

Adsorption Study of Micropore Structure of Tin Dioxide

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Received April 27, 1998

Abstract—The micropore structure of xerogels of tin dioxide prepared by precipitation is studied by the physical adsorption of N_2 , O_2 , and H_2 at $-195.6^\circ C$. The parameters of the microstructure as a whole depend on the adsorbate. The specific surface area of supermicropores measured by the oxygen adsorption exceeds that measured by nitrogen adsorption, and the extent of excess increases linearly with an increase in the supermicropore volume. The samples of tin dioxides have molecular-sieve properties, but they do not contain ultramicropores measurable by the adsorption of molecular hydrogen.

INTRODUCTION

Tin dioxide is widely used as a support in metal catalysts for low-temperature CO oxidation [1], as well as an ion-exchange resin [2, 3]. Therefore, the mechanisms of pore structure formation of its xerogel during low-temperature synthesis are important when a high concentration of the surface ion-exchangeable sites is maintained.

A change in the conditions of synthesis of the tin dioxide gels can lead to different textural parameters required for a specific problem [4]. In connection with this, it is necessary to pay special attention to the formation of micro- and supermicroporous constituents of the structure. The presence of these regions of a pore space significantly affects the properties of xerogels, especially their catalytic and ion-exchange properties.

In addition, the study of microporous objects becomes more and more important due to their wide use in heterogeneous catalysis [5].

The goal of this work is to study the micropore structure of the tin dioxide xerogels prepared by precipitation, which is most common, by adsorption methods.

EXPERIMENTAL

Tin dioxide hydrogels were prepared by precipitation from an aqueous solution of $SnCl_4$ by ammonia at a constant pH ranging from 2 to 9 at $20^\circ C$. The gels obtained were dried in air and then calcined in an oven at $150^\circ C$ for 6 h [4, 6].

The pore structure of the SnO_2 xerogels was studied on an automatic setup DigiSorb-2600 Micromeritics by measuring the adsorption isotherms of nitrogen, oxygen, and hydrogen at $-195.6^\circ C$. The samples were previously treated in a vacuum at $180^\circ C$ for 6 h. The adsorption isotherms of nitrogen and oxygen were treated by a comparative method using reference isotherms presented in [7, 8]; the adsorption isotherms for hydrogen were treated according to an original proce-

dure, the so-called “volumetric” comparative method proposed earlier [9, 10].

The true density of samples ρ was measured against helium on an Autopycnometer-1320 Micromeritics apparatus. X-ray diffraction analysis was carried out on a DRON-1.5 diffractometer with monochromatic CuK_α irradiation. The amount of the crystalline phase of cassiterite was determined by the (110) line using SnO_2 calcined at $500^\circ C$ as an external standard.

RESULTS AND DISCUSSION

As was shown in [4, 6], SnO_2 xerogels precipitated at pH from 2 to 9 contain a significant volume of micropores. However, at pH > 5 , only the micro- and supermicropore textures are formed. According to the XRD data and the true density values ρ , a negligible amount of the cassiterite phase is present in the samples under the conditions of synthesis; that is, the amorphous framework of the xerogel is generally formed.

Our data presented in part in Figs. 1 and 2 suggest that the capillary-condensation hysteresis is absent on the adsorption isotherms of N_2 and O_2 on the samples prepared at pH > 5 . This in turn can indicate the absence of a marked mesopore volume. However, whereas the adsorption isotherms of O_2 are reversible in the whole range of the relative pressures, the adsorption isotherms of N_2 have a small hysteresis ($2-3 \text{ cm}^3/\text{g}$), which extends to the region of the relative pressures that are lower than the start of the usual capillary-condensation hysteresis (it is not seen on the scale of Fig. 1). This phenomenon is likely associated with the presence of pores whose sizes are comparable with the kinetic size of the nitrogen molecule ($\sigma_k = 0.364 \text{ nm}$). In this case, the adsorption-desorption processes are retarded because of the activated diffusion of the sorbate molecules into ultramicropores [11]. The diffusion of the O_2 molecules with a smaller kinetic diameter ($\sigma_k = 0.346 \text{ nm}$) [12] into the pores of this size is nonactivated, and this fact is confirmed by the experimental data.

