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Soft X-ray absorption spectroscopy at the cutting edge for nanomaterials used in heterogeneous catalysis: the state of the art

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The state of the art in numerical simulation of soft X-ray absorption spectra at the L edge of different elements such zinc and gallium is presented. Significant progress has been achieved recently on the quality of the numerical simulation coming from qualitative agreement to a quantitative one. Moreover, it is possible to obtain the local density of states associated with each element. Works are in progress to take into account the different structural characteristics of materials such the lacunar aspect of solids or the distribution of vacancies inside clusters.

KEY WORDS: Zn- and Ga-based catalyst; soft X-ray absorption; DeNO$_x$.

1. Introduction

Modern materials studies integrate almost systematically *in situ* characterization techniques [1]. Regarding synchrotron radiation techniques, most of the structural and electronic investigations of nanomaterials are based on hard X-ray absorption spectroscopy [2,3] or on anomalous wide-angle X-ray scattering [4] using photons whose energy lies in the range between 3 and 25 keV. In heterogeneous catalysis [5], such material consists of high specific surface area light oxides on top of which are dispersed nanometer-scale entities (metallic or non-metallic) and the lack of long-range order of the supported phase means this technique is particularly suited [6].

Recent advances in the theoretical background [7,8] as well as in the instrumentation [9–11] have motivated several studies dedicated to the application in heterogeneous catalysis of X-ray absorption spectroscopy at low energy (for a recent review see Bazin and Guczi [12]). Different recent studies illustrate the breakthroughs. One can quote, for example, the NEXAFS study of the nitrogen K edge NO adsorption of $ZnAl_2O_4/Al_2O_3$ powder [13], the electronic investigation performed at the L edge of Co-based catalysts [14,15] or a quantification of aluminum coordinations in alumina and silica alumina by Al K edge XANES [16,17].

In this paper, oxide metallic compounds and more precisely $GaPO_4$ and $ZnAl_2O_4$ used as reference compounds for heterogeneous catalysts [18,19] are investigated using soft X-ray spectroscopy with a particular emphasis on the numerical simulations of the edge part of the absorption spectra. The different results demonstrate the nature of the information obtained and lead to a discussion on the advantages and the limits of such an approach.

2. Experimental

The soft X-ray absorption spectra can be collected at the LURE synchrotron facility at the SACO storage ring running at 800 MeV with an average current of 300 mA and a lifetime of 5 h.

Regarding the Zn L edge, photoabsorption measurements have been carried out on the SA 32 beam line using a focusing toroidal mirror and total electron yield detection [20,21]. A double crystal monochromator (fixed exit) made of beryls, quartz or InSb can be used depending on the element of interest. It is worth mentioning that the energy range can be limited by the composition of the crystals (as is the case for the collection at the K edge of Mg and Al using beryls or quartz).

Finally, the K edge spectra were recorded at LURE on the D44 station of the DCI storage ring running at 1.85 GeV with an average current of 300 mA and a lifetime of 200 h. The X-rays were monochromatized by two Si(311) single crystals. The incident I_0 and transmitted I_1 intensities were recorded using two ionization chambers filled with argon. This monochromator, operating with 1 mm vertical slits, had an energy resolution of 2.3 eV at 10 keV. Calibration of the experiment was made with a reference zinc metal foil.

3. From the multiplet theory to the FeFF approach

Recent theoretical advances have led to the development of several *ab initio* codes for the simulation of X-ray absorption spectra whatever the system considered.

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Among them, one can quote Continuum [22], Excurve [23], FeFF [24], GNXAS [25] or WIEN98 [26]. A recent paper [27] reviews the key concepts of the theoretical formalism, and summarizes some current developments as well as the different challenges for future development. Here, we focus on the nature of the information obtained using soft X-ray absorption spectroscopy in the case of nanomaterials used in heterogeneous catalysis from a theoretical as well as an experimental point of view.

3.1. The "multiplets" approach

In the case of nanomaterials dedicated to Fischer–Tropsch catalysis, cobalt-based catalysts are used. For the numerical simulation of the L edge of $3d$ transition metals, the theoretical approach using "multiplets" [28,29] is based on the evaluation of dipole transitions, ignoring basically the details of the electron scattering processes [30].

