

Zeolitization of geological and waste materials at low temperature in KOH solutions

Carlos A. Ríos^{*§}, Craig D. Williams^{**}, Clive L. Roberts^{**}

^{*} Escuela de Geología, Universidad Industrial de Santander, Colombia

^{**} School of Applied Sciences, University of Wolverhampton, England

§ carios@uis.edu.co

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Abstract

In this work, several zeolitic materials were prepared by geological and waste materials activation using potassium hydroxide as activating agent. The alkaline reaction was done by the classic hydrothermal treatment method at a constant temperature of 100 ° C and autogenous pressure. The synthetic products were characterized by X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy and thermogravimetric analyses. Different poorly crystalline zeolite-like materials were obtained, including K-chabazite (CHA), zeolite K-F (EDI), hydroxysodalite (SOD) and K-phillipsite (PHI). The K⁺ ion is a suppression factor during zeolite synthesis, which causes a slow crystallization rate, revealing a low conversion efficiency of the starting materials in KOH solutions.

Palabras Claves: Zeolitization, Geological and waste materials, Potassium hydroxide, Zeolite-like materials

Zeolitización de materiales geológicos y residuales a bajas temperaturas en soluciones de KOH

Resumen

En este trabajo, varios materiales zeolíticos se prepararon a partir de la activación de materiales geológicos y residuales usando hidróxido de potasio como agente activador. La reacción alcalina se llevó a cabo por el método clásico de tratamiento hidrotérmico a una temperatura constante de 100 ° C y presión autógena. Los productos sintéticos se caracterizaron por difracción de rayos X, microscopía electrónica de barrido, espectroscopía de infrarrojo por transformada de Fourier y análisis termogravimétrico. Diferentes materiales zeolíticos fueron obtenidos, incluyendo K-chabazita (CHA), zeolita K-F (EDI), hidroxisodalita (SOD) y K-filipsita (PHI). El ion K⁺ es un factor de supresión durante la síntesis de zeolitas, lo cual causa una lenta tasa de cristalización, revelando una baja eficiencia de conversión de los materiales de partida en soluciones de KOH.

Keywords: Zeolitización, Materiales geológicos y residuales, Hidróxido de potasio, Materiales zeolíticos

1. Introduction

Zeolites are porous crystalline aluminosilicate molecular sieves, which have been widely used in petrochemical cracking, water purification or separation and removal of gases and solvents. Alkaline pH solution - raw material reactions occur in a variety of geological environments as well as those where the environment has been modified by human activity in various engineering projects. Experimental data from the syntheses in potassium aluminosilicate systems are contradictory and confusing. In addition, the nomenclature for potassium zeolites has evolved over a period of decades since the early discovery of hydrothermal synthesis routes by Barrer (1978). Under high pH conditions (0.1–4 mol kg⁻¹ KOH), kaolinite transformed in sequence to: illite zeolite K-F K-phillipsite K-feldspar, and the transformation rates depended on solution composition, temperature, and reaction time (Bauer et al., 1998). A series of crystalline phases summarized by the reaction sequence kaolinite K-chabazite zeolite K-F unidentified potassium aluminosilicate phase kalsilite + leucite was identified in the system K₂O-SiO₂-Al₂O₃-H₂O by Ríos (2008). Other authors (Barrer et al., 1968; Barrer & Munday, 1971; Tuyé et al., 2005; Vicente & Belvert, 2006) reported easy ways to synthesize zeolite K-F from kaolin with appropriate cation exchange and ion selectivity properties. To our knowledge, no previous effort has been made to use clinoptilolite as a raw material in the synthesis of K-zeolites. Traces of zeolite phases (zeolite K-F and K-chabazite) can be

formed after activation of natural clinker in KOH solutions (Ríos, 2008; Ríos & Williams, 2008; Ríos et al., 2009). Ríos and co-workers have evaluated the hydrothermal reaction of fly ash at low temperature using KOH as a mineralizer. The formation of fly ash-based zeolites in KOH solutions should be promoted at longer reaction times and the dissolution of fly ash's aluminosilicate phases (mullite and quartz) in the KOH medium, except using higher activation solution/fly ash and lower temperature (Ríos, 2008). Juan (2007) synthesized several zeolite-like materials, including zeolite K-F, K-phillipsite and K-chabazite, which maintain their granular form and this could favour their use in some particular applications for environmental waste treatment. Similar synthesis products have been reported by Ríos (2008), Ríos & Williams (2008) and Ríos et al. (2009).

