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THERMAL CHARACTERIZATION OF THE METAL-SILICALITES OBTAINED FROM AQUEOUS NONALKALINE FLUORIDE GELS

A. Tavolaro

Department of Chemical Engineering and Materials, University of Calabria, I-87030 Arcavacata di Rende (Cosenza), Italy

Abstract

Thermal analysis of crystalline Metallosilicalite-1 precursors with various heteroatoms was carried out in a nitrogen atmosphere. Different interactions between tetrapropylammonium species and the zeolitic environment were evidenced, depending on the type of metallic complexes in the reaction medium. The results support the mechanism of Metallosilicalite-1 formation through a condensation process from the liquid phase.

Isomorphous substitution of T element in a molecular sieve material is very interesting in order to modify its acidity or redox catalytic properties [1–6].

Normally zeolites are synthesized in hydrothermal mixtures. Alkaline hydroxides, TPABr, silica and water are typically required to obtain Silicalite-1. Recently, MFI zeolitic structures have been obtained from near-neutral nonalkaline reaction mixtures containing fluoride ions [7–8].

Using tetrapropylammonium bromide (TPABr) as a template, molecular sieve Bi-, Ce-, Cu-, Cr-, Mo-, Pb-, Sb-, Ti-, V- and W-Silicalite-1 was the only phase obtained in the presence of fluoride ions.

In this paper, it is investigated how the thermal decomposition of TPA ions is influenced by the presence of heteroatoms in the framework of crystals.

Keywords: fluoride containing gels, isomorphous substitution, Silicalite-1

Introduction

In recent years increasing attention has been directed toward the study of new zeolitic materials, especially crystalline microporous metallosilicalites, due to their new catalytic properties. These properties of the zeolites are very much depending on both their chemical and physical features. Above all, zeolites have active sites where acidic, basic or redox-type reactions, interesting for catalysis, may occur.

From a general point of view, silicalite can be considered as a regularly structured lattice into which metal atoms (different from Si and Al) can be introducted up to certain concentration. The purpose of obtaining isomorphous substitution in the lattice of silicalite is obviously to modify the basic structure, the chemical features and therefore to study the new catalytic properties of the zeolites obtained.

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Normally, zeolites are synthesized in hydrothermal mixtures. Alkaline hydroxides, TPABr, silica and water are typically required to obtain Silicalite-1. Recently MFI zeolitic structures were obtained from near-neutral nonalkaline reaction mixtures containing fluoride ions.

The replacement of OH^- by F^- for the formation of soluble framework building species facilitates the incorporation of T elements which are sparingly soluble (e.g. Ti(IV)) or do not readily undergo polycondensation in alkaline medium.

In order to clarify different properties and mechanisms of crystallization between fluoride and alkaline reaction media, syntheses with different metals in identical amount were performed in batch reaction mixtures. Different ways to perform such a substitution are well established during synthesis for element like iron [1], boron [2], gallium [3] or germanium [4]. The substituted element may be strongly or weakly bound to the framework i.e. may remain stable or may give rise to well dispersed metallic oxide particles entrapped in the cavities [5].

Because of the importance of supported metal oxides as selective oxidation catalysts, several attempts have been made with the aim of introducing different atoms into the zeolite framework [6].

We have selected a reaction medium characterized by near-neutral *pH* values and by the presence of fluoride ions.

Previously, we have optimized such a method of synthesis for the crystallization of Silicalite-1 [7].

Since the thermal behaviour (DTG, TG and DSC) is sensitive to structural changes, thermal analysis has already been successfully applied to obtain data on new types of zeolites synthesized in the presence of organic molecules, such as B- and Fe-silicalite obtained from alkaline media.

This work, which is part of an extensive and systematic study on the incorporation of heteroatoms in the framework of silicalite, is devoted to the research of the qualitative proof of the isomorphous substitution of silicon by Bi, Ce, Cu, Cr, Mo, Pb, Ti, Sb, Ti, V and W within the zeolitic framework. The metallosilicalite-1 zeolites were crystallized from fluoride systems in the presence of tetrapropylammonium bromide which is embedded into the channels and cavities of the MFI structure. The thermal behaviour of this molecule reveals new information about the physicochemical properties of metallosilicalite-1 zeolites.

