Electron microscopy characterization of ferrisilicates synthesized with two different silicon sources

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Ferrisilicates have been synthesized by isomorphous substitution of Al by Fe using two silicon sources, to determine the influence of the silicon nature. The X-ray results are similar to that of ZSM-5 zeolite, but SEM and TEM show that the samples are different.

Keywords: Ferrisilicate; synthesis; silicon sources; characterization

1. Introduction

Iron supported on silica alumina is an active and flexible catalyst for the conversion of synthesis gas to hydrocarbons and water [1]. ZSM-5 zeolite was also used in the conversion of methanol to "gasoline range" hydrocarbons with high yield [2,3]. Mobil researchers tested the ability of ZSM-5 to control the products of the Fischer–Tropsch (FT) reaction by reacting CO and H_2 over the physical mixture of catalytically active iron and ZSM-5 powder [4,5] and the results were very promising. Researchers from all over the world have been trying to optimize the distribution of iron inside the ZSM-5 channels in order to produce a better FT catalyst [6–9]. Synthesized zeolites with structures containing cations other than Si^{4+} and Al^{3+} at the framework sites are gaining in importance because of their interesting catalytic and structural properties. The catalytic interest of these materials arises from the positive influence of the heteroatoms on the fine-tuning of the strength of the acidic sites and also from introducing a bifunctional nature to the catalyst [10]. For example, incorporation of iron includes hydrogenation centres in the catalyst and reduces the number of superacid sites.

The isomorphous substitution of tetrahedral aluminium in the zeolite structure with catalytically active elements such as iron [11–17] results in ferrisilicate material which comprises a class of molecular sieves in which only Si and Fe occupy tetrahedral framework sites [18]. It has been shown [19,20] that iron can simultaneously be present in the aluminosilicate framework sites and as oxides of Fe precipitated on the zeolite crystals [21]. These new materials have different catalytic acidities [11,17,22] which lead to altered activity, selectivity and stability [23]. The structural interest is justified because the isomorphous substitution modifies the pore size and hence the shape selectivity. Higher aluminium content in the ZSM-5 framework is also known to decrease the transition temperature of the monoclinic to orthorhombic phase change. Isomorphous substitution of iron in the MFI framework (Mobil FIve, ZSM-5 type zeolites) is well established [24–26], and the Fe substitution for Si results in the normal Brønsted acid sites due to the compensation of the negative charge on Fe induced by its tetracoordination [27]. This induced acidity is of rather moderate strength and results in catalytic activity for methanol conversion and the toluene alkylation reaction [27].

Iron can be substituted during synthesis into the tetrahedral framework sites of a molecular sieve structure [9,11,12,14]; however, the amount of iron incorporated and the purity of the resulting zeolite depends on the conditions of synthesis [9,28]. The quantity of silica which reacts with Fe depends on the polymerization grade of the silicon source; it has been reported [29] that silica with short chain is the more effective to synthesize these materials. In this paper we present the results of the characterization of ferrisilicates synthesized using the template method but with varying silicon sources: one of colloidal nature and the other one in powder form. The characterization techniques used were X-ray diffraction and scanning and transmission electron microscopy.

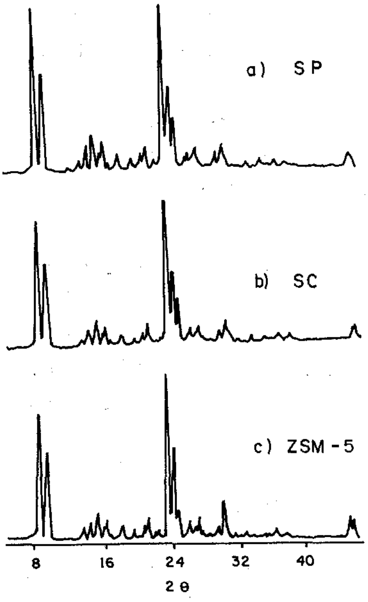

Fig. 1. X-ray diffraction patterns for (a) PS and (b) CS samples, with the pattern corresponding to ZSM-5 zeolite in (c).

