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Enthalpy change and temperature of the reversible monoclinic-orthorhombic phase transition in MFI type zeolitic materials

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Abstract

Calorimetric investigations show that the enthalpy change corresponding to the reversible and displacive monoclinic ($P2_1/n.1.1$)↔orthorhombic (Pnma) solid state phase transition in MFI type zeolitic materials presenting several Si/Al ratios is very sensitive versus the framework aluminum content. For $\approx 0.01 < \text{Al/uc} < 4.57$ the enthalpy change ΔH corresponds to $18.3 > E > 1.8$ kJ/mol. ΔH rapidly decreases with increasing Al content and the transition temperature T_t for strictly anhydrous materials is always above 50°C. In the case of air-equilibrated phases, the extra-framework water content increases with Al/uc and beyond $\approx 1.3 - 1.4$ Al/uc T_t is below 20°C. T_t is also sensitive versus the nature and the amount of sorbed or encaged guest molecules (e.g., water, aliphatic and aromatic hydrocarbons).

Keywords: MFI zeolites; silicalite; ZSM-5; Calorimetry; ^{29}Si *mas*NMR; X-Rays

1. Introduction

Zeolites presenting the MFI [1] topology (silicalite, ZSM-5 and post-synthesis modified phases) are microporous materials widely investigated and commercially used because of their shape-selective, adsorptive and/or catalytic properties. The unit cell (*uc*) content of an ammonium exchanged, calcined and evacuated H_x·ZSM-5

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material corresponds to the $H_xAl_xSi_{96-x}O_{192}$ chemical composition. The proton concentration, which depends on the Si/Al ratio (usually $0 < x < 8$), corresponds to the Brönsted acidity. It has been reported that for lower aluminum contents ($x < 1.2$–1.4 Al/uc) the calcined MFI material exhibits a reversible monoclinic ($P2_1/n.1.1$)↔orthorhombic (Pnma) solid state phase transition [2]. This transition has been investigated by variable temperature X-ray powder diffraction on a ZSM-5 material [3] and on highly crystalline silicalite [4]. In ref. [4] it has been shown that the displacive and reversible polymorphism of silicalite, which is very *progressive*, is spread over the 20-83°C temperature range, which is rather rare for a solid state phase transition. Koningsveld et al. have shown that the monoclinic form of H·MFI is *ferroalastic* [5]. Very little is presently known on the energetics of this transition: the only work dealing with the subject is reported by Endoh [6]. The present work has been undertaken in order to get a better knowledge of the energetics of the monoclinic-orthorhombic phase transition in a series of H·MFI materials corresponding to the $\approx 0.01 <$ Al/uc < 4.57 range.

2. Experimental

The source, aluminum content and Si/Al ratios of the H·MFI materials investigated in the present work are reported in the Table. The parent S115 zeolite from Union-Carbide™ has been dealuminated (water vapor steaming at 850°C) for 1 day ($S115W_1$ sample) and 10 days ($S115W_{10}$). The $S115W_{10}$ sample has further been dealuminated one day in boiling concentrated nitric acid ($S115W_{10}N$ sample). Samples 2, 3, 8 and 9 have been sythesized in fluoride medium with a templating TPAF (tetrapropylammonium fluoride) agent [7]. Samples 5 and 7 were obtained from Conteka™ (Sweden) and sample 10 was synthesized in a templateless alkaline medium [8]. The enthalpy and temperature changes were determined by using a Mettler™ TA 2000 B type differential scanning calorimeter (DSC). Calibration for temperature and heat flow determination was carried out using the melting point and heat of fusion of high purity metals and solids [9]. It is well established that the sorption of organic molecules and/or atmospheric water drastically influences the framework structure of H·MFI materials [10–13]. Accordingly, all the DSC experiments have been run in *strictly anhydrous* conditions: for each sample, the first two heating/cooling runs ($0.166/0.083°C s^{-1}$ rate) correspond to thermal cycles in the $-100 < T < 350°C$ temperature range in a dry nitrogen flow; the third *heating* corresponds to the effective DSC run from which the enthalpy change has been computed. The ^{29}Si *mas*NMR spectra were recorded on a Bruker™ MSL-300 spectrometer. The variable temperature step-scanned X-ray powder diffraction profiles were recorded on a Philips™ diffractometer as already reported in [4]. The presently investigated solid phases were selected among a collection of about eighty MFI materials. Among those, ten samples presenting the following two criteria were selected: (a) -*sharp* and well-defined X-ray diffraction peaks and a *flat* background (no characteristic bumps corresponding to nanocristalline material or partial amorphisation; (b) -room temperature *p*-xylene sorption isotherms corresponding to a two-step mechanism: a first plateau at *exactly* four molecules/uc and a second one at saturation for *exactly* eight molecules/uc as in