Experimental

The samples were prepared under hydrothermal conditions in modified Morey-type PTFE-lined 20 cm^3 autoclaves, without agitation. Syntheses were carried out at 170+2°C in unstirred teflon-lined autoclaves. The gels of various compositions are described in Table 1. They are characterized by the following global atomic composition:

$$10NaF–0.5Me_2O_x–1.25TPABr–10SiO_2–330H_2O$$

where *M*=Bi, Cu, Ce, Cr, Mo, Pb, Sb, Ti, V and W.

Table 1 Gel composition, *pH* and thermal analysis data of the crystals obtained in the system: $10NaF–0.5Me_2O_x–1.25TPABr–10SiO_2–330H_2O$

			Crystalline phase			
No.	Sample	*pH* gel	*T*/°C		Metal-Salt	*pH* fin.
1	Bi-MFI	6.8	415	478	$Bi(NO_3)_3$	6.8
2	Ce-MFI	7.2	406	460	CeO_2	6.5
3	Cu-MFI	7.0	415	465	$CuSO_4$	7.2
4	Cr-MFI	6.9	409	475	$CrCl_3$	6.9
5	Mo-Sil	7.5	406	467	Na_2MoO_4	6.9
6	Pb-Sil	6.8	417	514	PbAc	6.9
7	Sb-Sil	7.0	417	476	$SbCl_3$	6.9
8	Ti-Sil	6.9	406	462	TEOT	7.1
9	V-Sil	6.2	414	480	$VOSO_4$	6.9
10	W-Sil	7.5	418	505	WO_3	7.4
11	Silicalite-1	6.8	429	521	–	7

Fumed silica (Serva) was used as a silica source. The other reactants were pure TPABr (Fluka), reagent grade NaF (Baker), $Bi(NO_3)_3$ pentahydrate, pure (Merck), CeO_2, purum (Merck), WO_3, purum (Carlo Erba), $CrCl_3$ hydrate, $SbCl_3$ (Merck), $Pb(C_2H_3O_2)_4$ trihydrate, pure (Carlo Erba), Na_2Mo_4 dihydrate, pure (Carlo Erba), $C_8H_{20}O_4Ti$ (TEOT), $CuSO_4$ pentahydrate, pure (Carlo Erba), $VOSO_4$ pentahydrate pure (Merck). The reagents were mixed in the following order: silica, distilled water, TPABr solution, fluoride salt solution, metal source, and the resulting gel was subjected to vigorous mechanical action until complete homogenization.

After being heated at 170°C for predetermined times, the autoclaves were quenched in tap water, the products were filtered off and washed with distilled water, dried at 100°C for 8–12 h and analyzed.

The products were identified and their crystallinity was determined by means of a Philips PW 1730/10 diffractometer, using CuK_α radiation. The 2θ scanning rate for crystallinity determination was $1.2\ 2\theta\ min^{-1}$ and $0.6\ 2\theta\ min^{-1}$ for unit cell parameter calculations.

Simultaneous TG, DTG, DSC analyses of the end-products were performed by a NETZSCH thermal analyser 414/409 equipped with a HP VECTRA ES/12 computer. The mass losses and thermal effects due to the release of decomposition products in a dry nitrogen atmosphere (flow rate 10 $cm^3\ min^{-1}$) were evaluated. The heating rate was 10°C min^{-1}.

Results

The most interesting question characterizing high-silica zeolites such as pentasil (Silicalite-1) is whether isomorphous substitution of framework silicon atoms by atoms of other elements may or may not occur.

All the products obtained from the syntheses listed in Table 1 are characterized by an XRD powder pattern typical of pure Silicalite-1 structure type (Fig. 1). The metallosilicalite-1 was the only phase obtained, showing an X- ray pattern with relative peak intensities similar to the typical pattern of the MFI crystalline structures synthesized in a nonalkaline system in the presence of fluoride ions. These effects are probably due to the morphology and large size of the crystals. The colour of the crystals as-made is white and their morphology is different from those obtained for similar Silicalite-1 systems.

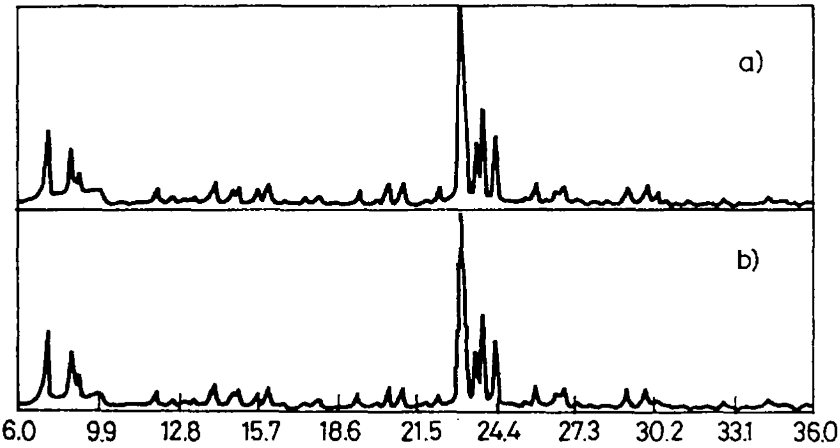

Fig. 1 X-ray diffraction patterns of Silicalite-1 (a) and sample 9 (b)

