THE SYNTHESIS OF THE MOLECULAR SIEVE CLOVERITE IN THE PRESENCE OF HETEROATOMS*

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Various cloverite samples containing a series of heteroatoms have been synthesized at optimized HF : Ga_2O_3 ratios and characterized by XRD, adsorption measurements, infrared and ESR spectroscopy. The results show that the pure cloverite structure is only formed in the presence of Ti, Si, Zn, and Mg ions. However, no real evidence can be given for an isomorphous substitution of phosphorus or gallium by the heteroatoms. Conditions for the storage of detemplated cloverite samples are given, which avoid amorphization under the influence of moisture.

During the last few years great attention has been paid to the synthesis of new large pore molecular sieves. The main interest results from catalytic reasons because these molecular sieves are assumed to be able to convert larger molecules than do the classic zeolites. One of the results of these efforts is the new gallium phosphate molecular sieve cloverite which contains supercages of 30 Å with 13.2 Å windows[1–3]. Several works have been published to further characterize the structure and properties of this sieve. In contrast, only few attempts have been published at the incorporation of heteroatoms into lattice or extra-lattice sites. These solely concerned Si where, with the exception of a ^{29}Si MAS-NMR measurement, no details were given[2]. A partial incorporation into the cloverite framework was reported from ^{27}Al and ^{19}F MAS-NMR studies[4]. As shown for other types of molecular sieves, a more or less strong modification of its catalytic properties by the presence of heteroatoms can be expected as, in dependence on charge, ionic radius etc., many properties can be influenced by these parameters.

EXPERIMENTAL

The samples were synthesized by slightly modifying the method described by Bedard et al.[3], using quinuclidine as template. The reaction mixtures had the following composition: $1.0\ Ga_2O_3 : 1.0\ P_2O_5 : 2.2\ HF : 6.0$ quinuclidine : x EIO : $70\ H_2O$ where EIO represents the oxide of the heteroatom used and x its molar concentration which has been varied between 0.03 and 0.48. The following chemicals were used: gallium(III) sulfate (99.99%, Aldrich), orthophosphoric acid (85.0%, Laborchemie Apolda), quinuclidine (97%, Fluka), hydrofluoric acid (48.0%, Aldrich). The heteroatoms were introduced in the form of tetraethyl orthotitanate, cobalt(II) sulfate, Aerosil-200 or tetraethyl orthosilicate, nickel(II) sulfate, ferric(III) sulfate, magnesium acetate, zinc(II) sulfate, manganese(II) sulfate, vanadium(IV) sulfate oxide.

The gels were prepared as follows: gallium(III) sulfate and deionized water were stirred for 24 h and then for another 2 h after a diluted orthophosphoric acid has been added. A mixture containing dissolved quinuclidine and HF was then added and homogenized for 2 h. Finally, the salts of the above mentioned metals or the appropriate Ti and Si sources were added. The crystallization was performed in a Teflon-lined autoclave at 433 K for 24 h under autogeneous pressure. The products were washed with deionized water until neutral pH and dried at room temperature. The removal of the template was performed in a flow of dry air in a furnace using a temperature program: 1st step: up to 573 K with the rate of 10 K/min, 2nd step: up to 823 K with a rate of 7 K/min. The samples thus synthesized were denoted as Me-CLO.

For the determination of the adsorption volume, the samples were put into predried (at 333 K) ampoules immediately after drying, and then evacuated at 673 K. Elemental analysis of the products was carried out by using ICP measurements, the concentration of silicon was determined gravimetrically as SiO_2 after ashing of the filter. XRD powder diffraction patterns were obtained by a Bragg–Brentano diffractometer using CuKα radiation. An ASAP 2000 M device (micromeritics) was used for the adsorption measurements at 77 K with nitrogen. IR spectra were obtained by the common transmission KBr wafer technique on a Mattson 5000 FTIR spectrometer of Unicam. ESR measurements were carried out at 77 K and room temperature at x-band on an ERS 220 spectrometer (ZWG).