Table 1
Source, aluminum content and Si/Al ratio of the H·MFI materials investigated in this work

H·MFI	Al/uc	Si/Al	origin of the zeolite
1a S115W$_{10}$N	≈0.01	> 10000	S115 steamed 10 days + boiling HNO_3
1b S115W$_{10}$			S115 steamed 10 days
1c S115W$_1$			S115 steamed 1 day (850°C)
2 SILMUL	≈0.02	≈5000	fluoride medium [7]
3 F328	≈0.02	≈5000	fluoride medium [7]
4 Endoh's sample	0.15	639	cited in [6]
5 CBV1	0.60	160	Conteka
6 *parent* S115	0.72	132	Union-Carbide
7 CBV2	1.32	72	Conteka
8 F802	2.34	40	fluoride medium [7]
9 F669	3.84	24	fluoride medium [7]
10 K53	4.57	20	without template, alkaline medium [8]

[14, 15]. These two criteria insures a high cristallinity and the absence of any extra-framework species (e.g., cations, defects, octahedral Al) in the starting MFI (silicalite, H·ZSM-5) material.

Results and Discussion

Selected DSC curves corresponding to samples 1a, 2, 3, 6 and 9 (see the Table) are shown in Fig. 1. Interpretation of these curves and of those corresponding to the remaining samples (except 1b and 1c) yield the variations of transition temperature T_t (°C) and enthalpy change ΔH (kJ/mol) versus aluminum content, represented in Fig. 2.

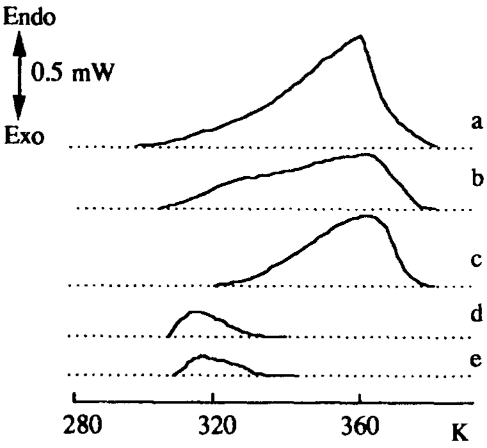

Fig. 1. Experimental DSC curves corresponding to some *anhydrous* H·MFI materials presenting several Si/Al ratios (see the Table): (a) S115W10N- (b) SILMUL- (c) F328- (d) F669- (e) parent S115.

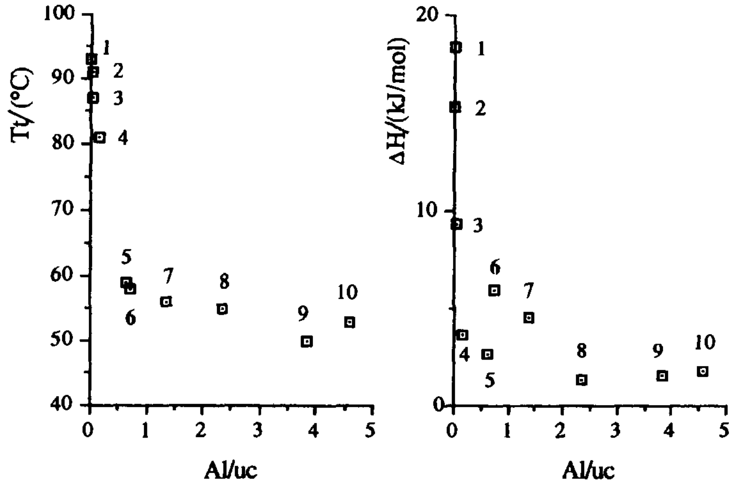

Fig. 2. Temperature and enthalpy change observed for the reversible monoclinic-orthorhombic phase transition in *anhydrous* H·MFI materials versus aluminum content of the zeolitic framework.