The unit cell parameters of the crystals were different for different atoms in the crystals and in the reaction gels, suggesting the isomorphous substitution in the framework of the MFI structure.

The DSC curves of the Silicalite-1 (synthesized in fluoride medium) recorded at 10°C min^{-1} exihibit an endothermic peak at 420°C, followed by a second one at 530°C. These two peaks were attributed to the decomposition of TPA$^+$ ions into tripropylamine and dipropylamine and propylene (at 420°C), and to the decomposition of dipropylamine into propylamine and finally to ammonia and propylene (at 530°C). On the other hand, relaxed TPA$^+$ ions, as it was proposed previously, could also be formed when part of the initial TPA$^+$ ions is decomposed at 430°C. The relaxed TPA$^+$ ions are those which do not interact with other neighbouring TPA$^+$ ions any more and are more strongly stabilized by the zeolite. Figure 2 shows the DSC curves obtained for Silicalite-1

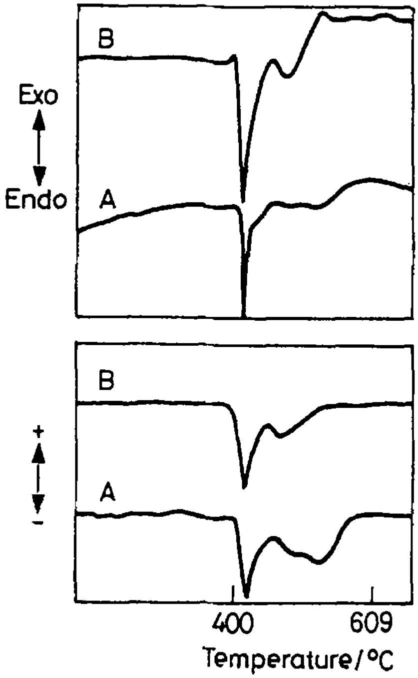

Fig. 2 DSC and DTG curves of Silicalite-1 (A) and the sample 9 (B)

and for the vanadium-containing silicalite-1 sample. In comparison with silicalite, a marked shift of peak II (by about 70°C) towards lower temperatures is observed in the case of V-Silicalite. This is a sure indication of the incorporation of vanadium in the lattice.

As shown in Fig. 3, the DSC curves of metallosilicate precursors are characterized by the same peaks as that of Silicalite. On the other hand, the effects observed occur at different temperatures than in the MFI-silicates crystallized from fluoride media.

In metallosilicate crystals the temperature of the first endothermic peak shifts from 430°C down to ca. 400°C due to the decomposition of the occluded TPAF, while the second peak at ca. 460°C is due to the decomposition of TPA^+ ions.

The micrograph in Figs 4 and 5 show the different external morphologies of Metallosilicalite-1 samples.

Conclusions

The results presented show the great potential of thermal analysis in the characterization of new types of zeolites, which are prepared with template molecules in fluoride medium.

