# Bonding States of Surface Vanadium(V) Oxide Phases on Silica: Structural Characterization by 51V NMR and Raman Spectroscopy

**Nandini Das and Hellmut Eckert***

*Department of Chemistry, University of California, Santa Barbara, California 93106*

**Hangchun Hu and Israel E. Wachs***

*Zettlemoyer Center for Surface Studies, Departments of Chemistry and Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015*

**John F. Walzer and Frank J. Feher***

*Department of Chemistry, University of California, Irvine, California 92621*

The coordination and local order of vanadium(V) surface oxides on silica are examined by 51V spin echo and MAS NMR, as well as by Raman spectroscopy. Comparison with corresponding data on two crystallographically characterized model compounds, [Ph₃SiO]₃VO and [(c-C₆H₁₁)₇(Si₇O₁₂)VO]₂, reveals unambiguously that the vanadia species found at the silica surface is a three-legged (SiO)₃V=O unit. These results support the hypothesis that silsesquioxanes are appropriate model systems for hydroxylated silica surfaces.

## Introduction

Supported vanadium oxide catalysts consist of a surface vanadium oxide phase on a high surface area oxide support (SiO₂, TiO₂, etc) and are of great importance as catalysts for the selective oxidation of hydrocarbons and for the selective catalytic reduction of NO$_x$.[1-5] There is much current interest in unraveling the molecular aspects of such catalysts, and consequently, many of the recent studies have focused on the molecular structural characterization of the surface vanadium oxide species.[6-13] This contribution deals with the silica-supported vanadium oxide system. Previous studies of this system under both ambient and dehydrated conditions have been carried out by Yoshida and co-workers, using X-ray absorption characterization techniques (EXAFS/XANES). Under ambient conditions, where the surface is hydrated, the surface vanadium oxide possesses a V₂O₅-like local environment, with close vanadium–vanadium distances, indicative of clustering. Under conditions where the surface is dehydrated, however, a dramatic change in the local environment is observed, and no close vanadium–vanadium distances are observable, suggesting that the vanadium surface species are dispersed. These authors propose a mono-oxo tetrahedral surface vanadate structure in the dehydrated state (see Figure 1a). Bell and co-workers employed Raman spectroscopy to structurally characterize the dehydrated vanadium oxide phase on silica and assigned a band at 1042 cm⁻¹ to a tetrahedral vanadium oxide species based on comparison with the spectra of gaseous tetrahedral VOX₃ (X = Cl, Br, I) compounds. Using oxygen isotope experiments, they conclusively demonstrated that this species at 1042 cm⁻¹ possesses only a single terminal V–O bond.[8] However, the assignment of the coordination geometry on the basis of a single Raman band carries uncertainties, since the band position is only a function of the shortest V–O bond length, and octahedral vanadium oxide species may also give rise to Raman bands in this region.[9] Deo and Wachs examined the hydrated surface vanadium oxide phase on silica with Raman spectroscopy under ambient conditions and found a broad band around 1000 cm⁻¹, which was assigned to an octahedrally coordinated decavanadate-like species.[10] In agreement with ref 8, they also found a strong Raman band at 1038 cm⁻¹ for the dehydrated silica supported surface vanadium oxide phase.[10] Unfortunately, attempts to provide further support for this
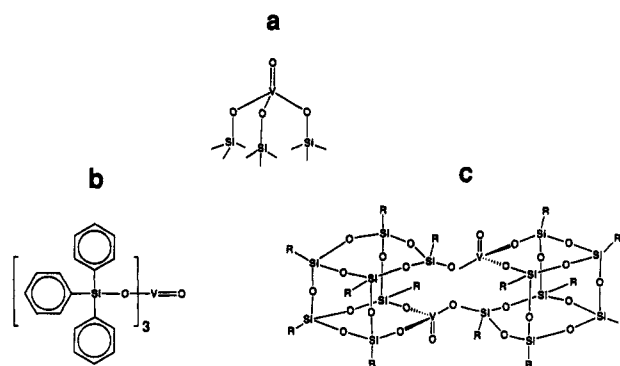
**Figure 1.** (a) Proposed local environment for vanadium(V) oxide on silica surfaces and (b, c) schematic structures of the two model compounds used in the present study.

assignment by solid-state NMR have been severely handicapped by poor spectroscopic resolution, signal distortions arising from dead time problems, and the lack of suitable model compounds.[11-13] In this contribution, we present new 51V magic angle spinning (MAS) and spin echo NMR data obtained on vanadia–silica catalysts and on the two crystallographically characterized vanadia–silica compounds shown in Figure 1b,c. These NMR results reveal unambiguously the bonding geometry of vanadia on the dehydrated silica surfaces. Complementary Raman results are also presented which provide additional insight into the silica-supported vanadium oxide system.