In this study, treatment with KOH at 100 °C led to very weak alterations in the composition and structure of kaolinite, clinoptilolite, natural clinker and fly ash, with the production of poorly crystallized zeolitic materials. The transformation of raw materials in KOH solutions can be explained by two different processes: (1) dissolution and (2) precipitation. A dissolution process of a series of crystalline phases summarized by the reaction sequence raw material zeolite phases + aluminosilicate geopolymeric phase was identified in the system K₂O-SiO₂-Al₂O₃-H₂O. In general, the synthesis

Table 1. Synthesis conditions for hydrothermal treatment of kaolinite in KOH solutions.

Raw material	Solution Molarity	RM (g)	NC ratio (ml/g)	Hydrothermal treatment		Zeolitic phases and other synthesis products	Residual phases
				T (°C)	t (h)		
KA01	3.99	3.1	4.47	100	24	CHA, EDI	---
KA02	3.99	3.1	4.47	100	240	CHA, EDI	---
KA03	3.99	3.1	4.47	100	528	CHA, EDI	---
CL11	3.99	3.1	4.47	100	72	*EDI	CLI
CL12	3.99	3.1	4.47	100	120	EDI	CLI
CL13	3.99	3.1	4.47	100	168	EDI	---
NC1	3.99	3.1	4.47	100	6	*CHA, *PHI, *SOD	Qtz
NC2	3.99	3.1	4.47	100	24	*CHA, *PHI, *SOD	Qtz
NC3	3.99	3.1	4.47	100	72	*CHA, *PHI, *SOD	Qtz
FA1	3.99	3.1	4.47	100	3	---	Qtz, Mul
FA2	3.99	3.1	4.47	100	24	---	Qtz, Mul
FA3	3.99	3.1	4.47	100	48	---	Qtz, Mul

KA0, Kaolinite; CLI, clinoptilolite; NC, natural clinker; FA, fly ash; CHA, K-chabazite; EDI, zeolite K-F; PHI, K-phillipsite; SOD, hydroxysodalite; Mul, mullite; Qtz, quartz; RM, raw material; L, alkaline solution.

* en trazas

products are characterized by the occurrence of a large amount of an amorphous aluminosilicate phase from which several crystalline phases formed, although with a low grade of crystallinity. Therefore, a higher concentration of KOH as an activating agent would be required in order to attack aluminosilicate phases from the starting raw material. In fact, according to Ríos (2008), a total dissolution of these raw materials would be achieved with high KOH concentration and temperature, with an amorphous potassium aluminosilicate phase at shorter reaction times. Longer reaction times were required to obtain crystalline phases (zeolites), which display a low grade of crystallinity. Therefore, to achieve a similar level of attack on the raw materials with KOH compared to that in the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$, it would be necessary to use higher KOH concentrations, alkaline solution/KAO ratios and longer reaction times, under controlled experimental conditions, to obtain the desired zeolitic phases.

2. Experimental procedure

2.1 Reagents

Kaolinite (English China Clay, Cornwall) as Supreme Powder supplied by ECC International; clinoptilolite (Miocene volcanic area of Tokay Mountains, Hungary); natural clinker (Cerrejón coal mining site, Colombia); fly ash (Rugeley Power Station, West Midlands, England); potassium hydroxide from Aldrich Chemical Company, Inc; and distilled water using standard purification methods.

2.2 Synthesis of zeolite-like materials

The synthesis conditions for transformation of raw materials in KOH solutions are schematized in Figure 1.

