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Change in the Dehydration and Crystallization Processes of V_2O_5 Xerogel due to Mechanical Pretreatment

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Dehydration and crystallization processes of vanadium pentoxide xerogels, $V_2O_5 \cdot 1.6H_2O$, with and without preliminary mechanical pretreatment, were examined by thermal and structural analyses. During the final step of dehydration of as-prepared xerogel, crystallization into orthorhombic V_2O_5 took place slowly but in one step, with a certain period of coexistence of the starting layer structure. The mechanically pretreated xerogel, in contrast, crystallized itself in two steps with a separated nucleation and growth, and allowed a smaller period of coexistence with the layer structure. These phenomena are associated with the disproportionation of the bonding state of interfoliar H_2O.

Introduction

Finely divided and highly pure metal oxide materials are often prepared from organic as well as inorganic sols (*1*). The reactivity and other important properties of the oxides prepared by these sol–gel processes could be controlled better if the dehydration and crystallization of the gels on heating were regulated more precisely.

Xerogels of vanadium pentoxide, $V_2O_5 \cdot nH_2O$, are attracting increasing interests in materials science in relation to the above-mentioned starting material for oxide materials and as a host material for intercalation (*2, 3*). Structural and chemical properties of vanadium pentoxide xerogels were studied thoroughly by Legendre and coworkers (*4, 5*), Aldebert *et al.* (*6, 7*), and Abello *et al.* (*8, 9*) by means of X-ray, neutron, or electron diffractometry and IR or Raman spectroscopies. Vanadium pentoxide xerogels are known to have a fibrous structure with a one-dimensional ordering. However, there is a close structural relationship with that of the crystalline, anhydrous vanadium pentoxide (*4, 5*). The dehydration is known to comprise three distinct steps (*8*). The final stage of the dehydration and the crystallization of the xerogel are believed to occur simultaneously when the number of moles of H_2O, n, per formula weight of V_2O_5, reduces to below 0.3. Little has been attempted, however, to control or separate these two processes.

In the field of mechanochemical studies, it is known that the effects of mechanical stress are quite diverse. This led us to an idea that there might be a possibility of changing the rates of dehydration and crystallization in different manners by applying mechanical stresses on xerogels. Most of the reported structural change and decomposition of inorganic materials due to mechanical treatments are interpreted as a result of crystallographical degradation or amorphization of the starting material. In contrast, only a few studies were reported on the effects of mechanical pretreatment on the noncrystalline materials (*10–12*).

The general purpose of the present study is to examine the change in the states of vanadium pentoxide xerogels due to mechanical pretreatment. More specifically,

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we tried to pursue the change in the binding state of water molecules in a xerogel upon treating them mechanically. At the same time, an attempt was made to seek a feasibility of controlling the dehydration and crystallization processes of V_2O_5 xerogels separately.

Experimental

1. Preparation of Xerogel

With an ion-exchange resin (Amberlite 1R-118), sodium metavanadate in a 0.4 *M* aqueous solution was converted to decavanadic acid. After aging the latter solution for 4 weeks in air at room temperature, a concentrated sol of $V_2O_5 \cdot nH_2O$ ($n > 100$) was obtained. The sol was then dried on a flat pan coated with PTFE under oxygen flow at 50°C for 4 hr to obtain a thin film of xerogel with n being approximately 1.6. A powdered gel, denoted sample VG, was obtained by crushing the gel film gently in an agate mortar.

Mechanical pretreatment was carried out with a small vibration mill of up-and-down motion (Glen-Creston) with amplitude 50 mm and frequency 12 Hz, for up to 24 hr. One gram of xerogel, 7.3 cm^3 cyclohexane, and two 12-mm agate balls were put together into an agate cylindrical vessel of 18.7-mm i.d. and 12-cm^3 capacity. Cyclohexane, being nonpolar and hence showing no sign of intercalation into the xerogel, was used to prevent the reduction of V(V) and the influence of atmospheric moisture during grinding. The mechanically pretreated gel is henceforth denoted as sample VG-M.

