

## SYNTHESIS AND CHARACTERIZATION OF ZINCOSILICATES WITH MFI-TYPE STRUCTURE

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### الخلاصة :

تم تحضير بلورات سليكات الزنك من محاليل تحتوي على أيونات تترا بروبييل الأمونيوم (TPA) بالتسخين مع وجود بخار الماء. وكان تركيب البلورات من نوع MFI. ولقد درست خواص هذه المواد وقورنت بمواد السليكات النقية التي لها نفس التركيب ومحملة بنفس الكميات من الزنك. وتم التحقق من النقاوة التركيبية لهذه المواد بواسطة انكسار الأشعة السينية والميكروسكوب الإلكتروني. وأظهر التحليل الكيميائي أن الزنك المحمل يؤثر على كمية الماء والصدويوم و(TPA) الموجودة في البلورة. ولقد اتضح بواسطة الميكروسكوب الإلكتروني أن شكل البلورة قد تغير عند إضافة الزنك، كما صاحب ذلك ارتفاع في درجة حرارة تحلل ال (TPA) مع زيادة كمية الزنك في العينة. إن المطيافية تحت الحمراء بيّنت زمرة عند الموجة 1084 سم<sup>-1</sup> وقد اختفت هذه الزمرة بعد تسخين العينة. وباستخدام طريقة الأمونيوم - (TPD)، تبين أن هناك بعض المواقع ذات الخاصية الحمضية (Lewis acid sites). وبالرغم انه لا يوجد دلالات واضحة لوجود الزنك في الهيكل التركيبي للبلورات، إلا أن طيف ال (XPS) وقياس حجم الثغرات دلّ على احتمال عالٍ جداً لإمكانية وجود الزنك في الهيكل التركيبي للبلورات.

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## ABSTRACT

Zincosilicates were hydrothermally crystallized in the presence of tetrapropylammonium cations (TPA). Crystals having the MFI-type structure were obtained. The isomorphous substitution and other physico-chemical properties of the samples were explored and to some extent compared with silicalite-I impregnated with zinc to similar levels. X-ray diffraction and scanning electron microscopy ensured the crystallinity and purity of the samples. Elemental composition showed that the level of zinc influenced the water, sodium, and TPA contents of the unit cell. Scanning electron microscopy showed the morphology of the crystals changed on introducing zinc in the synthesis. Thermal analysis showed that the temperature of the TPA decomposition increased with the zinc level in the samples. Mid-infrared spectroscopy of the as-synthesized zincosilicates has shown a band at  $1084\text{ cm}^{-1}$  in addition to the band at  $1100\text{ cm}^{-1}$ . This extra band disappeared upon calcination.  $\text{NH}_3$ -TPD showed that there is probably a low concentration of only Lewis acid sites. Although no direct evidence has been obtained indicating zinc isomorphous substitution in the framework, XPS showed that zinc is homogeneously distributed throughout the crystals of zincosilicate relative to zinc impregnated silicalite-I. The presence of zinc in the pores of zincosilicates reduces the pore volume of the materials relative to that of silicalite-I.

**Keywords:** silicalite, MFI, zinc, zeolite, isomorphous substitution, physico-chemical properties, synthesis

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### INTRODUCTION

Incorporation of zinc in zeolitic frameworks and pores produces interesting materials from both the fundamental and industrial viewpoints. These materials should have interesting chemical properties because of the negative charge concentration zinc may impart to the framework structure. There is also the question of where the zinc is in the structure and its movement during post-synthesis treatment steps, as well as during the course of a catalytic reaction. The crystallization of MFI-type and TON-type zirconosilicates has been claimed in the patent literature [1]. The synthesis was carried out from hydrogel precursors containing diethanolamine as an organic template. The use of zirconosilicates having MFI-type structure has been reported for the dehydrogenation of hydrocarbons [2, 3]. Zinc impregnated ZSM-5, however, was reported for the aromatization of LPG to produce gasoline-rich products [4].

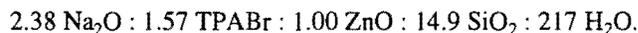
Probably the first reported synthesis of zirconosilicates having a 3-dimensional framework was that of Hesse *et al.* [5]. The material obtained had a feldspar-type structure and was synthesized hydrothermally from a hydrogel with composition of:  $\text{Na}_2\text{O} : \text{ZnO} : 3 \text{SiO}_2 : n \text{H}_2\text{O}$ . Crystallization was carried out at 1000 bar pressure and 450°C for several days. Study of the structure indicated zinc to be in a tetrahedral position. Dyer, Mehta, and McAnspine [6] synthesized zirconosilicates which appeared to be an isostructure with phase D reported by Litvin *et al.* [7]. In one study, it has been shown that incorporation of zinc in the synthesis of microporous silicates promotes the formation of three-member rings giving rise to some new structures such as those of VPI-6, VPI-7, and VPI-8 [8, 9]. The synthesis of zirconosilicate with MFI-type structure was reported from a hydrogel precursor containing tetrapropylammonium cation as an organic template [10]. The samples were shown to contain tetrahedrally-coordinated zinc oxide connected with the framework silica. However, upon post synthesis treatments, most of the zinc was dislodged from the framework.