RESULTS AND DISCUSSION

As known from literature, besides the use of template compounds, the presence of HF in the reaction gel is an important factor for the crystallization process[5]. In contrast to the gallium sources described in literature[3,4], the gallium sulfate used in the present synthesis does not contain water. This made it necessary to redetermine the conditions of crystallization, especially the quantitative influence of HF on the structure of the products.

Figure 1 shows XRD patterns of three samples synthesized with different amounts of HF. In the absence of HF, $GaPO_4$-a already described by Flannigen[6] is formed. Introducing HF into the gel and systematically increasing its amount shows that a HF : Ga_2O_3 ratio of about 2.2 is necessary to obtain the pure cloverite phase. At lower ratios, a mixture of the two phases is obtained.

The same conclusion can be drawn from IR spectra of framework vibrations where the characteristic band for cloverite appears at 634 and 598 cm^{-1} (Fig. 2). Despite of the presence of traces of cloverite in the crystallization product ($GaPO_4$-a), the bands are

best resolved and are of highest intensity for the samples prepared from the gel compositon $HF : Ga_2O_3 = 2.2$.

From scanning electron microscopic pictures, the two phases show completely different morphology. Cloverite crystals are cubic, whereas $GaPO_4$-a crystallizes in hexagonal rods. Remarkable is also the crystal size determination obtained with a laser particle size analyzer. Here, cloverite samples show a nice size distribution with a maximum at about 2 μm whereas $GaPO_4$-a crystals have a size up to 100 μm with a maximum of the size distribution at about 50 μm (Fig. 3). Samples having a medium F^- content show both maxima well separated.

FIG. 1
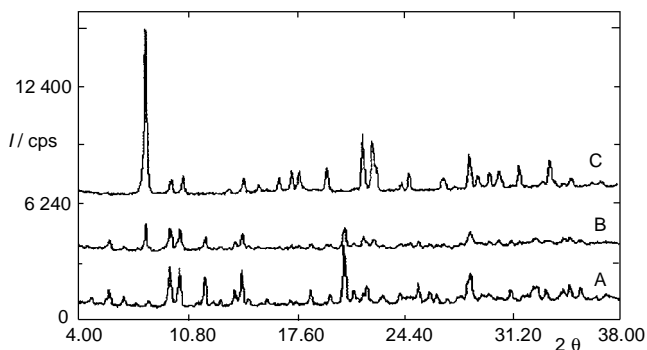XRD patterns. Variation of the $HF : Ga_2O_3$ ratio x in the synthesis gel. Samples A ($x = 2.2$), B ($x = 0.8$) and C ($x = 0$)
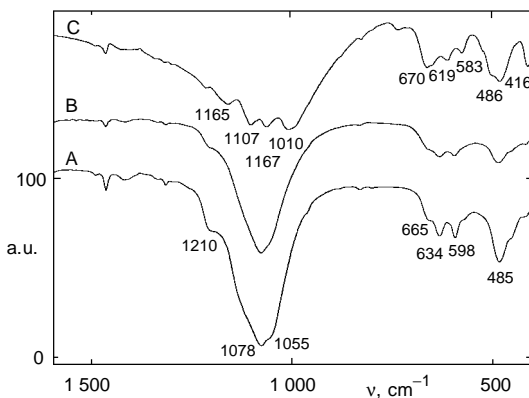

FIG. 2
IR spectra (for samples A, B, C see Fig. 1)

All the results obtained so far further document the tremendous effect of the presence of F^- ions on directing the crystallization process. Therefore, the results on the metal-containing cloverite samples were all carried out with gels containing a constant $HF : Ga_2O_3$ ratio of 2.2. Table I shows the series of samples synthesized under identical conditions. It is obvious that only in four cases cloverite is the only phase that crystallized in the presence of heteroatoms, i.e. Ti-CLO, Si-CLO, Mg-CLO and Zn-CLO. In the cases of Co, Ni, and Fe a second phase is co-crystallized which has not yet been identified. Under these conditions, the gels containing Mn and V did not crystallize the cloverite structure. Compared to the pure cloverite sample, the crystallinity decreased, in some cases dramatically, in dependence on the metal introduced. No indication of a correlation with the ion charge or the ionic radius of the metal ions has been observed.

