

FTIR AND THERMOGRAVIMETRIC STUDY OF SILICALITE TREATED WITH METHANOL*

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FTIR and TGA-DTA techniques were used for the high-defective Al-Na free silicalite characterization. Methanol reacting with external and internal silanols provides a sample modification evidenced by the combined use of these two techniques. A quantitative correlation between the FTIR and TGA data was drawn out although the incomplete methoxylation did not allow to quantify the total number of silanols. At least two distinct types of methoxylated sites were found according to their oxidation temperature which is unexpectedly high for one of them.

Key words: Silicalite; FTIR; TGA-DTA.

Silicalite is a pure siliceous zeolitic material of the MFI type. It was first patented in 1977 by Grose and Flanigen¹. During the time, the synthesis of this material has been modified towards Na and other contaminants (*e.g.* Al) free starting mixtures. Using tetraethyl orthosilicate (TEOS) as a source of silica, instead of Na-Ludox (Aldrich) pure tetrapropylammonium hydroxide (TPAOH) as a template molecule, in a Teflon-lined autoclave, it was possible to synthesize highly defective materials (*i.e.* containing a very high number of silanols²). The FTIR analysis of calcined samples, outgassed at room temperature, was performed to characterize SiOH groups³.

When treated with methanol, silicalite was strongly modified: the SiOH groups reacted to a very high degree forming stable methoxy groups (SiOCH₃). This behaviour is well-known with other types of zeolites⁴ and led to the recognition of different sites of adsorption^{5,6}. The thermogravimetric analysis (TGA-DTA) of our silicalite sample, performed in a stream of air, allowed us to determine the quantity of SiOCH₃ groups. These data are well-correlated with the integrated intensity of FTIR $\nu(\text{CH}_3)$ bands⁷ of methoxy groups.

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The aim of our work is to give evidence that, in absence of Al and Na, silicalite is easily methoxylated without coke formation and then regenerable by calcination without changes in its defective structure.

EXPERIMENTAL

Materials

Silicalite was synthesized under hydrothermal conditions starting from reactants (TEOS, TPAOH) completely Na and Al free in a Teflon-lined autoclave at 150 °C and autogenous pressure for 120 h, obtaining a material with Na and Al content ≤ 20 ppm for each of the elements (Inductive Coupled Plasma analysis). It was calcined in air at 550 °C for 4 h to eliminate the template molecule. The X-Ray Diffraction analysis (XRD) confirmed that silicalite was well-crystallized.

Methods

Sample powder (0.1 g) was treated with methanol ($0.1 \text{ cm}^3 \text{ h}^{-1}$) diluted with an argon flow ($100 \text{ N cm}^3 \text{ h}^{-1}$) in a quartz reactor up to 350 °C and 0.1 MPa for 20 h, with an on-line Mass Spectrometry analysis (MS) to control the outgoing products.

The FTIR spectra were taken on the outgassed self supported wafers with a System 2000 Perkin-Elmer equipped with the MCT detector cooled to 77 K.

The Thermogravimetric Analysis (TGA-DTA) was performed using air as oxidant at the heating rate of 4 °C min^{-1} in a Netzsch STA 409 system.

RESULTS AND DISCUSSION

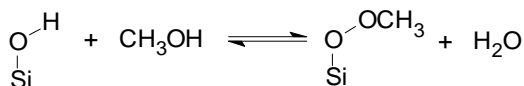
The FTIR spectra of silicalite and silicalite treated with methanol both outgassed at room temperature are shown in Fig. 1. According to Zecchina *et al.*^{3,7}, we distinguish three main ranges in the high frequency region:

1. $3\ 800\text{--}3\ 650 \text{ cm}^{-1}$: Stretching modes of hydroxyl groups not involved in hydrogen bonding. These groups include isolated and terminal OH groups³ (both external and internal).

2. $3\ 650\text{--}3\ 200 \text{ cm}^{-1}$: Stretching modes of hydrogen bonded hydroxyl groups³ (both external and internal).

3. $3\ 000\text{--}2\ 800 \text{ cm}^{-1}$: Symmetric and asymmetric stretching modes of CH_3 of SiOCH_3 groups⁷.