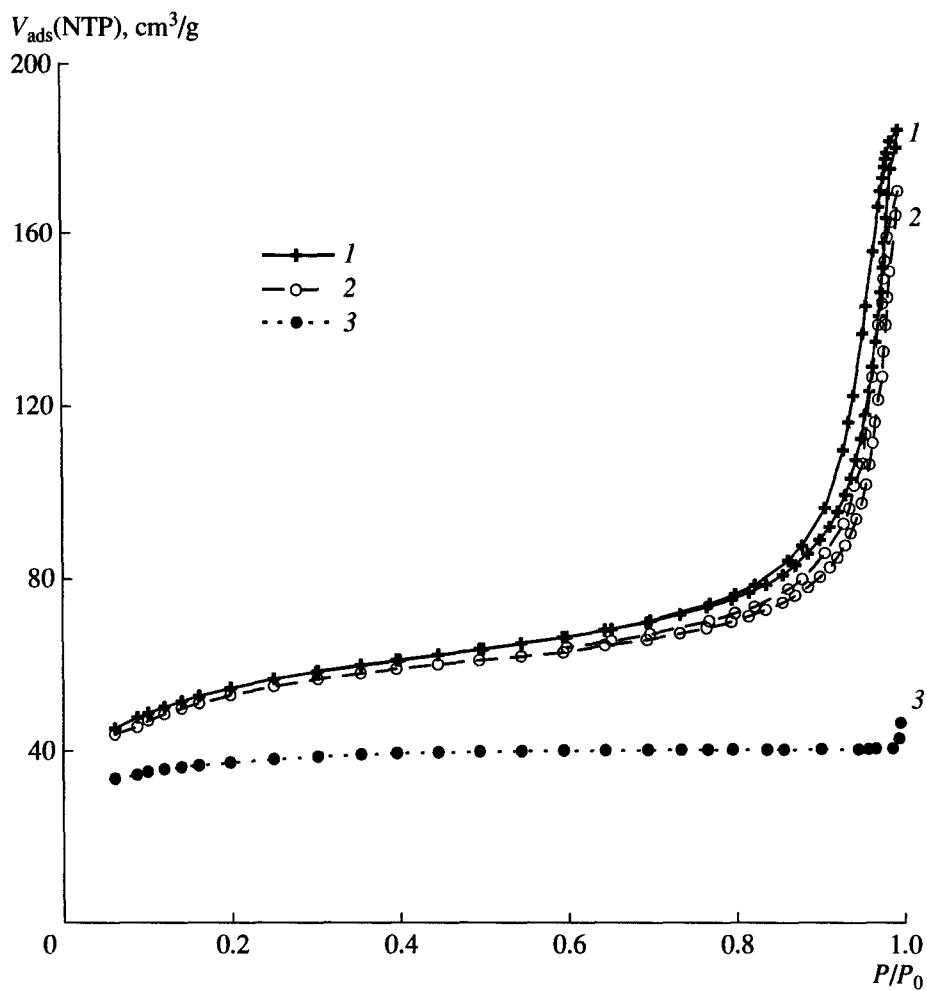


Fig. 1. Adsorption isotherms for nitrogen (-195.6°C) on the samples of tin dioxide prepared at pH (1) 4, (2) 3, and (3) 7.

Notably, the absence of the capillary-condensation hysteresis on the adsorption isotherms is a necessary but insufficient evidence for the absence of the capillary condensation in mesopores, which indicates the absence of mesopores in the samples. In principle, hysteresis-free (reversible) condensation can occur in conic or V-shaped pores in which the shape of the condensate meniscus does not change during adsorption-desorption [13]. The absence of capillary condensation and, hence, mesopores in the tin dioxide xerogels is confirmed by the linearity of adsorption isotherms at $P/P_0 = 0.7\text{--}0.9$ in the coordinates of the comparative method.

The adsorption isotherms of nitrogen and oxygen on the sample prepared at pH 5 have the pronounced capillary-condensation hysteresis, and the limited volume of the sorption space V_s for nitrogen significantly exceeds the value determined by oxygen (Tables 1, 2). A similar picture has been observed previously [14, 15], when the adsorption isotherms of nitrogen and argon at -195.6°C over the nickel mesopore catalysts were compared. The authors explained this fact by the phase tran-

sitions of argon in the overcooled state. In our work, adsorption measurements were also carried out at a temperature different from the oxygen boiling point. Hence, the behavior of the bulk phase of the sorbate in mesopores can be anomalous. The V_s values determined for O_2 and N_2 on all other xerogels in the absence of capillary condensation (samples 2–5) coincide satisfactorily.

