrinite, higher temperatures (200°C) and longer crystallization times (48 h) were required ⁹. However, the method developed in this study using an industrial byproduct enabled hydroxycancrinite to be obtained at 180°C after 4 h.

ZX was prepared with 0.35 eq of NaOH, SiO₂/Al₂O₃ ratio = 4, T_c = 120°C and t_c = 60 min. As a result of GS zeolitization, 20.7 g of a white powder was obtained. The XRD pattern in Fig. 3(b) shows reflections of zeolite ZX (60%), ZA (27%) and an amorphous material (13%). Although ZX was obtained together with zeolite A, the procedure followed here is advantageous, given that the chemical reagents used to produce zeolite X ³⁷ were replaced by GS. Previous reports have shown that zeolite X, when prepared from chemical reagents ^{45,46}, requires 3 to 6 h of heating, which is longer than the time required in the method described here (1 h). The optimal conditions for ZA synthesis were NaOH = 0.35 eq, SiO₂/Al₂O₃ ratio = 3, T_c = 120°C, t_c = 60 min, which yielded 20.3 g of a white powder. The XRD pattern in Fig. 3(c) confirms the presence of ZA as a crystalline phase (97%) along with an amorphous material (3%). The experimental run under the statistically calculated conditions to obtain ZS (NaOH = 0.55 eq, SiO₂/Al₂O₃ ratio = 4, T_c = 150°C, t_c = 240 min) yielded 19.8 g of a white powder. The XRD pattern in Fig. 3(d) reveals the presence of ZS (76.7%) as a crystalline phase. The method described here is an alternative to obtaining hydroxysodalite. Table 4 shows the optimal conditions for zeolite synthesis.

Fig.2. Effect of the synthesis parameters on zeolite content in zeolitization products, (a) hydroxycancrinite, (b) X zeolite, (c) A zeolite and (d) hydroxysodalite.

Table 4. Set of parameters calculated for zeolite synthesis.

	Factors	ZC	ZX	ZA	ZS
A	SiO ₂ /Al ₂ O ₃ ratio	4	4	3	4
B	T _c (°C)	180	120	120	150
C	t _c (min)	240	60	60	120
D	T _{tr} (°C)	200	200	200	200
E	t _{tr} (min)	120	30	60	30
F	NaOH (eq)	0.45	0.35	0.35	0.55

In summary, ZC, ZA and ZS were prepared in yields of 95, 97 and 76.7%, respectively. ZX was obtained together with ZA (87.6%) with a ZX/ZA ratio of 60/27.

3.6. Morphological characteristics of the experimental zeolites

The morphologies and particle sizes of the zeolites synthesized under the conditions established in Table 5 were examined by SEM (Fig. 3 (a')-(d')). As shown in Fig. 3(a'), cancrinite is a homogeneous material composed of quasi-spheres with diameters of approximately 5 µm; these particles are constituted by intercrossed laminar needles. The morphology of these needles is attributed to the high heating rate resulting from the use of microwaves. Under these conditions, the temperature increases sharply and different nucleation points are formed. This finding is consistent with earlier reports that have demonstrated that crystal size and morphology depend on the heating rate, although they depend on crystallization temperature, the particle size, purity and solubility in alkaline solutions of the precursor species⁴⁷.

The mixture of X and A zeolites consists predominantly of cubic particles with diameters of approximately 1 µm (Fig. 3(b')). Many of these particles are heaped plates that probably formed by the high heating rate induced by the accelerated microwave heating process. Fig. 3(c') shows that the experimental zeolite A presents a morphology of small, well-defined cubic particles with an average size of approximately 1 µm. The small particle size is attributed to the short induction and crystallization time used in the synthesis. Small particle size observed here agrees with reports of the conventional synthesis of zeolite, in which a small particle size has been associated with accelerated heating and fast reagent dissolution. Under these conditions, the reagents are rapidly consumed, and many nuclei are formed. The process promotes the formation of small crystals in a short period of time⁴⁷. Hydroxysodalite is mainly composed of particles with diameters of approximately 2 µm. These zeolite particles are formed by many intercrossed discs (Fig.3 (d')). The differences in the zeolite morphologies should be taken into consideration for the development of selective catalysts and adsorbents.