2. Experimental

The samples were synthesized by the template method [30], using two different silicon sources: one of colloidal nature (Ludox As) and the other one in powder form. The metal source was $Fe(NO_3)_3 \cdot 9H_2O$. Ammonium hydroxide, TPA-Br was the template and the Si/Fe ratio was ≈ 30.0. The synthesis of the sodic form (Na-FeZSM-5) was carried out under hydrothermal conditions at 190°C for 24 h. Acidic ferrisilicates were obtained by ionic exchange at ambient temperature using a 1 M solution of NH_4NO_3. The resulting NH_4-FeZSM-5 product was calcined to 500°C in a static air atmosphere yielding a H-FeZSM-5 solid of yellow color when the silicon source was in powder form, and of white color from the colloidal silicon.

The resulting samples were characterized by X-ray diffraction using a Siemens D500 diffractometer, and by electron microscopy in scanning and transmission modes, with the electron microscopes Jeol JSM-85 and Jeol 100CX, respectively. Electron microscopy plays an important role in the physical characterization of these catalysts, since scanning electron microscopy is used to characterize their morphologies and transmission electron microscopy is used for the identification

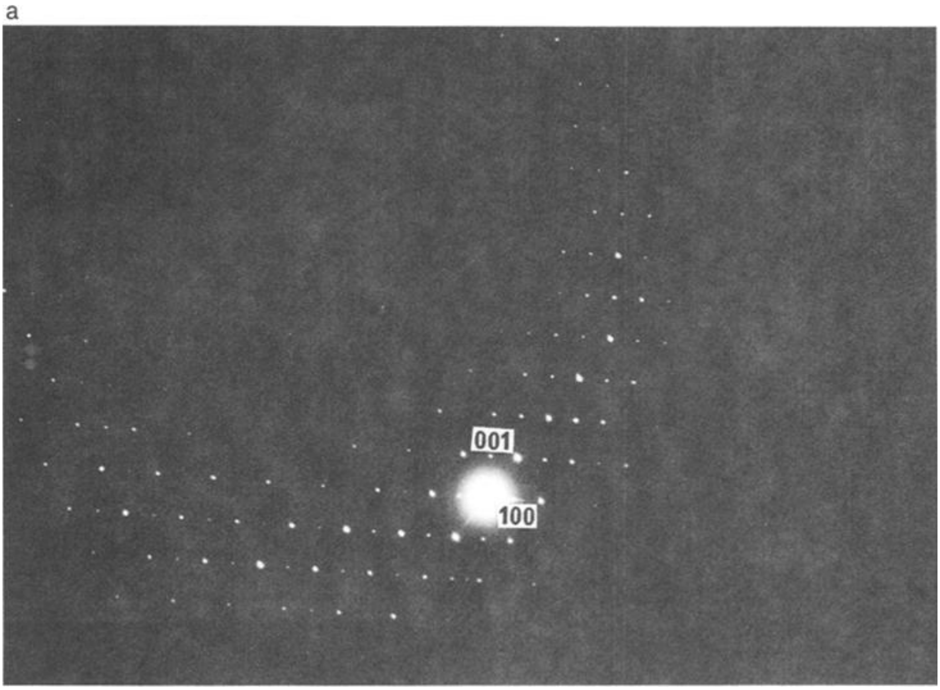

Fig. 2. Electron diffraction pattern for the CS sample with zone axis [010] and indexed as ZSM-5 zeolite (a), and for the CS sample with zone axis $[2\bar{4}5]$ and indexed as ZSM-5 zeolite (b).

