The solid-state rearrangement of the Wells–Dawson $K_6P_2W_{18}O_{62}\cdot 10H_2O$ to a stable Keggin-type heteropolyanion phase: a catalyst for the selective oxidation of isobutane to isobutene

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The thermal and structural stability of the Wells–Dawson-type heteropoly compound $K_6P_2W_{18}O_{62}\cdot 10H_2O$ was examined by FT-IR spectroscopy, X-ray powder diffraction, thermogravimetric analysis and HRTEM. It was found that calcination at temperatures higher than 850 K led to the formation of a Keggin-type compound "$K_3PW_{12}O_{40}$", containing small amounts of an additional phase originated from the high-temperature interaction between potassium phosphate (K_3PO_4, formed during the decomposition of the $K_6P_2W_{18}O_{62}\cdot 10H_2O$) and the Keggin-type compound itself. The Keggin-type product showed a higher activity in the selective oxidative dehydrogenation of isobutane to isobutene compared to both the Wells–Dawson precursor and to pure, authentic $K_3PW_{12}O_{40}$. This higher activity can be tentatively attributed to the presence of an amorphous layer of unknown stoichiometry at the surface of the thermally rearranged Wells–Dawson compound.

Keywords: Wells–Dawson heteropoly compounds; Keggin heteropoly compounds; phosphotungstates; isobutane oxydehydrogenation; isobutene synthesis

1. Introduction

Heteropolyanions are widely used as materials for catalysis in both fundamental and applied chemistry [1,2]. The success of their use lies in their potential multifunctionality with tunable redox and acid–base properties, coupled with their high structural stability, an important requirement in gas-phase heterogeneous catalysis. Among the different classes of heteropolyanions, Keggin-type complexes account for the majority of studies and application in heterogeneous gas-phase reactions [1,3], probably due to their high thermal stability under reaction conditions frequently combined with their easy preparation.

An important problem, which limits the application of heteropoly compounds as heterogeneous catalysts, concerns their tendency to decompose under reaction conditions. The stability of bare and supported Keggin-type heteropolyanions has been thoroughly investigated [4–9]; however, the solid-state reactions and the applications of other classes of polyanions are little investigated. For instance, Keggin-type heteropolyacids containing Mo are stable up to 600–650 K before decomposing to P_2O_5 and MoO_3 [4], while W containing heteropolyacids are reported to be more stable before decomposing to WO_3 and P_2O_5; a temperature of 773 K is reported for their upper limit of stability [5]. The substitution of H with a different cation increases the stability to higher temperatures; the stability of $K_xH_{3-x}PMo_{12}O_{40}$ is strongly dependent on the x value with no decomposition being observed for $K_3PMo_{12}O_{40}$ up to 920 K [6].

We report here our initial results concerning the thermolysis and microstructural rearrangement of the Wells–Dawson $K_6P_2W_{18}O_{62}\cdot 10H_2O$ heteropolyanion. In addition, the activity of the resulting Keggin-type product in the selective oxidative dehydrogenation of isobutane to isobutene is also reported and compared with that of the corresponding, authentic Keggin compound $K_3PW_{12}O_{40}$. The oxydehydrogenation of isobu-

tane is of particular interest nowadays, due to the increased need for isobutene as a raw material for the synthesis of MTBE (methyl *t*-butyl ether). Oxidative dehydrogenation may constitute a viable alternative to the capital- and energy-intensive dehydrogenation.

2. Experimental

The Wells–Dawson compound of composition $K_6P_2W_{18}O_{62}\cdot 10H_2O$ was prepared as detailed elsewhere [10]; its purity and composition were checked by FT-IR, solution ^{31}P NMR (with a peak at −12.3 ppm, relative to 85% external H_3PO_4), and elemental analysis. $K_3PW_{12}O_{40}$was prepared by precipitation from an aqueous solution containing $NaWO_3$ and H_3PO_4. HNO_3 was added to the solution until a pH lower than 1.0 was reached, and then $KNO_3$was added to precipitate the Keggin salt.

