

SYNTHESIS AND CHARACTERIZATION OF ZEOLITES, CALCIUM SILICATES AND KALSILITES FROM NATURAL MATERIALS

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INTRODUCTION

The purpose of this work consisted in the synthesis of useful minerals, *i.e.* zeolitic minerals (K-F and W-Merlinoite type), calcium silicates and kalsilite achieved through the use of natural materials. The high costs of chemical reagents in synthesis processes have led to research into the alternative and less expensive natural materials. Therefore there is a great economic potential for use of natural substitutes for chemical reagents in zeolite synthesis (Novembre, 2003; Novembre *et al.*, 2004). In this study starting materials are represented by two natural compounds: a tripolaceous rock from Crotona (Calabria, Italy) and a kaolinitic rock (Standard Porcelain IMERIS of Minerals Ltd). Zeolites are aluminosilicate hydrates of alkali metals and alkaline-earth metals, characterized by an acid and insoluble tetrahedral structure $(\text{Si,Al})\text{O}_4$ and a basic and soluble cavity hosting cations and H_2O . Presently zeolitic research is being greatly promoted and zeolitic use is extended to several new technological applications. Both cationic exchange and molecular sieving properties form the basis of several industrial applications, some of which dealing with radioactive waste-water treatments, industrial waste-water treatments and agricultural waste-water treatments (Akçay & Hatay, 2002; Andrews *et al.*, 2002; Coppola *et al.*, 2002). Calcium silicates are defined as mesoporous materials characterized by high specific surface and large pore volumes (between 2 and 5 nm). Thanks to their high porosity, calcium silicates show large water storage capacity, capillary transport and good insulating property; regarding these characteristics, such materials are useful for various applications, especially those in the field of cement and ceramic industry. Kalsilite crystallizes both in the hexagonal and in orthorhombic system; with regard to the latter form, it is characterized by macropores and strongly active potassium-based sites, for these properties its use is related to heterogeneous catalysis in trans-esterification process of triglycerides during the manufacturing of biodiesel (Wen *et al.*, 2010).

STARTING NATURAL MATERIALS

The opaline siliceous rock ("Tripoli" from Crotona, Italy) was employed in the synthesis of zeolites and of wollastonite, whereas the kaolinitic rock was used in the synthesis of orthorhombic kalsilite. Chemical treatments were performed on "Tripoli", in order to obtain K-silicatic solution, chemical reagent required for the synthesis of K-zeolites; thermal treatment was performed on kaolin, in order to obtain metakaolin.

ANALYTICAL METHODS

Starting materials and products of synthesis were analysed by powder X-ray diffraction (XRPD; Siemens D5000 operating with a Bragg-Brentano geometry; $\text{CuK}\alpha = 1.518 \text{ \AA}$, 40 kV, 40 mA, 2-45°, 2-90° scanning interval, step size 0.020° 2 θ).

Chemical characterization was performed by X-ray Fluorescence Analysis (Axios-Max Advanced Panalytical; KV: 60; mA: 160; W: 4000; 0.0001° 2 theta) and by induced coupled plasma optical emission spectroscopy (through previous fusion in lithium meta-tetra borate pearls and subsequent acid solubilization).

Microtextural and qualitative microchemical characterizations were obtained by means of scanning electron microscopy (JEOL JSM-840 served by a LINK Microanalysis EDS system, with operating conditions of 10 kV and a range of variation of 18 to 22 mm in window conditions).

Determination of crystallographic data of synthetic products was achieved by Rietveld method by the use of the software EXPGUI-GSAS (Toby, 2001). Density was calculated by He-pycnometry using an AccuPyc 1330 pycnometer. The specific surface and porosity were obtained using the BET method, from the data of absorbed volume of N₂ with a Micromeritics ASAP2010 instrument (operating from 10 to 127 kPa).

Dehydration and rehydration behaviour were studied by differential thermal analysis and thermo gravimetry (DTA-TG) by means of a Mettler TGA/SDTA851e instrument (10 °/minute from 30 to 1100 °C, using an approximate sample weight of 10 mg in Al₂O₃ crucible). The study of the thermal incidence on phase evolution was carried out using X-ray diffractometry at high temperature; the instrument was a X'PERT PROPANalitical (CuKα = 1.518 Å, 30 kV, 30 mA, counting time of 0.02-10 sec, with a high temperature camera ANTON PARA HTK-16).