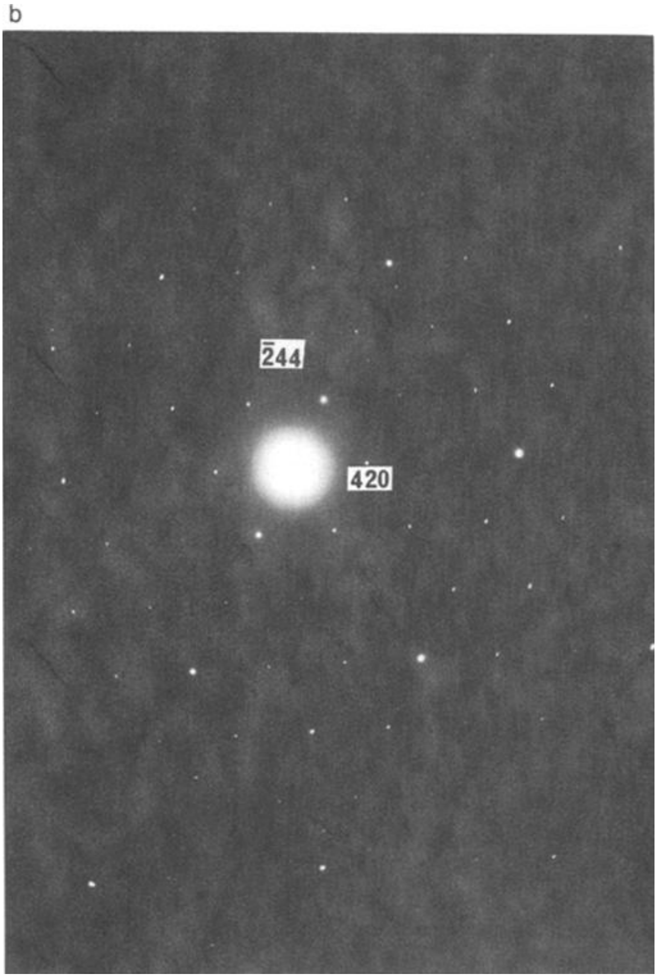

Fig. 2 (continued).

of the phases present in each sample. Characterization by X-ray diffraction ensured that the same phases were actually present in the bulk materials.

3. Results and discussion

The two samples of solid ferrisilicate type zeolite obtained as result of the synthesis with two different silicon sources were examined by X-ray diffraction. Fig. 1 shows the diffraction patterns of these two preparations. The ferrisilicate obtained using colloidal silicon is denoted CS and that corresponding to the powdered silicon as PS. The figure also shows the X-ray diffraction pattern of a

ZSM-5 zeolite synthesized by the same method. Comparison of the diffraction patterns shows that there are no differences in the positions or in the shapes and heights of the diffraction maximum. These three samples are therefore of the same nature and are identified as ZSM-5 type zeolites. Because of the impossibility of distinguishing these samples by X-ray diffraction, it was necessary to use other characterization techniques.

Studies of the CS and PS samples by transmission electron microscopy (TEM) were carried out in the diffraction mode in order to determine whether there were differences between them. Eight different diffraction patterns of the PS sample were examined and six of them were identified as silicalite and the two remaining were indexed as ZSM-5 zeolite. For the CS solid eight electron diffraction patterns were studied and all were indexed as ZSM-5 zeolite. Figs. 2 and 3 are typical electron diffraction patterns of various zone axes of the CS and PS samples, respectively. In table 1 we report the unit cell parameters obtained for the CS and PS samples as silicalite and ZSM-5 zeolite phases; these values are in accord with those reported in the literature [31,32].

The photographs in figs. 4a and 4b illustrate the typical appearance of the PS and CS samples, respectively. They were obtained via scanning electron microscopy (SEM) and show the uniformity in size of the particle aggregates for these samples. These images for the PS and CS samples were used for calculat-