Before catalytic tests, all compounds were calcined at 723 K for 3 h in air. The infrared spectra were collected as KBr pellet with a Digilab FTS-40 instrument. XRD patterns of powder were collected with an Inel instrument, using Co radiation. The DTA-TG analyses were carried out using a Netzsch STA equipment with a heating rate of 10 K/min up to 1500 K. Microstructural characterization by HRTEM was carried out with a Philips CM30 instrument operating at 300 kV. The samples were suspended in methanol and supported on copper grids with a holey-carbon-film support.

The catalytic activity for the gas-phase oxidative dehydrogenation of isobutane was examined using a stainless steel flow reactor operating at atmospheric pressure, as previously described [11]. Three grams of catalyst were loaded for tests; reaction conditions were as follows: feedstock composition 26 mol% isobutane, oxygen 13 mol%, water 12 mol%, remainder helium. Residence time was 3.6 s. Results were collected after approximately 50 h time-on-stream, and no effect of catalyst deactivation was observed up to 300 h time-on-stream. Analysis of the products was done as described previously [11].

3. Results and discussion

3.1. Thermolysis product characterization

Thermolysis in air of the Wells–Dawson heteropoly compound $K_6P_2W_{18}O_{62}\cdot 10H_2O$ (hereinafter referred to as WDHC), as a function of the temperature of calcination, has been followed by thermogravimetric analysis (TGA/DTA), ex situ XRD, FT-IR spectroscopy and HRTEM studies coupled with microprobe analysis.

Thermal analysis of $K_6P_2W_{18}O_{62}\cdot 10H_2O$ reveals that the compound is stable in air; loss of water occurs in the temperature range 373–473 K but there is no decomposition to P_2O_5 and/or WO_3 even after heating to 1100 K. However, significant modification of the structure takes place at higher temperatures, evidenced by the appearance in the DTA traces of an exothermic peak, at approximately 800 K. This modification must be a structural rearrangement, since there is no accompanying weight loss. Further treatment at temperatures up to 1173 K does not reveal any additional modification of the material.

Fig. 1 shows the XRD patterns of the WDHC sample as prepared, and of the sample after treatment at 1073 K (WDHC, 1073 K); the same pattern is already observed after calcination at 850 K, and is not modified by further treatment from room temperature up to 1173 K. Fig. 1 also shows the pattern of the Keggin reference compound, $K_3PW_{12}O_{40}$ (this sample will be referred to as KHC).

The features obtained by treatment of the WDHC at 850–1073 K closely resemble that of the KHC. Rietvelt analysis on the X-ray diffraction pattern of the WDHC treated at 1073 K reveals the presence of a cubic cell (Pn3m), with $a = 11.578$ Å, which is in agreement with the value found for pure $K_3PW_{12}O_{40}$ ($a = 11.571$ Å)

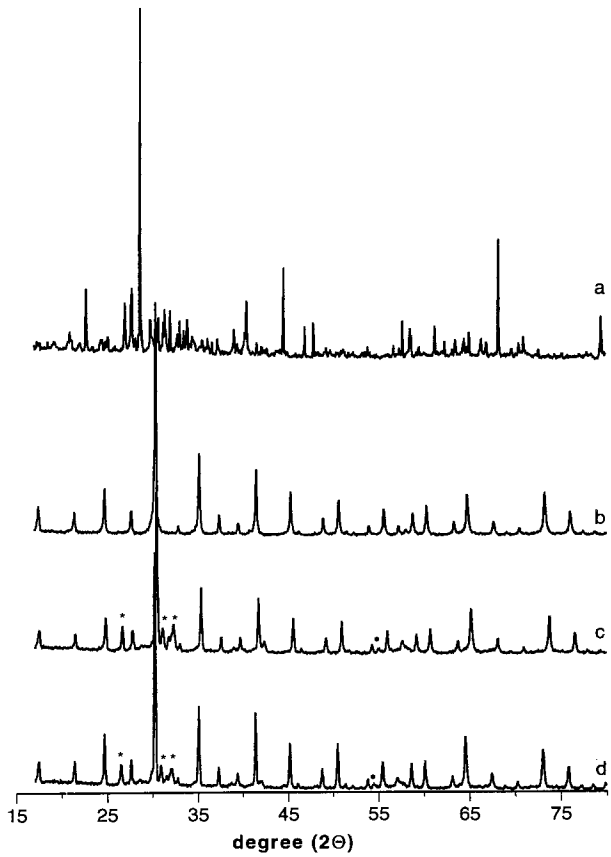

Fig. 1. Powder X-ray diffraction pattern of pure $K_6P_2W_{18}O_{62}\cdot 10H_2O$ (a = WDHC); $K_3PW_{12}O_{40}$ (b = KHC); $K_6P_2W_{18}O_{62}\cdot 10H_2O$ treated in air at 1073 K (c = WDHC, 1073 K) and a mixture of 98% $K_3PW_{12}O_{40}$ and 2% K_3PO_4 treated at 1073 K (d = K_3PO_4/KHC, 1073 K).

