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Selective synthesis of zeolite briquettes from conformed ashes†

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Abstract: The present study is devoted to the transformation of conformed ashes to zeolites by hydrothermal synthesis. A wide range of experimental conditions was tested to prepare selectively zeolites with different structures. Four different zeolites were synthesised: Na-P1, analcime, cancrinite and sodalite. Stabilisation of the cancrinite phase was achieved by modification of the silica/alumina ratio of the synthesis mixture. The transformation is not restricted to the external surface of the conformed ashes, on the contrary, different techniques have shown that a homogeneous transformation is produced and its yield does not decrease due to the use of a preconformed material. The main contribution of the proposed method is that the final zeolitic material is already compacted and does not require any conformation step or the use of a binder.

Keywords: zeolite; fly ash; hydrothermal treatment; XRD

1 INTRODUCTION

Coal combustion and gasification generate a wide variety of solids, most of which are used for landfill.[1] This huge amount of inexpensive residues merits transformation into more valuable materials. Until now, there have been few alternatives to remove, transform and use these by-products, among which, different procedures have been described to prepare (ie by hydrothermal treatment) zeolites and related materials.[2–7]

Fly ashes, from coal combustion, have been widely used as precursors for zeolite production, because they have both the appropriate active phases (silica and alumina) and the required high surface area.[2–7] However, there is a major drawback in zeolite synthesis from fly ashes in that the zeolites produced by this method have a small particle size. This makes their use in some application difficulty especially those in the liquid phase, which require a separation step to recover the zeolite. Additionally, a fraction of the fly ash is not transformed into zeolite, thus decreasing the overall yield of the process.

The solution of the above problem constitutes the main objective of the present work which deals with the synthesis and characterisation of zeolites by hydrothermal treatment of pelletised ashes (cylindrical shape), which originate from the burning of previously conformed coal pellets.

2 EXPERIMENTAL

The raw materials used in this study are pellets generated during the gasification of a pre-shaped coal produced by the Spanish company 'TECSA y HUSA' by pressing a lignite powder and lime mixture. The gasification of these carbon monoliths produces the ash pellet precursors which have high silica and alumina contents and large surface areas (Fig 1).

These monoliths were cut into discs (about 4 mm high and 8 mm diameter and 0.250 mg in weight) and hydrothermally treated in NaOH solutions. The effects of different experimental conditions were analysed (NaOH concentration, NaOH/conformed ashes, time and temperature). The starting and final materials were analysed by XRD, XRF, SEM and FTIR.

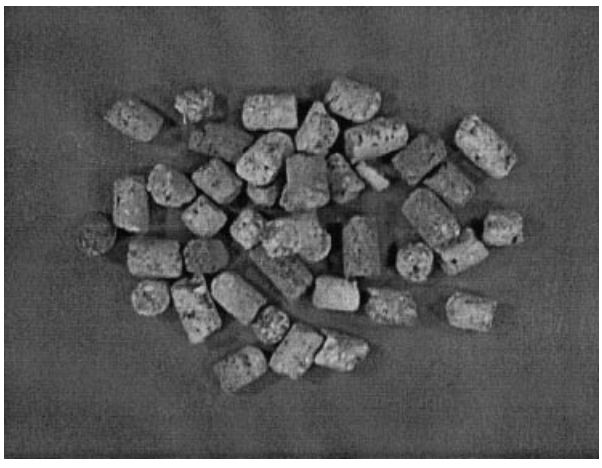

Figure 1. Conformed ashes used as raw material.

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XRD experiments were performed using a 2002 Seifer Diffractometer, with CuKα radiation (1.54Å), a graphite monochromator and an NaI (TI) detector. The copper cathode was used at 35 mA and 42 kV and the scan was carried out from 6° to 90° at 2° per min.

A Mattson infrared spectrometer (model Infinity MI60) was used for the DRFTIR analysis of the samples. This equipment has an MCT detector and a diffuse reflectance accessory (Spectra Tech, model Collector). The samples were diluted with KBr (sample:KBr ratio = 1:20). Each spectrum was collected after 100 scans at 4 cm^{-1} resolution.

To study the morphology of the crystals produced by the hydrothermal treatment, the samples were analysed by SEM (Jeol electronic microscope model JSM-840).