The infrared studies were conducted by means of a spectrometer FTLA2000, served by a separator of KBr and a DTGS detector; the source of IR radiation was a SiC (Globar) filament. Samples were treated following the method of Robert *et al.* (1989) by means of powder pressed pellets (KBr/sample ratio of 1/100, pressure undergone prior determination 15 t/cm²); spectra were processed by the program GRAMS-AI.

Nuclear magnetic resonance (²⁹Si MAS NMR) analysis was performed with a BRUKER AVANCE-SPECTROSPIN 300 MHz (speed of rotation at the magic angle 4000 Hz, variable number of scans from: 100, 200 to 400, pulse length (90°) p1 = 8µs and scanning time t1 = 5 sec); spectra were processed by the program Bruker WINNMR.

Characterization and chemical treatments on "Tripoli rock"

Tripoli rock used in this work crops out in the Crotona Basin (Calabrian Arc, Italy); the basin, filled with sedimentary rocks, is Messinian in age.

XRPD analysis revealed a mineral assemblage made of quartz, amorphous opaline silica, montmorillonite, chlorite, kaolinite, K-micas, and a minor amount of calcite (8% by calcimetric analysis). Chemical analysis revealed an abundant siliceous component (81.48%). Chemical treatments were performed on "Tripoli" in order to achieve the K_xSi_yO_z solution. Tripoli was first treated with HNO₃ to eliminate the calcitic and carbonatic fraction and Fe and Mn oxides. Finally the sample was immersed in an alkaline solution (KOH 10%) to induce the solubilization of the siliceous fossil fraction and the separation of the K₂SiO₃ nH₂O solution.

Characterization and thermal treatment on "Kaolin Rock"

A heat treatment at a temperature of 700 °C was conducted on the raw kaolin for the duration of one hour, in order to achieve calcination and the formation of the amorphous phase (metakaolin). Morphological and thermal analysis (thermogravimetric and differential analysis) and infrared spectroscopy were performed on both kaolin and metakaolin.

SYNTHESES

Synthesis of K-F and W Merlinoite-type zeolites

Syntheses of K-F and W Merlinoite-type zeolites were carried out by varying the ratio of the as above produced silicatic solution and the aluminatic one (56 cc of KOH-20% plus 12 g of Al(OH)₃-65%); then, three series of synthesis were performed for K-F zeolite. The molar composition of the three starting mixtures thus resulted:

- 1st Serie: 4K₂O – 3SiO₂ – ½Al₂O₃
- 2nd Serie: 3K₂O – 2SiO₂ – ½Al₂O₃
- 3rd Serie: 2K₂O – SiO₂ – ½Al₂O₃.

Similarly, two series were conducted for the synthesis of W Merlinoite-type zeolite. The molar composition of the two mixtures of synthesis resulted in:

- 1st Serie: 6K₂O – 5SiO₂ – ½Al₂O₃
- 2nd Serie: 8.4K₂O – 7.4SiO₂ – ½Al₂O₃.

All the mixtures were placed inside autoclaves at a temperature of 150 °C and ambient pressure.

Synthesis of wollastonite

Tripoli was mixed with a natural reagent, limestone (CaCO_3), together with sodium carbonate (Na_2CO_3) as triggering agent. Three series of synthesis were carried out, characterised by different stoichiometry, at constant temperature (1000 °C) and ambient pressure:

- 1st chemical system: 2 g Tripoli + 5 g CaCO_3 + 0.15 g Na_2CO_3
- 2nd chemical system: 3.3 g Tripoli + 2.5 g CaCO_3 + 0.09 g Na_2CO_3
- 3rd chemical system: 3 g Tripoli + 3 g CaCO_3 + 0.11 g Na_2CO_3

The three mixtures were placed inside of porcelain crucibles resistant to high temperatures and placed in oven at the selected temperature of 1000 °C.

Synthesis of ortho-kalsilite

The metakaolin was mixed in stoichiometric proportions with potassium nitrate (KNO_3). The experiments were conducted at ambient pressure for different temperatures (700, 800 and 950 °C), in order to point out the thermal transition from the hexagonal to the orthorhombic form of kalsilite.

CHARACTERIZATIONS

K-F zeolite

The crystallization of K-F zeolite, formerly associated with the metastable phase chabazite, was evident in the time intervals 10h-30h (in the 1st serie) and 7h-15h (in the 2nd serie); after these time intervals, crystallization of pure and isolated K-F zeolite was achieved for both the two series, as desumed by morphological observations. In the 3rd serie appearance of K-F phase as pure and isolated was instead verified after 3 hours. In Table 1 we report the values of the ratio $\text{Si}/(\text{Si}+\text{Al})$ calculated for the synthesized zeolites with reference to bibliographic data (Belver & Vicente, 2006).

