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Characterization of niobium pentoxide prepared by flame reaction

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Finely divided and well-crystallized niobium oxide has been prepared by flame reaction and identified as L–Nb_2O_5. The solid particles are non-porous, with a specific surface area in the range 30 to 50 $m^2 g^{-1}$. They are stable under oxygen or vacuum up to 673 K. A heat treatment under hydrogen, at temperature higher than 573 K, is sufficient to create some modifications in the absorption spectrum attributed to electrons solvated by the solid.

1. Introduction

In spite of various investigations of niobium pentoxide polymorphism, the existence and stability ranges of the different modifications are not well established.

Brauer [1] first reported on three polymorphic forms encountered at low (T), medium (M) and high (H) temperature. Later, Schäfer *et al.* [2] confirmed the existence of three phases, but the transition temperatures were somewhat different. Frevel and Rinn [3] observed a pseudo-hexagonal δ-form which Holtzberg *et al.* [4] believed to be a poorly crystallized state of the T-phase. Shafer and Roy [5] under high water pressure claimed the existence of four polymorphs named III, II, I low and I high, which progressively formed as the temperature was increased. Form II was believed to be Brauer's M-form. Another form, R–Nb_2O_5, was described by Gruehn [6], with a V_2O_5-type structure. According to Andersson [7], the substitution of O_2^- by OH^- and F^- transformed H–Nb_2O_5 to a new form, N–Nb_2O_5.

A summary and a correspondence table of symbols used to designate the various forms has been published [8]. Schäfer's nomenclature indicates either the transition temperature (TT, T, M, H) or the crystal habit (P prism, N needle . . .).

For Crawford and Anderson [9] H–Nb_2O_5 is the stable high-temperature structure into which all the polymorphs are transformed above about 1220 K. The differences in free energy between H–Nb_2O_5 and its metastable polymorphs are certainly small compared with the cohesive energy of the structures. There is a critical dependence of temperature, pressure and impurity content on the resulting form.

The strain field around a nucleus, modified by preparation conditions, either from solution or from gases, might be responsible for modifications of crystal order.

More recently Waring *et al.* [10] have proposed a pressure–temperature phase equilibrium diagram for Nb_2O_5 (Fig. 1), with four single-phase regions. The L-form (Brauer's T form) exists both in the low temperature–high pressure and in the high temperature–high pressure ranges. However, this form has also been reported to be a metastable phase resulting from low-temperature crystallization from solution [1]. L–Nb_2O_5 has an orthorhombic structure.

The B-modification, according to Schäfer *et al.*'s nomenclature [8], also named zeta-Nb_2O_5 by Laves *et al.* [11], was indexed on the basis of a monoclinic unit cell.

The high-temperature form, H, has been indexed on a monoclinic unit cell [4, 5].

More recently, interest in the catalytic properties of niobium pentoxide as an active phase or as part of a complex system has appeared. An Fe_2O_3–Nb_2O_5–Cr_2O_3 catalyst was reported to be active for the alkylation of phenol with methanol and selective for 2,6-xylenol production [12]. For Fischer Tropsch synthesis, an increase of selectivity for oxygen-containing compounds was observed going from an Rh–SiO_2 to an Rh–Nb_2O_5–SiO_2 catalyst [13]. Generally, the support effects, and more especially the ability for an Nb_2O_5 support to be in strong interaction with a metal, have been found important for CO hydrogenation; Rh–Nb_2O_5 and Ni–Nb_2O_5 catalysts exhibit high selectivity toward the production of higher hydrocarbons [14, 15].

For the reduction of NO_x by NH_3, a honeycomb V_2O_5–Nb_2O_5–TiO_2 catalyst has also been developed [16]. The main characteristics of such systems are an ability to withstand poisoning and a high thermal stability.