The raw materials were added, with stirring, to alkaline solutions, which were prepared by dissolution of KOH (pellets) in distilled water in reaction plastic beakers (150-250 ml). Calculated amounts of the raw materials were added to the KOH solutions and stirred until the reagents were dissolved and for homogenization of the reaction

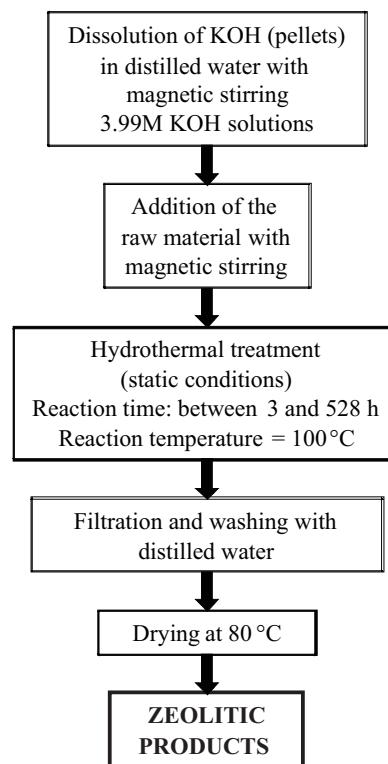


Figure 1. Schematic diagram of zeolite-like materials preparation by the hydrothermal treatment method

mixture. Then, pH of the reaction gels was measured. The crystallization was carried out by hydrothermal synthesis under static conditions in PTFE (polytetrafluoroethylene = Teflon) bottles (Cowie Technology Ltd) of 65 ml for preparations heated at 100 °C, which were previously weighted for preparations heated in an oven. The reactors were removed from the oven at the scheduled times and were quenched in cold water for product identification. Then, pH of the reaction mixtures was measured. After hydrothermal treatment, the reaction mixtures were filtered, washed with distilled water, and the products were dried in an oven at 80 °C. Synthesis conditions are summarized in Table 1. The dried samples were weighted and kept in plastic bags for analysis.

2.3 Characterization techniques

Powder X-ray diffraction data were collected on a Philips PW1710 type diffractometer operating in Bragg-Brentano geometry. The radiation applied was Cu-K α radiation (40 kV and 40 mA) and secondary monochromation. The samples were measured in step scan mode with steps of 0.02° 2 θ and a counting time of 1 s. Phase identification was made by searching the ICDD powder diffraction file database, with the help of Joint Committee on Powder Diffraction Standards (JCPDS) files for inorganic compounds. Fourier Transform Infrared Spectra were obtained on a Mattson Genesis II FTIR spectrometer. The microstructure of the as-synthesized zeolite-like materials was analyzed with a scanning electron microscope (ZEISS EVO50) in the back-scattered electron mode, under the following analytical conditions: I probe 1 nA, EHT = 20 kV, beam

current 100 μ A, Signal A = SE1, WD = 8.0 mm. Thermogravimetric analyses (TG) were carried out in a Mettler Toledo TG 50 type thermobalance under dynamic heating conditions (20 °C/min heating rate) under nitrogen gas flow (20 ml/min). A ceramic crucible was used for the experiments, filled with 15-20 mg sample in each case.

3. Results and discussion

3.1 X-Ray Diffraction analyses

The comparison of the diffractograms (Figure 2) with the JCPDS data file showed that poorly crystallized K-chabazite, zeolite K-F, hydroxysodalite and K-phillipsite were formed under these reaction conditions. The XRD patterns reveals that the hydrothermal treatment of the starting materials in KOH solutions is