The treatment of adsorption isotherms on micropores-containing xerogels by the BET method results in the known uncertainties in the interpretation of the specific surface area [13]. In this case, the use of the conventional version of the comparative method [16] for analysis of the adsorption isotherms is more reasonable.

The treatment of the adsorption isotherms of N_2 and O_2 by the comparative method makes it possible to determine the volume of accessible micropores V_μ and the surface area of supermicro- and macropores S_α (Tables 1, 2). In addition, the use of the comparative method in the region of $P/P_0 = 0.8\text{--}0.9$ for the samples that are characterized by the absence of the capillary-

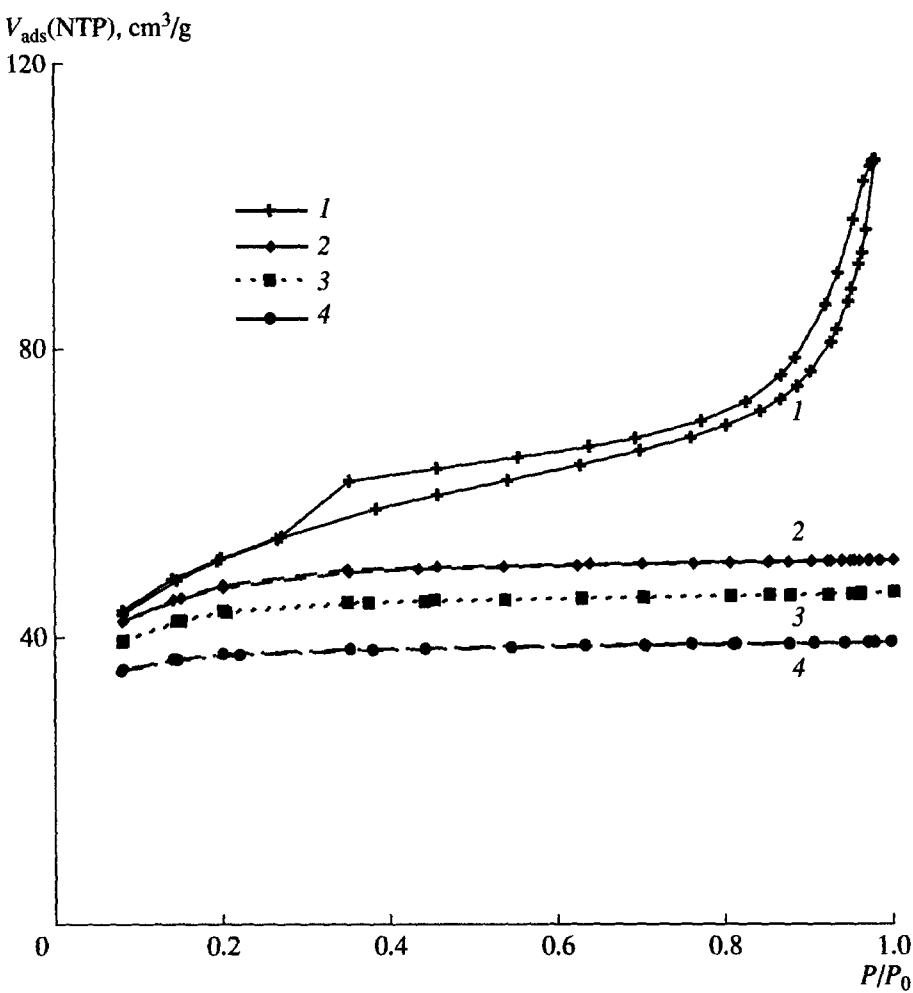


Fig. 2. Adsorption isotherms for oxygen (-195.6°C) on the samples of tin dioxide prepared at pH (1) 5, (2) 6, (3) 7, and (4) 9.

condensation hysteresis allows one to estimate the surface area of macropores S_m and the total volume of micro- and supermicropores $V_{\mu+s\mu}$.