2. Characterization

The dehydration and crystallization processes were monitored by thermal analyses (Rigaku, Thermoflex), i.e., thermogravimetry (TG) and differential scanning calorimetry (DSC). A linear heating condition, i.e., 10 K min^{-1} in a nitrogen flow at 100 cm^3 min^{-1}, was maintained throughout the present study, including the quenched samples

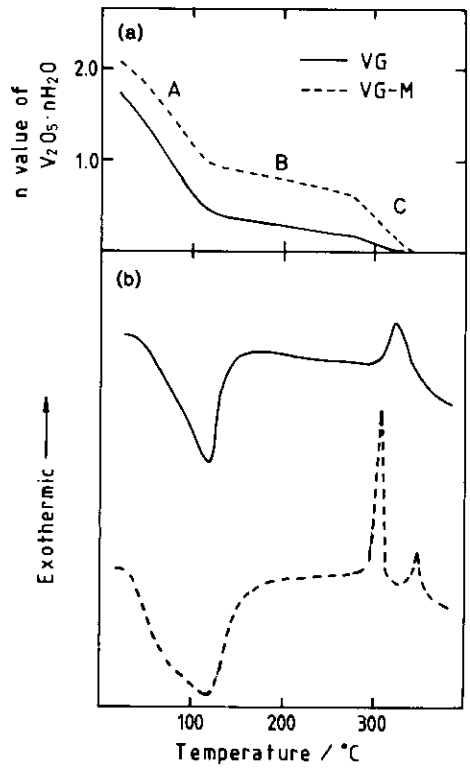

FIG. 1. TG (a) and DSC (b) profiles of xerogel: VG, untreated; VG-M, mechanically pretreated.

for the following X-ray and IR measurements. X-ray diffractometry (XRD) was carried out with Cu$K\alpha$ line source by a conventional method. The KBr disk method was employed for the FT-IR measurement (Bio-Rad, Digilab, FTS-65). X-ray photoelectron spectroscopy (JEOL, JPS-90SX) was carried out by using Mg$K\alpha$. Possible error due to charge up was corrected by using a standard binding energy, 87.0 eV of Au $4f_{3/2}$.

Results and Discussion

1. Process of Thermal Dehydration

In accordance with the report of Abello *et al.* (*8*), the dehydration process of V_2O_5 xerogels with and without mechanical pretreatment was divided into three steps, A–C, as indicated in Fig. 1a. A sample with a preliminary mechanical pretreatment

showed a larger amount of total weight loss. This might partly be attributed to the adsorption of environmental water. However, the relative extent of first step dehydration (step A) with regard to the total weight loss of each sample decreased from 75.5% for as-prepared gel (VG) to 53.6% for mechanically pretreated gel (VG-M). In contrast, the relative amount of the third-step dehydration (step C) increased from 8 to 30.8% after mechanical pretreatment. If the larger weight loss were attributed only to the adsorbed water, the first-step dehydration alone should have increased and not the third step. Therefore, it is clear that some qualitative change in the state of the remaining interfoliar water molecules took place.

2. *Change in the DSC Profile*

DSC profiles of the xerogels with and without mechanical pretreatment are compared in Fig. 1b. The broad endothermic peak at 120°C was common to both samples. By comparing with the results of thermogravimetry, it is clear that the endothermic peak is attributed to the first step dehydration. In contrast to the report of Abello *et al.* (*8*), however, no peak due to the second step dehydration was observed. It may be associated with the smaller amount of the water molecules detached at the second stage as compared to those from the reported results.

While a single broad exothermic peak due to crystallization was observed at 323°C on VG, the exothermic peak was split into two sharper ones with their top peaks at 309 and 348°C. The change in the DSC thermogram suggests the change in the mechanism of the crystallization and related energy liberation as a result of mechanical pretreatment, as discussed below, by referring the change in the dehydration behavior, mentioned in the previous section.