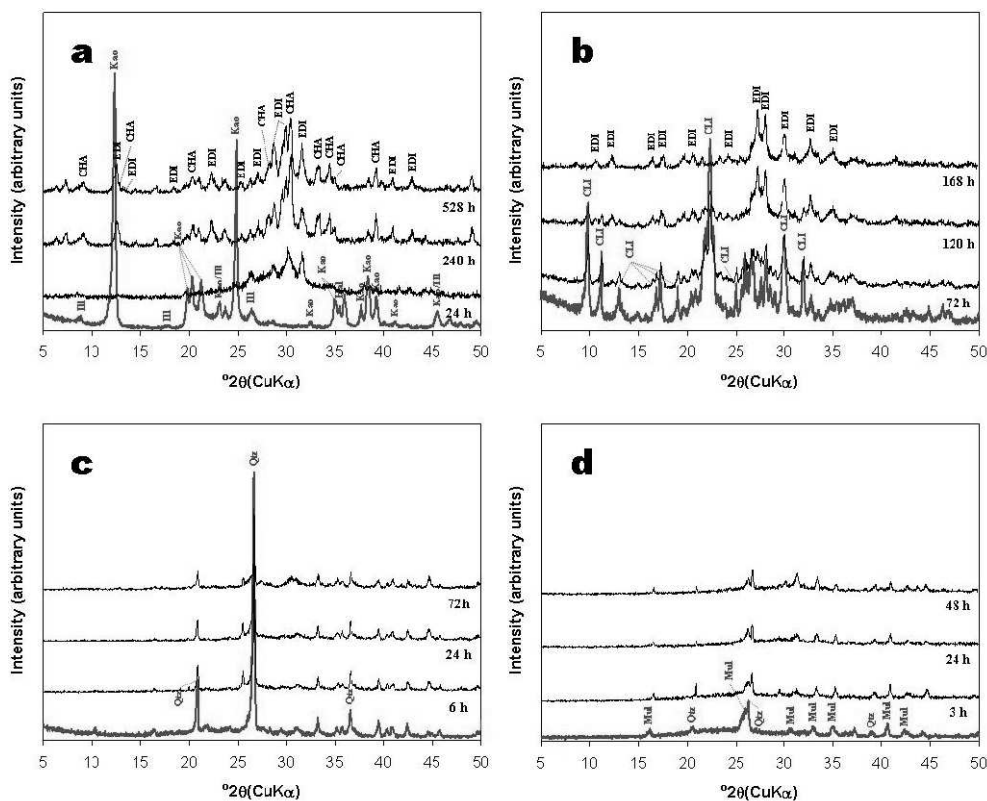


Figure 2. XRD patterns of the unreacted (background in red color) (a) kaolinite, (b) clinoptilolite, (c) natural clinker and (d) fly ash, and representative as-synthesized products obtained after their hydrothermal reaction in KOH solutions. CHA, K-chabazite; EDI, edingtonite (zeolite K-F); CLI, clinoptilolite; Kao, kaolinite; Ill, illite; Hal, halloysite; Qtz, quartz; Mul, Mullite.

characterized by a slow dissolution of raw materials and the formation of amorphous aluminosilicate and crystalline phases accompanied by residual phases of the raw materials.

As can be seen from the XRD patterns in Figure 2a, very weak peaks indicate that an intense dissolution of the starting kaolinite was accompanied by the precipitation of two different zeolitic phases (K-chabazite and zeolite K-F), which increased in crystallinity with reaction time. According to Ríos (2008), it could be said that KOH concentration increase promoted the zeolite K-F formation. In Figure 2b is illustrated the progressive crystallization of zeolite K-F with reaction time after activation of clinoptilolite. The X-ray diffraction patterns in Figure 2c of the activated natural clinker show evidence of the disappearance of some of the characteristic diffraction peaks of the starting material, whereas quartz showed a reduction of intensity of the reflection peak at $2\theta = 26.6^\circ$ with reaction time. The XRD patterns in Figure 2d show that quartz and mullite in fly ash were not attacked by the

KOH solutions, as shown by the approximately constant behaviours of their reflection peaks.

These results reveal low conversion efficiency of the starting materials using KOH as alkaline activator, taking into account that K^+ is a suppression factor for zeolite synthesis, which causes a slow crystallization rate.

3.2 Scanning Electron Microscopy

To characterize the morphological changes of the different starting materials, SEM images were obtained. As an illustrative example, Figure 3 displays SEM images for the treated raw materials, which reveal interesting morphologies that provide new clues on the phase reaction history after the hydrothermal transformation of kaolinite, clinoptilolite, natural clinker and fly ash in the system $K_2O-SiO_2-Al_2O_3-H_2O$.