Whether zinc resides in the framework of a zeolitic framework or in the pores of the structure, it should impart interesting catalytic properties at the intra-crystalline surface of these microporous materials. The aim of the work, reported in this paper, is to synthesize zirconosilicates of MFI-type structure and study their physico-chemical properties.

### EXPERIMENTAL

#### Synthesis of Zirconosilicate and Silicalite

In a typical synthesis procedure, 6.00 grams of zinc sulfate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) were dissolved in 50 cm<sup>3</sup> of distilled water. Dilute ammonia solution (*ca.* 10%) was added drop-wise with stirring until the pH of the solution approached 6. The formed precipitate was filtered, washed well with distilled water, and dried on the filter for approximately 15 minutes. The precipitate was added to a solution containing 3.98 grams of sodium hydroxide in 53.6 cm<sup>3</sup> of distilled water. The mixture was stirred for 15 minutes and then 8.74 grams of tetrapropylammonium bromide (TPABr) were added with stirring followed by 46.7 grams of Ludox AS40 (containing 40% by weight  $\text{SiO}_2$ ). The formed hydrogel was stirred until it became homogeneous. Its molar composition was:



The hydrogel was transferred into a 300 cm<sup>3</sup> autoclave and stirred at 175°C for 4 days under autogeneous pressure. The autoclave was then cooled to ambient temperature and the solid product filtered, washed well with distilled water, and dried at 100°C. The zinc levels in the crystalline product were varied by varying the amount of zinc incorporated in the hydrogel precursor.

Silicalite-I was synthesized as described before using the rapid crystallization method [11] and used for the preparation of zinc-impregnated materials as described below. For the purpose of comparing the crystal morphology, another batch of silicalite-I was synthesized using a hydrogel precursor with composition as close as possible to that used for the synthesis of the zirconosilicates. 3.85 grams of sodium hydroxide were dissolved in 55.0 cm<sup>3</sup> of distilled water. Whilst stirring, 8.85 grams of tetrapropylammonium bromide (TPABr) were added and when dissolved, 45.5 grams of Ludox AS40 were added. The hydrogel was stirred until it became homogeneous. The molar composition of the hydrogel was:



The hydrogel was transferred into a 300 cm<sup>3</sup> autoclave and stirred at 175°C for 4 days under the autogeneous pressure. The autoclave was then cooled to ambient temperature and the solid product filtered, washed well with distilled water, and dried at 100°C.

### Calcination and Ion-Exchange Treatments

The as-synthesized zincosilicate or silicalite was calcined in dry air at 550°C for 48 hours to remove the trapped organic template. The temperature of the furnace was raised at a rate of 50°C / hour. The sample was then given three consecutive one-hour ammonium nitrate ion-exchange treatments at reflux temperature. The concentration of the ammonium nitrate solution was 1 molar and the solid to solution ratio in the reflux mixture was 1 gram of solid per 10 cm<sup>3</sup> of solution. Finally the sample was calcined at 550°C in dry air for 18 hours to remove ammonia.

### Impregnation of Silicalite with Zinc

About 5 grams of the calcined silicalite were mixed with 20 grams of zinc acetate solution containing the correct amount of zinc acetate necessary to achieve the required zinc level. The slurry was mixed well and evaporated gradually to dryness under vacuum. The solid was then calcined at 550°C for 18 hours.

### Characterization

Samples were examined by X-ray diffraction for phase identification. The diffractometer used was a JEOL JDX3530 employing CuK<sub>α</sub> radiation from an X-ray tube operating at 40 kV and 30 mA. The instrument has a 1 degree divergence slit, 1 degree scatter slit, and a receiving slit of 0.2 mm. The scanning speed of data collection was 0.01° 2θ/step with a count time of 2 sec/step.

Crystals were characterized by a JEOL-JSM-840 scanning electron microscope. A small amount of the solid sample was mounted on a copper holder, and coated with gold evaporated under high vacuum.

Thermal analysis of samples was carried out on a Netzsch simultaneous thermal analyzer (STA-429). The reference material used was aluminum oxide (Ultrax grade Baker), and the heating rate was 10°C/min. The analyses were made over a temperature range of 20–1000°C in a dynamic atmosphere of air flowing at a rate of 100 cm<sup>3</sup>/min.

Fourier Transform Infrared (FTIR) vibrational spectra of various samples were measured to characterize zinc framework substitution. About 1 mg of zeolite sample was ground with about 300 mg of dry KBr in a small ball-mill apparatus. The fine and well-mixed powder was transferred into a die, 8 mm in diameter, and pressed for a few minutes at about 10 000 psi under vacuum. A transparent pellet was obtained by this method which was loaded into a Perkin-Elmer 16F PC FTIR. The spectra were recorded by taking 50 scans with a resolution of about 2.0 cm<sup>-1</sup> and a scan range of 450–4000 cm<sup>-1</sup>.

Bulk chemical analyses were carried by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) to determine Si, Zn, and Na levels. Sample preparation required fusion with lithium metaborate followed by dissolution in a hydrochloric acid solution.