In these examples, little is known about the structure of Nb_2O_5 directly derived from the initial preparation and about possible changes resulting from activation or regeneration upon heat treatments, even though

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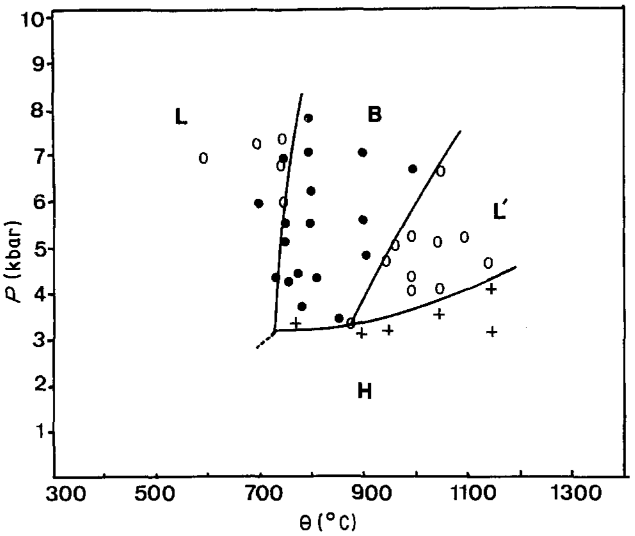

Figure 1 Pressure–temperature phase equilibrium diagram for Nb_2O_5, from Warring *et al.* [10]. 1 kbar = 10^8 Pa.

Nb_2O_5 polymorphism might have an influence on the catalytic properties.

Among the various preparation processes, gas phase methods are currently used to obtain divided oxides (Al_2O_3, SiO_2, TiO_2 etc.). The flame reaction method, developed in the laboratory [17, 18], is particularly suitable to prepare finely divided particles. By controlling thermodynamic parameters, the flame reaction temperature and the reactive species concentration, and a kinetic parameter, the residence time of the reactive species in the flame (i.e. in the reaction zone), it is possible to change the particle size, the size distribution, the morphological aspect and, in some cases, the crystalline structure [19].

2. Experimental procedure

2.1. Preparation of niobium oxide from a hydrogen–oxygen flame

Niobium oxide particles are obtained by hydrolysis and/or oxidation of niobium pentachloride. The reaction occurs in a hydrogen–oxygen flame. The oxide particles result from the condensation (homogeneous nucleation and growth) of the supersaturated vapour formed by the reaction in the gas phase.

The reactor used in the laboratory consists of four concentric tubes. The metallic chloride vapour carried out by a stream of oxygen and/or nitrogen is fed in through the central tube. Pure hydrogen or a mixture of hydrogen and nitrogen is injected into the third tube. The second tube is used to form a nitrogen screen between the reaction partners in order to avoid the formation of oxide on the wall of the central tube. Without this screen, in a few minutes a plug of oxide is formed. The fourth (outside) tube allows a suitable oxygen feed.

The reaction parameters may be modified by changing the mass flow rate of the different gases.

2.2. Physical characterization

The oxides were studied by a Jeol 100 CX transmission electron microscope after manual grinding, dispersion in ethanol under ultrasound shaking and deposition on a carbon-covered copper grid.

X-ray diffraction (XRD) data were collected using step-scan procedures (0.016°/2θ-step; counting time, 2 sec) on a Siemens D-500 diffractometer system. Incoherent background from nickel-filtered Cu$K\alpha$-radiation was reduced by a back graphite monochromator, quartz standard calibration being carried out as a routine. The Siemens Diffrac-11 software allows data collection and treatment on a PDP 11-23+ computer, including peak maximum and shape analysis, JCPDS standard fitting and direct semi-quantitative phase analysis.

The UV spectra were recorded at room temperature with a Perkin-Elmer λ9 spectrometer using the diffuse reflection technique and $BaSO_4$ as a reference.

3. Results

Two samples of Nb_2O_5 were prepared using the same total flow rate ($3.2 \times 10^{-4}\,m^3\,sec^{-1}$) but modifying the nature of the gas used to carry out the niobium chloride.

The first sample, Nb_2O_5 (I), was obtained by carrying out the chloride vapour with an oxygen stream and for the second sample, Nb_2O_5 (II), the carrier gas was nitrogen.

