



# STRUCTURAL CHARACTERIZATION OF THE FORMATION OF SAPO-34 FROM A LAMELLAR ALPO-KANEMITE PRECURSOR

Experiment  
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Names and affiliations of applicants (\* indicates experimentalists):

**M. Milanesio<sup>a,\*</sup>, G. Croce<sup>a</sup>, A. Frache<sup>a,\*</sup>, L. Marchese<sup>a,\*</sup>, D. Viterbo<sup>a</sup>, M. Cadoni<sup>a,\*</sup>, E. Boccaleri<sup>a</sup>, H.O. Pastore<sup>b</sup>, A. Albuquerque<sup>b</sup>**

<sup>a)</sup> Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale, Via Bellini 25/G, 15100 Alessandria, Italy; FAX: + 39 0131 287416; Tel.: + 39 0131 287414.

<sup>(b)</sup> Instituto de Química, Universidade Estadual de Campinas, CP 6154, CEP 13084-971, Campinas, SP, Brasil; FAX: + 55 19 3788 3023; Tel.: + 55 19 3788 3095.

## Introduction

H-SAPO-34 is a microporous molecular sieve analogous to natural chabazite (IZA structure code CHA).<sup>1</sup> Bronsted acidity guarantees that this material can be used for acid-catalysed reactions, such as methanol-to-olefins conversion.<sup>2</sup> Standard syntheses of SAPO-34 can be carried out either in the presence or in the absence of HF but always start from an amorphous gel [SAPO-34(*gel*)]. An NMR and XRD study of the kinetics of SAPO-34 formation in the presence of HF<sup>3</sup> indicated that intermediate layered phases are formed during the crystallization of the gels. Recently we were able to prepare new molecular sieves (named CAL-1 and CAL-2<sup>4,5</sup>) with chabazite-type structure, starting from a lamellar aluminophosphate,<sup>6</sup> hereafter named named ALPO(*kan*), structurally similar to silica kanemite.<sup>7</sup> Hexamethyleneimine (HMI) was added to ALPO(*kan*) as structure directing agent (SDA) to obtain this new isotype. When morpholine was used instead of HMI, SAPO-34 was directly produced [SAPO-34(*kan*)].

## Results

A *ex situ* high resolution X-ray powder patterns (XRPD) was carried out collecting data on samples of a starting mixture of composition [2 ALPO(*kan*): 0.4 SiO<sub>2</sub>: 1.5 HMI: 50 H<sub>2</sub>O], reacted for different times (3 h, 12 h, 24 h, 48 h) at 460 K in hydrothermal conditions<sup>4</sup> (Figure 1). After 3 hours reaction, the ALPO(*kan*) material is already slightly changed while after 12 hours, the CAL-1 structure is essentially formed. After 48 hours reaction the X-rays diffraction pattern contains signals of both trigonal and triclinic chabazite-type structure. When morpholine (MOR) is used as SDA, again a mixture of trigonal and triclinic phases is obtained. The thermal treatment causes the removal of the organic molecules and the formation of a pure trigonal SAPO-34 phase ("calcined SAPO-34" in figure 1). It is worth noting that no amorphous phases are detected during the whole reaction and this seems to indicate that the rearrangement of the solid is taking place at a local molecular level. Therefore, the process involves a solid state

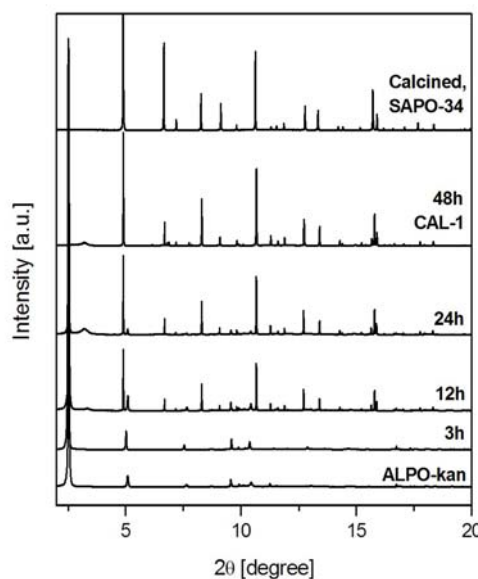


Figure 1: XRPD patterns of materials obtained after different reaction times with HMI in the starting mixture.

phase transition from bidimensional lamellar ALPO(*kan*) to a tridimensional zeolitic phase (CAL-1). The analysis of the XRPD pattern after 48 h reaction (Figure1b) allowed the determination of CAL-1 lattice parameters and crystal structure.<sup>4,5</sup> The Rietveld refinements of the collected data, in addition, allowed a structural characterization of the intermediate phases. Table 1 shows the lattice parameters of CAL-1 and those of SAPO-34-related materials containing different SDA molecules and obtained with different synthesis strategy. SAPO-34(*kan*) and SAPO-34(*gel*) show very similar lattice parameters, thus suggesting that the preparation route does not influence significantly the crystal structure, although the resulting morphology is very different. Conversely, the presence of HMI in CAL-1 causes structural rearrangements likely due to the different size and shape of the SDA.

Table 1: Lattice parameters of as made CAL-1 and SAPO-34 (*kan*) compared to a SAPO-34 from *gel*.<sup>8</sup>

Material*	SDA	a=b	c	Volume
CAL-1	HMI	13.702(2)	15.132(2)	2460(1)
SAPO-34 ( <i>kan</i> )	MOR	13.737(2)	14.968(4)	2446(1)
SAPO-34 ( <i>gel</i> )	MOR	13.782(1)	14.873(1)	2446.4(4)

\* SAPO-34(*kan*) = SAPO-34 prepared from ALPO(*kan*), SAPO-34(*gel*) = SAPO-34 prepared by conventional methods from aluminum hydroxide and phosphoric acid.

## Conclusions

The cell parameters of the trigonal CAL-1, a CHA-type molecular sieve, were obtained and compared to those from SAPO-34 samples obtained by different synthesis strategies. A triclinic polymorph of CAL-1 has been also detected. *Ex situ* high-resolution synchrotron X-ray powder diffraction experiment allowed to monitor the relevant steps of the ALPO(*kan*) to CAL-1 reaction and the CAL-1 calcination to H-SAPO-34. After 3 h reaction, the ALPO(*kan*) is only slightly changed whereas after 12 h the CAL-1 phases begins to appear. After 24-48 h reaction (depending on the synthesis conditions) the X-rays diffraction pattern contains signals of both trigonal and triclinic CAL-1, the trigonal phase being predominant. Amorphous phases were not detected during the *ex situ* XRPD study of the ALPO(*kan*) transformation into CAL-1.

The Rietveld refinement of the intermediate steps of CAL-1 crystallization is useful to shed some light on the kinetics of this solid state reaction. Nevertheless the *ex situ* approach might introduce a bias in the experiment, since some phase (amorphous or crystalline) could be modified and/or lost during the washing, filtration and drying, needed to prepare the samples for the XRPD analysis, after extraction from the reactors. Besides the XRPD techniques has some know limitation in detecting small changes of the organic molecules employed as SDA in the crystallization. Therefore we intend to carry out an *in situ* combined RAMAN/HR-XRPD study of CAL-1 crystallization<sup>9</sup> for a full comprehension of the kinetics of this reaction.

**Publication:** A short communication has been submitted on January 2005 to *Studies in Surface Science and Catalysis*. A full paper reporting the structural analysis, by Rietveld refinement, of the intermediate step of CAL-1 crystallization and of the CAL-1 crystal structure (a novel chabasite-type material) is under development.

## References

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