STUDIES OF THE SYNTHESIS OF LARGE VAPO-5 CRYSTALS AND INCORPORATION OF VANADIUM IONS*

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Received September 13, 1991
Accepted October 14, 1991

The molecular sieve VAPO-5 has been synthesized hydrothermally in form of large crystals up to 660 μm in length. They have been used as a model substance for the study of vanadium incorporation into the framework. Our results show that vanadium was incorporated into the framework though in relatively small amounts. The results are in agreement with earlier findings for powder preparations of VAPO-5, except for the oxidation state of the vanadium ions and its stability. These conclusions agree with those arrived at previously for vanadium silicalite KVS-5.

Molecular sieves based on microporous aluminophosphates are increasingly interesting as adsorbents and/or catalysts. Catalytic activity can be achieved by incorporation of heteroatoms into the framework of molecular sieve crystals. Fine tuning as well as an appropriate adaption of a molecular sieve to distinct catalytic processes can be obtained by a suitable choice of incorporated elements. Transition elements are particularly useful.

The catalytic properties of vanadium compounds and especially of its oxides are well known. They are mainly due to the ability of vanadium to change its oxidation state easily. Vanadium catalysts were commonly supported on silica or alumina[1-4] and on phosphorus oxide[5]. Lately efforts were undertaken to prepare self-supporting porous vanadium catalysts, that is zeolitic materials containing either occluded vanadium and/or vanadium incorporated into the framework[6]. It was an obvious consequence to attempt the synthesis of vanadium containing microporous aluminophosphates analogous to zeolites.

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[*] Presented as a poster at the *International Symposium "Zeolite Chemistry and Catalysis", Prague, September 8—13, 1991.*

Syntheses of numerous substituted aluminophosphates have been already claimed[7,8] but only some of these materials have been investigated after the synthesis in much detail[9–14]. Synthesis of vanadium containing aluminophosphates has been claimed already in 1985 (ref.[8]), however, without any proof of vanadium incorporation into the framework. Later, in 1989, Miyamoto et al.[15] reported the catalytic properties of VAPO-5 synthesized using vanadium(III) compounds. It is surprising that after the synthesis, V^{4+} ions were present in the crystals. These ions appeared stable and were not oxidized during calcination. These results when compared to our findings on V-silicalite (KVS-5) (ref.[6]) of MFI topology seem to indicate quite an opposite effect, namely that the vanadium compounds are only occluded within the framework of the crystals. The incorporation of vanadium in 4+ and 5+ oxidation states into the framework of $AlPO_4$-5 molecular sieve, synthesized as spherulitic growth aggregates (diameter $\approx 20\,\mu m$), was studied recently[16] except that the unit cell dimensions in this work were determined on large crystals. However, based on our experience and conclusions with vanadium silicalite[6], some of the details of interpretation of the experimental data regarding the state of vanadium ions in the crystals and the changes of their oxidation state are questionable. Therefore, we tried to synthesize large crystals of VAPO-5 which could be used as a model substance for the study of both the incorporation and the oxidation state of vanadium ions in this material. In this paper we are presenting the first results.

EXPERIMENTAL

The molecular sieve VAPO-5 was synthesized without agitation at 170—190°C and under autogeneous pressure for 2—10 days in Teflon-lined autoclaves following the method described elsewhere[17–19]. The hydrothermal synthesis proceeded from gels of formal molar compositions

$$1\ Al_2O_3\ .\ 0{\cdot}8{-}0{\cdot}95\ P_2O_5\ .\ 0{\cdot}05{-}0{\cdot}2\ V_2O_5\ .\ 1{\cdot}2{-}1{\cdot}5\ T\ .\ 250{-}1\,000\ H_2O\ .$$

The reagents used were: aluminium oxide hydrate sol (pseudoboehmite-like)[18], orthophosphoric acid, triethylamine (TEA) or tripropylamine (TPA) as the template T, and as the source of vanadium V_2O_5, $VOSO_4$, $NaVO_3$ and NH_4VO_3.

After the reaction was completed, the autoclaves were cooled down and the resulting crystals were washed by multiple decantation with the aim of separating them from the remainder of the unreacted gel and/or the byproducts. Subsequently they were filtered and dried at 110—120°C for 24 h.

The calcination of the VAPO-5 crystals was performed in a quartz-tube oven at 500°C under a stream of dry air for a minimum of 24 h and then at 500—550°C under a stream of oxygen for at least 48 h.

The samples of VAPO-5 were investigated by XRD, SEM, EPM, MAS NMR, ESR and DTA/DTG techniques.

