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FT-IR STUDY OF THE OH SURFACE GROUPS ON CORDIERITE AEROGEL

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Résumé - Nous avons étudié une cordiérite à haute surface spécifique par spectroscopie infrarouge en transmission. Après activation des échantillons, nous avons mis en évidence la présence des groupes hydroxyles. L'action du méthanol et l'échange isotopique avec le deutérium ont prouvé que tous ces groupes sont liés aux atomes de silicium de surface.

Abstract - A high specific surface area cordierite has been investigated by infrared transmission spectroscopy. After activation of the samples, we have evidenced the presence of hydroxyl groups. Treatments with methanol and isotopic exchange with deuterium have proved that all of them are bound to the surface silicon atoms.

1 - INTRODUCTION

Cordierite is a ceramic material promising in the electronic and catalytic fields. The study of these catalytic properties goes through the investigation of the surface. From this viewpoint, the Fourier transform infrared (FT-IR) spectroscopy is a very useful tool as long as the specific surface area of the compound is high enough. The sol-gel preparation process provides us with such a surface area which allows to characterize the OH groups on cordierite as a first step of a surface study.

2 - EXPERIMENTAL

The preparation of cordierite aerogel has been related elsewhere /1,2/. According to this process, the aerogel is obtained with a high specific surface area ($400 \text{ m}^2 \cdot \text{g}^{-1}$), a low density (0.3) and hydrophylic character. The properties of the bulk have previously been studied /3/.

The spectra are recorded using a FT-IR spectrometer (Nicolet 5DX) with a 4 cm^{-1} resolution. Cordierite is pressed in grid-supported pellets. The samples are introduced inside a vacuum heatable cell allowing in-situ experiments. We have activated them by heating up to 723 K and then cooling down to room temperature, both under evacuation. Prior to any introduction of adsorbates the pressure is about 10^{-6} mB.

Methanol (RP Normapur from Prolabo) is dried on molecular sieves before adding. D_2 (from Alphagaz-Air liquide) is used as provided.

3 - RESULTS AND DISCUSSION

The spectrum of an activated sample presents a sharp absorption band at 3747 cm^{-1} (figure 1a). As in silica /4,5/, it is assigned to the $\nu(\text{OH})$ stretching vibration of the surface silanol groups, free from any hydrogen bond. On the cordierite surface, we can expect to find OH groups bound to Al and Mg atoms whose vibration frequencies are at 3700 , 3745 , 3760 and 3785 cm^{-1} (Al-OH on γ -alumina) and at 3752 and 3610 cm^{-1} (Mg-OH on magnesia) /6/. However, we have been unable to evidence these absorptions. This lack of the expected bands has already been noticed on silica-alumina /4/ and Mg Al_2O_4 /7/.

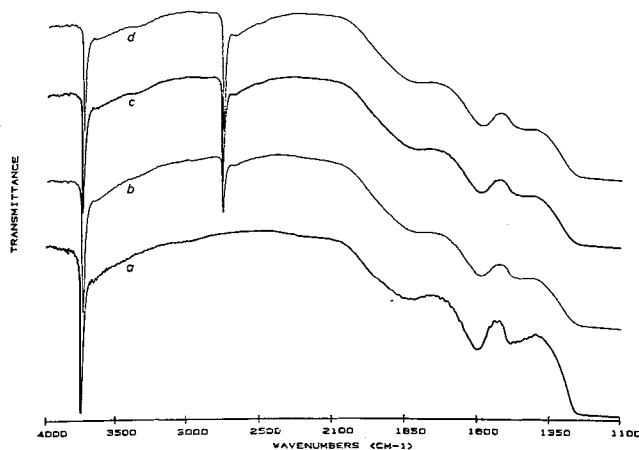


Fig. 1 - Evolution of the cordierite spectrum after addition of D_2 : Spectrum of the activated cordierite (a). Addition of 7 mB D_2 at 673K for 10mn (b), 30mn (c) and 60mn (d).

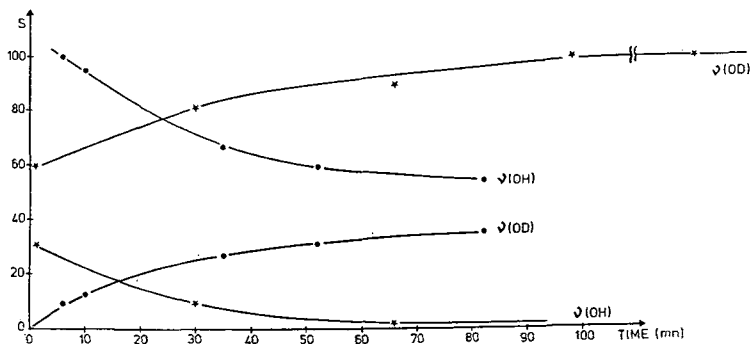


Fig. 2 - Isotopic exchange - Integrated surface (S) versus time : ● 1st dose $P(\text{D}_2) = 6\text{ mB}$ - ★ 2nd dose $P(\text{D}_2) = 355\text{ mB}$.

After adding 7 mB of D_2 at 673 K to the activated sample, we observe a sharp band occurring at 2760 cm^{-1} (figure 1) attributed to the $\nu(OD)$ stretching mode, while simultaneously the intensity of the $\nu(OH)$ band decreases. The isotopic exchange does not proceed to completion under a low pressure, even by adding subsequent doses. The intensity ratios of the $\nu(OD)$ and $\nu(OH)$ bands have been calculated as functions of the contact times, the temperatures of the sample and the doses. Some results are given in figure 2 : whatever the dose and the pressure are the curves $\nu(OH)$ and $\nu(OD)$ versus the time follow the same evolution, with an asymptotic behavior corresponding to the exchange equilibrium.