This figure includes Endoh's result [6]. The general shape of the thermal effect is compatible with a ferroelastic solid state phase transition. Such thermal effects occuring in rather large temperature ranges have already been observed in the case of rare-earth pentaphosphates [16]. The temperatures reported in Fig. 2 are determined at the maxima of the thermal effects and the numbering of the experimental points corresponds to the *anhydrous* samples reported in the Table. It is clearly observed that T_t and ΔH drastically decrease with increasing aluminum content in the H·MFI material. Nevertheless, the temperature is always above 50°C; in other words, at room temperature all anhydrous H·MFI temperature is always above 50°C; in other words, at room temperature all anhydrous H·MFI phases correspond to the monoclinic polymorph. As soon as the zeolitic material is in contact with atmospheric water T_t decreases, and for Si/Al ≈ 100 the room temperature form corresponds to the orthorhombic polymorph.

Solid state NMR investigations have shown that the line-broadening of the ^{29}Si *mas*NMR peaks depends on the Si/Al ratio in zeolitic materials [10, 11]. Some NMR spectra corresponding to the presently investigated samples are represented in Fig. 3. The highly resoluted profile at the top of the figure has been reported in [11]. The asymmetric unit in the crystal structure of the monoclinic MFI polymorph contains 24 independent silicon atoms [5]. Accordingly, the ^{29}Si *mas*NMR spectrum should exhibit 24 peaks. Numerical desummation and simulation techniques performed on the observed NMR profiles shows that all the spectra correspond to the superposition of the same 24 elementary peaks of increasing width at half maximum.

The results reported in Figs. 2 and 3 show that the phase transition temperature, the enthalpy change and the NMR peak line-broadening are in correlation with the Si/Al ratio. It must be emphasized that these correlations hold only if the investigated solids

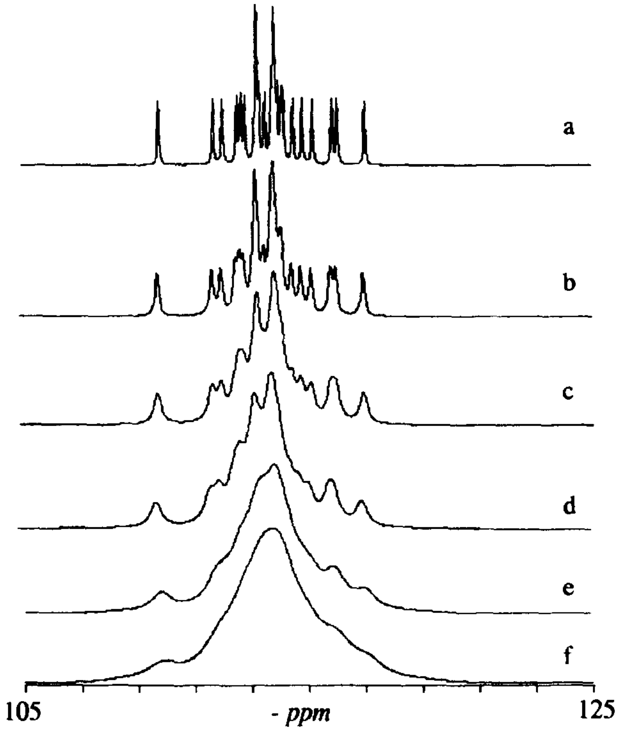

Fig. 3. Experimental line broadening in the ^{29}Si *mas*NMR spectra corresponding to H·MFI materials presenting several Si/Al ratios. (a) Highly dealuminated silicalite, see [11]- (b) water steamed (10 days) S115 further dealuminated in boiling nitric acid- (c) calcined silicalite, see [7]- (d) water steamed S115 for 10 days- (e) water steamed S115 for 1 day- (f) initial parent S115 sample (Si/Al = 132).

are in their strictly *anhydrous* form. In order to illustrate this point, the effects of benzene and atmospheric water adorption on the crystal structures of some H·MFI phases are reported in Fig. 4.

Two selected experimental X-ray diffraction profiles (22–25 °2θ domain) corresponding to the F669 sample (Si/Al = 24) for its benzene loaded (4 molecules/uc) and water saturated ($\approx$ 28 molecules/uc) forms are represented in Fig. 4 (a) and (b) respectively. The arrows clearly reveal that the broader peak corresponds to the benzene loaded sample. Profile simulation techniques and subsequent structure refinements (Rietveld method) show that for up to four benzene molecules/uc the structure of the zeolite is single-phased and monoclinic, whereas the water saturated sample exhibits the orthorhombic form.