Finally, the samples were also analysed by gas adsorption. Both N_2 adsorption at 77 K and CO_2 adsorption at 273 K were carried out in a Autosorb-6 apparatus. Prior to the analysis, all the samples were degasified in an Autosorb Degasser, for 4 h at 523 K and 5×10^{-5} bar.

3 RESULTS AND DISCUSSION

The characterisation of the conformed ashes by XRD shows that this is mainly an amorphous material although some minerals typically present in coal such as quartz, mullite, haematite, magnetite and cristobalite were detected (Fig 2). The chemical composition of the conformed ash obtained by XRF (Table 1) shows that silica (47.7%) and alumina (33.8%) are the main components of the solid. However, a significant amount of iron oxide was also observed (12.2%).

Figure 3 shows an SEM picture of the raw material. No crystalline phases could be observed by this technique. On the contrary, the appearance of this material is typical of an amorphous solid, corroborating the XRD results. In addition, the cenospheres, which are present in the fly ashes, are not observed in these conformed ashes due, probably, to the lower temperature applied to the carbon monoliths during gasification.

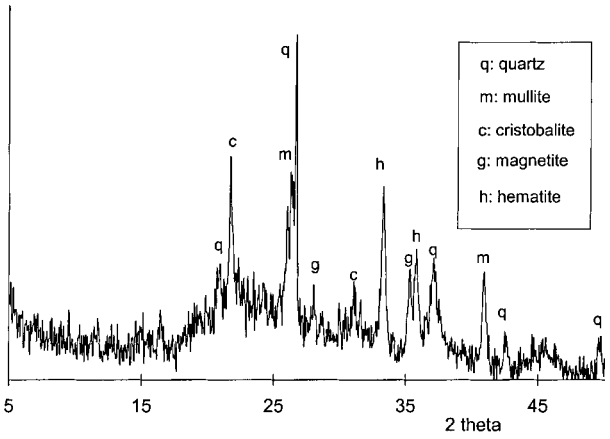

Figure 2. XRD pattern of the conformed ashes used as raw material.

Table 1. Chemical composition of the raw material estimated by XRF, shown as wt% of the most stable oxide of each element whose concentration is higher than 0.1 wt%

Composition (oxide)	*Content (%)*	*Composition (oxide)*	*Content (%)*
SiO_2	47.7	CaO	1.3
Al_2O_3	33.8	TiO_2	0.9
Fe_2O_3	12.2	MgO	0.8
K_2O	1.4	Na_2O	0.1

Hydrothermal treatment of the conformed ashes produces a wide variety of zeolites. Control of the synthesis conditions (NaOH concentration, temperature, time, NaOH/conformed ashes ratio) allowed the selective preparation of four different materials, ie Na-P1, analcime, sodalite and cancrinite. Table 2 describes the synthesis conditions used for the preparation of these materials and some of their main properties, such as chemical formula (obtained from Ref 8), pore size, framework density, and unit cell type.[9] The selective synthesis of cancrinite was possible after adding extra silica to obtain a silica/alumina ratio equal to 6.

It is worth highlighting that the hydrothermal treatment of the conformed ashes produces zeolite briquettes, which keep their shape and mechanical properties. These zeolite briquettes were studied by XRD, and, as an example, Fig 4 shows the XRD patterns of the conformed ashes after hydrothermal treatment in 1 mol dm^{-3} NaOH at 431 K for different periods of time (4, 8, 24, 32 and 64 h). This figure shows the evolution of the XRD as a function of the reaction time and the gradual, and selective, transformation of the raw material, which is mainly amorphous, into a crystalline compound identified as analcime.[10] It must be noted that the transformation does not occur when the pH of the solution is not high enough. This indicates that the silica and alumina present in the raw material need to be dissolved to be able to assemble into a crystalline solid, as is usual in zeolite synthesis. In addition, the same transformation was followed by DRFTIR. As shown in Fig 5, the original material (conformed ashes) shows some peaks related to the presence of amorphous silica (at

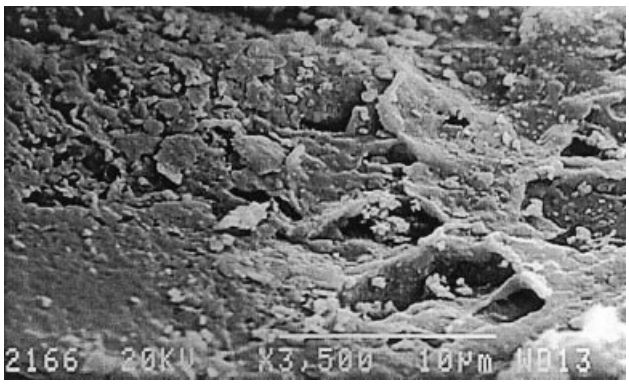

Figure 3. SEM image of the conformed ashes.