3. *State of H_2O in Xerogel*

Infrared bands due to O–H stretching from the intact and mechanically pretreated xerogels are shown in Fig. 2. The adsorption band from as-prepared xerogel, VG, is rather broad, suggesting a wide and more or less continuous distribution of the state of water. After mechanical pretreatment, a stronger absorption around 3600 cm^{-1} was observed with a remaining shoulder around 3400 cm^{-1}. According to the thorough spectroscopic study on amorphous V_2O_5 by Sanchez *et al.* (*13*), the absorption at 3610 cm^{-1} is attributed to relatively free water molecules, while that at 3370 cm^{-1} to water molecules associated through hydrogen bonds.

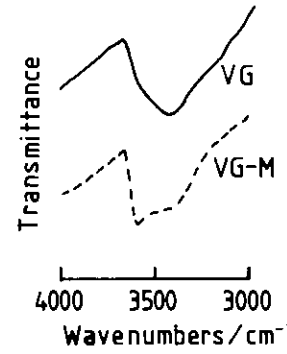

FIG. 2. IR absorption spectra; VG, untreated; VG-M, mechanically pretreated.

The physical significance of the change in the bonding state is more explicitly shown by O_{1s} profile of the X-ray photoelectron spectroscopy (XPS), shown in Fig. 3. According to Erre *et al.* (*14*), the binding energy of the O_{1s} from free H_2O, from hydrogen-bonded oxygen, and from the V_2O_5 latatice are well distinguished, as denoted by A, B, and C, respectively, in Fig. 3. The increase in the relative significance of the oxygen atoms taking part in the hydrogen bonding is quite obvious.

The results of IR and XPS consistently suggest the shift of part of the interfoliar water in the direction of higher energy and the rest in the opposite direction, resulting in a kind of disproportionation of the bonding state. Splitting of the DSC peaks from one at 323°C into two at 309 and 348°C, respectively, with their sharpening by mechanical pretreatment must also be an indication of

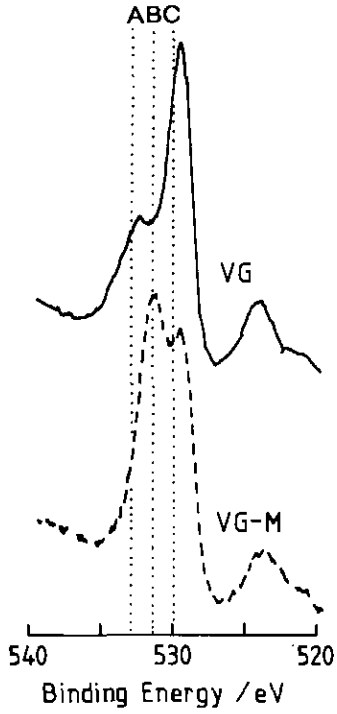

FIG. 3. X-ray photoelectron spectra: VG, untreated; VG-M, mechanically pretreated.

the disproportionation of the bonding state of H_2O, in accordance with the spectroscopic observations discussed just above.

Weakly bound H_2O molecules are likelier to become free or detach and readsorb during mechanical pretreatment, whereas enhancement of the hydrogen bonding took place. Out of the two possibilities of hydrogen bonding, i.e., either by linking two fibrils or falling into the large cavities of the V_2O_5 "crystals," Abello *et al.* concluded that the water molecules in the cavities are more likely, as they studied the thermal dehydration of V_2O_5 xerogels (*8*). In the case of change in the state of water as a result of mechanical treatment, the situation may not necessarily be the same. By the mechanical pretreatment, change in the coordination number of vanadium atom could take place as a result of bond breakage in the decavanadate units specific to the V_2O_5 xerogel. This brings about the change in the electronic state of oxygen, which, in turn, could change the extent of polarization of interfoliar water (*5*). This is discussed below in relation to the crystallization process.