As can be seen from Tables 1 and 2, although micropore volumes V_μ calculated from the adsorption of oxygen and nitrogen are nearly the same for the samples synthesized at $\text{pH} > 5$, the V_μ values obtained with oxygen are less scattered and are probably closer to the true value of this parameter. Obviously, the scattering

of the micropore volumes measured by nitrogen adsorption is primarily associated with the effect of the activated diffusion of sorbate molecules.

A comparison of the values presented in Tables 1 and 2 shows that the S_α values for samples 4 and 5 measured using various adsorbates coincide. However, the S_α values for samples 1–3 measured by oxygen adsorption are higher than those measured by nitrogen adsorption. Overall, the S_α values include the surface areas of supermicro-, meso-, and macropores. In samples 2–5, the surface areas of meso- and macropores are negligible. Hence, the surface area of supermicropores contributes mainly to the S_α value.

Figure 3 shows the $S_\alpha(\text{O}_2)/S_\alpha(\text{N}_2)$ ratio as a function of the volume of supermicropores calculated as $V_{s\mu} = V_{\mu+s\mu} - V_\mu$ from the data presented in Tables 1 and 2. It is seen that for $V_{s\mu} > (0.01-0.015) \text{ cm}^3/\text{g}$, an excess of the surface areas measured by oxygen adsorption over those measured by nitrogen adsorption increases linearly with an increase in the supermicropore volume. When the supermicropore volume in the samples is

Table 1. Parameters of the pore structure of the SnO_2 xerogels calculated from the N_2 adsorption isotherms

No.	pH	V_{ads} , cm^3/g	V_s , cm^3/g	S_{BET} , m^2/g	S_α , m^2/g	V_μ , cm^3/g	$V_{\mu+s\mu}$, cm^3/g	ρ , g/cm^3
1	5	116.2	0.180	146	102	0.036	—	5.22
2	6	43.8	0.068	136	62	0.036	0.065	5.15
3	7	33.1	0.051	105	55	0.023	0.050	4.97
4	8	37.3	0.058	112	31	0.039	0.055	4.93
5	9	33.8	0.051	107	32	0.036	0.050	4.96

smaller than the $V_{s\mu}^*$ value mentioned, the S_α values estimated using both adsorbates coincide satisfactorily; that is, the following conditions determining the $V_{s\mu}^*$ value are fulfilled:

$$\text{at } V_{s\mu} \leq V_{s\mu}^* \quad S_\alpha(O_2)/S_\alpha(N_2) = 1,$$

$$\text{at } V_{s\mu} > V_{s\mu}^* \quad S_\alpha(O_2)/S_\alpha(N_2) > 1.$$

The experimental curves (Fig. 3) are linearized in the coordinates of simple linear equations with two terms and with similar slopes, 13.87 for nitrogen and 13.5 for oxygen. This coincidence is barely accidental. Let us examine possible reasons for this phenomenon.

It is hardly probable that the complex threshold character of the above dependence is due to geometric (textural) origins. It is well known that the surface area of the unit model pore (S) is simply related to its volume (V): $S = kV/r$, where k is the coefficient of the pore shape independent of the sorbate nature and r is the pore radius (a parameter that in the case of supermicropores could depend on the size of the adsorbate molecule). It can be seen that the ratio between the surface areas can be presented as $S_1/S_2 = (r_2/r_1)(V_1/V_2)$, where the subscripts 1 and 2 refer to parameters measured using different adsorbates. It is obvious that this dependence cannot adequately describe the experimental data in Fig. 3.

One can suggest that this experimental character of the dependence is due to the specific behavior of the molecules of various sizes in the pore space of supermicropores. It should be noted that a similar phenomenon was observed for the samples of zirconium dioxide; that is, this effect is not accidental and requires more detailed study.

Figure 4 shows adsorption isotherms for hydrogen on the samples of tin dioxide at -195.6°C . The data give evidence that the isotherms are completely reversible. Therefore, the procedure of the comparative method [9, 10] is usable in their analysis. Figure 4 shows that the isotherms are still close to each other; hence, the adsorption properties of the xerogels with respect to this adsorbate are indistinguishable.

Table 3 presents the parameters of the micropore structure of a series of samples of tin dioxide studied, V_μ and $V_{u\mu}$, calculated from hydrogen adsorption isotherms by the comparative method.