Na-P1			
NaOH concentration	2 mol dm^{-3}	Composition	$Na_8(Al_8Si_8O_{32})\cdot 16H_2O$
Temperature (K)	363	Channels (Å)	4.5×3.1; 4.8×2.8
NaOH/conformed ashes	2	Fd[a]	15.4 T/1000 Å^3
Time (h)	12,24,72,144	Unit Cell	Monoclinic
Analcime			
NaOH concentration	1 mol dm^{-3}	Composition	$Na_{16}(Al_{16}Si_{32}O_{96})\cdot 16H_2O$
Temperature (K)	431	Channels (Å)	Distorted eight membered rings
NaOH/conformed ashes	1	Fd[a]	18.6 T/1000 Å^3
Time (h)	4,8,24,32,64	Unit cell	Cubic
Sodalite			
NaOH concentration	10 mol dm^{-3}	Composition	$Na_6(Al_6Si_6O_{24})\cdot NaCl$
Temperature (K)	363,463	Channels (Å)	–
NaOH/conformed ashes	10	Fd[a]	17.2 T/1000 Å^3
Time (h)	12,24,72,144	Unit cell	Cubic
Cancrinite[b]			
NaOH concentration	10 mol dm^{-3}	Composition	$Na_6(Al_6Si_6O_{24})\cdot Na_2CO_3\cdot 2H_2O$
Temperature (K)	463	Channels (Å)	5.9 Å
NaOH/conformed ashes	10	Fd[a]	16.7 T/1000 Å^3
Time (h)	24, 48, 96	Unit cell	Hexagonal

[a] Fd: Framework density expressed as T atoms (T = Si or Al) in each 1000 Å.^{3}
[b] SiO_2 was added to give a silica/alumina ratio equal to 6.

Table 2. Synthesis conditions used to prepare the different materials produced by hydrothermal treatment of the conformed ashes, with, some of the main properties of these materials[8,9]

1091 cm^{-1}) and alumina (1240 and 1150 cm^{-1}).[11] Hydrothermal treatment of this material produces a shift of these peaks to lower wavenumbers even at short times. New bands appear at 1005 and 1120 cm^{-1}, which correspond to the external and internal antisimmetric stretching of the TO_4 units (T = Si or Al) of the zeolites.[12]

Using other experimental synthesis conditions, the transformation of the ashes into a zeolitic compound follows other more complex synthesis routes. As an example, Fig 6 shows the results obtained by treating the conformed ashes in a 10 mol dm^{-3} NaOH solution at 463 K. Cancinite (CAN) formation was first observed. This zeolite experiences a solid-state transformation into sodalite (SOD) with time. Although the SOD and CAN structures are quite different both are closely related[13] and the transformation from one into the other can occur by short range changes. A more exhaustive systematic study of the experimental conditions could increase the number of zeolites prepared from conformed ashes. Thus, zeolite Na-P1 has been

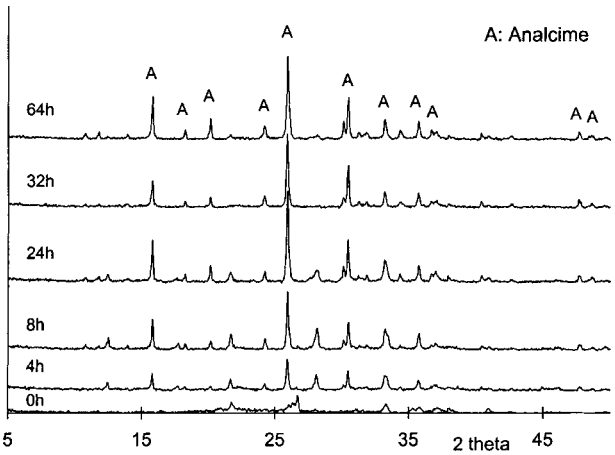

Figure 4. Evolution of the conformed ashes treated in 1 mol dm^{-3} NaOH at 431 K for different periods of time, analysed by XRD.