Electron microscopy for chemical analysis (ESCA) of the samples surface was carried out using an PHI5300 X-ray photoelectron spectroscopy system (XPS) from Perkin-Elmer. It is equipped with a dual Mg/Al anode. Unmonochromated MgK<sub>α</sub> radiation (1253.6 eV) at a power output of 200 W is used under a vacuum during analysis maintained at 10<sup>-8</sup> Torr. The samples in powder form are affixed onto the sample holder with the aid of double-sided Scotch tape. The surface atomic ratios are calculated by a resident computer program [12]. The binding energy peaks were measured with reference to the C<sub>1s</sub> line at 284.5 eV.

Temperature-programmed desorption of ammonia was carried out on the calcined, ammonium ion-exchanged, and calcined samples. The procedure used was as described by the ASTM method, D-4824-88. 500.0 mg of the sample was degassed at 400°C under a continuous flow of helium gas for two hours. The temperature was raised from room temperature to 400°C at a rate of 10°C/min. The sample temperature was reduced to 100°C and ammonia gas was introduced to the sample to the point of saturation. The temperature was raised to 175°C at the rate of 10°C/min and kept

at this temperature for one and a half hours in order to remove physisorbed ammonia. Desorption was then carried out by raising the sample temperature to a temperature of 700°C at the rate of 10°C/min in a flow of helium.

## RESULTS AND DISCUSSION

Isomorphous substitution of zinc in zeolitic framework structures has been demonstrated before in the literature [5–10]. X-ray structural analysis, NMR, and synthetic conditions were presented as evidence. In one publication, zinc was shown to come out of the framework of MFI-type structure upon calcination [10].

The work reported in this paper compares the physico-chemical properties of hydrothermally-synthesized zincosilicates with silicalite impregnated to the same levels with zinc. No tangible evidence has been obtained supporting isomorphous substitution in the framework of MFI-type framework. However, some evidence is presented supporting substantial incorporation of zinc in the intracrystalline pores of the materials when zinc is incorporated in the hydrogel precursor.

Whether zinc is residing in the framework or finely dispersed in the pores of the structure, the material should have interesting properties at least from the catalytic application viewpoint. Such materials would have the zinc within the shape selective environment of the micropore structure. Characterization of zinc-impregnated samples of silicalite-I has shown zinc to be predominantly on the external surface of the crystals.

### Crystallinity

The crystallinity of the samples is examined by X-ray powder diffraction and scanning electron microscopy. Figure 1 shows the representative x-ray diffraction patterns of zincosilicates as compared with silicalite-I. The patterns show the samples to have all the characteristics of MFI-type structure. There are minor changes in the relative intensities of some peaks as expected due to the removal of the template. There is also change in the splitting of some diffraction reflection upon calcination. These changes are perhaps due to transformation from orthorhombic symmetry to monoclinic symmetry that is notable for aluminosilicates and other metasilicates with MFI-type structure [13]. In addition, there is an enhancement in the intensities of the reflections at  $2\theta = 13.9^\circ$  and  $27.5^\circ$  especially in the samples rich in zinc. The reason for this is not clear at present; however the possibilities may be (a) part of the peaks are due to impurities whose crystallinity is reduced upon calcination, or (b) the enhanced intensity is due to zinc substitution in the framework and zinc is dislodged upon calcination. These peaks have been checked against impurities such as zinc hydroxide and/or sulfate species and no correspondence has been found. No notable shift in the  $d$ -spacing values has been observed.  $Zn^{2+}$  is clearly larger than  $Si^{4+}$  resulting in a longer T–O bond when T=Zn. A corresponding shift in the  $d$ -spacing values would, therefore, be expected providing the average T–O–T angle does not change for the two materials. However, the Zn–O–Si angle is substantially smaller than the Si–O–Si angle in many structures [14], and an increase in the T–O bond length can be offset to some extent by a reduced T–O–T. In the cases of borosilicate and ferrosilicate, the difference in the unit cell size was much more clearly in favor of isomorphous substitution [15, 16].

The scanning electron micrographs are shown in Figure 2. A change in the crystal morphology is evident as zinc is introduced in the hydrogel precursor. Even with two extremely different methods of silicalite synthesis the crystal morphology is somewhat similar but substantially different from those obtained when zinc is incorporated. Figure 2a shows the morphology of the crystal synthesized using the rapid crystallization method [11]. Figure 2b shows silicalite crystals synthesized from hydrogel composition very similar to those used for the crystallization of the zincosilicates. Both samples have morphologies of slab-like. However, the crystals of the zincosilicate samples appear to have morphologies different from those of both sets of silicalite samples. The reason for these difference may be attributed to the gel chemistry associated with the presence of zinc. Zinc is an amphoteric metal and can be present in a tetrahedral environment in zeolitic framework [5–10]. Presence of zinc in the synthesis mixture is perhaps expected to form zincosilicate hydrogel and take part in the polymerization and de-polymerization reactions of the hydrogel. These compositional differences with respect to pure silica would be expected to introduce differences in the relative rates of crystallization and nucleation as well as in the growth rate of the three aspects of the crystals. These events would, in turn, give rise to crystals with different morphologies as compared with the silicalite synthesis. The scanning electron micrographs of the samples, as shown in Figure 2, show a clear change in the crystal morphology upon inclusion of zinc in the synthesis.