In Fig. 1, sample 1 is very rich in silanols. When treated with methanol, the silanol bands strongly decrease and methoxy group bands appear (Fig. 1, sample 2). Methanol reacts with silicalite according to the Scheme 1. The residual bands of SiOH groups in Fig. 1, sample 2, point out the incomplete conversion of SiOH to SiOCH_3 .



SCHEME 1

This is an equilibrium reaction; in fact, a previous work⁸ using Temperature Programmed Desorption with on-line Mass Spectrometer (TPD-MS) showed that at 350 °C, in presence of water, methoxy groups are easily hydrolyzed.

Under our experimental conditions, despite the large excess of methanol and long time of treatment, we cannot exclude the presence of water in reaction environment:

Al (even in traces) inserted in the zeolitic framework forms Brönsted acidic sites (SiOAl)H that catalyze methanol reaction to gasoline⁹ with water production. Most likely, steric hindrance does not allow the existence of too many neighbouring methoxy groups when a high concentration of defects exists. Furthermore, some external less stable methoxy groups can be hydrolyzed by atmospheric humidity at room temperature when the sample is exposed to air after the methoxylation procedure.

On the other hand, SiOCH₃ groups are completely stable under vacuum up to 350 °C: The methoxy group bands do not change at all with heat treatment (Fig. 2), while

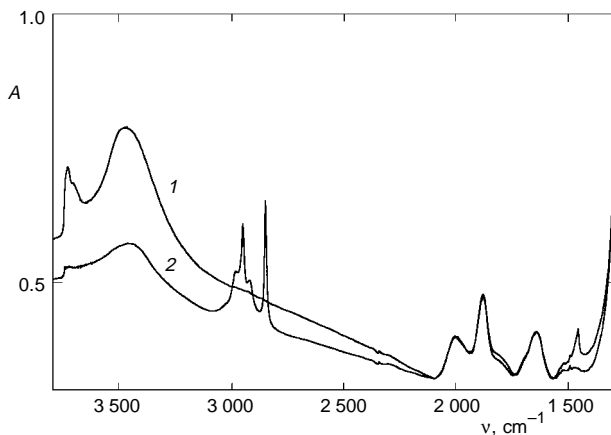


FIG. 1
FTIR spectra of silicalite out-gassed at room temperature: 1 calcined, 2 calcined and treated with methanol (A absorbance, ν wavenumber)

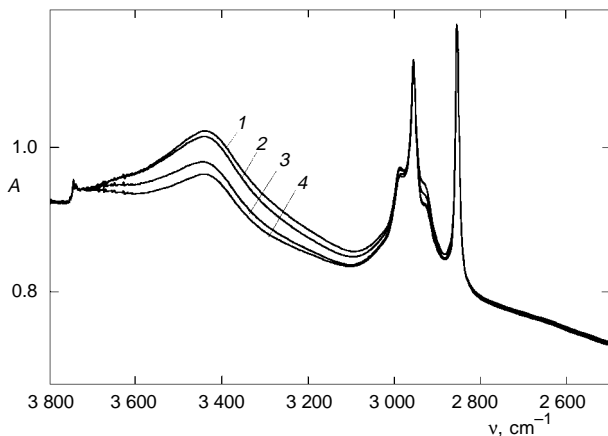
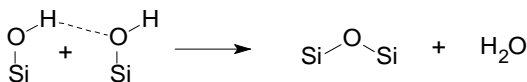
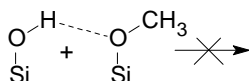


FIG. 2
FTIR spectra of the sample calcined, treated with methanol, out-gassed at different temperatures: 1 room temperature, 2 120 °C, 3 240 °C, 4 350 °C

residual hydrogen bonded silanols decrease. The condensation reaction, with formation of siloxane bridges (SiOSi), occurs with water but not with methanol elimination (Schemes 2 and 3).

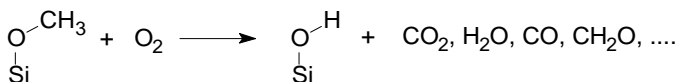


SCHEME 2



SCHEME 3

In inert atmosphere, methoxy groups pyrolyze only at very high temperature⁸. After oxidizing treatment performed in TGA-DTA apparatus, SiOH groups are completely regenerated from SiOCH₃ groups with production of CO₂, CO, CH₂O and H₂O (MS analysis) according to the Scheme 4.