In accordance with the procedure [9], the adsorption of H_2 on a microporous xerogel can be described as

$$V = V_{u\mu} + V_\mu \beta,$$

where β is the effective density of the adsorbed phase determined by the adsorbate pressure and $V_{u\mu}$ is the volume of ultramicropores. The hydrogen adsorption isotherm on the uniformly microporous zeolite ZSM-5 was used as a reference. The treatment of isotherms was carried out without taking into account the contri-

Table 2. Parameters of the pore structure of the SnO_2 xerogels calculated from the O_2 adsorption isotherms

No.	pH	V_{ads} , cm^3/g	V_s , cm^3/g	S_{BET} , m^2/g	S_α , m^2/g	V_μ , cm^3/g	S_m , m^2/g	$V_{\mu+s\mu}$, cm^3/g
1	5	106.8	0.125	187	125	0.030	—	—
2	6	51.0	0.060	166	75	0.032	0.6	0.059
3	7	46.5	0.054	152	63	0.032	1.0	0.053
4	8	41.8	0.049	129	32	0.035	1.7	0.046
5	9	39.7	0.046	127	32	0.034	0.7	0.045

Table 3. Parameters of the pore structure of the SnO_2 xerogels calculated from the H_2 adsorption isotherms

No.	pH	V_μ , cm^3/g	$V_{u\mu}$, cm^3/g
1	5	0.042	—
2	6	0.044	—
3	7	0.038	≈ 0.002
4	8	0.039	≈ 0.001
5	9	0.039	—

bution from the adsorption on the surface of supermicropores S_α . As was shown in [10], this adsorption should be taken into account when the surface areas are large, for example, at $S_\alpha > 100 \text{ m}^2/\text{g}$. The micropore volume V_μ was calculated from the slope of a straight line on the comparative plot, and the accessible volume of ultramicropores $V_{u\mu}$ was evaluated from the intercept of the ordinate axis. Figure 5 shows the example of such a plot in the coordinates of the comparative method.

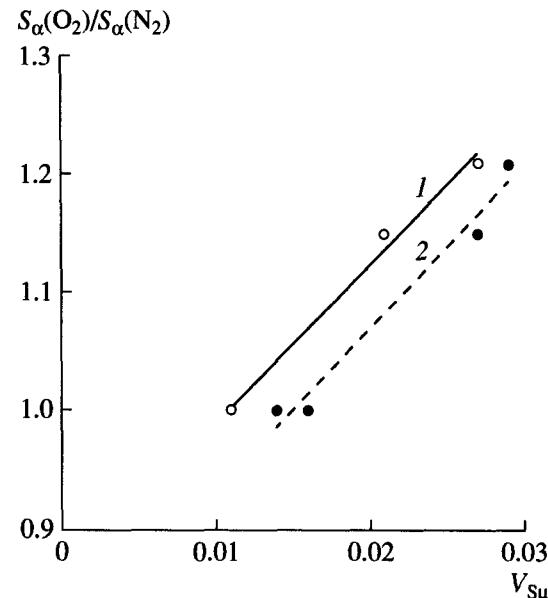


Fig. 3. Dependence of the $S_\alpha(O_2)/S_\alpha(N_2)$ on the supermicropore volume ($V_{s\mu}$) measured by (1) oxygen and (2) nitrogen.