[12]. Some additional weak reflections are also observed, labeled in the diffraction pattern with an asterisk.

FT-IR spectra of the same compounds are given in fig. 2; the spectrum of WDHC is different from the spectrum of the KHC [10]. When the WDHC is treated at 850 K, the characteristic bands due to P–O, W–O and W–O–W vibrations, which are present in authentic KHC at approximately 1080, 990 and 805 cm^{-1}, are observed at the same frequencies. Additional bands in the region of P–O vibrations, at 1203 and 1143 cm^{-1}, plus a band at 945 cm^{-1}, and other bands in the region of W–O vibrations which cause a broadening of the peak at 805 cm^{-1}, are also apparent in this new phase.

The close similarity between XRD and IR of the WDHC (calcined at temperatures higher than 850 K) and of the KHC suggests that a high-temperature solid-state rearrangement from the Wells–Dawson to the Keggin-type structure has occurred, according to an idealized reaction scheme with the stoichiometry shown in eq. (1). This rearrangement is apparently possibly due to the stability of the Keggin fragments [2] at these temperature (a point we verified with the pure $K_3PW_{12}O_{40}$ which was found thermally stable to 1173 K)

$$2K_6P_2W_{18}O_{62} = K_3PO_4 + 3\text{“}K_3PW_{12}O_{40}\text{”} \quad (1)$$

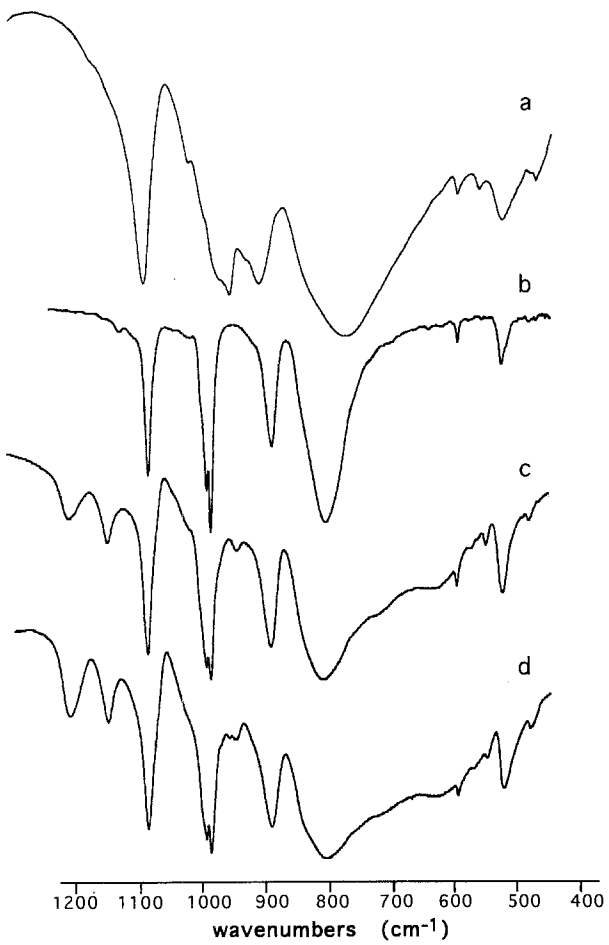

Fig. 2. Infrared spectra of pure $K_6P_2W_{18}O_{62}\cdot 10H_2O$ (a = WDHC) (bands at 1093, 960, 914, 779, 530 cm^{-1}); $K_3PW_{12}O_{40}$ (b = KHC) (1081, 991, 982, 890, 805, 529 cm^{-1}); $K_6P_2W_{18}O_{62}\cdot 10H_2O$ treated in air at 1073 K (c = WDHC, 1073 K) (1203, 1143, 1081, 991, 983, 894, 804, 524 cm^{-1}) and a mixture of 98% $K_3PW_{12}O_{40}$ and 2% K_3PO_4 treated at 1073 K (d = K_3PO_4/KHC, 1073 K) (203, 1143, 1081, 991, 983, 890, 804, 524 cm^{-1}).