Finely divided particles were obtained; the specific surface areas determined by using the BET method were 32 and 47 $m^2\,g^{-1}$ for Nb_2O_5 (I) and Nb_2O_5 (II), respectively. As shown on the electron micrograph of Nb_2O_5 (I) (Fig. 2), the particles mainly exhibit isometric shapes and frequently appear as isolated one from the other. The particle size distribution tends to be narrow

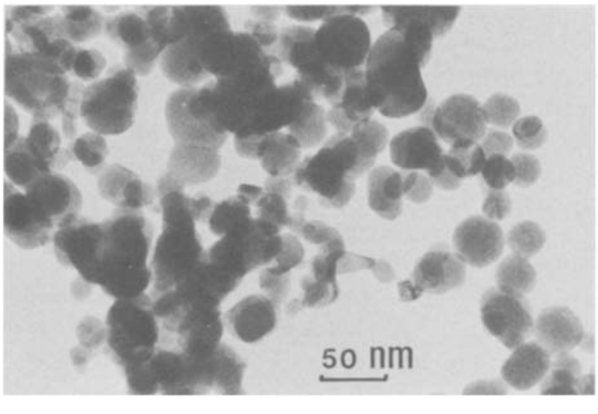

Figure 2 Electron micrograph of Nb_2O_5 (I).

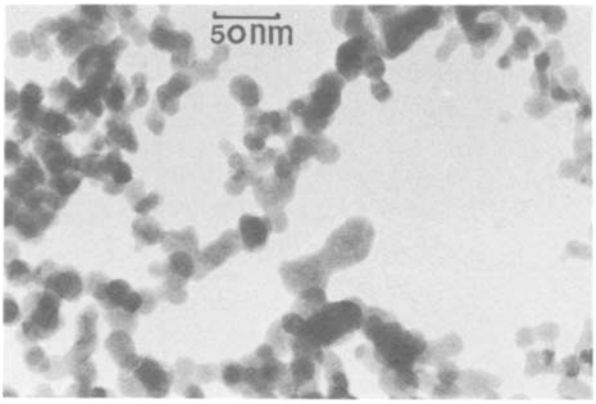

Figure 3 Electron micrograph of Nb_2O_5 (II).

with a mean diameter in the range from 25 to 45 nm. For Nb_2O_5 (II) (Fig. 3) there is also evidence of pseudo-spherical particles, but in contrast to Nb_2O_5 (I) a chain-like formation between the particles is frequently observed. The mean diameter is in the range from 15 to 30 nm.

Taking 4.5 as the specific gravity of Nb_2O_5, the mean particle diameters obtained from the BET surface areas (42 and 28 nm for Nb_2O_5 (I) and Nb_2O_5 (II), respectively) are in fair agreement with the range of particle size evidenced by microscopic examination. This agreement confirms that the solids are non-porous, as expected from a preparation process involving nucleation as the first step of crystallization followed by a growth mechanism.

Fig. 4 shows the X-ray powder diffraction pattern of Sample I directly derived from the flame reaction, without further heat treatment. It matches the 27-1003 ASTM pattern of Nb_2O_5.

By X-ray line broadening analysis (XRLBA) it is possible to calculate a mean diameter of the crystallized areas. For example, using either (0 0 1) or (0 0 2) line broadening, it was possible to calculate mean particle sizes of 22 and 18 nm for Nb_2O_5 (I) and Nb_2O_5 (II), respectively.

The UV-visible and near-infrared absorption spectrum of Sample I is represented in Fig. 5a. A main absorption band appears at 260 nm and two minor bands are observed at 1380 and 2210 nm. No modification of the initial spectrum results from heat treatment under oxygen at 673 K, followed by desorption under vacuum at the same temperature.

TABLE I Electron configuration and maximum absorption bands of niobium species [22]

Species	λ (nm)
Nb (IV) $4d^1$	480, 700
Nb (III) $4d^2$	440, 530, 650
Nb (II) $4d^3$	450
Nb (I) $4d^4$	900

The sample was then treated stepwise, in 13 kPa of H_2, at 473, 573, 673 and 773 K. Up to 473 K, the hydrogen treatment gave no noticeable change. After reduction at 573 K, the sample turned light blue due to a continuous absorption ranging from the visible (about 500 nm) to the near-infrared (2500 nm) (Fig. 5b).

Enhancement of this effect was observed when the temperature of the hydrogen treatment was increased (Fig. 5c). The desorption under vacuum at 773 K did not further change the characteristics of the spectrum (Fig. 5d). Oxygen was then adsorbed on the sample, at room temperature. The intensity of this last-observed wide absorption band rapidly decreased, as illustrated in Fig. 6; oxygen seems to bleach the solids.