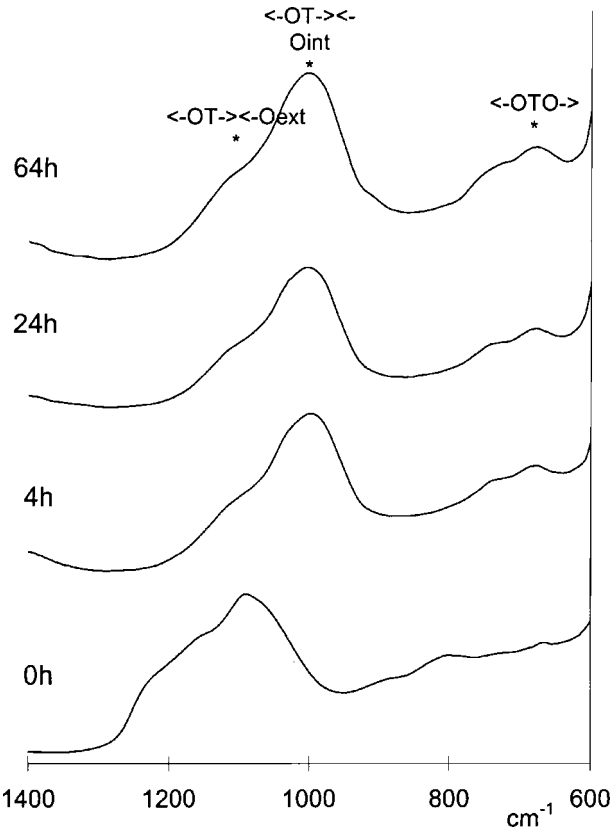

Figure 5. Evolution of the conformed ashes treated in 1 mol dm^{-3} NaOH at 431 K for different periods of time, analysed by DRFTIR.

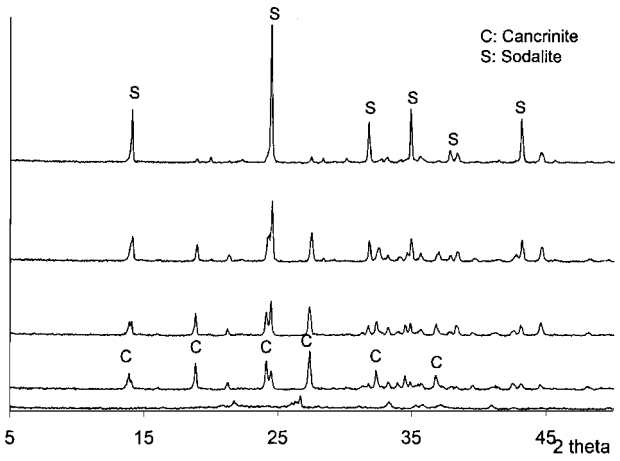

Figure 6. Evolution of the conformed ashes treated in 10 mol dm^{-3} NaOH at 463 K for different periods of time, analysed by XRD.

successfully prepared, which has important applications, especially in water treatment due to its high ion exchange capacity for heavy metals[14–16] and ammonium,[16] and its gas adsorption capacity, for example for SO_2.[17]

It is interesting to note that by changing the experimental conditions the cancrinite phase can be stabilised, preventing its transformation into sodalite. This can be made by adding, an extra amount of silica to the synthesis mixture (Table 1). A high silica/alumina ratio seems to stabilise the cancrinite phase. Both the transformations of cancrinite into sodalite and sodalite into cancrinite have been observed by other authors.[18–20] The first transformation (as observed in this study) occurs at high silica/alumina ratios and the second one when the synthesis mixture is alumina-rich.

The porous texture of the samples was studied by both N_2 adsorption at 77 K and CO_2 adsorption at 273 K. Figure 7 shows the N_2 adsorption isotherms of the conformed ashes and the prepared zeolites. It is quite remarkable that the transformation of the conformed ashes into Na-P1 (prepared using soft conditions) produces a significant increase in the pore volume of the solid. On the contrary, in the case of analcime, cancrinite and sodalite (prepared using more aggressive conditions) a decrease in porosity is observed, probably because these are quite dense phases. The micropore volume of Na-P1, estimated by N_2 adsorption at 77 K, is 0.08 $cm^3 g^{-1}$ which is lower than expected. However, the micropore volume of the same sample estimated by CO_2 adsorption at 273 K is significantly higher (0.3 $cm^3 g^{-1}$). The limitations of N_2 adsorption at 77 K to characterise narrow microporous solids such as zeolites have been shown previously.[21]