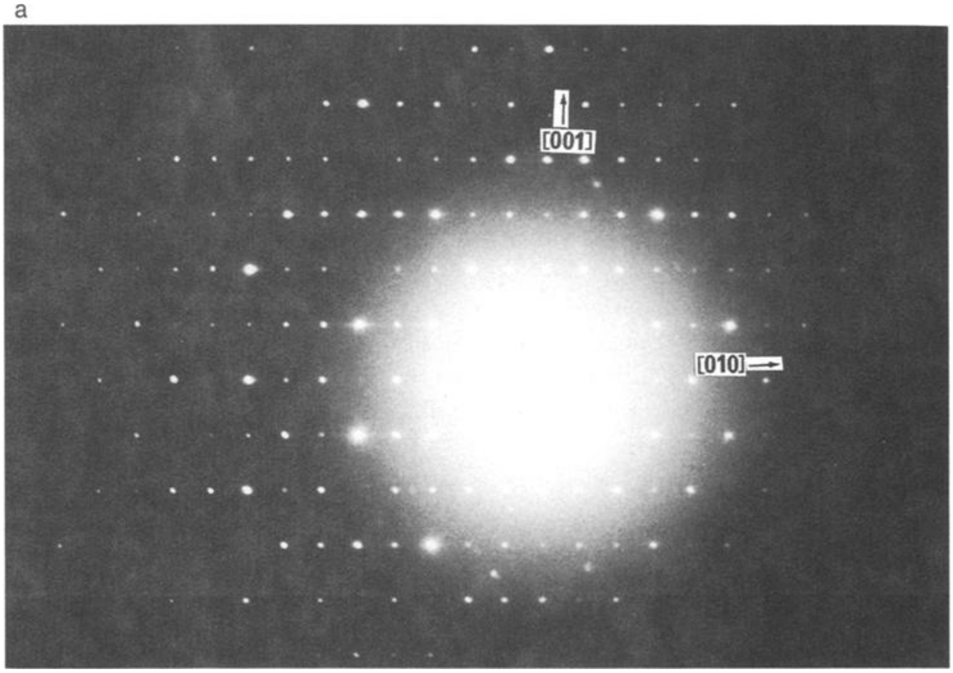

Fig. 3. Example of electron diffraction pattern for the PS sample with zone axis [100] and identified as silicalite (a) and for the PS sample with zone axis [10$\bar{4}$] and indexed as silicalite (b).

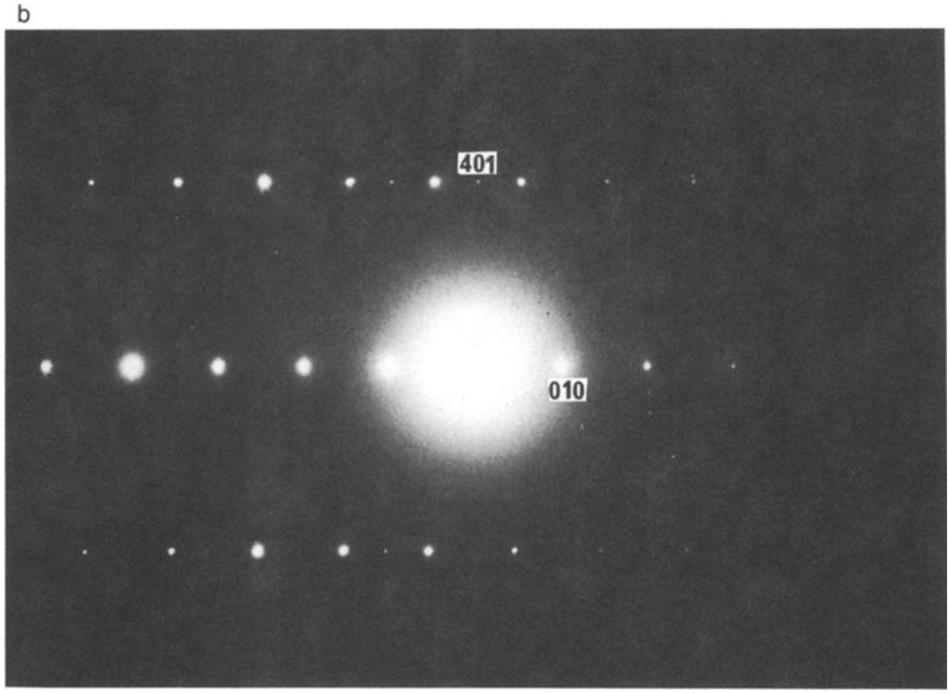

Fig. 3 (continued).

ing the size distributions of their crystalline aggregates, shown in figs. 5a and 5b, respectively. These graphs show that the CS samples present a better uniformity in the size of the aggregated crystallines, with a localized maximum for the particles of 1 micron of diameter, than the one presented by the PS sample, which does not have a well defined maximum. Therefore, the CS sample presents a much narrower size distribution of particle aggregates than the PS sample.