Table 1 - Chemical characterization of synthesis runs. (*): Belver & Vicente, 2006; (**): Passaglia *et al.*, 1977; (***) : Gallo *et al.*, 1984. (w): Weak; (m): medium; (s): strong.

Samples	Al (wt.%)	Si (wt.%)	K (wt.%)	(Si/Si+Al) (wt.%)	Time (hours)	XRD Spectrum
K-F (2nd serie)						
ICP-8	26.5	47.96	24.6	0.64	80	K-F (w/m)
K-F zeolite (3rd serie)						
ICP-11	26	49.46	24.3	0.655	30	K-F (s)
K-F (*)	23.19	32.33	28.94	0.60	/	K-F zeolite
W zeolite (1st serie)						
ICP-14	20.5	60.17	18.79	0.74	106	W (s)
W zeolite (2nd serie)						
ICP-17	21	57.57	20.98	0.733	70	W (s)
W (**)	18.04	51.82	7.53	0.71	/	W zeolite
O-kalsilite 800 °C						
ICP-3	25.9	44.07	28.3	0.630	379	O-kalsilite (s)
O-kalsilite 950 °C						
ICP-6	27	44.87	26.6	0.624	164	O-kalsilite (s)
Kalsilite (***)	27.9	39.7	27.9	0.60	/	kalsilite

DTA-TG analyses conducted on monomineralic powders (containing isolated KF), revealed a continuous water loss for the all samples, followed by an exothermal peak corresponding to the removal of organic cations, with a marginal loss of crystallinity; the structure held up to 1100 °C, in agreement with Matsumoto *et al.* (2006); the exothermic peaks are located at 520 and 878 °C for sample at 63h (1st serie), at 880 °C for sample at 30h (2nd serie) and at 900 °C for sample at 104h (3rd serie). The study of thermal incidence on phase evolution was performed on the sample at 30h (2nd serie); in particular, three structural changes were detected: the first at 100 and the second 200 °C, both relative to the dehydration of zeolitic structure; the third at 800 °C relative to the removal of organic cations (Belver & Vicente, 2006). Infrared spectra showed that the main band, related to tetrahedral asymmetric stretching, is located at 989 cm⁻¹ for sample at 56h (1st serie), at 994 cm⁻¹ for sample at 30h (2nd serie) and at 991 cm⁻¹ for sample at 128h (3rd serie). Locations of the other peaks are shown in Table 2 together with values reported by Belver & Vicente (2006) and Gorjainov & Belitsky (1988) for K-F zeolite. Synthetic samples were also characterised by ²⁹Si MAS NMR analysis, the resulting values being in agreement with bibliographic data (Rios Reyes & Williams, 2010).

W Merlinoite-type zeolite

The crystallization of W zeolite, formerly associated with the metastable phase chabazite, was evident in the time interval 18h-34h (in the 1st serie) and at only 7h (in the 2nd serie); after these time intervals crystallization of pure and isolated W zeolite was achieved for both the two series, as desumed by XRPD- and IR-analyses as well as by morphological observations. In Table 1 we report the values of the ratio Si/(Si+Al) calculated for the synthesized zeolites with reference to bibliographic data (Passaglia *et al.*, 1977). DTA-TG analyses conducted on monomineralic powders (containing isolated W), revealed a continuous water loss for all samples, followed by an exothermal peak corresponding to the removal of organic cations (Barret *et al.*, 1998); the structure held up to 1000 °C; the exothermic peaks are located at 620 and 842 °C for sample at 130h (1st series) and at 622 and 845 °C for sample at 141h (2nd series). The study of thermal incidence on phase evolution was performed on the sample at 130h (1st series); in particular, three structural changes were detected: one at 100, another at 200 °C both regarding the dehydration of zeolitic structure; the last one at 1100 °C is relative to the structural collapse. IR spectra showed that the main band, related to tetrahedral asymmetric stretching, is located at 1008 cm⁻¹ for sample at 82h (1st series) and at 1009 cm⁻¹ for sample at 117h (2nd series). Locations of the other peaks are shown in Table 2 together with values by Flaningen (1971) for W zeolite. The synthetic samples were also characterized by ²⁹Si MAS NMR analysis, the resulting values being in agreement with bibliographic data (Bieniok *et al.*, 1996).