The microporous volume for cloverite was found to be 0.22 cm^3/g. There is a distinct decrease of the microporous volume if the crystallinity is decreased, however, without a clear quantitative correlation. Remarkably, the Ti-CLO sample shows a sligthly higher microporous volume than the pure cloverite sample.

Nitrogen adsorption isotherms show a similar picture at $p/p_0 = 0.5$. Three groups are shown, i.e. CLO and Ti-CLO show the highest adsorption capacity of about 0.28 – 0.30 cm^3/g, Si, Ni and Co show 0.17 – 0.22, and Fe, Zn and Mg below 0.15 cm^3/g. The amorphous V sample does not show practically any adsorption capacity, as expected.

Infrared spectra of framework vibrations of the as-synthesized metal-containing samples are shown in Fig. 4. With the exception of the amorphous V sample all other samples show similar spectral features. Again, in depence on the metal introduced (or the crystallinity formed), the resolution of the spectra decreased in the same way as did the crystallinity of the samples. A broad band at about 1 078 cm^{-1} with shoulders at

Fig. 3
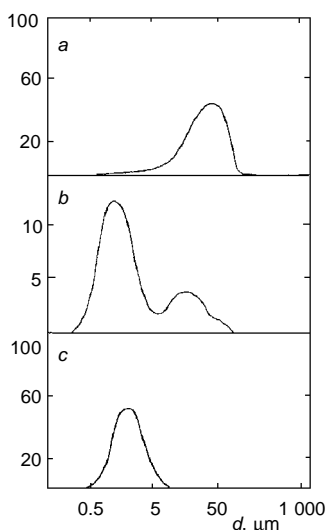
Particle size (*d* in µm) distribution of samples with different $HF : Ga_2O_3$ ratio (sample designation see Fig. 1)

TABLE I

Properties of metal-containing $GaPO_4$ (CLO) samples

Sample	Phase[a]	Crystallinity[b] %	V^c cm^3/g	s^d m^2/g	Adsorption capacity[e] cm^3/g
CLO	CLO	100	0.22	500	0.28
Ti-CLO	CLO	129	0.25	583	0.30
Co-CLO	CLO[+]	84	0.22	499	0.17
Si-CLO[f]	CLO	74	0.15	354	0.19
Ni-CLO	CLO[+]	76	0.18	419	0.22
Fe-CLO	CLO[+]	63	0.13	306	0.15
Mg-CLO	CLO	61	0.09	217	0.11
Zn-CLO	CLO	63	0.11	245	0.12
Mn-GaPO₄	amorphous				
V-GaPO₄	amorphous				

[a] CLO[+] denotes the detection of an additional unknown "phase" indicated by an enlarged peak at $d = 0.328$ nm. [b] The crystallinity of the pure cloverite sample is defined as 100%, the values are deduced for comparison as an estimation from the XRD pattern by forming the ratio of the $d = 0.432$ nm intensity to the underground. [c] Microporous volume, N_2 adsorption, $\Delta_{max} = 0.005$ cm³/g. [d] Microporous area, $\Delta_{max} = 3$ m²/g. [e] Taken at $p/p_0 = 0.5$. [f] Si source was Aerosil-200.
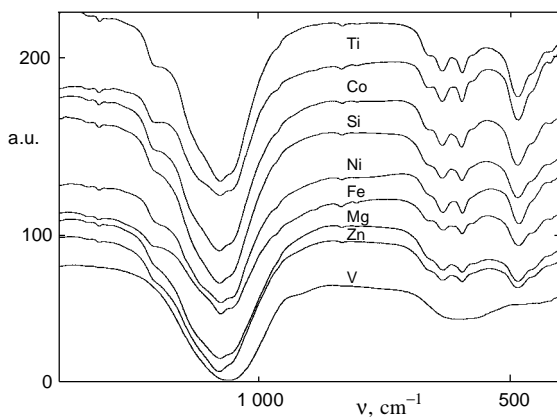