SCHEME 4

The FTIR spectra in Fig. 3 confirm the disappearance of CH₃ stretching peaks and show only a slight change in SiOH distribution with an increase of high frequency hydroxyl group bands.

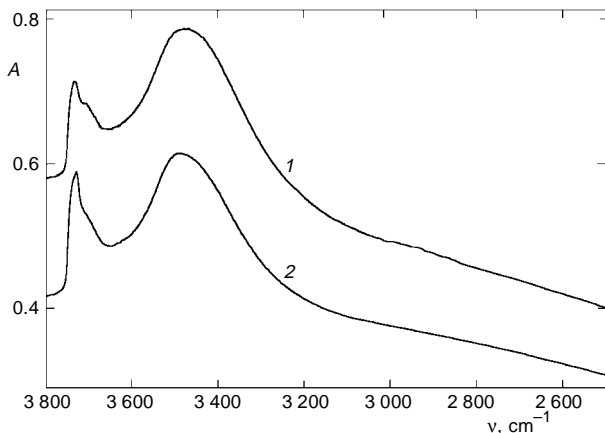


FIG. 3

FTIR spectra of silicalite: 1 calcined, 2 treated with methanol and then oxidized with air up to 550 °C at a heating rate 4 °C min⁻¹

The TGA signal (Fig. 4) shows three well-defined steps:

1. Room temperature–200 °C: Initial loss of weight due to evaporation of physisorbed water and/or methanol.
2. 200–400 °C: Oxidation of SiOCH_3 accompanied by a broad exothermic DTA peak.
3. 400–550 °C: Further oxidation at very high temperature characterized by a very sharp exothermic DTA peak.

Since the TGA of initial silicalite (not reported) shows only loss of weight due to the water elimination both from physisorbed molecules (up to 200 °C) and from silanol

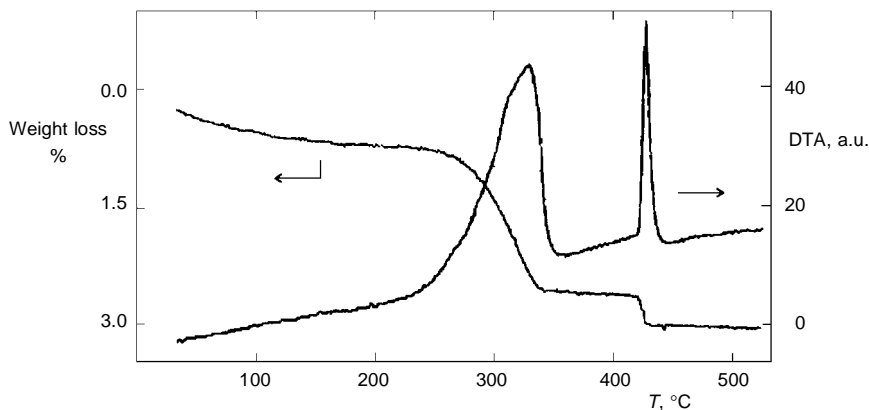


FIG. 4

Thermogravimetric analysis performed in air (heating rate 4 °C min^{-1}) of the sample treated with methanol

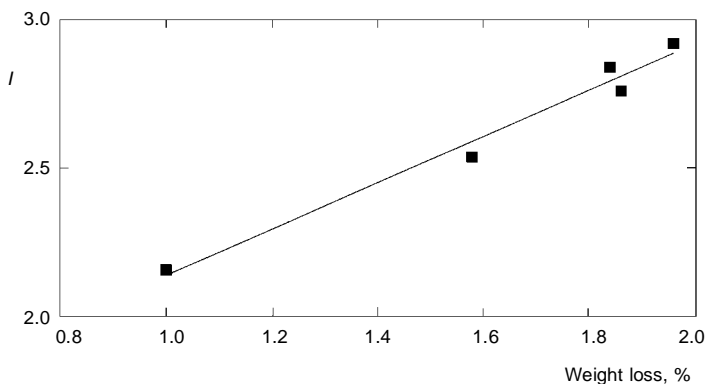


FIG. 5

Integrated intensity of $\nu(\text{CH}_3)$ IR bands I vs loss of weight in the range 200–550 °C (samples treated with methanol from 325–360 °C)