Table 2 - Infrared data for the synthesized K-F and W zeolites.

(*): Goryainov & Belitsky, 1988; (**): Flaningen *et al.*, 1971. (w): Weak; (m): medium; (s): strong.

	Time (hours)	Asymmetric stretch	Simmetric stretch	Double rings	T-O bends	Phase
KF-128	128	1104-1047-991-946	665	618-529	499-431-395-359	K-F zeolite (s)
EDI (*)		1103-1056-993-956	656	599-530	494-432-407-357	
W-117	117	1125-1009	785-756-691	635-593-485	433	W zeolite (s)
W (***)		1128-1006	786-756-691	637-590-483	432	

Wollastonite

The first chemical system showed crystallization of wollastonite with associated lime, larnite (dicalcium silicate), and rankinite (tricalcium disilicate); the second chemical system showed synthesis of wollastonite and tridymite, as also confirmed by chemical analyses reported in Table 3. The third chemical system was the best one since it showed crystallization of wollastonite associated with a very little amount of tridymite. IR spectra showed that the main band, related to tetrahedral asymmetric stretching, is located at 898 cm⁻¹ for sample at 313h (2nd serie).

The locations of the other peaks are shown in Table 4 together with values reported by Ptacek *et al.* (2010) and Atalay *et al.* (2001) for wollastonite. The synthetic samples were also characterized by ^{29}Si MAS NMR analysis, the resulting values being in agreement with bibliographic data.

Table 3 - Chemical analysis of the wollastonite synthesis series. (*): Teir *et al.* (2005).

Samples	Si (wt.%)	Ca (wt.%)	(SiO ₂ /CaO)%	Time (hours)	XRD Spectrum
ICP-12	61.04	31.50	1.93	313	Wollastonite (s)
Woll-2M (*)	51.56	47.73	1.0	/	Wollastonite

Table 4 - IR data for the synthesized wollastonite and kalsilite-O. (*): Wollastonite by Ptacek *et al.* (2010); (**): wollastonite by Atalay *et al.* (2001); (***): KAlSiO₄-O₁ by Dimitrijevic & Dondur (1995).

Sample	Time (hours)	Asymmetric stretch	Simmetric stretch	Phase
woll-313	313	1086-1063-1012-962-936-898	683	Wollastonite (s)
Woll (*)		1081-1060-1016-965-925-900	682	
Woll (**)		1087-1056-1019-964-925-904	680	
Kal-800-331	331	1108-1067-1033-990-944-874	700-665	Kalsilite O (s)
Kal-950-164	164	1108-1073-1036-990-944-874	693-665	Kalsilite O (s)
KAlSiO ₄ -O ₁ (***)		1100-1070-1040-990-940-880	700-665	

O-kalsilite

Run synthesis at 800 °C showed the formation of orthorhombic kalsilite, proving that its first appearance temperature was lowered to at least 800 °C contrarily to the temperature of 850 °C indicated by Tuttle & Smith (1957). The experiments performed at 700 °C and 950 °C revealed the emergence of hexagonal and orthorhombic kalsilites, respectively. The values of the ratio Si/(Si+Al), calculated for the all synthesized samples together with data from Gallo *et al.* (1984), are reported in Table 1. IR spectra showed that the main band, related to tetrahedral asymmetric stretching, is located at 990 cm⁻¹ either for sample at 331h (serie at 800 °C) and sample at 164h (serie at 950 °C).

The locations of the other peaks are shown in Table 4 together with the values reported by Dimitrijevic & Dondur (1995) for orthorhombic kalsilite. The synthetic samples were also characterized by ^{29}Si MAS NMR analysis and the resulting values were in agreement with data from Gregorkiewitz *et al.* (2008).

CONCLUSIONS

Synthesis of useful minerals, zeolites (K-F and W-Merlinoite-type), calcium silicates and kalsilites were achieved through the use of natural materials, *i.e.* tripalaceous and kaolinitic rocks. Easy chemical treatments operated on these natural rocks were performed in order to achieve reagents required for the synthesis process. These innovative protocols reduce high costs of industrial synthesis schemes, which involve the utilization of pure and expensive reagents, and also improve the economic value of the geo-resources (Novembre, 2003; Novembre *et al.*, 2004; 2005; 2011).

There is a good agreement between characterization of the synthesized crystals (morphological, crystallographic data, density values, thermal and infrared behaviour, and ^{29}Si MAS NMR response) and those reported in bibliography regarding the same mineralogical phases.

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