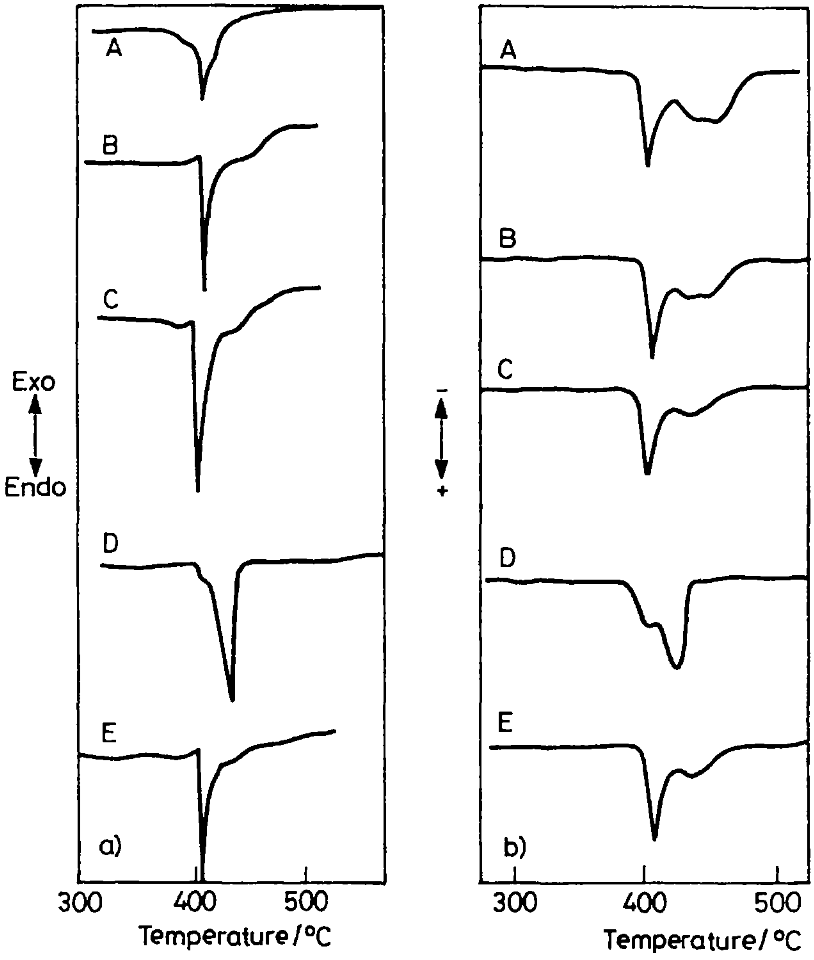

Fig. 3 DSC (a) and DTG (b) curves of samples 5(A), 10 (B), 1 (C), 3 (D) and 7 (E)

The present study was entered upon with a view to characterize the TPA^+ template occluded in precursors of M-Silicalite-1 zeolites. Thermal methods (DTA, TG, DSC) provide a means for discriminating between the species occurring as ion pairs and those corresponding to the compensation of the negative charge of the framework. The latter are bonded to the zeolite by stronger interaction energies and their endothermal decomposition starts at higher temperatures.

For fluoride anion, the relative intensities of the peaks connected with the decomposition of TPA^+ change as a function of the metal type. In fact, the DSC curves of metallosilicate precursors are characterized by two peaks at different temperatures than those observed for the Silicalite-1 crystallized from fluoride media. Furthermore, the temperatures of decomposition of TPA^+ species in all metallosilicalite samples are different.

The distinct variation of the decomposition temperature relative to silicalite already for a Si/*M* ratio of 10 can be taken as strong evidence for the incorporation of metals.

The results reported confirm the assumption that the metal atoms studied can be introduced into the Silicalite-1 structure by direct synthesis in nonalkaline medium.