To investigate this point further, a mechanical mixture of 2 wt% K_3PO_4 and 98% of freshly prepared $K_3PW_{12}O_{40}$ (as required by the above stoichiometry; this sample will be referred to as K_3PO_4/KHC) was prepared and heated at 1073 K. It gives rise to the formation of a compound whose IR features (fig. 2d, K_3PO_4/KHC 1073 K) and XRD (fig. 1d) are identical to those of the WDHC treated at temperatures higher than 850 K. Also the two IR bands at higher frequency are well reproduced; they probably belong to P–O vibrations relative to a phase developed by K_3PO_4 interacting with $K_3PW_{12}O_{40}$ at high temperature. The additional peaks in the XRD pattern, labelled in fig. 1 with an asterisk, also appear following the high temperature treatment of $K_6P_2W_{18}O_{62}\cdot 10H_2O$, and probably belong to the same phase. However, a clear assignment of these reflections to a specific phase was not possible. The two bands at 1203 and 1143 cm^{-1} in the FT-IR spectrum, and the additional reflections in the XRD pattern, do not belong to K_3PO_4, whose spectral features are not modified by calcination at 1073 K.

HRTEM of the WDHC treated at 1073 K indicates that the sample contains two kinds of particles (fig. 3). Particles labeled A are the most abundant, while particles labeled B are minority; they differ in their morphology, chemical composition and internal structure. Particles of type A are relatively large and have a very well-developed platelet morphology, as illustrated in the micrograph. They give electron-diffraction patterns consistent with the presence of cubic $K_3PW_{12}O_{40}$; moreover, EDX analysis is in accordance with the presence of W, K and P in the required proportions as for $K_3PW_{12}O_{40}$ (i.e., only the oxygen analysis could not be verified). High resolution details of particle A (fig. 4) indicate that growth of an amorphous layer occurs on the surface of $K_3PW_{12}O_{40}$ during decomposition (see the areas between the white arrows). The HRTEM analysis of the compound obtained by calcination at 1073 K of the K_3PO_4/KHC (which FT-IR and XRD analysis demonstrated to be structurally identical to the compound obtained by decomposition of the WDHC at temperatures higher than 850 K), does not show the formation of this amorphous layer. Therefore, the growth of this surface compound is not due to the high-temperature interaction between the formed Keggin-type product and K_3PO_4, but rather is generated during the WDHC decomposition process.

Owing to the amorphous nature of this layer, it was not possible to determine its composition; however, on the basis of indications given by Mioc et al. [13], who described the formation of a bronze-like species from