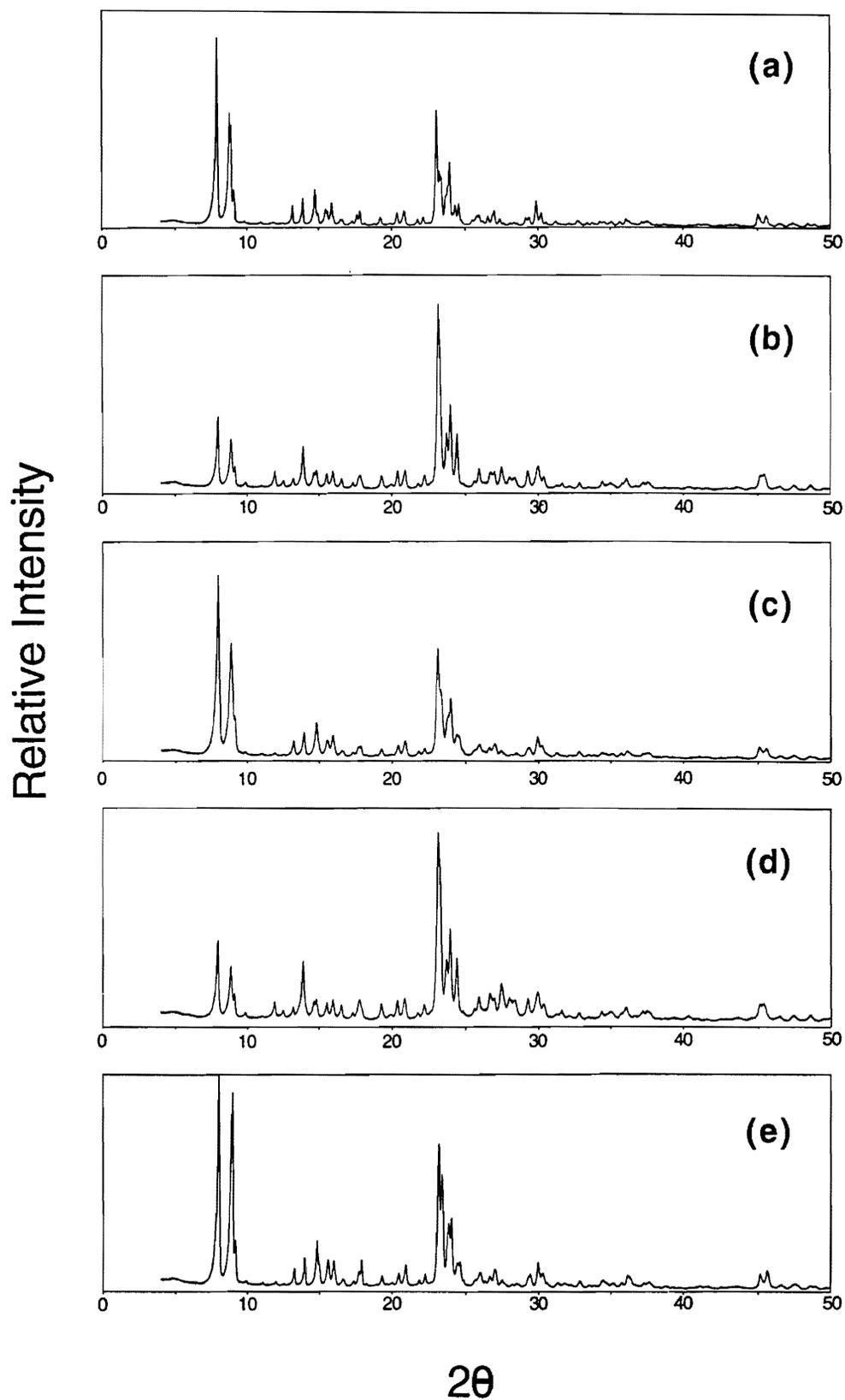


Figure 1. X-ray diffraction patterns of: (a) calcined Silicalite AS-1; (b) as-synthesized zinc-containing silicate AS-2; (c) ASZ-2 calcined; (d) as-synthesized zinc-containing silicate ASZ-4; (e) ASZ-4 calcined.