Figure 3a reveals the presence of neoformed crystals of zeolite K-F and an unidentified potassium aluminosilicate, which have grown at the expense of spheroidal aggregates of K-

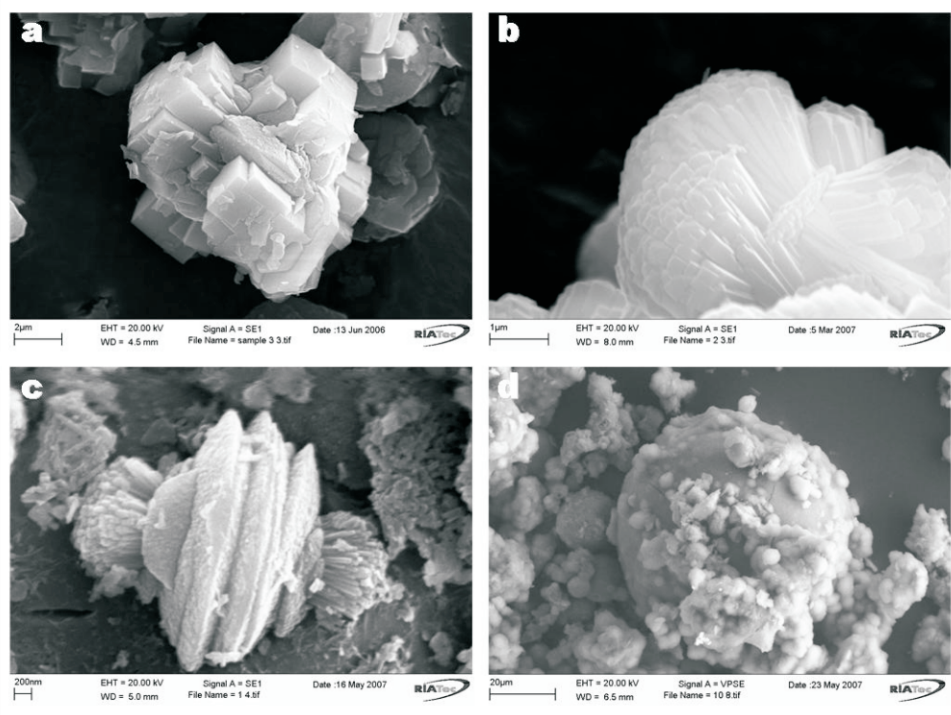


Figure 3. SEM images showing the occurrence of representative synthesis products obtained via hydrothermal treatment of (a) kaolinite, (b) clinoptilolite, (c) natural clinker and (d) fly ash in KOH solutions at $100^\circ C$.

chabazite after activation of kaolinite. Observe the intergrowth between prismatic crystals of zeolite K-F developing cruciform penetrating twinning and a potassium aluminosilicate phase with hexagonal plate-like morphology. A petal flower morphology characteristic of zeolite K-F obtained from hydrothermal treatment of clinoptilolite is shown in Figure 3b. Using natural clinker as starting material promoted the formation of (1) K-chabazite, which occurs as pseudo-hexagonal crystals forming star-shaped discoidal with a characteristic complex interpenetrating twins ('phacolic habit') that develop rosette aggregates, and (2) K-Phillipsite occurring as prismatic, well-terminated, moderately striated crystals developing cruciform penetrating twinning, which coat and project outwards from K-chabazite (Figure 3c). The growth of the K-phillipsite in a radial array from the centre of K-

chabazite shows a typical growth mechanism from a nucleating point in an essentially amorphous material. The unreacted surface of the starting fly ash spheres is observed in Figure 3d. Observe how very small crystals of unidentified phases start growing onto amorphous material. Therefore, the reaction between fly ash with KOH did not change significantly the microscopic structure of the starting material.

3.3 Fourier Transform Infrared Spectroscopy

Figure 4 illustrates the FT-IR spectra of the raw materials and as-synthesized products obtained after their hydrothermal treatment in KOH solutions. The characteristic peaks of kaolinite y clinoptilolite disappeared after reacting with KOH, while those of natural clinker and fly ash weakened. However, the IR vibration bands reveal