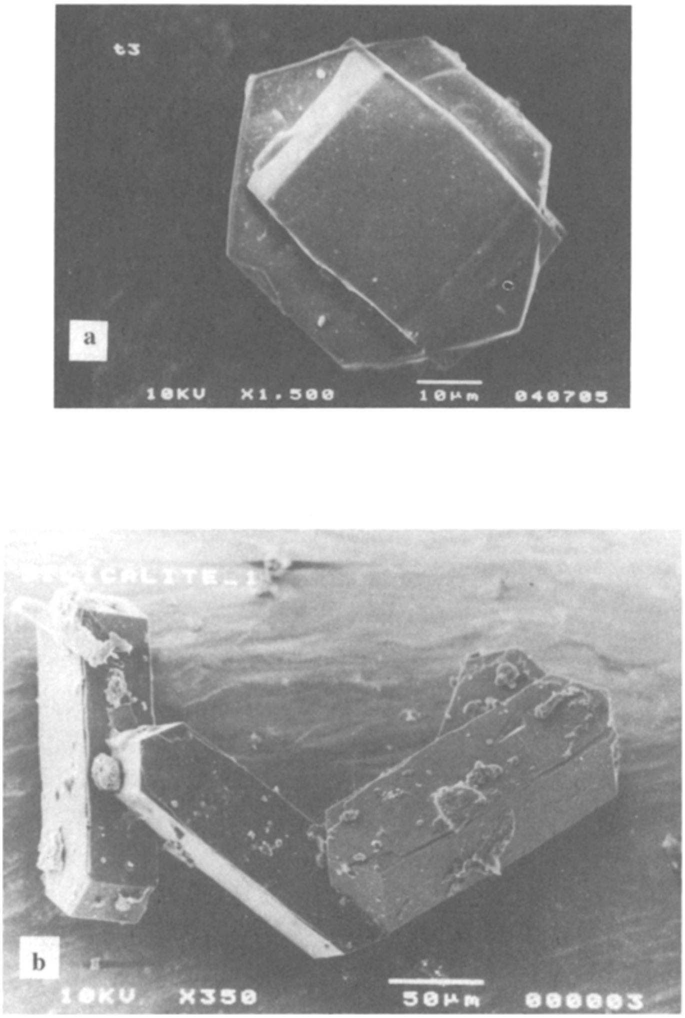

Fig. 4 Scanning electron micrographs of samples 9 (a) and 11 (b)

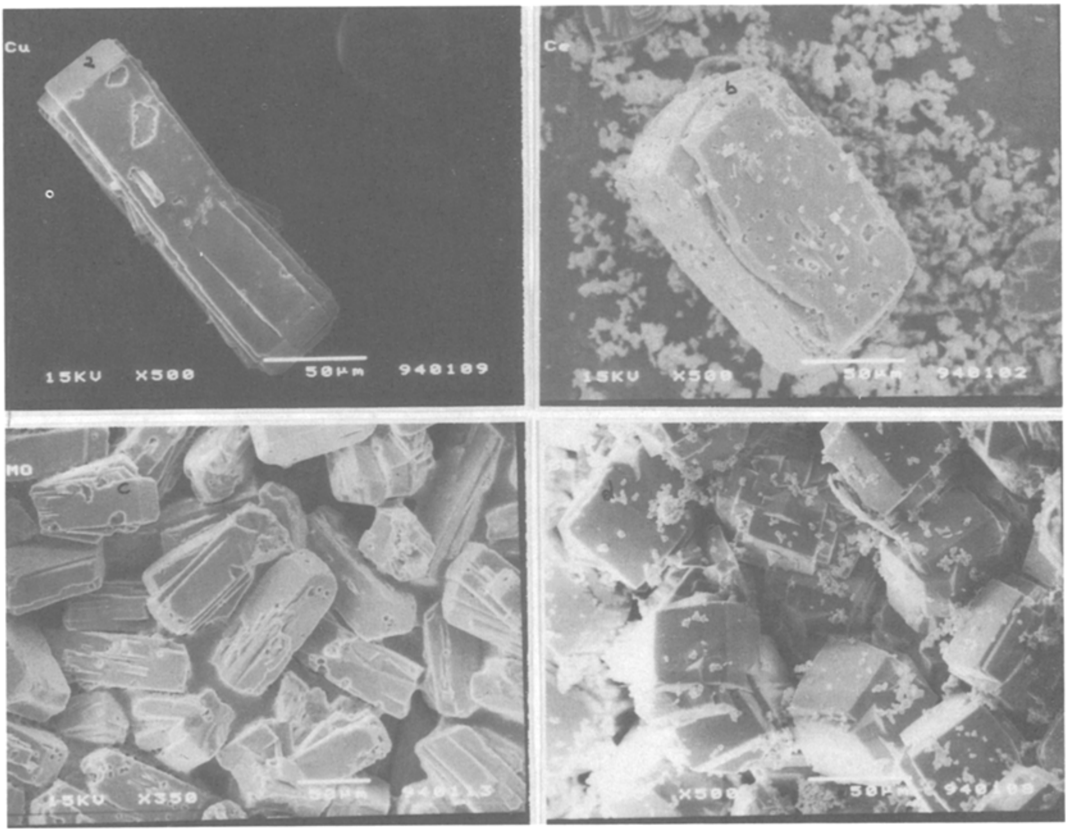

Fig. 5 Scanning electron micrographs of samples 3 (Cu), 2 (Ce), 5 (Mo) and 7 (Sb)

Of course, the synthesis of metallosilicalite from non-traditional gels is the subject of preliminary research, and the elucidation of the local symmetry and the oxidation state of the possible species of metals in the zeolitic crystals requires further analysis.

This research, together with the experimental results obtained in previous studies, points to the peculiarities of this method applied to study the synthesis of high-silica materials, and the partial isomorphous substitution of silicon by metal atoms.

The results reported confirm the existence of different mechanisms of crystallization between Metallosilicalite-1 obtained in fluoride and alkaline media.

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