## Experimental Section

**Sample Preparation and Characterization.** Fumed Cab-O-Sil (Cabot, EH-5) possessing 380 m²/g surface area was used as the silica support. The handling characteristics of this material were improved (without reduction in surface area) by treatment with distilled water, drying at 120 °C overnight, and subsequent calcination at 500 °C for 24 h. The silica-supported vanadium oxide catalysts were prepared in inert atmosphere (N₂ flow) by the incipient wetness impregnation method using vanadium triisopropoxide oxide (Alfa, 95–98%) dissolved in methanol. The samples were initially dried for 2 h at room temperature and further dried at 120 °C overnight in a nitrogen environment and

were subsequently calcined at 500 °C under flowing oxygen. All the catalyst loadings in the figures are presented as nominal loadings. Inductively coupled plasma mass spectrometry (ICP-MS) analysis of the 10% $V_2O_5/SiO_2$ sample revealed that only 8.4 wt % $V_2O_5$ was present on the silica support. This loss is probably due to the volatilization of the alkoxide precursor during the calcination process.

The Raman spectra were recorded on both hydrated and dehydrated materials, under conditions similar to those reported in ref 10. The preparation and characterization of the two model compounds employed in this study, $[(c-C_6H_{11})_7(Si_7O_{12})VO]_2$ and $[Ph_3SiO]_3VO$, have been described elsewhere.[14]

**Solid-State NMR Studies.** Solid-state NMR studies were carried out at 79.0 MHz using a General Electric GN-300 spectrometer equipped with a Nicolet fast digitizer and a high-speed MAS probe from Doty Scientific. Wide-line NMR spectra were obtained using a $\theta_1-\tau-\theta_2$ ($\theta_2 = 2\theta_1$) spin echo pulse sequence, with a delay time $\tau$ of 50 $\mu$s and a relaxation delay of 1 s. In all of the samples studied only the central $^1/_2 \rightarrow -^1/_2$ transition of the quadrupolar $^{51}V$ nucleus ($I = ^7/_2$) is being detected. A pulse length of 1 $\mu$s was chosen, corresponding to a flip angle $\theta_1$ of 45° in the selective excitation limit. Variation of $\theta_2$ between 1 and 2 $\mu$s did not affect the results, but at larger pulse lengths, signal distortions due to nonuniform excitation appeared. Appropriate phase cycling was applied in order to cancel the contribution arising from "feedthrough" FID signal following the refocusing pulse.[15] Following acquisition, the time-domain data set were left-shifted to the top of the echo prior to Fourier transformation. $^{51}V$ magic angle spinning NMR spectra were obtained with 45° solid flip angles at variable spinning speeds between 4 and 8 kHz. Prior to the NMR studies, the silica-supported vanadia samples were dehydrated in a furnace at 700 °C, subsequently transferred to a glovebox, and packed into an air-tight MAS rotor in an anhydrous atmosphere.

## Results and Analysis

The Raman spectra from the hydrated 0–10% $V_2O_5/SiO_2$ samples are presented in Figure 2a. The silica support possesses Raman features at 450 and 800 cm$^{-1}$ (siloxane bridges), 600 and 480 cm$^{-1}$ (three- and fourfold siloxane rings), and 980 cm$^{-1}$ (surface silanol groups). The deposition of vanadium oxide on the silica surface gives rise to additional Raman bands at 1016–990, 700–670, 512, 418, 320, 263, and 150 cm$^{-1}$. Previous Raman studies have shown that silica-supported vanadium oxide samples are very easily dehydrated by the laser beam even when low laser power and extremely rapid sample rotation are employed.[10] Due to this partial dehydration effect, the Raman band at 1016 cm$^{-1}$ in Figure 2a occurs at an intermediate position between the bands for hydrated (990–1000 cm$^{-1}$) and dehydrated (1038 cm$^{-1}$) surface vanadium oxide species. The band at 1016 cm$^{-1}$ is characteristic of a terminal V=O bond, the Raman bands at 200–300 and 500–800 cm$^{-1}$ are characteristic of V–O–V vibrations, and the Raman band at 150 cm$^{-1}$ is assigned to a lattice vibration. These Raman bands do not closely match those of crystalline $V_2O_5$ (which possesses sharp Raman bands at 994, 702, 527, 404, 284, and 146 cm$^{-1}$), but the somewhat similar band positions suggest that the structures of hydrated surface vanadium oxide on silica and of $V_2O_5$ may be related. Contrary to a previous suggestion,[10] the structure of the hydrated phase is not related to a decavanadate-like species, because the latter gives rise to very different Raman band positions.