4. Discussion

Flame reaction of niobium pentachloride gave rise to a crystallized phase which has been identified to the L–Nb_2O_5 orthorhombic form as described by Waring *et al.* [10]. For these authors, during the preparation, the samples were maintained under high temperature and high pressure until equilibrium was reached. On the other hand, a metastable L–Nb_2O_5 form can be obtained by precipitation and low-temperature crystallization (Brauer's T form). In the same way, during a flame reaction process, equilibrium conditions are unlikely to be reached leading to the formation of metastable phases such as δ-Al_2O_3, γ-Fe_2O_3 and TiO_2 (anatase) [17–19].

The mean diameters of crystallized domains calculated using XRLBA appear smaller than particle mean diameters determined through electron microscopy, or BET surface area measurements. Twinned

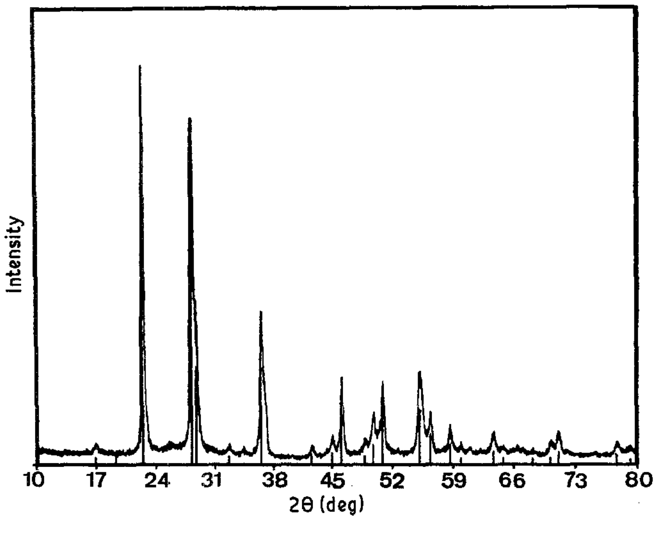

Figure 4 X-ray powder diffraction pattern of Nb_2O_5 (I).

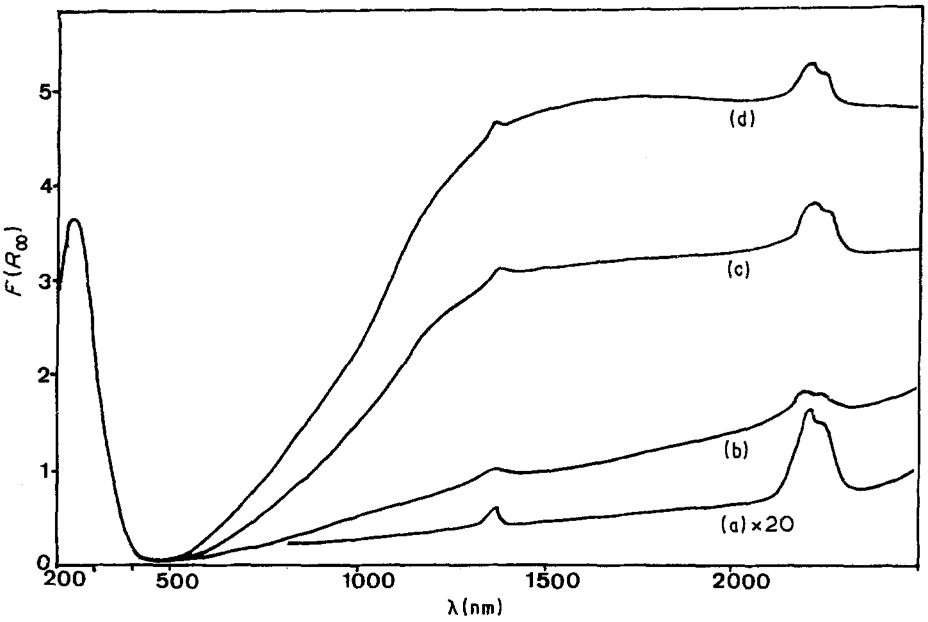

Figure 5 Absorption spectra of Nb_2O_5 (I): (a) as prepared from flame reaction procedure; (b) after hydrogen treatment at 13 kPa and 673 K; (c) after hydrogen treatment at 13 kPa and 773 K; (d) after (c) treatment, then desorption at the same temperature. $F(R)_\infty$ = the remission function or Kubelka–Munk function.

particles may explain these results. For Nb_2O_5 (II) an important background, possibly due to a poorly crystallized phase, is superimposed on the X-ray pattern due to a well-crystallized material.