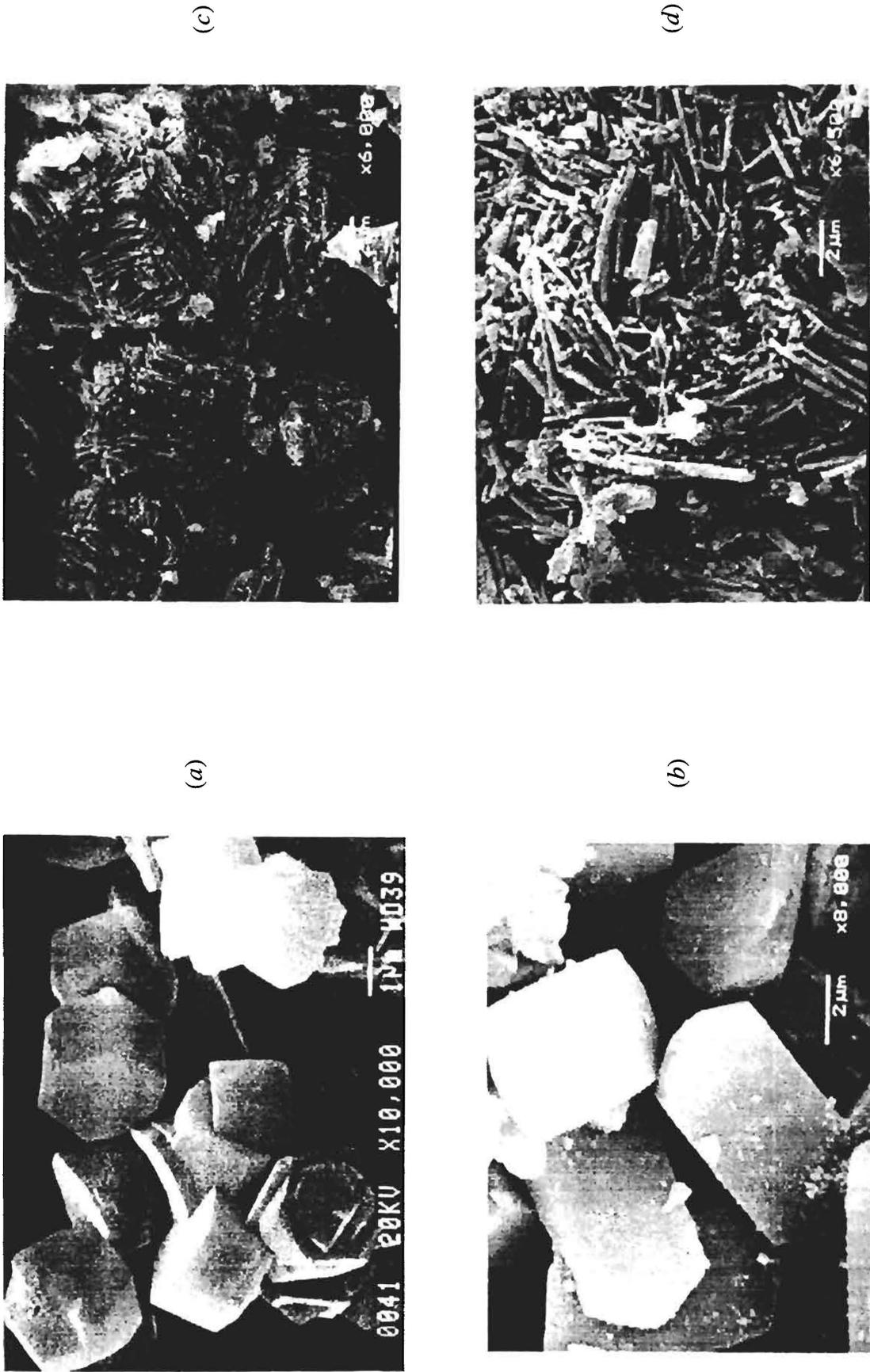


Figure 2. Scanning electron micrographs of representative crystals: (a) silicalite AS-1; (b) silicalite AS-2; (c) zincosilicate ASZ-2; (d) zincosilicate ASZ-4.

## Composition

The composition per 96 moles of  $\text{TO}_2$ , where  $T = \text{Si} + \text{Zn}$ , is given in Table 1. If all the zinc is located in the framework, the composition would be truly that of a unit cell. The sodium level seems to follow closely that of the zinc and one may assume that there are approximately two sodium ions per zinc anion species. However, the  $\text{Na}_2\text{O}/\text{ZnO}$  ratio is marginally but consistently below unity as shown in Table 1. This may be attributed to hydroxyl groups attached to the zinc and even perhaps to penta-coordinated zinc species. The water molecules per sodium cation vary within the range 1.5–1.8 molecules of water per sodium cation. The water content, however, may well be influenced by the hydrophobicity of the framework and by the presence of the varying level of template molecules. The inclusion of the tetrapropylammonium (TPA) cations in the pores is apparently a function of the zinc level, as seen in Figure 3. A similar trend has been reported for the aluminosilicate analogue of MFI zeolite [11]. In silicalite there appears to be on average 3.6 TPA molecules/uc (per unit cell) [17]. As the zinc level increases the number of TPA/uc declines reaching a value of 2.6 molecules/uc at zinc content of 7.8 zinc atoms/uc. The X-ray diffraction pattern of both materials shows high crystallinity. Therefore, the correlation of the TPA content with the zinc level may appear in the first instance to be due to (a) an increased sodium content (competing with the TPA cations) and/or (b) a corresponding decrease in the hydrophobicity of the framework. From the chemical analysis, there may be two cations required per zinc atom. Such an electrostatic position favors cations with small radius. In a competition between sodium and TPA cations, clearly sodium would be preferred at the expense of the bulky TPA cation. However, there is a third possibility that the presence of zinc in the pores (rather than in the framework) causes reduction in the pore volume available for the TPA. The effect of the zinc levels in the sample on the micro-pore volume is discussed below.

## Thermal Analysis

Figure 4 shows a representative thermal analysis profile for the zincosilicates. The thermal gravimetric analysis (TGA) profile features two stages of weight loss. The first stage is within a temperature range below  $250^\circ\text{C}$  and attributable to loss of intra-crystalline water. The second stage occurs in the temperature range  $300\text{--}500^\circ\text{C}$  and characterizes the removal of the tetrapropylammonium template. The differential thermal analysis (DTA) supports this assignment giving (a) an endothermic band below  $200^\circ\text{C}$  for the water desorption process, and (b) a relatively sharp exothermic band at a temperature in the range of  $350\text{--}550^\circ\text{C}$  for the combustion of the organic template.