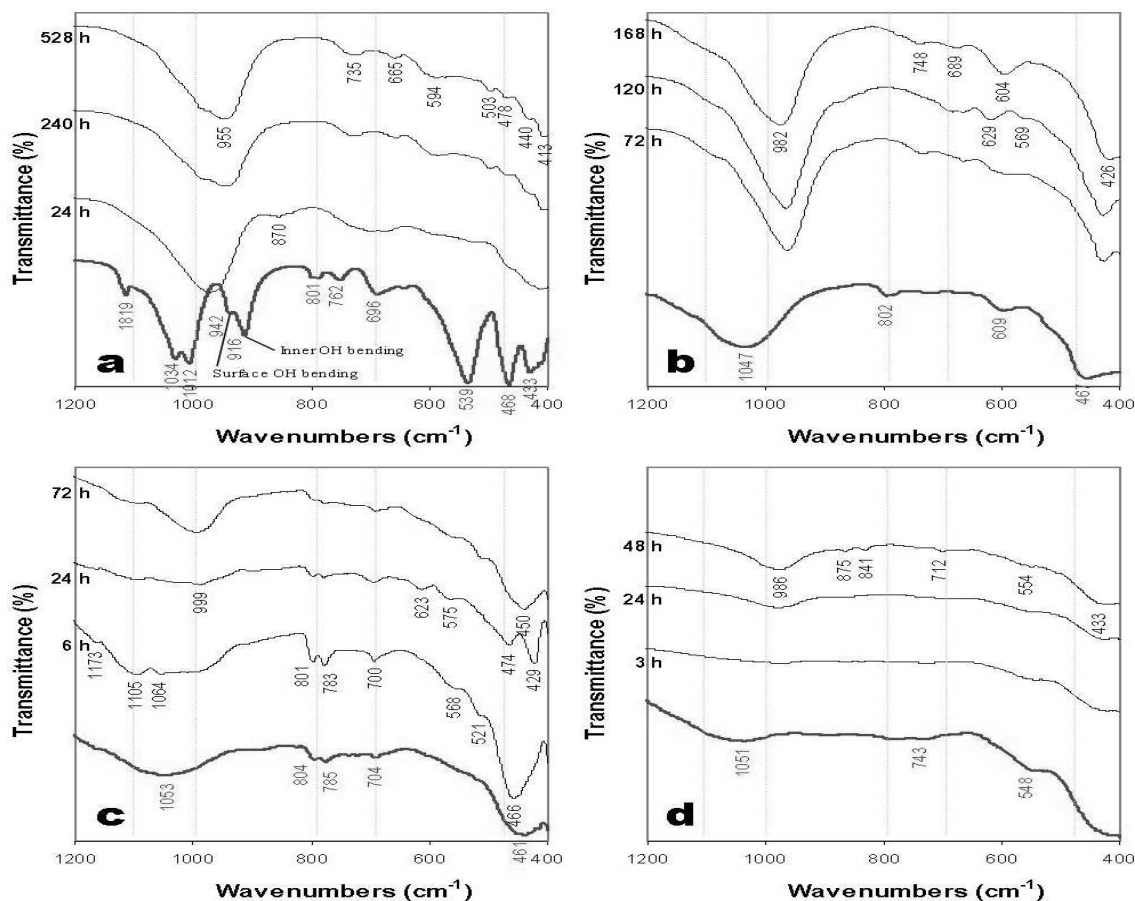


Figure 4. FT-IR spectra of the unreacted (background in red color) (a) kaolinite, (b) clinoptilolite, (c) natural clinker and (d) fly ash, and representative as-synthesized products obtained after their hydrothermal reaction in KOH solutions.

the appearance of new vibration bands corresponding to the formation of several zeolitic phases. The synthesis products are characterized by IR absorption spectra, with no sharp peaks revealing a material with low grade of crystallinity, which has a very constant behaviour in spite of the reaction time.