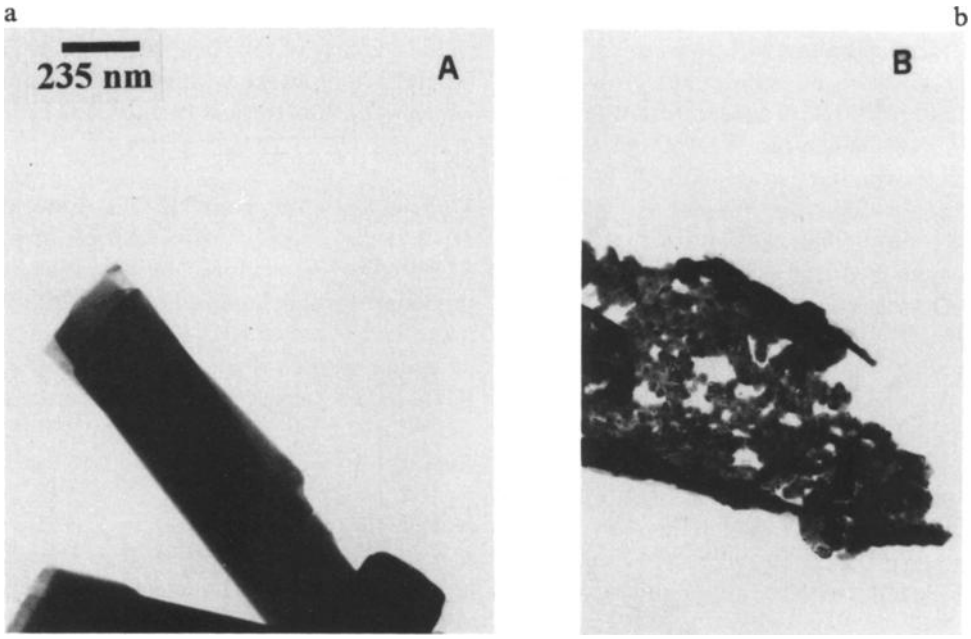

Fig. 3. Low magnification transmission electron micrographs of particles labelled A (a) and B (b) (see text for details) derived from thermal treatment of $K_6P_2W_{18}O_{62}\cdot 10H_2O$ in air at 1073 K.

decomposition of $H_3PW_{12}O_{40}$, we can envisage that surface decomposition of the WDHC may lead to the development of an additional surface "bronze-like" species of composition $(WO_3)_n$–PO_4. Alternatively, following earlier observations on Mo-based heteropolyanions [6], a dehydrated form of $H_3PW_{12}O_{40}$, "$(PW_{12}O_{40-x})$", can be formed covering the surface of $K_3PW_{12}O_{40}$.

Particles B contain agglomerates of rounded, smaller particles, which are crystalline as evidenced by HRTEM and electron diffraction patterns. EDX analyses indicate that particles B do not contain W, but they do contain K and P, and thus they may be attributed to the additional phosphate-containing phase, which is responsible for additional absorptions in FT-IR spectrum (fig. 2) and for the extra peaks in the XRD pattern (fig. 1).

3.2. *Catalysis of isobutane oxydehydrogenation*

The compounds derived from treatment of WDHC at 1073 K have been tested in the oxydehydrogenation of isobutane to isobutene, and the activity has been compared with that of the WDHC precursor and of the KHC. In addition, catalytic tests were made on the K_3PO_4/KHC calcined at 1073 K. The results are sum-

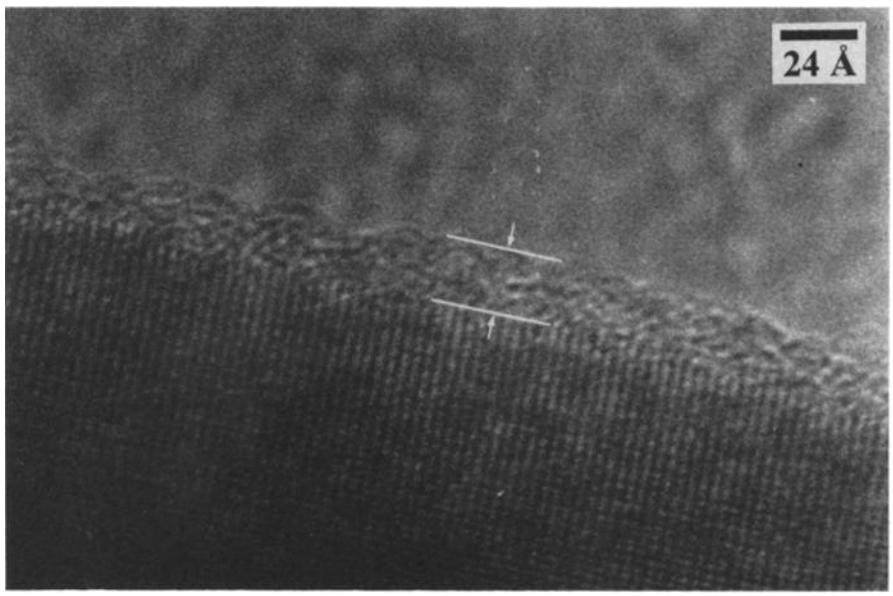

Fig. 4. High resolution transmission electron micrograph of particle labelled A in fig. 3a.