RESULTS AND DISCUSSION

As it can be seen from the conditions given in the Experimental, we investigated the synthesis conditions over a relatively wide range of parameters: dilution of the gel, source of the vanadium ions, and two different templates. In addition we studied also the influence of temperature and reaction time. In part, the results are consistent with those obtained for the synthesis of the $AlPO_4$-5 molecular sieve itself[17-19]. Decrease of temperature as well as higher dilution require a longer time of crystallization and vice versa, respectively. A lower rate of crystal growth (longer time of crystallization) favours the growth of larger crystals but at the same time also the formation of byproducts. It can lead even to a damaging of the largest crystals due to a secondary dissolution in the mother liquor[19]. So, as usual for this method of large crystals growth, the synthesis has to be stopped in an appropriate moment which should be determined experimentally to get the highest possible yield, the largest possible crystals, and the lowest possible content of byproducts[18-20].

The result of synthesis depends to a very large degree on the source of vanadium applied. The two vanadate salts, i.e. $NaVO_3$ and NH_4VO_3 yield the worst results. The reaction proceeds extremely slowly and nearly pure byproducts contaminated by less than 2% of the VAPO-5 phase can be obtained. A good reactivity is shown by V_2O_5. Recently, however, the use of $VOSO_4$ yielded even better results. A qualitative estimation based on the colour of the crystals and the mother liquor seems to show a considerably higher content of vanadium in the VAPO-5 phase. Similarly, application of TPA instead of TEA seems to favour the incorporation of higher amounts of vanadium but, on the other hand, it causes a decrease of crystal dimensions. Such effect has been observed for SAPO-5 (ref.[21]) where, as opposed to the present VAPO-5 system, no byproducts have been formed. Further work is in progress.

How the results depended on the synthesis conditions is shown by several examples in Table I. The dimensions, morphology and phase purity have been estimated from light and scanning electron microscopy as reported in ref.[20]. The scanning micrographs are not shown as they are not differing from those reported previously[18-21].

Electron probe microanalysis (EPM) was performed for the samples from the V_2O_5/TEA system and they show a vanadium content of always less than 1 mole % e.g. 0·711% and 0·247% for samples 1 190/24 and 1 190/22, respectively. It is worth noting that these figures agree with the decrease of phosphorus content as compared with a pure $AlPO_4$-5 phase. The second interesting observation is that the vanadium ions in VAPO-5 are easily detectable by the EPM method though they were not detected in KVS-5 (MFI structure) at the same or even slightly higher vanadium content[6]. This might show another distribution of these ions in these two materials relative to the surface. The EPM measurements as well as the XPS method applied by Sung et al.[16] give the composition of the surface layer. This might indicate that the vanadium ions in the VAPO-5 material are more concentrated in the external layer of the crystals as opposed to KVS-5. This would explain why vanadium was not detected by the EPM method in V-silicalite.

The X-ray diffraction spectra of the VAPO-5 preparations agree very well with those of $AlPO_4$-5. The lattice constants a, b and c measured for the as-prepared TEA containing samples are 1·3606(6), 1·3606(6) and 0·8445(3) nm, respectively. They are considerably smaller than those of $AlPO_4$-5, which are $a = b = 1{\cdot}3726$ and $c = 0{\cdot}8484$ (ref.[22]). Our finding is in agreement with the smaller cell constants found for FAPO-5 (ref.[10]) and partially (c value) for CoAPO-5 (ref.[12]), while actually an expansion of the lattice would be expected. A small expansion of 1 – 2 pm for both directions has been recently reported for VAPO-5 (ref.[16]).

Thermogravimetric analysis results are shown in Fig. 1. The shape of the TG curve is apparently different from that presented by Sung et al.[16] as it has no sharp steps but instead a smooth slope. This difference might be due to two different reasons (whereby we must keep in mind the different scales used in presenting the respective results):

- the removal of the decomposition products is slowed down by diffusion phenomena;
- the amount of oxygen is too small under static conditions.