The Raman spectra of the dehydrated $V_2O_5/SiO_2$ samples are shown in Figure 2b. At all vanadium oxide loadings there is a sharp Raman band at 1037 cm$^{-1}$ characteristic of the terminal V=O bond of the surface vanadium oxide species, and the bands due to V–O–V bonds are absent, suggesting an isolated structure. For the 10% $V_2O_5$ sample a trace of crystalline $V_2O_5$ is also detected. In addition, two weak Raman bands are observed at
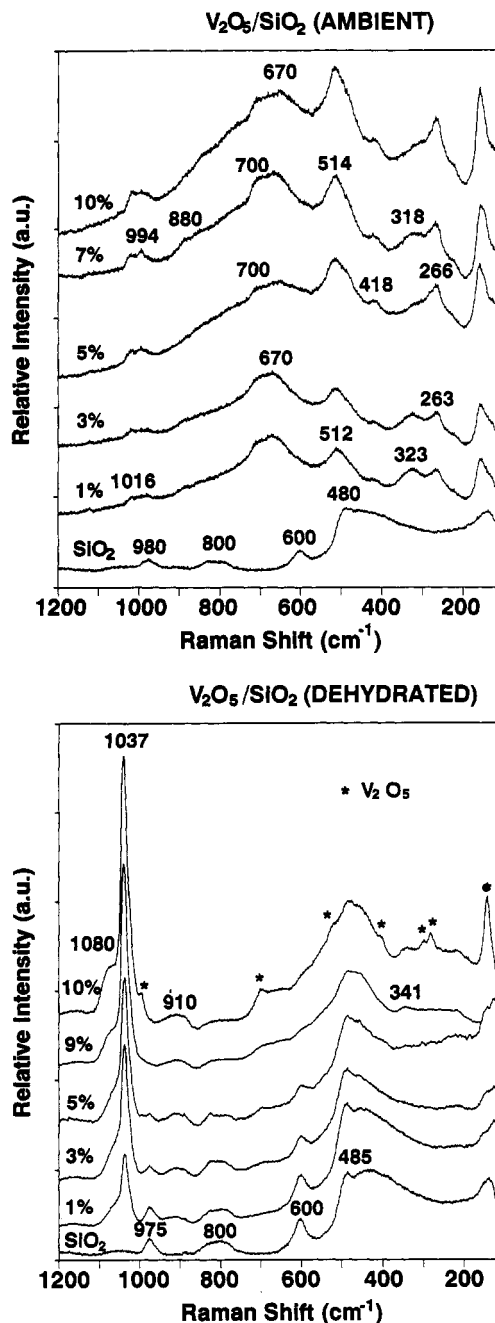


**Figure 2.** Raman spectra of vanadium(V) oxide on silica surfaces under (a, top) hydrated (ambient) and (b, bottom) dehydrated conditions.

1080 and 910 cm$^{-1}$ which are characteristic of Si–O$^-$ and Si(–O$^-$)$_2$ functionalities.[16] This reveals that the surface vanadium oxide species are breaking some Si–O–Si bridges upon bonding to the silica surface in addition to reacting with the Si–OH bonds. Unfortunately, Raman spectroscopy does not provide any information about the V–O–Si bonds because these bonds are most likely slightly ionic and consequently Raman inactive.

The Raman spectra of the two crystalline model compounds were also examined. However, the hydrocarbon portion of the model compounds gives rise to very strong Raman bands near 1030 cm$^{-1}$ which overshadow the V=O vibration in this region. For these compounds, the element specific NMR technique is more suitable for the characterization of the vanadium sites.