Table 1. Nominal Unit Cell Composition of Zincosilicates Samples.

Sample Code	composition per 96 moles of $\text{TO}_2^*$								
	ZnO	$\text{SiO}_2$	$\text{Na}_2\text{O}$	TPA	$\text{H}_2\text{O}$	$\text{H}_2\text{O}$	$\text{Na}_2\text{O}$	Zn	TPA
						Na	ZnO	Si	Si
AS-1**----	96.0	1.1	3.6	7.2	----	----	----	0.038	
AS-2***	----	96.0	0.5	3.8	6.9	----	----	----	0.040
ASZ-1	2.6	93.4	2.3	2.7	7.4	1.6	0.88	0.028	0.039
ASZ-2	3.4	92.6	3.3	3.2	12.0	1.8	0.87	0.037	0.037
ASZ-3	4.0	92.0	3.5	3.7	20.6	2.9	0.88	0.043	0.031
ASZ-4	6.0	90.0	5.4	2.7	15.7	1.5	0.90	0.067	0.030
ASZ-5	7.8	88.2	6.9	2.6	20.2	1.5	0.89	0.088	0.030

\*T is a tetrahedral atom in the framework either Si or Zn. This assumes an ideal case where all the zinc is isomorphously substituted in the silicalite framework.

\*\* Synthesized by the rapid crystallization method [10].

\*\*\* Synthesized by the same method used for the zincosilicates without adding any zinc.

The peak position of the exothermic band of the DTA shifts to a higher temperature with increasing zinc content of the zincosilicate. The temperature of the peak maximum is plotted against the zinc content in Figure 5. It has been reported before that the temperature of template decomposition for metal substituted MFI-type molecular sieves is higher than that of silicalite-I [18]. This correlation between framework Si/M ratio (where M is an isomorphously substituting metal) and the decomposition temperature of the TPA template does not necessarily provide an indirect evidence for metal substitution. One has to consider, for example, the interaction of the TPA or its decomposition product with non-framework metal. Non-framework zinc is a well-known Lewis acid and thus has hydrogen or hydride acceptor properties. Another factor may be just a concentration effect. Figure 3 shows that the TPA content decreases with increasing zinc. Higher concentration of TPA is likely to create higher intensity of combustion leading to total combustion at a lower applied temperature. Pore blocking may well also be a reason for the higher temperature of combustion.

### Mid-Infrared Spectroscopy

Mid-infrared spectroscopy has been employed before to verify the isomorphous substitution of amphoteric metals such as gallium and iron in the framework of silicalite [17–21]. Shifts in the asymmetric vibrations band at  $1100\text{ cm}^{-1}$  have been observed and taken as indication of substitution of the metals. As seen in Figure 6, there is a new band appearing at  $1084\text{ cm}^{-1}$  (in addition to the band at  $1100\text{ cm}^{-1}$ ) and one may take this as a possible indication of isomorphous substitution. The band claimed for titanium substitution is at  $960\text{ cm}^{-1}$  and since zinc is heavier than titanium, a lower wavenumber would be expected for zinc substitution. Le Fèvre *et al.* [21] have suggested that variation in the position of the bands around  $1100\text{ cm}^{-1}$  can be best ascribed to difference in the crystal size. In this work, however, the extra band disappears upon calcination at high temperature, as seen in Figure 6, suggesting that it is not related to the crystal size or morphology.

### $\text{NH}_3$ -Temperature-Programmed Desorption (TPD)

Figure 7 shows the  $\text{NH}_3$ -TPD profiles of all the hydrothermally crystallized zincosilicates. As seen, all the samples are characterized by single peaks at approximately  $260^\circ\text{C}$ . These may be attributed to the presence of Lewis acid sites which demonstrates the absence of Brønsted acidity. The total levels of ammonia adsorbed are very low, ranging from 0.090 to 0.130 mmole/g, increasing consistently with the level of zinc. This data is in agreement with the conclusions drawn above about the existence of the zinc in the pores as a non-framework species.

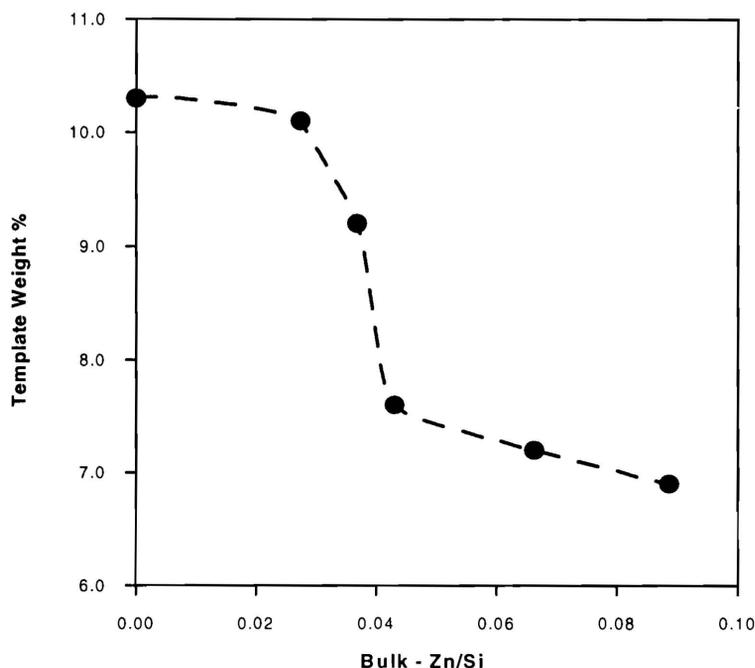


Figure 3. Content of tetrapropylammonium cation as a function of bulk Zn/Si ratio.