3.7. Chemical composition and calcium binding capacity of the end products

The chemical compositions of the synthesized zeolites, determined by XRF as percentages of oxides, indicate that they are mainly composed of Al₂O₃, SiO₂, Na₂O and volatile materials, as shown in Table 5. Furthermore, CaO, K₂O, Fe₂O₃ and ZnO were detected in smaller amounts, and MnO, SO₃, TiO₂ and ZrO₂ were found in all the synthesized zeolites in percentages less than 0.1 weight %. Calcium carbonate was only detected in cancrinite, at a concentration of 0.68%. The concentrations of some elements in GS, such as Ca, K, Fe, Zn, and Cl, were decreased during zeolitization.

Table 5. Chemical composition of experimental zeolites (wt%)

Zeolites	SiO ₂	Al ₂ O ₃	Na ₂ O	CaO	K ₂ O	Fe ₂ O ₃	ZnO	LOI ^a
Hydroxycancrinite	37.9	29.0	22.4	----	0.0	0.1	0.1	10.0
X	37.8	23.8	14.0	0.4	0.1	0.2	0.2	23.5
A	35.9	27.9	16.0	0.3	0.1	0.2	0.1	19.4
Hydroxysodalite	38.2	29.0	17.1	0.3	0.1	0.2	0.1	16.8

^aLOI: Loss on ignition.

Fig.3. XRD patterns of zeolites obtained under statistically calculated conditions (a-d) and SEM images that indicate their morphologies ((a')-(d')). (a) Cancrinite and an unknown zeolite (●), (b) X zeolite with A zeolite (*), (c) A zeolite and (d) hydroxysodalite. Morphologies of the experimental zeolites by SEM: (a') cancrinite, (b') mixture of A and X zeolites, (c') A zeolite and (d') hydroxysodalite.

The resulting SiO₂/Al₂O₃ molar ratios in the final zeolites were 2.2, 2.7, 2.2 and 2.2 for ZC, ZX, ZA and ZS, respectively. These molar ratios were lower than the SiO₂/Al₂O₃ molar ratio in the starting gel compositions, which were 4, 4, 3, and 4 for ZC, ZX, ZA and ZS, respectively.

The CBC results show that ZX zeolite exhibits a CBC of 5.01 meq/g (87.6% crystalline phase), whereas A zeolite presents a CBC of 5.09 meq/g (97% crystalline phase). As a reference, the CBCs of commercial X and A zeolites were measured, and the zeolite percentages were calculated. The CBC and zeolite percentages were 5.58 meq/g and 99.3% for commercial zeolite X and 5.24 meq/g and 99.8% for zeolite A. The lowest values of CBC were obtained for HS and HC, which exhibited CBC values of 4.55 and 4.17 meq/g, respectively. The ion-exchange capacity is relevant when zeolites are used as adsorbents in water-treatment processes. The CBC depends on the sodium content of the zeolite. Thus, CBC serves as an indicator of the ability of other ions, such as heavy metals in wastewater, to replace the sodium ions. This study has defined the conditions for synthesizing some low-SiO₂/Al₂O₃-ratio zeolites, starting from washed and thermally pretreated GS.

CONCLUSIONS

The zeolitization of GS using microwaves as an energy source constitutes an alternative method with economic and environmental advantages for obtaining the zeolites hydroxycancrinite, A, X and hydroxysodalite. The method described here required shorter times and lower temperatures for GS zeolitization compared with the conventional heating method. The Taguchi experimental design provided the optimum conditions for synthesizing these zeolites and for gaining an insight into the effect of the synthesis parameters. The synthesized X and A zeolites exhibited physicochemical properties similar

to and CBC values as high as the corresponding commercial zeolites. These properties indicate that the synthesis of zeolites from GS using microwaves is a good alternative for obtaining low-cost zeolites that are potentially useful as ion exchangers for water-treatment applications.

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