3.4 Thermal analysis

Figure 5 shows the TGA and its first derivative (DTG) curves of representative as-synthesized products obtained after hydrothermal reaction of raw materials in KOH solutions. For the edingtonite (zeolite K-F)-K-chabazite mixture obtained from kaolinite (Figure 5a), three DTG curves were observed, which reveal that most of the water was lost in four stages. H₂O was lost under vacuum at 25°C, and additional H₂O was lost in three steps between 25-85°C, 85-150°C and 150-

250°C. An additional peak at 490 °C was observed. For edingtonite (zeolite K-F) obtained from clinoptilolite (Figure 5b), two DTG curves were observed, which reveal that most of the water was lost in three stages. H₂O was lost under vacuum at 25°C, and additional H₂O was lost in two steps between 25-75°C and 160-250°C. The synthesis products obtained by the activation of natural clinker (Figure 5c) show five DTG peaks dehydration step. The DTG peaks observed in the range of 25–175 °C correspond to the zeolite dehydration steps (up to 3 DTG peaks). Two additional peaks at 312 and 606 °C were observed. The fly ash-based zeolitic product (Figure 5d) show four DTG peaks dehydration step. Zeolite dehydration process is revealed by the occurrence of DTG peaks between 25–150 °C. Two additional peaks at 312 and 531 °C were observed.

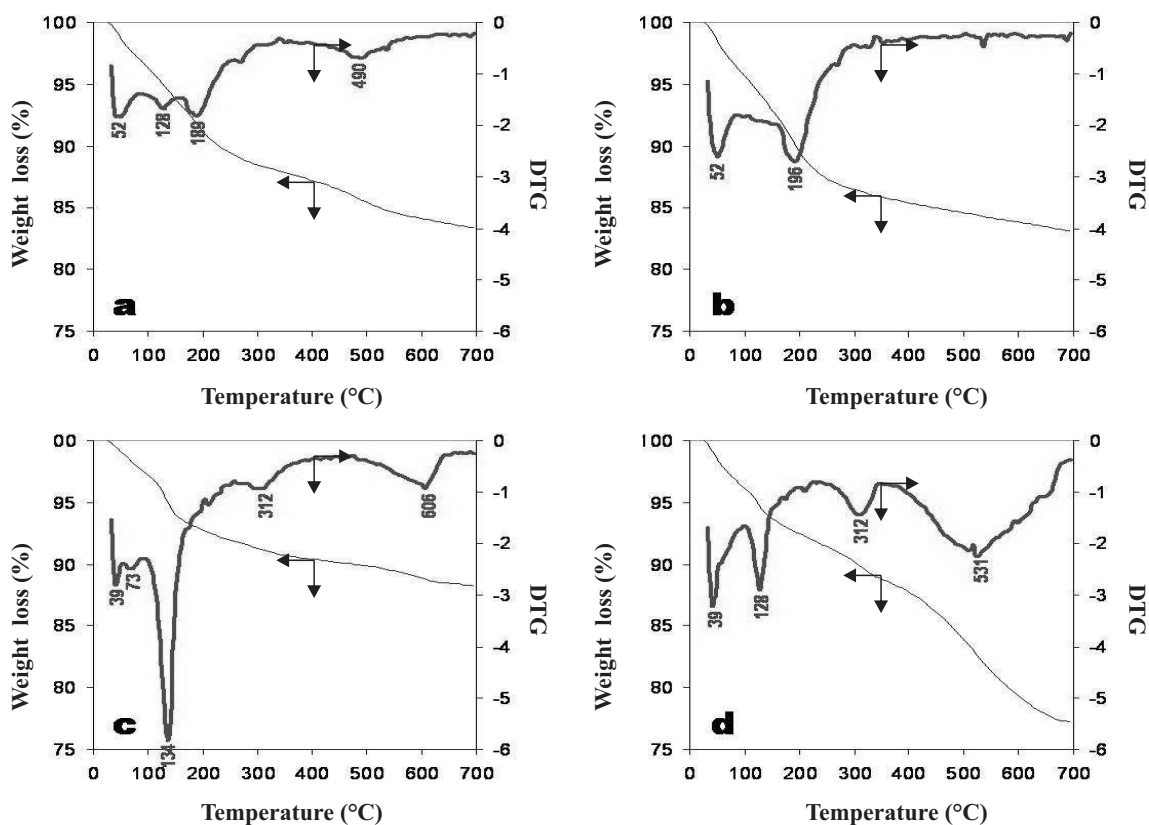


Figure 5. TG/DTG curves between 25-700 °C of representative synthesis products obtained after alkaline activation of (a) kaolinite, (b) clinoptilolite, (c) natural clinker and (d) fly ash using KOH as mineralizer.