Thus, the L edge calculation is quasi-atomic: only the symmetry breaking among the neighboring oxygen atoms—from atomic to cubic or to octahedral—is important. A significant limit of this approach is thus the fact that the exact position as well as the chemical nature of the neighboring atoms cannot be determined.

3.2. The FeFF approach

In multiple scattering, the calculation concerns the scattering of the emitted electron. As we will see in the next sections, full multiple scattering calculations can be performed using the FeFF code [24,31,32] based on calculated curved-wave and multiple scattering. In this case, the X-ray absorption spectrum is a sum of different multiple scattering contributions and each such contribution can be written in the form

$$\chi_n(k) = \chi_0^n(k)\exp(-L_n/\lambda_n - 2k^2\sigma^2)$$

and

$$\chi_0^n(k) = F_n(k)\sin[kL_n + \theta_n(k)]$$

where n represents different single or multiple scattering paths, L_n is the total path length and λ_n is the mean free path associated with each path. $F_n(k)$ and $\theta_n(k)$ are the amplitude and phase of the backscattered wave, which depend on k, on the scattering path involved and on the atomic potential parameter. For XANES spectra, these paths, by path terms, can also be summed to all orders by matrix inversion methods, as implemented in the full multiple scattering (FMS) algorithms in FeFF8.

More precisely, only the mean square variation in bond length is treated, the angular variation being ignored. Some aspects regarding the disorder can be thus treated. For example, as we will see in the next section, structural parameters may affect significantly the shape of the edge, such as the size of the cluster as well as its lacunar aspect (cation vacancies, anion vacancies or their distribution inside the cluster).

3.3. Experimental limitations

Soft X-ray spectroscopy offers the possibility to perform *in situ* experiments. More precisely, if the temperature of the sample as well as the nature of the reactive gas can be considered as "free" parameters, then this is definitely not the case for the pressure. The value taken by the pressure on the sample during the experiment has to be in line with the low energy of the incident photon (as well as the energy of the photons/electrons coming from the sample). Such a limitation supposes that the value of the gas pressure during the experiment is close to 10^{-10} Pa. Note that high-pressure experiments (*e.g.*, $p > 20$ bar) can be considered in a preparation chamber, the catalyst being then transferred. In fact, as we have already shown [14], this technique enables a real improvement in the knowledge of the structural evolution of the material under reaction conditions.

4. Zn K edge: the latest breakthrough in the theoretical simulation of the XANES part of the absorption spectra

The decomposition of nitrogen oxides, which are unwanted pollutants in the atmosphere, has been widely studied. In this context, the copper-exchanged zeolite ZSM-5 is considered as a reference material [33]. There are many published studies of catalysts for this process, among which we can distinguish different groups such as metallic particles supported on light oxides (alumina or zeolite) or supported metal oxides. Recently, we have studied ternary AB_2O_4 spinel oxides [18,34,35].

More precisely, the material selected was a supported catalytic system $ZnAl_2O_4/\gamma_c\text{-}Al_2O_3$ (atomic composition: 2.3% Zn, 38.1% Al and 59.6% O) provided by Rhodia. A model of the zinc distribution inside the alumina particle has been proposed, in which the zinc atoms are mostly located at the surface of the alumina particle with a concentration gradient between the surface and the particle center.

4.1. Complementarity between the K and the L edge

An interesting starting point is given by a comparison between the Zn K and L_{III} edge for the reference compound $ZnAl_2O_4$ (figure 1). For this compound, the electronic state of Zn atoms is 2^+ corresponding to a $3d^{10}$ configuration. Thus, the strongest bonding effect in this $3d$ oxide is given by the overlap between the oxygen $2p$ band (filled) and the Zn $4s$ and $4p$ bands (empty). This overlap forms the shape of the oxygen $2p$ valence band and also the Zn $4s$ and $4p$ conduction band.