condensation (at higher temperature), we can say that the last two features between 200–550 °C are all due to the oxidation of methoxy groups. Moreover, the intensity of CH₃ peaks in the FTIR spectra is well-correlated with the TGA loss of weight, in the same range, performed over five samples having different degree of methoxylation: Fig. 5 shows linear relationship (correlation coefficient $R^2 = 0.97$) between the integrated intensity I (2 800–3 100 cm⁻¹ range) and the loss of weight.

Attempting to explain the TGA evidence, a FTIR spectrum was taken after oxidation up to 350 °C (sample 2 in Fig. 6). The residual CH₃ stretching peaks still appear unaltered in frequencies (curve 2' of Fig. 6) so we can exclude the presence of other species (rising from, *e.g.*, partial oxidation) adsorbed on the surface. The difference spectrum (4) between the total (3) and the partially oxidized (2) sample points out the incomplete regeneration of the hydroxyl groups at the 350 °C oxidizing temperature. The missing hydroxy groups still methoxylated are those particularly involved in mutual hydrogen bonding characterized by lower frequency bands ($\approx 3\ 400$ cm⁻¹).

The persistence of the last type of methoxy groups, unexpectedly resistant to oxidation, not detected with other techniques than TGA, can be ascribed to the additional stabilization due to hydrogen bonding with hydroxy groups.

CONCLUSIONS

The synthesis of silicalite with reagents free of Na and Al produces highly defective materials, *i.e.* those with a very high number of silanols: their quantity and quality strongly depend on the synthesis conditions and post-synthesis treatments.

When treated with methanol, silicalite is methoxylated with elimination of water. In our experimental conditions, the methoxylation is incomplete owing to the difficulty in reaching a completely anhydrous reaction environment or more likely to the steric hindrance when a high concentration of large defects exists.

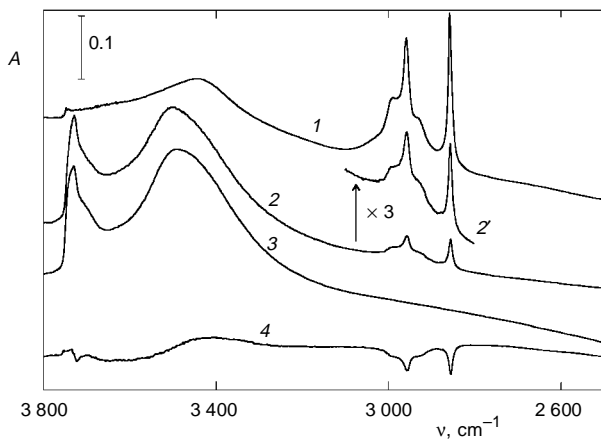


FIG. 6
FTIR spectra of silicalite: 1 treated with methanol, 2 treated with methanol and then with air up to 350 °C, 2' 3 100–2 800 cm⁻¹ range of curve 2 magnified three times, 3 treated with methanol and then with air up to 550 °C, 4 difference (3) – (2)

Methoxy groups are very resistant to heat treatment in inert atmosphere but in an oxidizing stream, they burn off completely up to 550 °C restoring silanols.

FTIR and TGA determine the quantity of SiOCH₃: The CH₂ loss of weight and integrated intensity of ν(CH₃) bands are well-correlated.

The TGA-DTA analysis of methoxylated samples performed in air shows the existence of two oxidation peaks, one of them at a surprisingly high temperature. The FTIR difference spectrum between the sample oxidized up to 550 °C and up to 350 °C points out that the more strongly hydrogen bonded silanols, characterized by a lower stretching frequencies (≈3 400 cm⁻¹), are restored at higher temperature.

The study of methoxylated silicalite by means of the combined commonly applied techniques reported in this work is a new proposal to further characterize silanols.

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