A pressure higher than 200 mB is needed to reach the complete exchange even though it is not spontaneous but a rather slow process. It is totally reversible by introducing H_2 .

So we can conclude that all the OH groups are located on the surface.

Adsorbed methanol on the cordierite surface gives rise to many bands over two main regions : $3700 - 2800\text{ cm}^{-1}$ and $1500 - 1300\text{ cm}^{-1}$. We were particularly interested in the first range corresponding to the absorption of the $\nu(OH)$ stretching vibrations (figure 3). Adding 0.07 mB of methanol at room temperature leads to the disappearance of the $\nu(OH)$ at 3747 cm^{-1} and the appearance of a broad band centered at 3375 cm^{-1} and of two sharp bands (2966 and 2853 cm^{-1}) with shoulders (2997 and 2921 cm^{-1}).

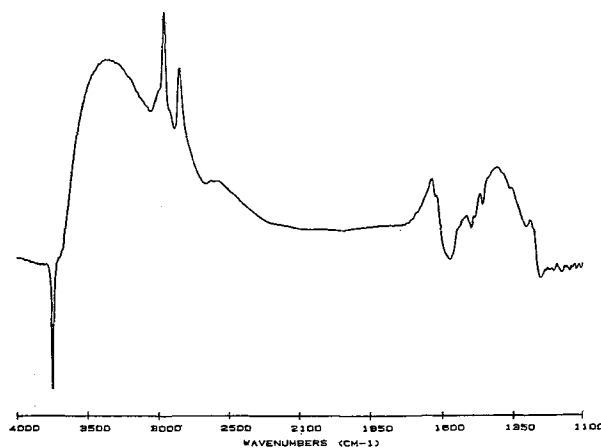


Fig. 3 - Difference spectrum featuring the modification of the cordierite spectrum after adding 0.07 mB of methanol at room temperature.

The first two features result from the formation of a hydrogen bond between the surface silanols and the methanol OH group. The $\nu(CH)$ stretching frequencies of H-bonded methanol should be slightly perturbed compared with the free molecule.

Under evacuation at room temperature, a very few silanol groups are restored, but at 373 K we observe the decreasing of the 3350 cm^{-1} band and of both 2966 and 2841 cm^{-1} bands, included their shoulders (figure 4). We therefore assign them to the $\nu(CH)$ stretching vibrations of the H-bonded methanol.

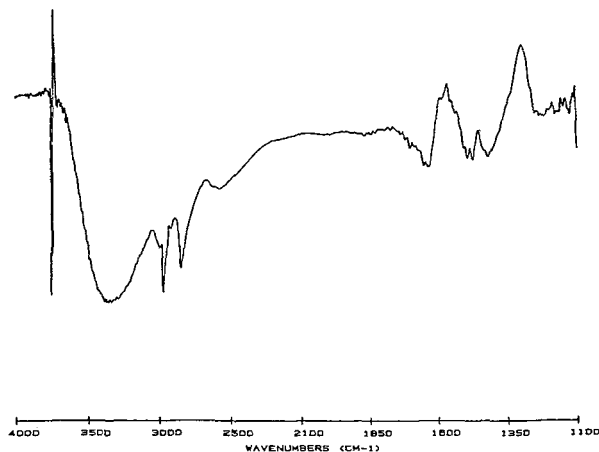


Fig. 4 - Difference spectrum : the evolution of the spectrum of methanol adsorbed on cordierite by evacuation at 373 K. The modification of the band at 3747 cm^{-1} ($\nu(\text{OH})$) is partly due to a temperature effect /10,11/.

However, after pumping off for one hour at 673 K the spectrum of cordierite still presents two weak bands at 2964 and 2856 cm^{-1} (figure 5). At this temperature the H-bond no longer exists. Comparing with silica /8/, we attribute them to methoxyl group on silicium (Si-OCH_3). Not all the sample is methylated at room temperature and under that pressure. Neither was the silica surface even at higher temperature and under saturated methanol vapour, because of the steric hindrance preventing a complete reaction /9/.

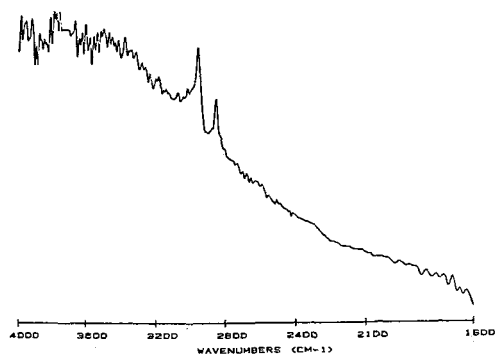


Fig. 5 - Difference spectrum : adsorbed methanol on the cordierite surface after evacuation at 673K.

4 - CONCLUSION

By FT-IR spectroscopy we have pointed out that all the OH groups of cordierite are located on the surface. Their stretching vibration frequency and their behavior regarding deuteration and methylation look very much the same as in silica.

So we can conclude that all the evidenced OH groups belong to the silanol species. No absorption frequency corresponding to Al-OH or Mg-OH surface groups has been observed so far. Experiments are still running for characterizing the other catalytic sites on the cordierite surface and their acidic or basic activities.

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