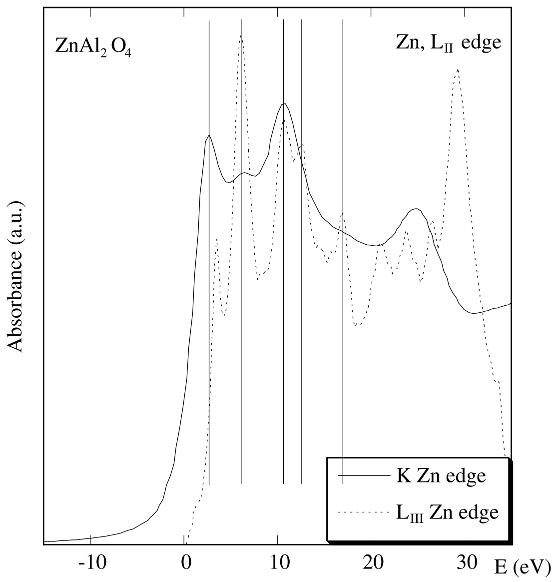

Figure 1. Comparison between the Zn K and L_{III} edge for the reference compound $ZnAl_2O_4$.

The similarity observed between the K and the L edge leads to the fact that some overlap exists between the conduction band (zinc 4*s* and 4*p* with oxygen 2*p*) and the 3*d* band, creating very weak 3*d* character following the same shape as the 4*p* states. Note that a similar approach has been made in an early paper by Grunes [36] in the case of transition metals in pure and oxide form.

Note that soft X-ray absorption spectroscopy seems to be very interesting in the case where the metal is deposited by sublimation from high-purity wires. Rodriguez *et al.* [37] have studied the behavior of silver, cesium and zinc with α-alumina surfaces through thermal desorption and photoemission studies. The results of photoemission experiments indicate that the interaction between Zn and alumina is relatively weak. More precisely, the adsorption of zinc induced only a very minor negative shift in the position of Al 2*p* and O 1*s* peaks of the alumina substrate.

The nature of the preparation method as well as the nature of the alumina thus seems to be very important. Metal deposition by sublimation leads to a very weak interaction between the zinc and the alumina. Conversely, an impregnation method gives a stronger metal/support interaction, an insertion of the Zn^{2+} cation in the support being observed. Moreover, as proposed by Rodriguez *et al.* [37] through photoemission studies, soft X-ray spectroscopy can give information on the mixing of the different atomic orbitals through a comparison between K and L absorption edges of the metal.

4.2. The challenge for nanomaterials

Regarding the study of nanomaterials, the near edge region of the model compound ($ZnAl_2O_4$) and the catalyst are compared at the K and L edge (figures 2 and 3). Regarding the shape as the well as the position of the edge, the great similarity that exists between the catalyst and the $ZnAl_2O_4$ spinel above the edge indicates that the electronic state of the zinc atom is 2^+.

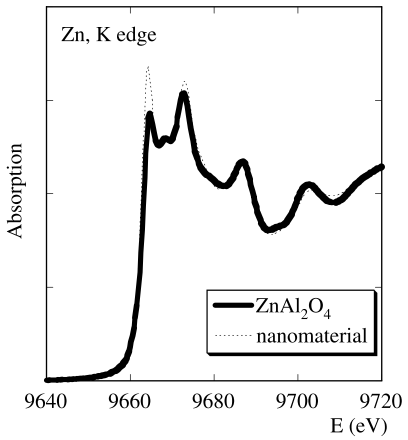

Figure 2. Near edge region at the zinc K edge of the model compound $ZnAl_2O_4$ (line) compared with the near edge region associated with the catalyst (dots).

Nevertheless, a careful analysis of the X-ray absorption spectra indicates that significant differences exist between the reference compound and the nanomaterial. At the K edge, the amplitude of the first peak of the catalyst is clearly lower than the one associated with the reference compound. At the L edge, even if each feature present at the edge exists, the amplitudes are significantly different between the two compounds. In order to link these differences to structural parameters, a quantitative simulation is performed using the structural parameters derived from the numerical simulations of the EXAFS modulations collected at the Zn K edge [18].

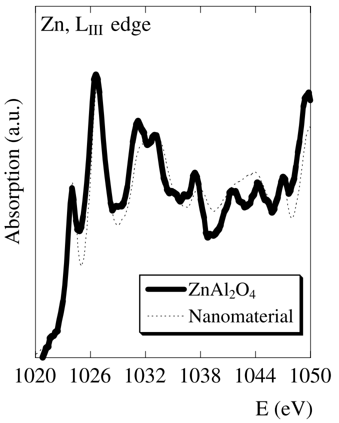

Figure 3. Near edge region at the zinc L_{III} edge of the model compound $ZnAl_2O_4$ (line) compared with the near edge region associated with the catalyst (dots).