The position of these DTG peaks and the number of dehydration steps has been attributed to the different compensating cation–water binding energies as well as to the different energy associated with the diffusion of the desorbed water through the porous structure of the zeolites (Covarrubias et al., 2006). The first group of peaks are in the range of 25–85 °C and correspond to water desorption; the second group of peaks are in the range of 85–250 °C and are attributed to occluded water. Additional DTG peaks at 490 (for the mixture chabazite-edingtonite), 312 and 606 (for natural clinker-based zeolitic product), and 312 and 531 (for fly ash-based zeolitic product) °C, can be attributed to framework dehydroxylation of the zeolitic materials.

The as-synthesized zeolitic materials show up to five dehydration steps, depending on the thermogravimetric evolution of the zeolitic materials, which could be explained as a consequence of water molecules dehydrated at lower temperatures that could re-enter the zeolite with or without affecting its framework linkages.

4. Conclusions

It was successfully demonstrated the production of poorly crystalline potassium zeolites by hydrothermal treatment of different raw materials at 100°C in KOH solutions. The synthesis products include zeolite K-F as the main zeolitic phase and K-chabazite and K-phillipsite generally as trace phases. This study provides valuable scientific knowledge on the transformation of the starting materials, which can be summarized by two main stages: (1) the dissolution of the raw material releasing Si and Al, with a progressive formation and dissolution of an amorphous aluminosilicate gel, and (2) the crystallization of zeolite-like materials.

The chemistry of zeolite synthesis was subject to perturbations caused by the presence of impurities in the starting material, which may remain insoluble during the crystallization and make undesired species to nucleate, developing mixtures of different zeolitic materials coexisting in the as-synthesized products. In some cases, zeolite formation was assessed to be fairly

unsuccessful, taking into account that the synthesis products contain the mineral phases of the starting material (fly ash), which reveals its low conversion efficiency using KOH as alkaline activator.

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6. References

- Barrer, R.M. (1978). *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*. London: Academic Press.
- Barrer, R.M., Cole, J.F., & Sticher, H. (1968). Chemistry of soil minerals. Part V. Low temperature hydrothermal transformations of kaolinite. *Journal of the Chemical Society A: Inorganic, Physical, Theoretical* 2475-2485.
- Barrer, R. M., & Munday, B.M. (1971). Cation exchange in the synthetic zeolite K-F. *Journal of the Chemical Society A: Inorganic, Physical, Theoretical* 2914-2921.
- Bauer, A., Velde, B., & Berger, G. (1998). Kaolinite transformation in high molar KOH solutions. *Applied Geochemistry* 13(5), 619-629.
- Covarrubias, C., Garcia, R., Arriagada, R., Yanez, J., & Garland, M. (2006). Cr(III) exchange on zeolites obtained from kaolin and natural mordenite. *Microporous and Mesoporous Materials* 88(1-3), 220-231.

Juan, R., Hernandez, S., Andres, J.M., & Ruiz, C. (2007). Synthesis of granular zeolitic materials with high cation exchange capacity from agglomerated coal fly ash. *Fuel* 86(12-13), 1811-1821.

Ríos, C.A. (2008). *Synthesis of zeolites from geological materials and industrial wastes for potential application in environmental problems*, Doctoral Thesis, School of Applied Sciences, University of Wolverhampton, Wolverhampton, England.

Ríos, CA., & Williams, C.D. (2008). Synthesis of zeolitic materials from natural clinker: A new alternative for recycling coal combustion by-products. *Fuel* 87(12), 2482-2492.

Ríos, CA., Williams, C.D., & Roberts, C.L. (2009). A comparative study of two methods for the synthesis of fly ash-based sodium and potassium type zeolites. *Fuel* 88(8), 1403-1416.

Tuỳ, Đ.Q., Quyên, V.N., Binh, H.T., & Phuong, V.H. (2005). Study on conversion from Vietnam kaoline mineral to KF zeolite. *Hoá học và ứng dụng*, (12), 25-28.

Vicente, M.A., & Belvert, C. (2006). Easy synthesis of K-F zeolite from kaolin and characterization of this zeolite. *Journal of Chemical Education* 83(10), 1541-1542.