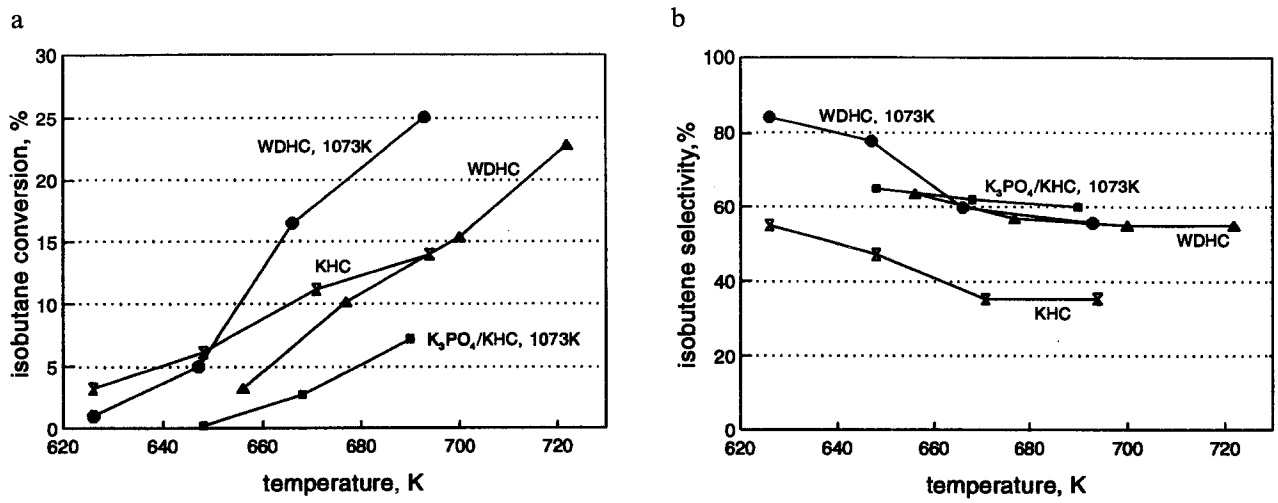

Fig. 5. Isobutane conversion (a) and selectivity to isobutene (b) as functions of the reaction temperature for $K_6P_2W_{18}O_{62}\cdot 10H_2O$ (WDHC), $K_3PW_{12}O_{40}$ (KHC), $K_6P_2W_{18}O_{62}\cdot 10H_2O$ treated in air at 1073 K (WDHC, 1073 K) and a mixture of 98% $K_3PW_{12}O_{40}$ and 2% K_3PO_4 treated at 1073 K (K_3PO_4/KHC, 1073 K). Residence time 3.6 s; feed composition: 26 mol% isobutane, 13 mol% oxygen, 12 mol% water, remainder helium.

marized in fig. 5, which gives the isobutane conversion (fig. 5a) and the selectivity to isobutene (fig. 5b) as functions of the reaction temperature. Other by-products were CO_2, CO, and low amounts of propylene, methacrolein and methacrylic acid.

All the samples examined were active for the oxidation of isobutane in the range of temperature 600–700 K; however, significant differences of activities and selectivities are observed. The most active catalyst is the one obtained by treatment of the WDHC at 1073 K. The WDHC and KHC have comparable activities, while the lowest activity is shown by the K_3PO_4/KHC heated at 1073 K. Fig. 5b shows that the KHC is the least selective all over the temperature range examined, while the WDHC treated at 1073 K shows the highest selectivity at low temperatures. If we compare the selectivity for the same level of conversion, the WDHC treated at 1073 K is the most selective, because it can operate at lower levels of temperature.

It is worth noting that the WDHC treated at 1073 K has a reactivity which is different from that of the K_3PO_4/KHC heated at 1073 K. This confirms the HRTEM finding that, though the WDHC (1073K) and the K_3PO_4/KHC (1073 K) compounds are characterized by identical bulk structural composition (as indicated by FT-IR and XRD), they are different in their surface composition.

In conclusion, results substantiate the previously unreported observation that the Wells–Dawson $K_6P_2W_{18}O_{62}\cdot 10H_2O$ transforms to a Keggin-type "$K_3PW_{12}O_{40}$" heteropolyanion phase (plus some of an ill-defined phase) after thermal treatment in air at 850 K. This observation is also the first reported solid-state rearrangement between different classes of polyanions. The high temperature rearrangement produces an active and amorphous surface layer, which is a better isobutane oxidation catalyst than the precursor $K_6P_2W_{18}O_{62}\cdot 10H_2O$ (Wells–Dawson compound), and than pure Keggin $K_3PW_{12}O_{40}$ polyanion.

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