Figure 3 shows the wide-line $^{51}V$ NMR spectra obtained by the spin echo method and the MAS-NMR spectra of both an ambient (surface-hydrated) and a dehydrated sample containing 10 wt % $V_2O_5$ on silica. Essentially identical features (with lower signal-to-noise ratios) have been observed for samples with lower vanadia contents, in agreement with the Raman results.
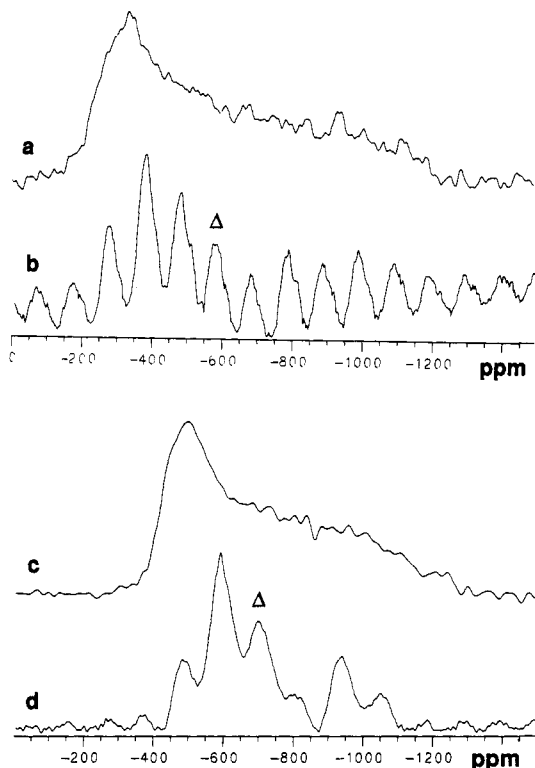
**Figure 3.** The 79.0-MHz solid-state $^{51}V$ NMR spectra of vanadia supported on silica (10 wt % $V_2O_5$): (a) wide-line NMR spectrum of the hydrated material present under ambient conditions, (b) MAS-NMR spectrum (at 8-kHz spinning speed) of this sample, (c) wide-line NMR spectrum following dehydration at 700 °C, and (d) MAS-NMR spectrum (at 8-kHz spinning speed) of the dehydrated sample. The central resonances of the MAS-NMR spectra are indicated by the symbol Δ.

Figure 4 compares the wide-line and MAS-NMR spectra of the dehydrated sample with those of the crystalline model compounds. As found previously for many other vanadium-containing systems,[17-20] the $^{51}V$ solid-state NMR line shapes at a field strength of 7 T are dominated by the chemical shift anisotropy, whereas second-order quadrupolar effects on the line shapes are negligible. Accordingly, the $^{51}V$ chemical shift
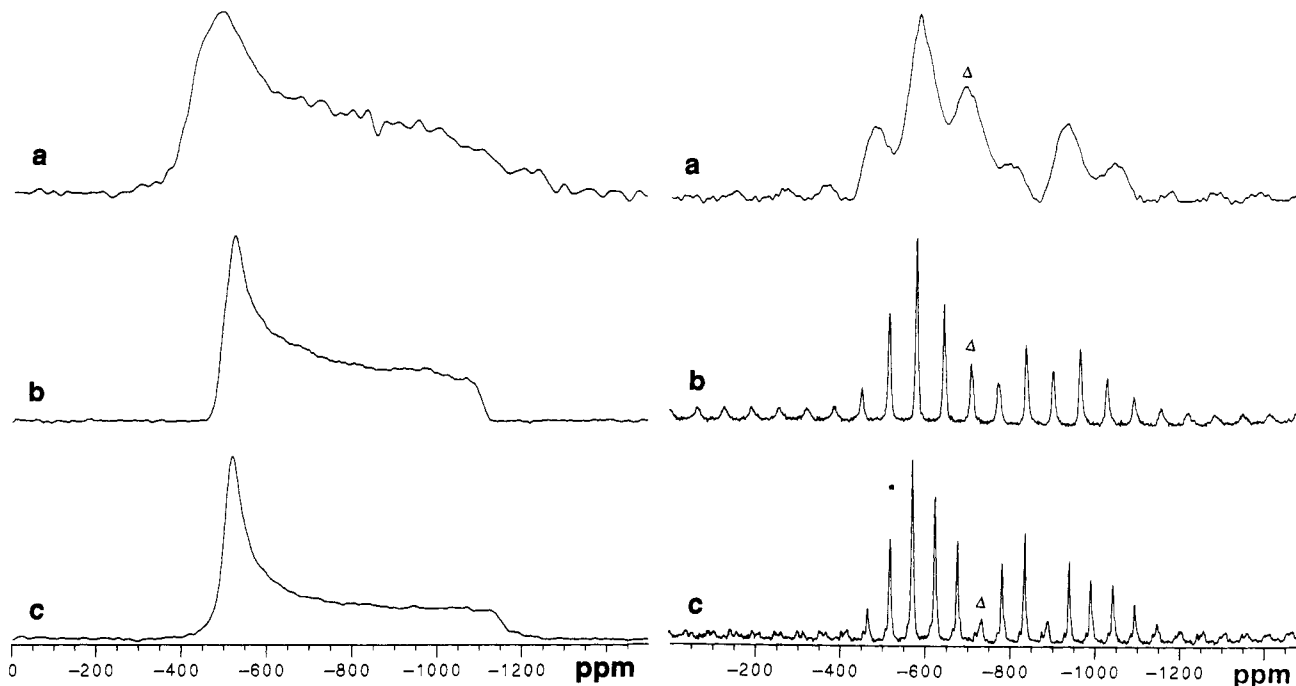
**TABLE I: Chemical Shift Parameters[a,b] of the Samples under Study**