The selected X-ray diffraction traces (12.5–18.5 °2θ domain) represented in Figs. 4 (c) and (d) compare the observed profiles corresponding to the hydrated (bold lines) and anhydrous forms of two H·MFI phases presenting different Si/Al ratios. In both cases the anhydrous samples present the monoclinic structure. The crystal structures of the

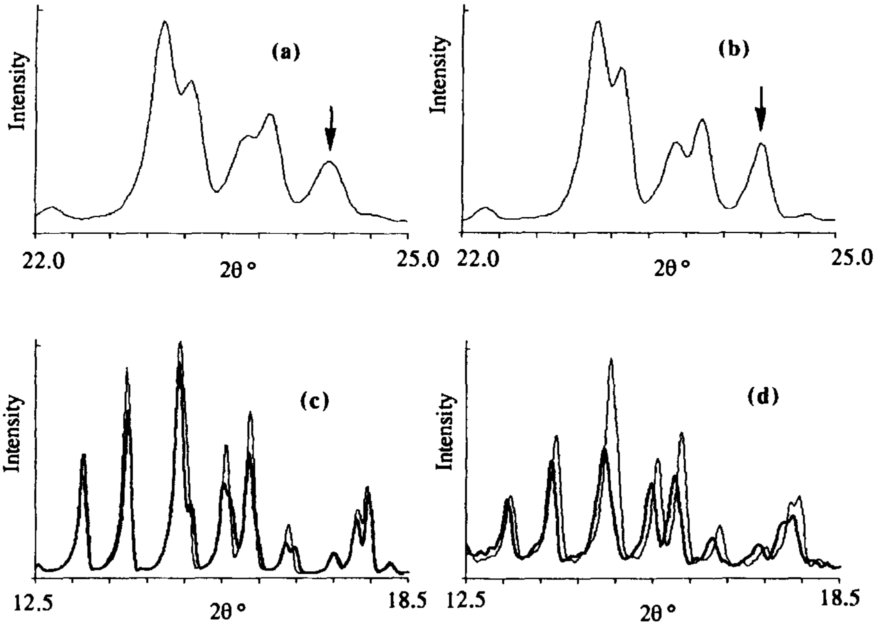

Fig. 4. Influence of benzene and atmospheric water absorption on selected X-ray diffraction profiles. (a) H·MFI/4benzene complex (Si/Al = 24)- (b) its hydrated form- (c) the hydrated (bold line) and anhydrous H·MFI phase for Si/Al = 132- (d) the same for Si/Al = 20.

hydrated phases corresponding to the S115 (Si/Al = 132) and K53 (Si/Al = 20) zeolites are monoclinic and orthorhombic respectively.

Conclusions

The present work shows that in strictly anhydrous conditions, the temperature of the reversible monoclinic-orthorhombic polymorphic phase transition corresponding to *all* the investigated H·MFI samples takes place above 50°C. This transition temperature (T_t) and the associated enthalpy change (ΔH) are strongly correlated. It must be emphasized that although the investigated samples correspond to different sources (see the Table), the results represented in Figs. 1, 2 and 3 are very coherent. ΔH and T_t drastically increase when the zeolitic material is highly dealuminated and corresponds to a *critical* aluminum concentration which might be estimated around 0.5 Al/uc (Si/Al $\approx$ 190), *i.e.*, one Al atom in two MFI unit-cells ($\approx$ 10700 Å^3). The unit-cell parameters of the monoclinic polymorph of silicalite are a(Å)/b/c/α(°) = 20.1007(9)/19.8721(9)/13.3646(7)/90.616(4) [17], and if we assume that the aluminum atoms are distributed over a minimum number of sites, the estimated mean Al... Al distance is (a + b + c)/3 $\approx$ 35.6Å, which is far beyond the usual short and medium range van der Waals interactions ($\approx$ 10Å). In that case only residual Coulombic charges corresponding to long range interactions might be considered. Nevertheless, given that the exact aluminum distribution in the zeolitic framework of the MFI phases is not known, no definitive interpretation for the existence of the observed critical Si/Al ratio can presently be proposed.

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