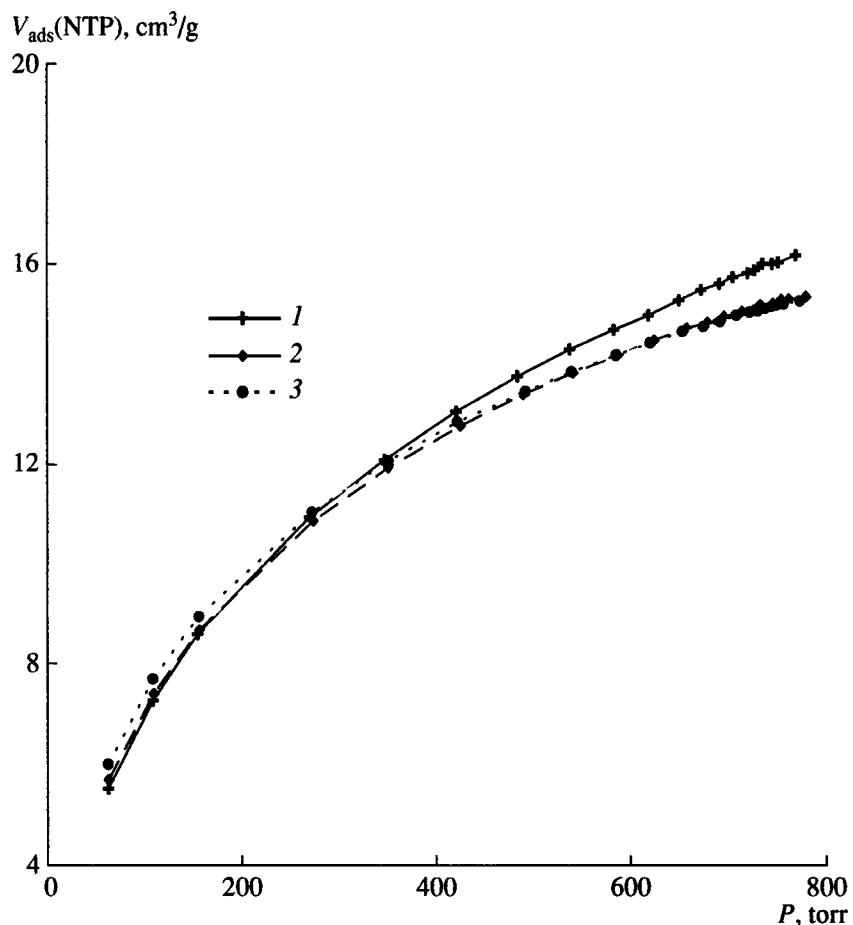


Fig. 4. Adsorption isotherms for hydrogen (-195.6°C) on the xerogels of tin dioxide precipitated at pH (1) 5, (2) 7, and (3) 9.

It is seen from Table 3 that micropore volumes obtained for H_2 by the above method are somewhat higher than those obtained for nitrogen and oxygen. This phenomenon can be due to the presence of a pore

space in xerogels accessible only by those H_2 molecules whose kinetic diameter σ_k is 0.289 nm; that is, tin dioxide xerogels studied in this work exhibit noticeable molecular sieve properties.

Note also that the higher the pH of the gel precipitation, the smaller the difference in the volumes of accessible micropores calculated from the adsorption of the molecules of various sizes. This can be due to an increase in the micropore sizes at a higher pH of precipitation, which is accompanied by a decrease in the molecular sieve action.

The volume of ultramicropores measurable by hydrogen adsorption is negligibly small in the samples. The extrapolation of the adsorption isotherms to a zero pressure on the comparative plots usually gives the negligible intercepts on the ordinate axis (either positive or negative), which are within the accuracy of the experimental measurements.

Thus, using the adsorption of various molecules including unconventional adsorbates, oxygen, and hydrogen for the study of the micropore structure of tin dioxide, we found the presence of textural regions with the molecular sieve properties and their change due to variations in the preparation conditions.

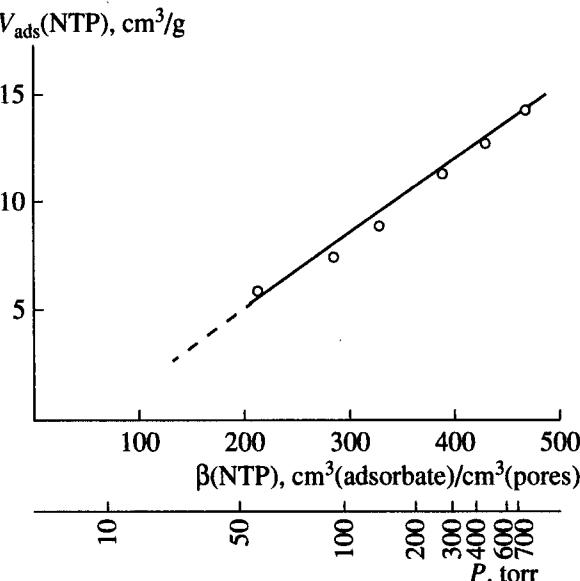


Fig. 5. Adsorption isotherm for hydrogen (-195.6°C) on the xerogel of tin dioxide precipitated at pH 9 in the coordinates of the comparative method [9].

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