The DTA curve shows a considerable shift of the exothermal effect of the combustion of the template in VAPO-5 as compared with $AlPO_4$-5. This agrees exactly with

TABLE I

Some examples of the VAPO-5 synthesis conditions and their results

Sample No.	Source of V and amine		Water in gel mol	Yield of VAPO-5 wt. %	Colour of crystals[a]	Largest crystals µm
990/27	$NaVO_3$	TEA	750	<2	l. gr.	300 × 30
1 090/25 – 27	V_2O_5	TEA	750	≈ 20	v.l. bl.	660 × 60
1 190/21 – 30	V_2O_5	TEA	250	≈ 60	v.l. bl./y.	160 × 80
291/17 – 23	V_2O_5	TEA	265	≈ 50	l. bl./y.	200 × 80
291/37 – 41	NH_4VO_3	TEA	265	<2	l. gr./bl.	20 × 5
591/7 – 12	V_2O_5	TEA	270	≈ 65	v.l. gr.	260 × 85
691/56 – 59	$VOSO_4$	TPA	300	≈ 40	d. gr.	70 × 30
691/60 – 63	$VOSO_4$	TEA	300	≈ 80	d. dir. gr.	85 × 70
691/64 – 67	V_2O_5	TPA	300	≈ 50	d. dir. gr.	130 × 55

[a] l. light, v. very, bl. blue, y. yellow, gr. green, d. dark, dir. dirty.

the statement by Sung et al.[16] that the template molecules are clearly stronger bound in VAPO-5 due to interactions with the charge centres created by the V^{4+} ions in the framework.

The ESR spectrum (Fig. 2) of vanadium in VAPO-5 shows a well resolved hyperfine structure as it was already reported by Sung et al.[16] and found by us for V-silicalite KVS-5 (ref.[6]). That proves the existence of vanadium in the 4+ oxidation state and in monoatomic dispersion. After calcination, our samples show no ESR signal at all, as opposed to the findings of Sung et al.[16] where the intensity of the signal was only decreased. It proves that in our samples the vanadium ions are completely oxidized to V^{5+}. As we have stated for the KVS-5 zeolite[6], the V^{4+} ions in the framework are easily oxidized while those outside of the framework are difficult to oxidize. On the other hand, Sung et al.[16] report that their samples have more than approx. 60% vanadium in the 4+ oxidation state.

A comparison of these findings shows that: *a*) either the samples of Sung et al.[16] contain a certain amount of extra-framework vanadium which is impossible to oxidize during calcination; *b*) or the calcination process used by them is incorrect, i.e. too short and/or without an appropriate amount of oxygen (muffle furnace).

Comparing the above considerations with those by Miyamoto et al.[15], one can conclude that the statement in ref.[15] that V^{4+} ions are more stable in VAPO-5 than in V-silicalite can not be correct.

The first ^{51}V MAS NMR measurements gave no result. This is probably due to a too small amount of vanadium. Further work is in progress.

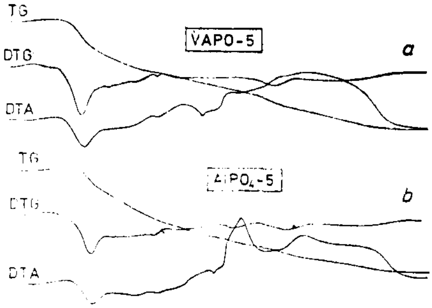

FIG. 1

Thermogravimetric analysis of large crystals of *a* TEA-VAPO-5 and *b* TEA-AlPO$_4$-5: 200 mg sample, static atmosphere, heating rate 10 K/min

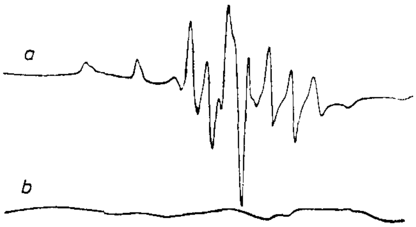

FIG. 2

ESR spectra of as-prepared (*a*) and calcined (*b*) TEA-VAPO-5

CONCLUSIONS

It is possible to synthesize large crystals of VAPO-5 molecular sieve with a good yield. The as-prepared samples contain vanadium in the 4+ oxidation state. These ions are located in the aluminophosphate framework substituted for phosphorus atoms and they can easily be oxidized into V^{5+} and reduced back to V^{4+} by an appropriate redox treatment without leaving the framework. The vanadium ions are concentrated most probably more in the external layers of the crystals than on the inside. The lattice constants of VAPO-5 crystals are significantly smaller than those of $AlPO_4$-5. The template molecules are more strongly bound in VAPO-5 than in $AlPO_4$-5, possibly due to an interaction with framework V ions. As it is shown by ESR and TGA measurements, the complete removal of the template molecules from the crystals requires very carefully chosen treatment conditions.

The authors are indebted to O. Podrezov and A. Vashchenko for the SEM and EPM investigations. The work was partially supported by Bundesministerium für Forschung und Technik, the Polish Committee for Scientific Research (KBN) and NTTM of the State University of Kiev.

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