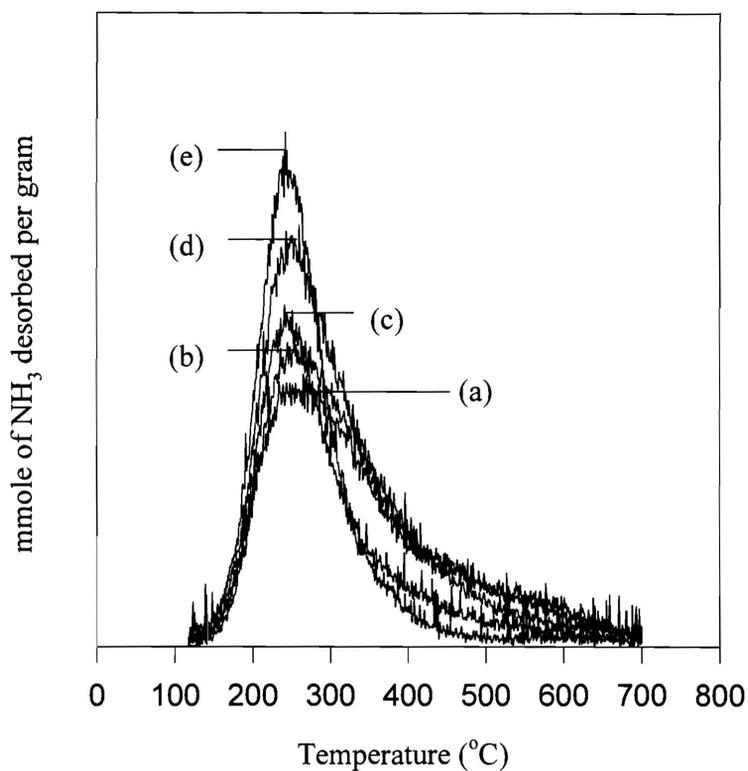


Figure 7  $\text{NH}_3$ -TPD profile of: (a) ASZ-1; (b) ASZ-2; (c) ASZ-3; (d) ASZ-3; (e) ASZ-5.

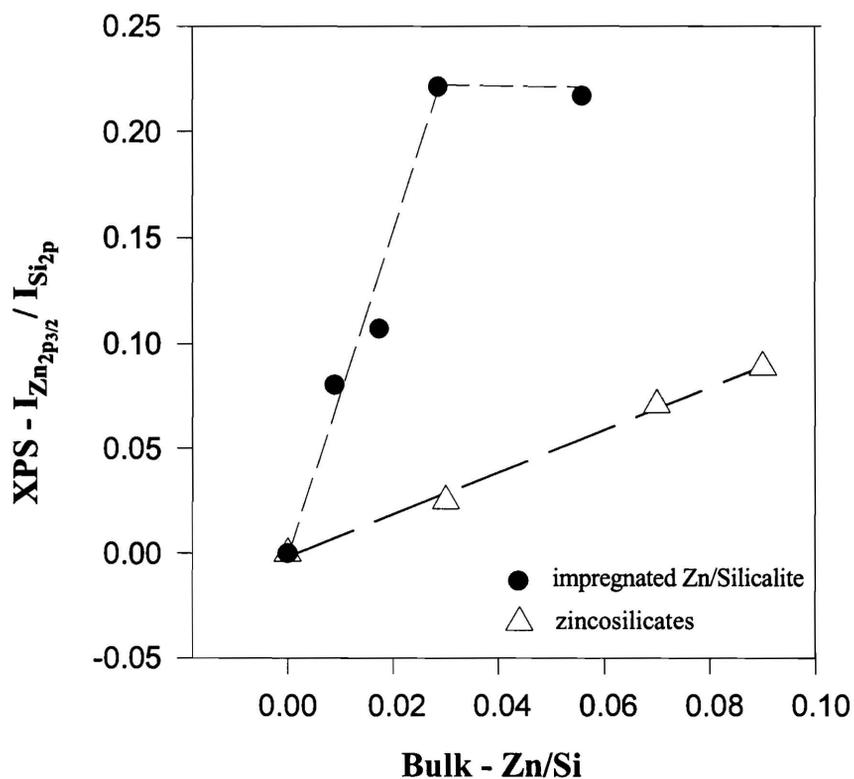


Figure 8. Surface Zn/Si ratio as determined by XPS as a function of the bulk Zn/Si.

