INFLUENCE OF PARTICLE-SIZE AND CONCENTRATION ON THE INFRARED SPECTRUM OF V_2O_5

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Transmission curves of V_2O_5 powder imbedded in KBr or suspended in paraffine oil werse measured in the IR spectral range. It was found that the position of the absorption bands doe not change with the particle-size or concentration of the V_2O_5, while the shape of the curves and the transmission values undergo changes.

Vanadium pentoxide is a catalyst frequently used in oxidation processes of organic compounds. Its catalytic effect was studied, chiefly with IR methods, by several authors [1—3]. As well known, for measuring IR transmission spectra, the powder of the material to be studied is imbedded in compressed KBr tablets. The shape of the absorption curves and the position of the absorption bands give valuable information concerning the stretching vibrations of the various atom groups, as well as about chemical and physical processes important for the catalysis. It is, however, essential to secure favourable conditions for measuring the spectra to be analyzed. In this respect the particle-size and concentration of the powder, compressed in the KBr tablet, may play an important role. The purpose of the present paper was to investigate this problem in V_2O_5 tablets.

Methods and results

Transmission measurements were made with V_2O_5 powders of different particle-size and concentration, compressed in KBr tablets of 20 mm diameter and 0.92 mm thickness, or suspended in paraffine oil. The samples were prepared from (REANAL) a.p. grade V_2O_5 with KBr and paraffine oil of spectroscopical purity (MERCK products).

For preparing the tablets, 800 mg KBr was mixed with the corresponding quantity of V_2O_5 powder and ground in a vibrator. For separating the V_2O_5 powders of different particle-size, sieves (from 90 to 40 μ) and sedimentation (for particles 0 to 36 μ) were used. The specific surface area of the V_2O_5 powders of different particle-size was determined with the method of BRUNAUER, EMMET and TELLER (BET method) by measuring the nitrogen quantity adsorbed on the surface. For compressing the tablets, the V_2O_5 was thoroughly mixed with the KBr imbedding material and the samples compressed to tablets in a ZEISS DP 36 decimal hydraulic press with 220 kp/cm^2 pressure.

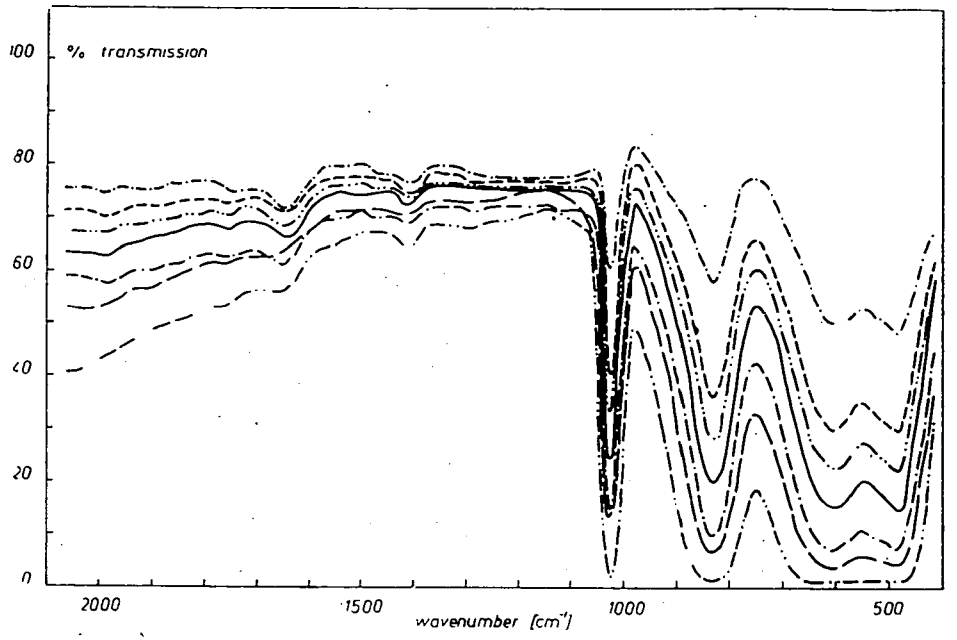

Fig. 1. Transmission curves of V_2O_5 powder of different concentration imbedded in KBr: —·— 0.4 mg, ------- 0.6 mg, —··—·· 0.8 mg, —— 1.0 mg, ——· 1.2 mg, ——— 1.6 mg, ——·· 3.0 mg, V_2O_5 in 800 mg KBr.