| compound | $\delta_{11}{}^c$ | $\delta_{22}{}^c$ | $\delta_{33}{}^c$ | $\delta_{iso}$ |
|---|---|---|---|---|
| 10% $V_2O_5$ on $SiO_2$ (ambient) | −250 | −330 | −1200 | −580 ± 10[d] |
| 10% $V_2O_5$ on $SiO_2$ (dehydrated) | −450 | −470 | −1190 | −710 ± 10[d] |
| $(Ph_3SiO)_3VO$ | −510 | −525 | −1150 | −736 ± 1[d] |
| $[(c\text{-}C_6H_{11})_7(Si_7O_{12})VO]_2$ | −500 | −535 | −1115 | −714 ± 1[d] |

[a] In ppm relative to $VOCl_3$. [b] Second-order quadrupolar shifts are negligible within experimental error. [c] From simulated wide-line spectra, ±10 ppm. [d] From MAS-NMR.

principal tensor components have been obtained from these spectra with the help of standard line shape simulation programs available in the FT NMR software package. The results are summarized in Table I, illustrating that in all of the materials studied here the $^{51}V$ chemical shift tensors possess close-to-axial symmetry, as predicted from the anticipated point symmetry ($C_{3v}$) at the vanadium center.

**Discussion and Conclusions**

The wide-line $^{51}V$ NMR line shapes obtained for vanadia on silica (and the chemical shift tensor values extracted from them) under ambient (surface hydrated) conditions (Figure 3a) closely resemble, but are not quite identical with, those previously published for bulk crystalline $V_2O_5$. A similar resemblance was previously noted for vanadia on surface-hydrated amorphous silica–aluminas.[22] We thus conclude that, in the presence of surface water, vanadium(V) is predominantly five-coordinated (as in $V_2O_5$) and present in the form of a hydrated surface phase. We note that this environment is structurally significantly different from the distorted octahedral decavanadate-like environment observed on alumina and titania catalyst surfaces.[17] As discussed previously, under hydrated conditions, the coordination number and symmetry of surface vanadia are largely controlled by the net pH at which the surface possesses point zero charge (PZC) of the metal oxide support.[10] Hydrated silica with a surface pH at PZC of 3–4 provides an acidic aqueous environment, on which the vanadia species cannot be dispersed but rather coagulate to form hydrated amorphous $V_2O_5$-like clusters, as is also expected from the aqueous chemistry of vanadium.[10] This conclusion from NMR is identical to that reached from EXAFS/XANES[7] and



**Figure 4.** The 79.0 solid-state $^{51}V$ wide-line (left) and MAS (right) NMR spectra of (a) dehydrated vanadia supported on silica (10 wt % $V_2O_5$), (b) $[(c\text{-}C_6H_{11})_7(Si_7O_{12})VO]_2$, and (c) $(Ph_3SiO)_3VO$. The central resonances of the MAS NMR spectra are indicated by the symbol Δ.