FIG. 4

IR spectra of metal-containing cloverite samples

1 210 and 1 055 cm^{-1} dominates all the spectra and is assigned to TO asymmetric stretching vibrations of the GaPO$_4$ tetrahedra[7], the band at 485 cm^{-1} to their deformation vibrations. The doublet at 634 and 598 cm^{-1} with a very weak shoulder at higher wavenumbers (665 cm^{-1}) is the structure-sensitive band of cloverite; its intensity decreased with decreasing crystallinity of the samples.

Calcination of the samples in vacuum or in air results in desorption of water and template or of its destruction products. Hydroxyl groups which had been interacting with water or the template become visible in the OH vibration region. The most characteristic bands in this region, shown here for the Ti-CLO sample (Fig. 5), appeared at 3 676 cm^{-1} and 3 704 cm^{-1}. Both have been attributed to POH groups by Barr et al.[8]. The spectrum is nearly identical with that of the pure cloverite, i.e. no evidence for an isomorphous substitution of Ga by Ti is provided in this case.

It is well known that detemplating of the cloverite decreases dramatically the stability of the cloverite structure in the presence of moisture[3]. As Ti-CLO samples seemed to be the Me-CLO sample of the highest crystallinity and, additionally, showed an increased microporous volume compared to the pure cloverite (Table I), a few experiments were undertaken to see whether Ti stabilizes the cloverite structure or not. As an indication of such changes, the microporous volume and surface area were taken. The first results are, however, not encouraging. Putting Ti-CLO in an open ampoule led to its complete amorphization after 24 h. After 5 and 7 day's-storage in a closed, dried and with N$_2$-filled ampoule, the microporous volumes and areas decreased by about 50 to 70%, respectively (Fig. 6). This instability thus demands very careful handling of Me-CLO samples and a cautious interpretation of the results obtained from detemplated samples.
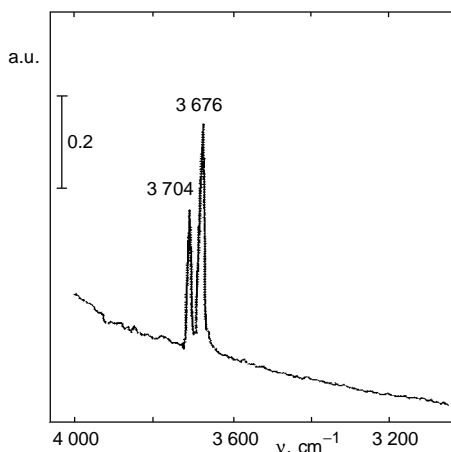

Fig. 5

IR spectrum of the hydroxyl region of the cloverite Ti-CLO

Two methods have been developed to store the detemplated samples without a remarkable loss of crystallinity:

1. The samples can be stored in closed ampoules in liquid nitrogen. This suppresses any attack of moisture on the cloverite structure. After 6 day's-storage, the microporous volume shows a loss of only 4%, which can be neglected.

2. The pores can be filled with a certain amount of liquid hexane. After storage for 5 days and evacuation of hexane (72 h at 723 K), the sample shows no loss of the microporous volume.
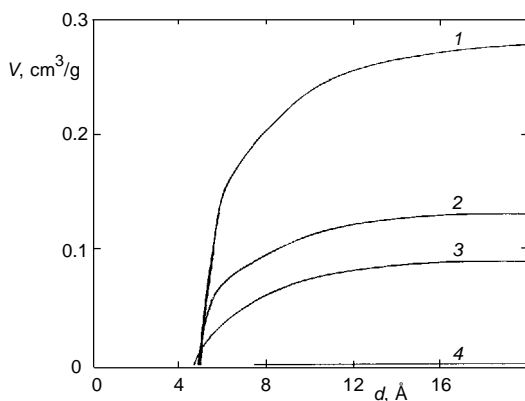