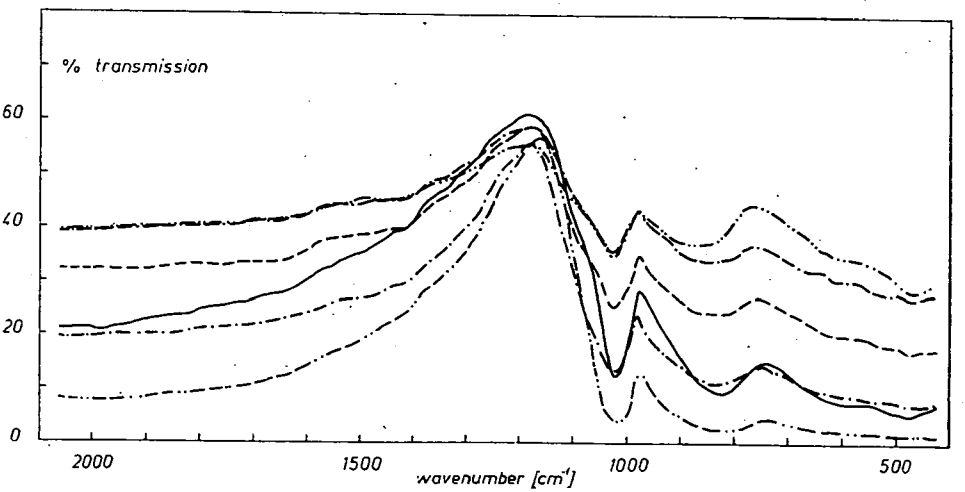

Fig. 2. Transmission curves of V_2O_5 powder of different particle-size (10 mg V_2O_5 imbedded in 800 mg KBr): ——— "unselected" powder as obtained from the factory, ——·· 0—36 μ, —·—· 40—45 μ, ——— 45—63 μ, ——· 63—80 μ, —·· 80—90 μ particle-size.

For the paraffine oil suspensions V_2O_5 was ground with the oil in an agate mortar; the transmission curves were measured in a dismountable cuvette.

The IR spectra of the samples were measured with a ZEISS UR-20 IR spectrophotometer using the double-beam method in the wavenumber range $\tilde{\nu}=400\ cm^{-1}$ to $2000\ cm^{-1}$, with respect to the position of the absorption bands important for the catalytic effect. The transmission curves of the samples prepared as described above are to be seen in Figs. 1 to 4.

Fig. 1 shows the transmission curves of tablets containing 0.4 to 3.0 mg V_2O_5 powder each. In accordance with results published in literature [4—7] we found sharp absorption bands at $\tilde{\nu}=1025\ cm^{-1}$ and $\tilde{\nu}=830\ cm^{-1}$, to be attributed to the stretching vibrations of the V=O and the V-O-V group, respectively. In the wavenumber range $400\ cm^{-1}$ to $600\ cm^{-1}$ a comparatively broad absorption band can be seen, which, according to literature, is attributed to lattice vibrations. As can be seen from the figure, the position of the absorption bands remains unchanged with warying V_2O_5 concentrations, while the width of the bands undergoes changes.