4. Crystallization Processes

Mechanical pretreatment did not bring about an appreciable change in the basal spacing of the layer structure, as determined from the X-ray diffractograms shown in Figs. 4 and 5. No appreciable increase in V(IV) from ca. 1.5% due to mechanical pretreatment was observed either. The only change in the X-ray diffractograms due to mechanical pretreatment before heating is weakening and broadening of the diffraction peaks, indicating an increase in the disorder in a layer and/or stacking.

The XRD peaks of the samples after heating to different temperatures and quenching are also shown in Figs. 4 and 5. Profiles of

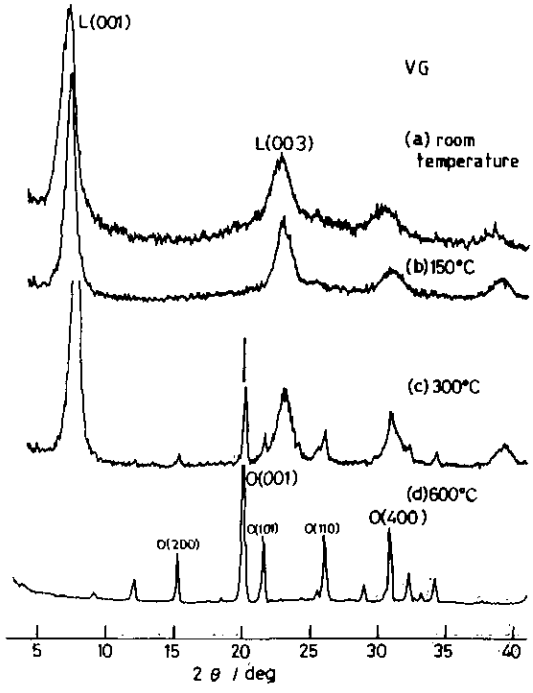

FIG. 4. Profiles of X-ray diffractograms of untreated xerogel heated up to different temperatures and quenched. L and O denote layer and orthorhombic structures, respectively.

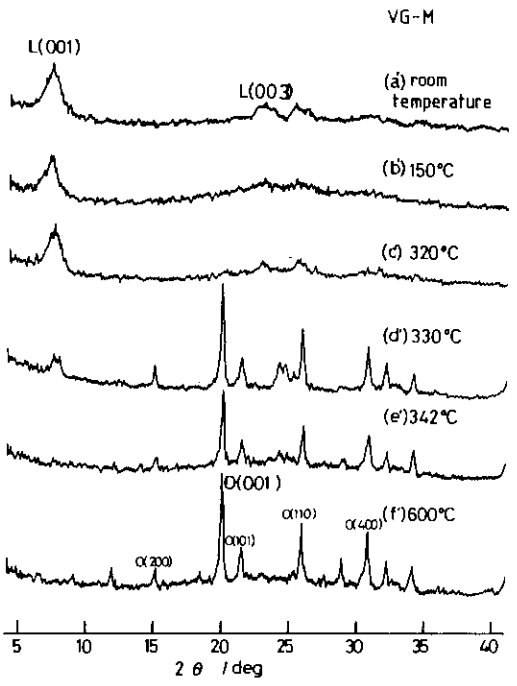

FIG. 5. Profiles of X-ray diffractograms of mechanically pretreated xerogel heated up to different temperatures and quenched. L and O denote layer and orthorhombic structures, respectively.

each sample remained practically unchanged when they were heated to the temperature just below the onset of the third-step dehydration. They comprise only the diffraction peaks from the planes of the layer structure, with a substantial broadening after mechanical pretreatment.

It is to be noted that the orthorhombic phase did not appear from the sample VG-M at 320°C, just after the first sharp exothermic peak. Therefore, the first one out of two exothermic processes seems to be associated with the liberation of stored energy during a structural relaxation with simultaneous dehydration. An exothermic process of mechanically pretreated materials associated with the liberation of stored energy is often observed in various materials (*16–19*). The content of the first step relaxation is not quite evident. However, it should be kept in mind that the energy released due to this first-step relaxation, after compensating the energy absorption due to dehydration, is almost three-quarters of the total heat evolved in the course of entire crystallization. In addition, no sign of the recovery of the layered structure was observed on heating the mechanically pretreated xerogel. Therefore, such kind of large energy liberation cannot be explained without taking the nucleation of the crystalline V_2O_5 into account. On the other hand, the second exothermic peak, above which X-ray diffraction peaks were observed, is obviously associated with a crystal growth process, or development of long-range ordering of anhydrous, orthorhombic V_2O_5, accompanied by a simultaneous final stage dehydration.