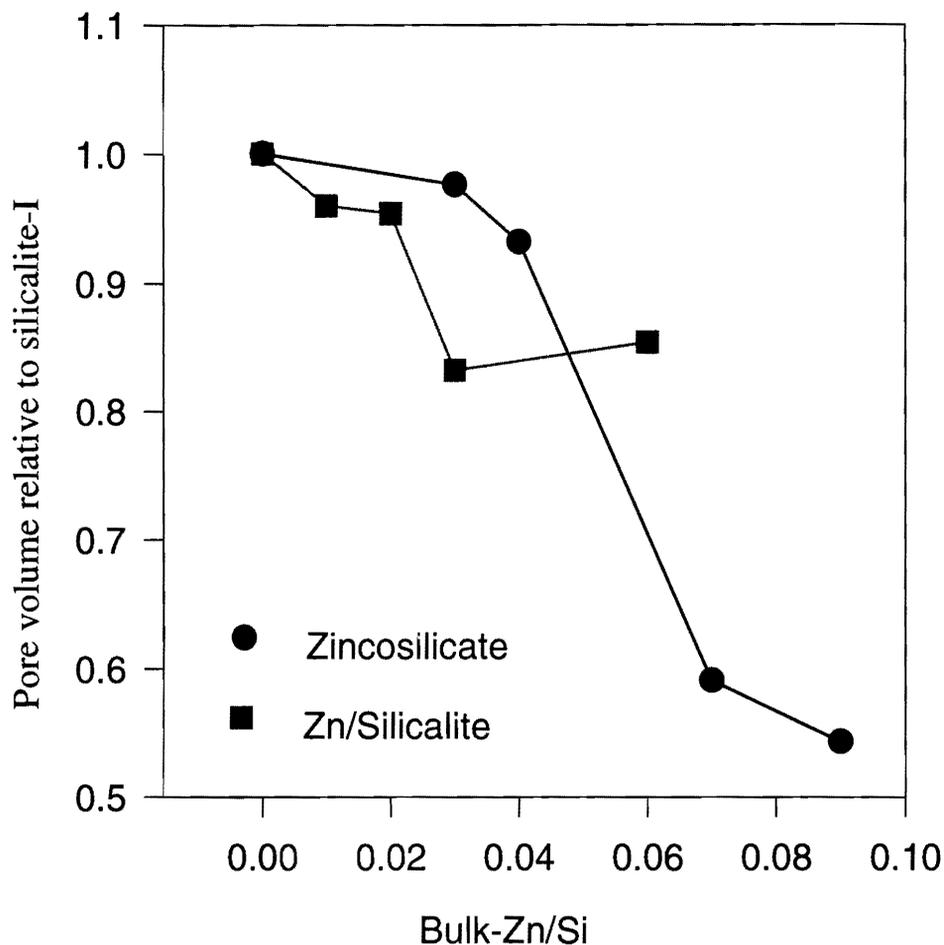


Figure 9. Pore volume of the calcined zincosilicates relative to silicalite as a function of Zn/Si ratio

### Intracrystalline Pore Volume (PV)

The relative intracrystalline pore volumes (PV) of the zincosilicates and the zinc impregnated silicalite samples are shown in Figure 9. The values of the PV are normalized relative to unmodified silicalite sample whose PV is  $0.21 \text{ cm}^3/\text{g}$ . It is quite clear from Figure 9 that incorporation of zinc reduces the PV of the samples. In case of the zincosilicates in particular, more than 40% of the pore volume is reduced when increasing the Zn/Si ratio from zero to 0.10. The reduction in PV is most probably caused by the presence of non-framework zinc in the intracrystalline pores of the samples. The relationship of the pore volume and Zn/Si ratio is progressively downward confirming the conclusion of the XPS that zinc is probably homogeneously distributed and most of which is probably present as non-framework species.

### CONCLUSIONS

There is strong indirect evidence for the homogeneous distribution of zinc throughout the structure in the case of the hydrothermally synthesized zincosilicates, compared with zinc impregnated silicalite. Substitution in the framework of the MFI-type structure, however, has not been proven. Characterization of the hydrothermally synthesized materials with varying zinc levels shows that there are significant and continual changes in the properties of the materials as more zinc is introduced. The crystal morphology changes substantially with increasing zinc level, indicating some influence of the presence of zinc on the hydrogel chemistry. Mid-infrared spectra shows a band at  $1080 \text{ cm}^{-1}$  for the as-synthesized zincosilicates that disappears upon calcination. XPS shows zinc to be homogeneously distributed throughout the crystal,

with the surface concentrations of zinc being very close to those of the bulk. Thermal analysis of the template de-composition is consistent with the presence of zinc in the pores of the structure if not substituted in the framework.

The pore volume of the structure decreases with increasing zinc levels, while crystallinity is maintained as evidenced by X-ray powder diffraction. This has been attributed to the presence of the zinc in the micropore structure and seems to be entirely consistent with the XPS data. Acidity characterization by NH<sub>3</sub>-TPD has shown evidence for the presence of dilute Lewis acidity.

If zinc has been, indeed, substituted in the framework, the material would have interesting properties. Zinc has an oxidation state of 2, which would have the effect of introducing a higher anionic charge (two negative charges per zinc atom) to the framework structure than in the case of aluminosilicates. However, what appears more likely is that zinc resides in the intracrystalline pores of the structure at least in the calcined samples. The presence of zinc within the shape selective pore structure of silicalite should give some interesting catalytic properties.

## ACKNOWLEDGEMENTS

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