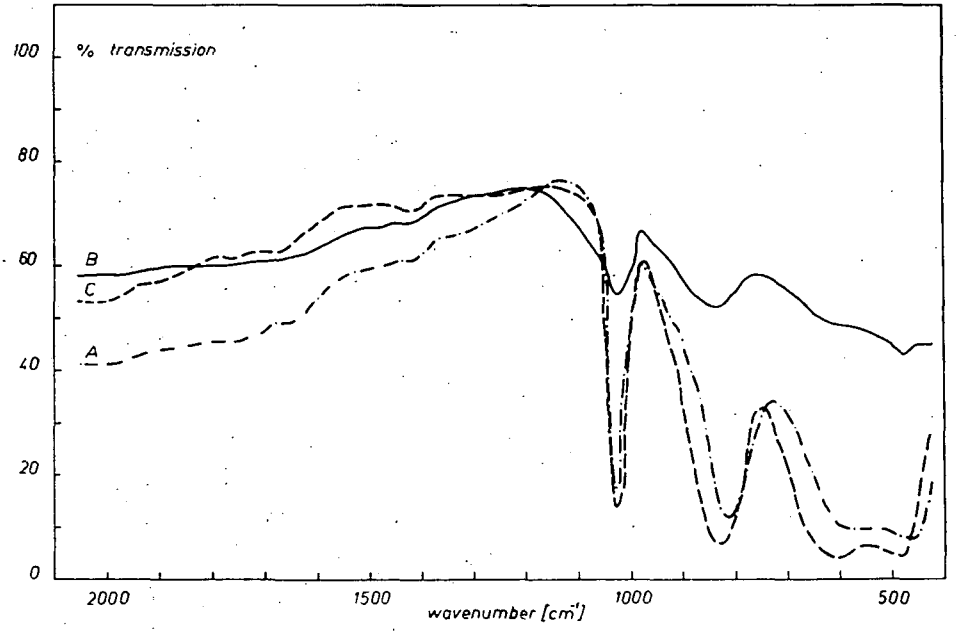

Fig. 3. Transmission curves of V_2O_5 powder prepared by different methods, imbedded in KBr (1.6 mg V_2O_5 in 800 mg KBr). *A:* powder ground from V_2O_5 single crystals, *B:* "unselected" powder as obtained from the factory, *C:* powder ground with KBr in a vibrator.

In Fig. 2 the changes in transmission due to changes in particle-size can be seen for constant concentration of the V_2O_5 powder. The specific surface areas corresponding to the particle-size 0 to 36 μ, 40 to 45 μ, 45 to 63 μ, 63 to 80 μ, 80 to 90 μ, determined with the BET method, are 2.745 m^2/g, 2.538 m^2/g, 2.332 m^2/g, 2.082 m^2/g and 2.077 m^2/g, respectively. Fig. 2 contains also the transmission curves of the "unselected" powder, as obtained from the factory. As can be seen from the

curves, changes in particle-size are without influence on the position of the absorption bands, whereas the transmission values and the width of the sharp band at 1025 cm^{-1} undergo significant modifications.

In Fig. 3 the transmission curves of V_2O_5 powders prepared in different ways and imbedded in KBr, are presented. Curve *A* was measured with powder ground from V_2O_5 single crystals, curve *B* with the "unselected" V_2O_5 powder thoroughly

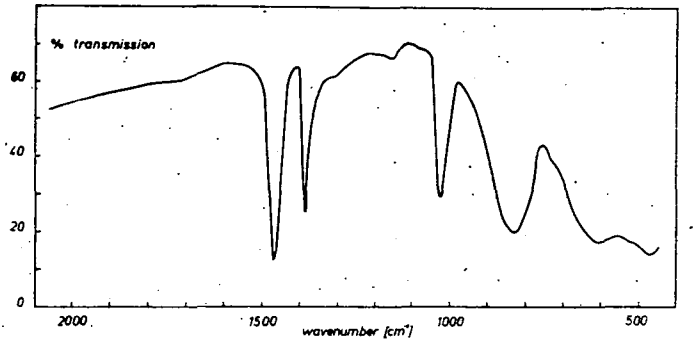

Fig. 4. Transmission curve of V_2O_5 ground in paraffine oil.

mixed with KBr, curve *C* with the same V_2O_5 powder ground with the KBr in a vibrator. The transmission curves *A* and *C* are quite similar, only a small shift in the position of the stretching vibrations attributed to V-O-V groups and in that of the broad absorption band corresponding to lattice vibrations can be found. The transmission curves *B* of the "unselected" powder show significant deviations from curves *A* and *C*, which proves the influence of the particle-size in modifying the transmission values.

Fig. 1 to 3 may be used as a basis for determining the optimal experimental conditions of preparing samples which can be expected to give the best results in studying the absorption bands attributed to stretching vibrations and lattice vibrations.

Fig. 4 shows the transmission spectrum of V_2O_5 suspended in paraffine oil. It can be seen that, apart from the absorption bands at $\tilde{\nu}=1385\ cm^{-1}$ and 1470 cm^{-1} due to the deformation vibrations of the CH group, the bands corresponding to stretching vibrations and lattice vibrations can be well determined and appear at the same wavenumbers as in the compressed samples.

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ВЛИЯНИЕ ВЕЛИЧИН ЗЕРЕН И КОНЦЕНТРАЦИИ НА ИНФРАКРАСНЫЙ СПЕКТР V_2O_5

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Мы сняли пропускание впрессованного в KBr и взвешенного в парафиновом масле порошка V_2O_5, в инфракрасной области спектра. Было установлено, что положение полос поглощения с ростом величин зерен или изменением концентрации V_2O_5 не меняется, но изменяются формы кривых и интенсивности пропускания.