Table 1
Structural parameters associated with the spinel $ZnAl_2O_4$ and with the nanomaterial

	$ZnAl_2O_4$			Nanomaterial		
Nature	N	R (Å)	σ^2 (Å^2)	N	R (Å)	σ^2 (Å^2)
Zn–O–Zn	4	1.95	3.6	4	1.95	3.6
Zn–Al–Zn	12	3.36	4.9	10.9	3.34	4.9
Zn–O–Zn	12	3.40	11.1	10.9	3.38	11.1
Zn–Zn–Zn	4	3.50	9.3	0.9	3.49	9.3
Zn–Al–O–Zn	24	3.62	2.5	23.9	3.62	2.5
Zn–O–Zn	12	4.27	2.1	6.6	4.27	2.1
Zn–Al–O–Zn	24	4.36	2.8	14.3	4.36	2.8

Note: For the Debye–Waller factor, we report σ^2 (Å^2) $\times 10^3$.

4.3. Numerical simulations performed using the FeFF code

We first recall the structural characteristics of the $ZnAl_2O_4$ reference compound [18]. Table 1 gathers the results of a quantitative analysis of the EXAFS oscillations beyond the Zn K edge. The absorption spectroscopy here provides a key result, the high vacancy concentration in the nanomaterial.

Based on these structural parameters, numerical simulations have been performed using the new code FeFF8MPI and a NERSC parallel machine with a cluster of 200 atoms. Regarding the K edge, as can be seen in figures 4 and 5, recent progress is significant. Even if quantitative agreements have been obtained in several cases (*e.g.*, for platinum) it seems that quantitative agreement is replacing qualitative ones.

5. Ga K edge: the lastest breakthrough in the theoretical simulation of the XANES part of the absorption spectra

5.1. The XANES K edge

Regarding the XANES part of the gallium K edge (figure 6), the starting point is given by several reference compounds in which the coordination of gallium is 6 ($ZnGa_2O_4$), 4 ($GaPO_4$) or between these two values (Ga_2O_3). If we consider the nanomaterial, the shape of the XANES part at the Ga K edge indicates clearly

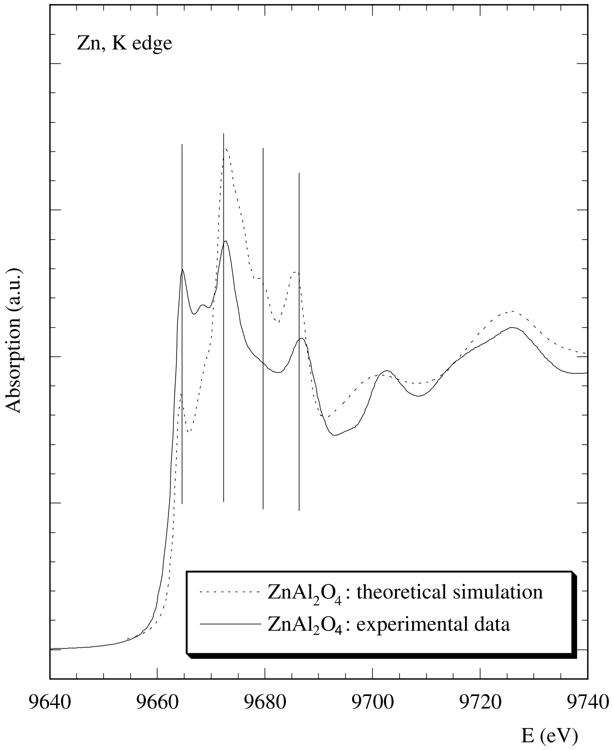

Figure 4. Numerical simulation based on the FeFF code and experimental data for the reference compound $ZnAl_2O_4$ at the Zn K edge.