Figure 8 shows SEM pictures of some zeolite samples prepared by the hydrothermal method described in this study. The figure contains: (a) the zeolite Na-P1, prepared at 366 K, 0.2 mol dm^{-3} NaOH, 24 h, and (b) cancrinite prepared at 463 K, 10 mol dm^{-3} NaOH, 24 h. Both zeolites display their well known morphology. These observations were obtained after breaking the monoliths, indicating that the transformation of the almost amorphous raw material (Fig 3) occurs not only on the external surface but also in the bulk of the monolith.

On the other hand, it is remarkable (as confirmed by XRD and SEM) that the parallel study carried out with the powdered ashes gives zeolites (and zeolite conversions) similar to those obtained from the ashes in briquette form. This observation indicates that the

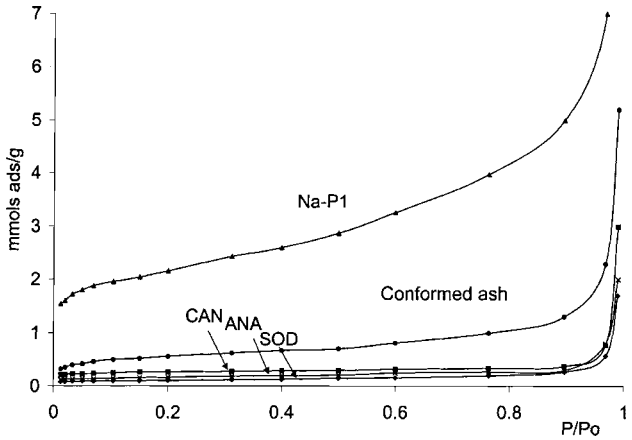

Figure 7. Isotherms of N_2 at 77 K of the conformed ashes, Na-P1, cancrinite, analcime and sodalite.

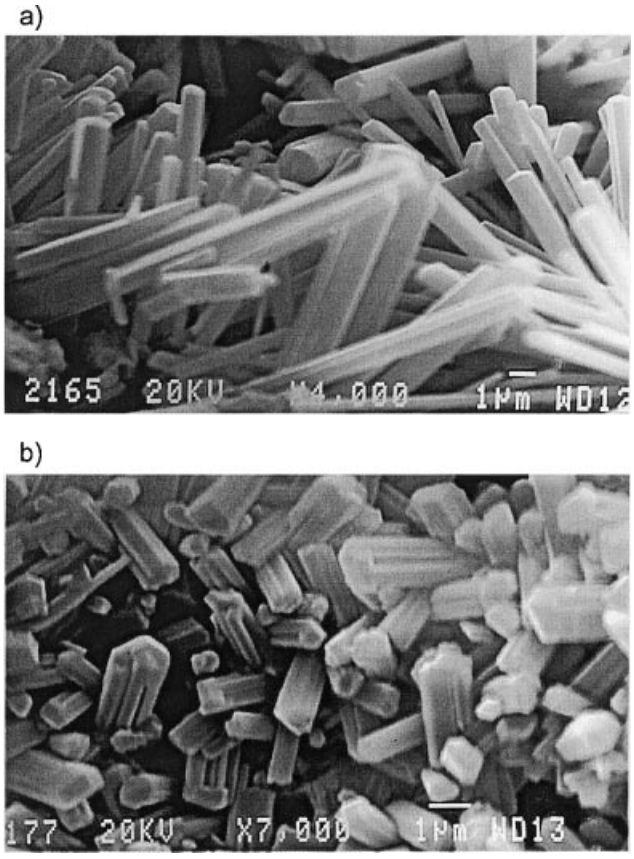

Figure 8. SEM images of some zeolites prepared by hydrothermal treatment; (a) zeolite Na-P1 and (b) cancrinite.

basic medium reaches and reacts, not only with the external surface of the briquettes, but also with the inside, giving an homogeneous conversion of the briquette. This also shows that the briquette has an open structure to the basic medium which has to be related to its preparation process. The briquettes used in this study are ash briquettes which have been obtained after burning the raw briquette which contains carbon. The burning of the carbon seems to favour the porosity of the briquettes and hence the contact between the basic solution and the internal parts of the briquette.