Raman studies[10] on the hydrated silica-supported vanadium oxide phase. The [51]V MAS-NMR spectrum (Figure 3b) illustrates that this environment is structurally similar to but clearly distinct from that in crystalline $V_2O_5$. The hydrated vanadium(V) surface oxide sites give rise to a broad sideband pattern centered at –580 ppm. In addition, a small amount of bulklike $V_2O_5$ gives rise to distinct shoulders on the upfield sides of this pattern. This peak manifold is centered at –609 ppm, the known resonance shift of crystalline $V_2O_5$.

Figure 3c,d shows the wide-line and MAS [51]V NMR spectra of the same sample after surface dehydration. The spectra illustrate a dramatic change in the vanadium coordination environment. The most striking features are (a) the near-axial symmetry of the chemical shift tensor and (b) the relatively narrow distribution of isotropic chemical shifts, accounting for the effectiveness of MAS line narrowing. These results illustrate that, despite the amorphous character of the vanadium(V) oxide surface layer, the vanadium atoms are in fairly well-defined chemical environments. The spectral feature at $\delta_\parallel$ appears to be smeared out over a wider frequency region, presumably because of variations in local environments causing a distribution of chemical shift anisotropies.

We note that the spectra shown here differ substantially from those published by others for vanadium(V) oxide on silica surfaces.[11-13] Invariably, those spectra were obtained on incompletely dehydrated samples and by employing only simple one-pulse techniques. As is well-known, unrecoverable signal decay during the receiver dead time can dramatically distort the resulting NMR spectrum, particularly if the lines are very broad. Apparently for these reasons, the spectra previously published for surface vanadium oxides on partially dehydrated silica surfaces have only shown the dominant "perpendicular" component of the axially symmetric chemical shift powder pattern near –500 ppm. In contrast to these studies, our MAS-NMR spectra (Figure 3, bottom), reveal that the isotropic chemical shift lies around –710 ppm. Curiously, the separations in the peak maxima of the broadened MAS sideband patterns are not exactly identical. This effect can arise if the various sites contributing to the broadened MAS centerbands possess widely different chemical shift anisotropies. We believe this to be a likely explanation for this phenomenon, in view of the wide distribution of $\delta_\parallel$ observed in the static spectrum.

Figure 4 compares [51]V wide-line and MAS-NMR spectra obtained for 10% $V_2O_5$ on silica with the corresponding data obtained for $[(c\text{-}C_6H_{11})_7(Si_7O_{12})VO]_2$ and $[Ph_3SiO]_3VO$. According to X-ray crystallography, in both model compounds the vanadium(V) sites are three-legged $(SiO)_3V{=}O$ species.[14] Inspection of the [51]V chemical shift database[17-20] reveals that the spectra shown in Figure 4 identify the structural environments shown in Figure 1 in a unique manner. All other known vanadium coordination environments are characterized by substantially different chemical shift tensor values. Figure 4 shows further that, aside from the line broadening induced by disorder effects, the spectra of dehydrated surface vanadia on silica are in excellent agreement with those of the two model compounds studied here, indicating that the assignment of the local structure shown in

Figure 1a is correct, consistent with the EXAFS/XANES[7] and Raman[8] characterization studies. Regarding the dramatic effect of surface dehydration, there is also an interesting analogy with the EXAFS/XANES and Raman findings on silica-supported molybdenum oxides: Under ambient conditions, Mo is present in the form of hydrated heptamolybdate clusters, whereas under dehydrated conditions isolated mono-oxo $MoO_5$ surface species are formed.[23]

The results presented here unequivocally identify the bonding state of surface vanadium oxides on silica supports and confirm a previous hypothesis[24,25] that silsesquioxanes can serve as excellent structural models for hydroxylated silica surfaces. The present findings for the silica-supported surface vanadium oxide phase should also assist in the structural identification of the dehydrated surface vanadium phases on other oxide supports ($TiO_2$, $Al_2O_3$, etc.) where somewhat more complex spectroscopic features are observed.

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