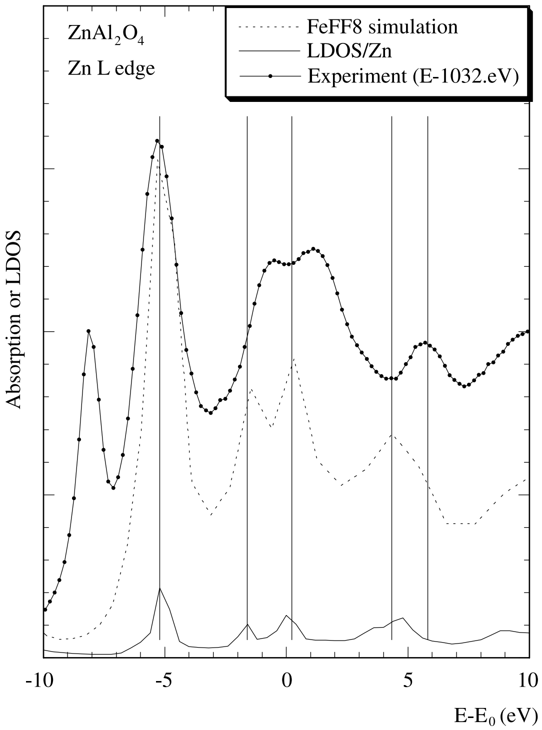

Figure 5. Numerical simulation based on the FeFF code and experimental data for the reference compound $ZnAl_2O_4$ at the Zn L edge.

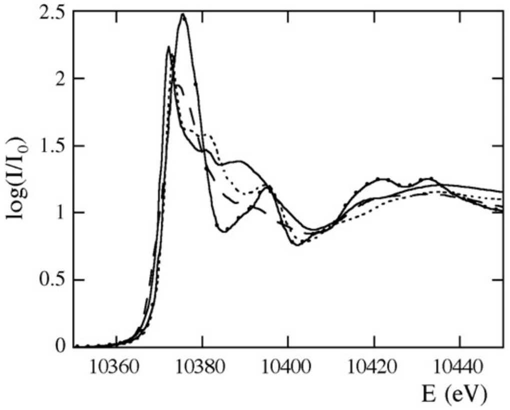

Figure 6. Ga K XANES for the catalyst SnO$_2$: (Zn,Ga)/Al$_2$O$_3$ (-----) and the reference compounds Ga$_2$O$_3$ (— —), GaPO$_4$ (——) and ZnGa$_2$O$_4$ (—•—).

that the coordination of gallium atoms is 4. At this point, this information is in contradiction to the EXAFS analysis, which gives for the composition of the first coordination sphere 4.8 oxygen atoms, the interatomic gallium–oxygen distance being equal to 1.85 Å. While the value of coordination number is between 4 and 6, the interatomic distance is close to the value of the interatomic distance which corresponds to the GaPO$_4$ compound (GaPO$_4$, $R_{\text{Ga-O}} = 1.79$ Å, ZnGa$_2$O$_4$, $R_{\text{GaO}} =$ 1.99 Å). In fact, Ga RMN experiments confirm that Ga atoms are positioned at tetrahedral sites [38]. Here, we consider the L absorption edge to confirm the environment of gallium given by the K absorption edge.

5.2. Complementarity between the K and the L edge

If we consider the L edge (figure 7), we find again a similarity between the Ga K and L$_{\text{III}}$ edge. This experimental result leads to the fact that some overlap exists between the conduction band (Ga 4*s* and 4*p* with oxygen 2*p*) and the 3*d* band, creating very weak 3*d* character following the same shape as the 4*p* states.

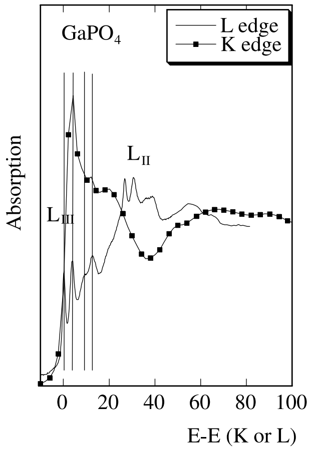

Figure 7. Comparison between the Ga K edge and Ga L$_{\text{III}}$ edge for the reference compound GaPO$_4$.

5.3. Local density of states and the L_{III} absorption edge

In the case of a platinum nanometer-scale metallic cluster, a major improvement in the numerical simulation of the edge part can be done through a comparison between the density of states calculated by the FeFF program and one based on a tight-binding model [39, 40]. Through previous calculations dedicated to the electronic structure of nanometer-scale Pt clusters and the Pt L$_{\text{II,III}}$ edge, we have shown that a strong correlation exists between the intensity of the white line and the size of the cluster.