Finally, it should be highlighted that the metal oxides present in the raw material which are not soluble in basic media, such as Fe_2O_3 (Table 1), are unlikely to be incorporated into the zeolite structure. Most probably, they are unchanged during the hydrothermal treatment. As observed in Fig 4 and 6, the peak located at 33 2θ (assigned as haematite, see Fig 2) is unaltered during the whole hydrothermal treatment, which confirms that the Fe_2O_3 retains its original structure. The part of the briquette which is unchanged after treatment probably helps maintain the mechanical stability of the final material.

4 CONCLUSIONS

Conformed ashes are suitable raw materials for the synthesis of zeolite briquettes and can be a promising alternative to the most common use of powders, such as fly ashes. The transformation can be achieved by conventional one-step hydrothermal treatment of the conformed ashes in NaOH solution. Modification of the experimental conditions allows the preparation of specific zeolite phases. Mild conditions, low temperature and NaOH concentration favour the formation of an open structure (Na-P1), increasing the conditions produces closer structures (analcime) and high temperatures and NaOH concentrations produce dense phases (cancrinite and sodalite).

The use of conformed ashes does not decrease the yield of the zeolite which is homogeneously localised on both the external surface of the monolith and in the bulk of the material. Moreover, even the more aggressive experimental conditions do not damage the integrity of the briquette.

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REFERENCES

1 IEA Coal Research, *Reviews in Coal Science, The Problems of Sulphur*, Butterworths (1989).
2 Querol X, Plana F, Alastuey A and López-Soler A, *Fuel* **76**(8):793 (1997).
3 Shigemoto N, Hayasho H and Miyaura K, *J Materials Science* **28**: (1993).
4 Stout WL, Hern JL, Korcak RF and Carlson CW, *Manual for Applying Fluidized Bed Combustion Residue to Agricultural Lands ARS-74*, US Department (1995).
5 Shigemoto N, Sugiyama S, Hayashi H and Miyaura K, *J Materials Science* **13**:660 (1994).
6 Mondragón F, Rincón F, Sierra L, Escobar J, Ramirez J and Fernandez J, *Fuel* **69**:263 (1990).
7 Querol X, Plana F, Alastuey A and López-Soler A, in *Coal Science and Technology*, Vol 24, Elsevier, Amsterdam (1979).
8 Margaret K and McClune WF, Powder Diffraction File. Inorganic Phases, Sets 1–42, International Centre for Difraction Data, Pennsylvania, USA (1992).
9 Meier WM, Olson DH and Baerlocher Ch, *Atlas of Zeolite Structure Types*, Elsevier (1996).
10 Treacy MMJ, Higgins JB and von Ballmoos R, *Collection of Simulated XRD Powder Patterns for Zeolites*, Elsevier (1996).
11 Nyquiest Richard A and Kagel Ronald O, *Infrared Spectra of Inorganic Compounds*, Academic Press Inc, London (1971).
12 Szostak R, *Molecular Sieves: Principles of Synthesis and Identification*, Van Nostrand Reinhold, New York. pp 53–54 (1989).
13 Hassan I, *Kuwait Journal of Science and Engineering* **24**(1):163 (1997).
14 Lee MG, Yi G, Ahn BJ and Roddick F, *Korean J Chem Eng* **17**(3):325–331 (2000).
15 Streenburggen G and Hollman GG, *J Geochem Explor* **62**(1–3):305–309 (1998).
16 Baccouche A, Srasra E and El Maaoui M, *Appl Clay Sci* **13**(4):255–273 (1998).
17 Srinivasan A and Grutzeck MW, *Environ Sci Technol* **33**(9):1464–1469 (1999).
18 Mundus C, Mueller-Warmuth W and Buhl JC, *Eur J Mineral* **8**(2):231 (1996).
19 Hackbarth K, *Microporous and Mesoporous Materials* **30**(2–3):347 (1999).
20 Mark Barnes C, Addai-Mensah Jonas and Gerson Andrea R, *Microporous and Mesoporous Materials* **31**(3):287 (1999).
21 García-Martínez J, Cazorla-Amorós D and Linares-Solano A, in *Studies in Surface Science and Catalysis. Characterization of Porous Solids*, Ed by Unger KK, Kreysa G, and Baselt JP, Elsevier. pp 438–442 (2000).