FIG. 6

Cumulative pore volume *V* of 0.05 Ti-CLO sample (according to Horvath–Kawazoe): *1* immediately after detemplating, *2* after 5 day's storage in a closed ampoule, *3* after 7 day's storage in a closed ampoule and *4* after 24 h storage of the detemplated sample (*1*) on air
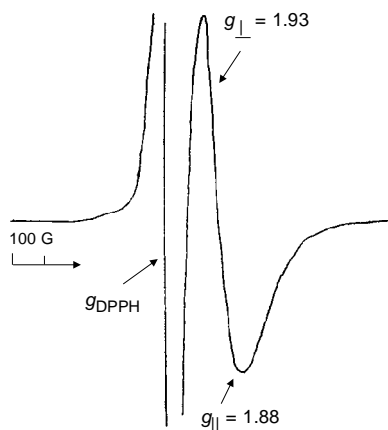

FIG. 7

ESR Ti^{3+} spectrum of the 0.05 Ti-CLO sample after its reduction in hydrogen (2 h, 823 K) recorded at 77 K

One of the most interesting questions is whether heteroatoms are able to substitute the lattice atoms or not. First ESR measurements were undertaken on various Ti-containing cloverite samples. Though Ti^{4+} ions are not detectable by ESR, the reduction with hydrogen leads to the trivalent state which can be easily observed. The reduction was carried out at temperatures up to 873 K in steps of 50 or 100 K. The results show that the reduction starts at about 573 K leading to a Ti^{3+} signal, the intensity of which increased with increasing reduction temperature. Figure 7 shows a typical, slightly asymmetric and not well resolved Ti^{3+} signal. This shows a relatively strong temperature dependence, i.e. the intensity of the room temperature signal is much lower than that expected from the Curie law. (The sharp strong signal at about $g = 2.0$ that overlaps the DPPH signal results from destruction products of the template and lattice distortions and will not be further discussed). The result is similar to that found in TS-1 samples[9]. The strong temperature dependence of the Ti^{3+} signal could be taken as an indication that Ti is incorporated in tetrahedral coordination into the cloverite lattice, making this temperature behaviour reasonable. On the other hand, the temperature at which the reduction starts seems to be rather low for the lattice Ti species. This leads to the assumption that preferentially extra-lattice Ti species were reduced. It should be emphasized that also IR measurements carried out on Ti-CLO samples do not show bridged OH groups caused by Ti atoms incorporated into the framework.

In the case of Ti silicate (TS-1) Raman spectroscopy could successfully provide evidence for the incorporation of Ti atoms to the framework positions. First Raman measurements on several Ti-CLO samples do not show, however, any characteristic bands of titanium species or of anatase because of the strongly dominating template bands. It seems, therefore, that this method is not suitable for characterizing template-containing cloverite samples.

CONCLUSIONS

The results show that the introduction of heteroatoms into the reaction gel strongly influences the course of crystallization and properties of the solid products. The presence of Ti, Si, Mg, and Zn has no or little effect, as the pure cloverite structure is formed in these cases. The introduction of Mg and V salts into the gel does not lead to crystalline products under the conditions used. In all other cases, a second phase was formed which could not yet been identified. Thermal stability of the samples is high. Detemplated metal-containing cloverite samples are extremely sensitive to moisture. However, the storage at liquid nitrogen temperature or pore-filling with hexane avoids their destruction.

Although the contents of heteroatoms in the products have not yet been finally quantified, most samples contain obviously heteroatoms, as found by ESR spectroscopy (see e.g. Ti-CLO). However, no conclusive evidence can so far be given for an isomorphous substitution of phosphorus and/or gallium by titanium in the cloverite framework.

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