More precisely, two physical phenomena can affect the intensity of the white line. The first is the size of the cluster which can be considered as an intrinsic effect (density of states of a nanometer-scale Pt cluster are far from the bulk one). The second is linked to a possible charge transfer between the cluster and the support, which can be considered as an extrinsic one [39]. These first results obtained with the FeFF program are encouraging. Nevertheless, it is clear that to go further in the analysis, the detailed geometric configurations present in the cluster surface have to be integrated much more precisely. This improvement will allow one to obtain quantitative effects, which would be more clearly related to the characteristics of the density of states. This approach will allow us to handle properly electronic transfer between the cluster and the support.

The latest version of the FeFF program is able to calculate the local density of states. In order to illustrate this new opportunity, we have plotted in figure 8 (respectively in figure 5) a comparison between the LDOS of oxygen and of gallium atoms and the Ga L$_{\text{III}}$ absorption

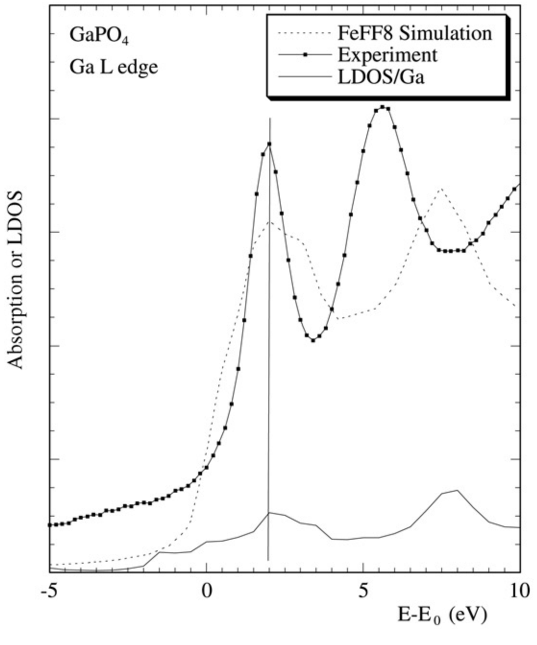

Figure 8. Comparison between the LDOS of oxygen and of Ga atoms and the Ga L$_{\text{III}}$ absorption edge of GaPO$_4$.

edge of $GaPO_4$ (respectively between the LDOS of oxygen and of Zn atoms and the Zn L_{III} absorption edge of $ZnAl_2O_4$). Note that it is possible that the discrepancy between the density of states and XAS in figure 8 is due largely to broadening, and partly due to self-energy corrections that shift the peak positions slightly. Work is in progress to link the different features located at the edge to the local density of states.

6. Conclusion and perspectives

Ab initio simulations of X-ray absorption spectra associated with nanomaterials used in heterogeneous catalysis constitute an important challenge. Part of the difficulty arises from their particular structural and electronic characteristics including their nanometer scale as well as their lacunar aspect. As we have seen in these examples, we arrive at the limit of the theoretical formalism currently used in the analysis of L edge absorption.

Regarding the transition metals, the blurring of details in the Co L_{III} edge absorption spectra gives an indication of structural disorder in the first coordination sphere of the Co atoms but up to now disorder has not been taken into account in the "multiplet" formalism. For other elements such Zn and Ga, significant progress has been made, replacing the qualitative agreement by a quantitative one.

The facts that (i) we can use the similarity between the K and the L edge to point out the overlap of atomic orbitals and (ii) we have access now to the local density of states through the FeFF code will allow us to take into account the particular structural and electronic characteristics of nanomaterials. Special attention has to be paid to significant parameters such as the size of the cluster as well as its lacunar aspect (cation vacancies, anion vacancies or their distribution inside the cluster).

Finally, as underlined by Somorjai and McCrea [40], characterization of the catalysts under reaction conditions is essential, as the catalyst restructures in the presence of the reactant mixture. The fact that it is possible to perform *in situ* X-ray absorption experiments constitutes clearly a major advantage to understand the molecular details of the catalytic process.

Acknowledgments

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