The electron configuration of the Nb (V) ion being $4d^0$, upon UV irradiation only a charge transfer absorption is likely to occur and has indeed been observed at 260 nm, in agreement with previously reported results [20, 21].

Bands observed at 3740 to 3665 cm^{-1} (2670 to 2730 nm) for Nb_2O_5 are due to O–H stretching of surface hydroxyl groups. Therefore, the bands at 1380 and 2210 nm shown in Fig. 5 could be attributed to the first overtone (2νOH) and to a combination band of (νOH + δNb–OH) of the OH groups, respectively.

The spectrum of Nb_2O_5 is modified by hydrogen treatment at temperature higher than 573 K. During such a process, valency states lower than Nb (V) should be formed.

In Table I are given the absorption bands of the various reduced niobium species [22].

Since no well-defined bands appear, we must assume that localized reduced niobium species have not been created by the hydrogen treatment.

The absence of well-defined bands in the adsorption spectra of TiO_2 reduced by hydrogen has also been reported. Similarly, in solution, the UV spectra of photochemically produced electrons or of electrons produced by radiolysis exhibit a broad adsorption band [22]: the wavelength corresponding to the maximum of absorption ranges from 500 to over 2000 nm, depending upon the polarity of the solvent. In the same way, we tentatively assume the observed UV–visible spectra to be due to electrons, and suggest

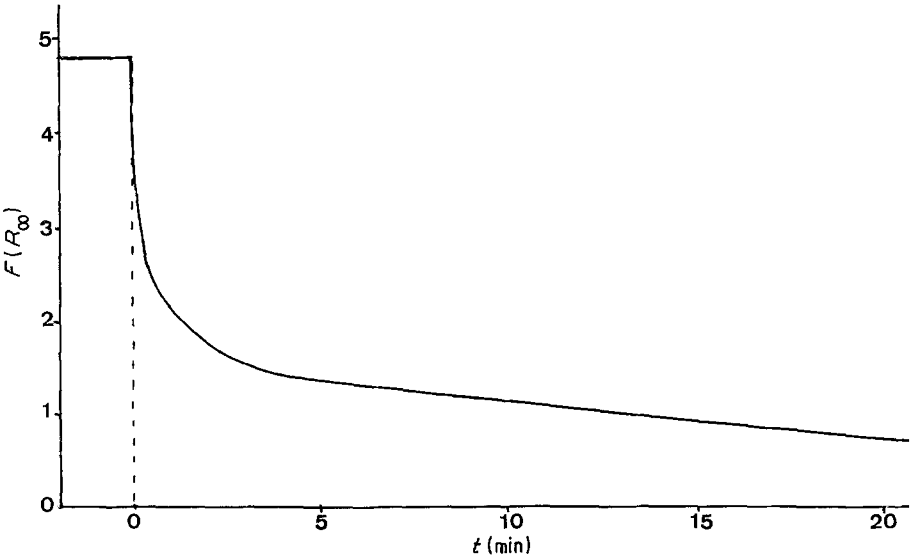

Figure 6 Variation of the intensity of the absorption band, λ = 1800 nm, against time, for Nb_2O_5 (I) treated under 13 kPa H_2 at 773 K, desorbed under vacuum and brought into contact with oxygen at room temperature.

the following reaction to take place:

$$\tfrac{1}{2}H_2 + 2Nb^{5+} + 5O^{2-}$$
$$\rightarrow 2Nb^{5+} + 4O^{2-} + OH^- + e^-$$

the electrons generated being solvated by the solid and not localized on Nb (V) ions, at least at room temperature. The system thus created can be destroyed by oxygen adsorption at room temperature, due to the high electron affinity of O_2.

5. Conclusion

The oxidation and/or hydrolysis of niobium pentachloride in a hydrogen–oxygen flame results in niobium pentoxide formation.

Particles thus formed are well crystallized, pseudospherical, non-porous and approximately homodispersed. According to the reaction conditions, the average diameter is either close to 30 or to 40 nm. By UV, visible and near-infrared absorption study, the samples are shown to be stable under oxygen or vacuum up to 673 K whereas modifications are brought about by hydrogen treatment at temperatures higher than 573 K.

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