As shown in Fig. 5, the appearance of the first X-ray diffraction peak of orthorhombic V_2O_5 shifted to higher temperatures after mechanical pretreatment. This leads us to the conclusion that the mechanical pretreatment accelerated the onset of the relaxation, coupled with the initiation of crystallization or nucleation, but retarded the formation of the long-range ordering, i.e., propagation or crystal growth.

The definite mechanism of nucleation of orthorhombic V_2O_5 from V_2O_5 xerogels is not yet proposed. It is clear, however, that VO_6 octahedra in the decavanadate ion should somehow be converted into V_2O_5 crystal, where the construction unit is the vanadium (V) ion surrounded by five oxygen atoms (*20*). It is also evident that dehydration is necessary for this kind of change in the coordination number and, accordingly, for nucleation of the orthorhombic phase.

5. Consequences of Mechanical Pretreatment

As discussed previously, the bonding state of the remaining water in the xerogel became looser for one case, and for the other, tighter after mechanical pretreatment. It is therefore reasonable to assume that the nucleation was accelerated, because some of the water molecules in the third-step dehydration were detached more easily, while the rest of the water entrapped

in the cavity of V_2O_5 unit blocked the long-range ordering and hence retarded the alignment of the repeating units into the orthorhombic crystal of V_2O_5.

Based on the careful analyses including ESR, Gharbi *et al.* concluded that V(IV), included inevitably in V_2O_5 xerogels, is surrounded by six oxygens (*20*). The sixth coordination site might be occupied by a water molecule. Crystallization cannot take place without removing that water molecule. After mechanical pretreatment, the amount of V(IV) did not appreciably increase from the ca. 1.5% contained in the as-prepared xerogel. However, only a trace of persisting water around V(IV) could block the entire crystallization. Thus, it can also be stated that the trace amount of water apparently stabilizes the amorphous V_2O_5 when the water molecules are incorporated in the gel structure, like those through a direct coordination to V(IV), just mentioned above.

In this moment, it is to be reminded that mechanochemical processes are much more heterogeneous than thermal processes. Thus, it is reasonable to assume that those local spots, where the water around either V(V) or V(IV), the latter being located as the sixth ligand, has been removed, nucleation can occur. However, in other spots where the last water molecules are stabilized by hydrogen bonding, the long-range ordering of the orthorhombic V_2O_5 is blocked. Thus the crystal growth after mechanical pretreatment, and accordingly, the appearance of the X-ray diffraction peaks, was retarded. Similar phenomena of separated nucleation and growth from mechanically activated gels were observed upon heating the mechanically pretreated gel mixture, $PbO–TiO_2$ (*21*), although in the latter case preexisting PbO crystallites may have played another important role.

Concluding Remarks

The disproportionation of the bonding state of interfoliar H_2O took place by mechanical pretreatment of V_2O_5 xerogel. This led to the promotion of nucleation and the retardation of long-range ordering, resulting in a two-step crystallization.

When H_2O or OH groups are deleted from a hydrated oxide, the "wound" must be healed and stabilized upon subsequent heating. However, it may not always be accompanied by a change in the long-range ordering which results in a change in the entire crystalline or noncrystalline state. Instead, a local stabilization by nucleation of orthorhombic V_2O_5, spot by spot, may well suffice for such types of energy compensation. Thus, the independent control of dehydration, nucleation, and growth processes by an appropriate mechanical pretreatment seems, if not to an unlimited extent, to be quite possible.

Acknowledgments

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