X-ray diffraction data obtained on the ferrisilicate samples indicate that it is difficult to distinguish between the CS, PS and ZSM-5 samples because the main reflections of the diffractograms show the same Bragg angles. Thus, the synthesized ferrisilicate sample, CS and PS, are considered to be ZSM-5 type

Table 1
Determination of the unit cell parameters (Å) for the PS and CS samples

	Silicalite		ZSM-5 zeolite	
	calc.	ref. [31]	calc.	ref. [32]
a	20.08	20.06	20.09	20.07
b	19.76	19.80	19.87	19.92
c	13.36	13.36	13.40	13.42

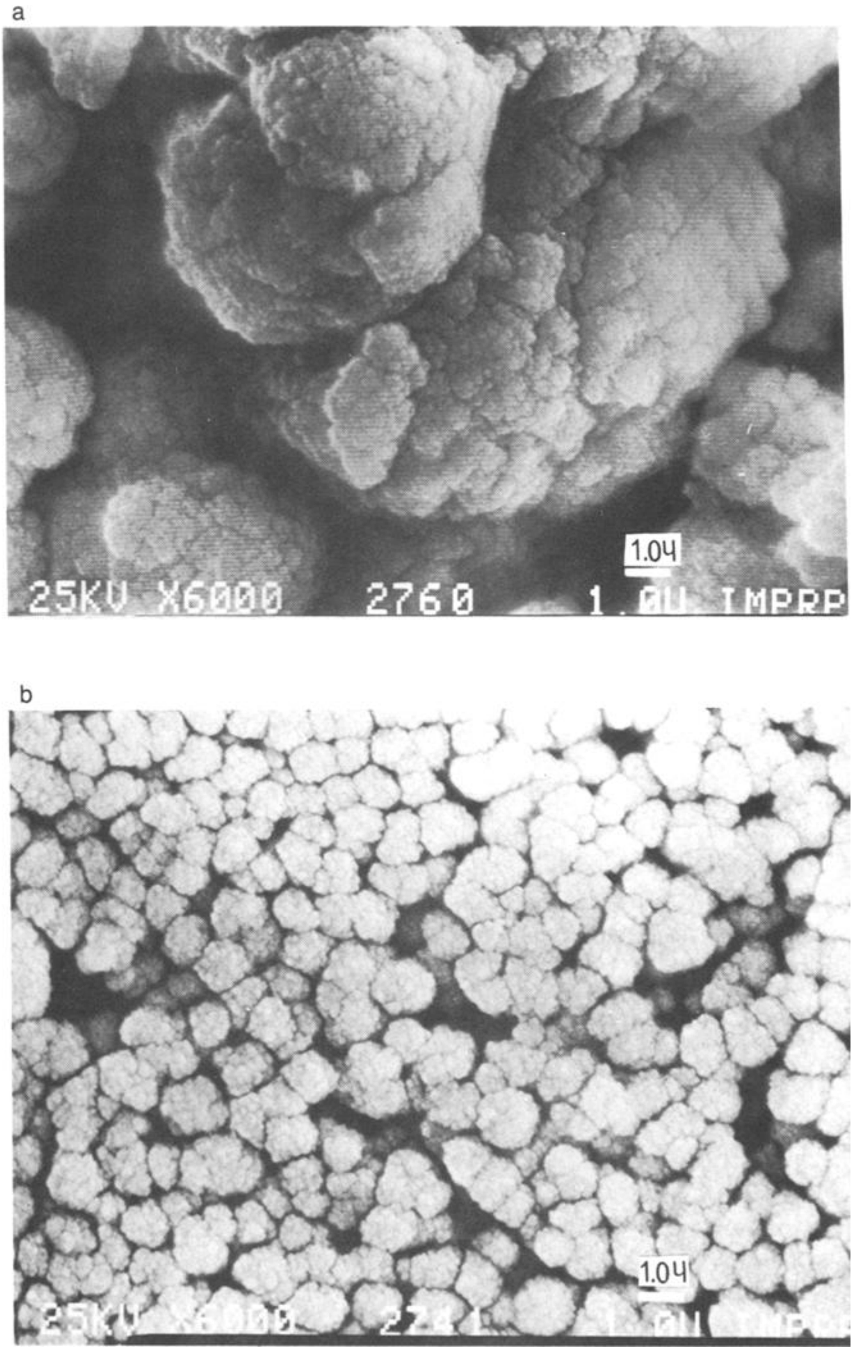

Fig. 4. SEM images for the (a) PS, (b) CS samples. The bar is 1 μm; the magnifications are equal.

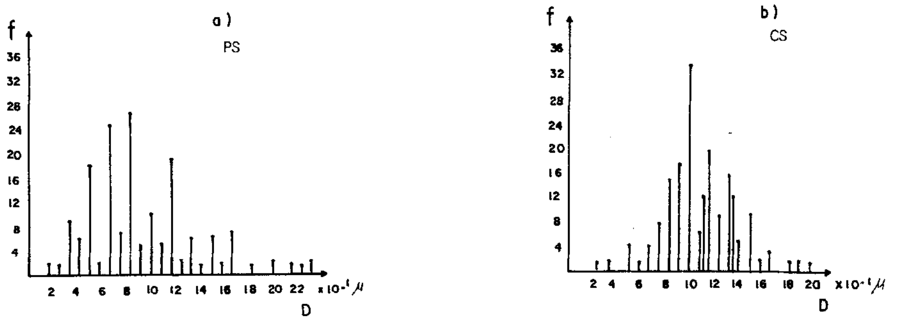

Fig. 5. Size distributions of crystalline aggregates for the (a) PS and (b) CS samples.

zeolites. Therefore, in accordance with X-ray studies, the nature of the silicon source is not important in the synthesis of ferrisilicate. Nevertheless, the analyses performed with TEM and SEM show that there are structural differences between te CS and PS samples. SEM analysis shows that the size distribution of particle aggregates of the CS sample is narrower than that of the PS sample.

The electron diffraction patterns of the PS and CS solids show that there are structural differences between the synthesized ferrisilicates. For instance, the CS sample is constituted by only one very crystalline phase and is a ZSM-5 type zeolite, whereas the PS sample is constituted by a mixture of ZSM-5 type zeolite and silicalite, the latter being present in a greater proportion. The results show that there is a difference in the structure of the two synthesized ferrisilicates. Therefore, one can conclude that the nature of the silicon source is important in the synthesis of these ferrisilicate materials.

X-ray analysis is not an appropriate technique for structurally distinguishing between the two samples, because the values of the parameters of the unit cells corresponding to ZSM-5 zeolite and silicalite are very similar, but in the case of transmission electron microscopy the differences between the lattice parameters are displayed by the better resolution of this technique as compared with X-ray diffraction.

4. Conclusions

The synthesis of ferrisilicates by isomorphous substitution of the Al cation by Fe was achieved under hydrothermal conditions using the template method, under autogenous pressure and utilizing silicon of colloidal and powder nature. The results of the characterization of these two preparations permitted the following conclusions:

The X-ray diffraction patterns of the two synthesized solids are similar to that of ZSM-5 type zeolite. Moreover, by transmission electron microscopy the solid synthesized with colloidal silicon has been identified as ZSM-5 type zeolite, and the sample generated with silicon powder consists of a mixture of silicalite and ZSM-5 zeolite, the former being present in greater proportion. The results of scanning electron microscopy show that the size of the crystalline aggregates of the sample synthesized with silicon of colloidal nature is more homogeneous than that of the sample synthesized with silicon in powder form. Thus, the general conclusion of this study is that in the synthesis of ferrisilicates, the phase-purity of this material is enhanced by using silicon of colloidal nature.

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