An EXAFS study of Cu/ZnO and Cu/ZnO–Al_2O_3 methanol synthesis catalysts

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Received 20 March 1993; accepted 19 April 1993

Cu K-absorption edge and EXAFS measurements on binary Cu/ZnO and ternary Cu/ZnO–Al_2O_3 catalysts of varying compositions on reduction with hydrogen at 523 K, show the presence of Cu microclusters and a species of Cu^{1+} dissolved in ZnO apart from metallic Cu and Cu_2O. The proportions of different phases critically depend on the heating rate especially for catalysts of higher Cu content. Accordingly, hydrogen reduction with a heating rate of 10 K/min predominantly yields the metal species ($>50\%$), while a slower heating rate of 0.8 K/min enhances the proportion of the Cu^{1+} species ($\sim 60\%$). Reduced Cu/ZnO–Al_2O_3 catalysts show the presence of metallic Cu (upto 20%) mostly in the form of microclusters and Cu^{1+} in ZnO as the major phase ($\sim 60\%$). The addition of alumina to the Cu/ZnO catalyst seems to favour the formation of Cu^{1+}/ZnO species.

Keywords: EXAFS; XANES; methanol synthesis catalysts; Cu/ZnO; Cu/ZnO–Al_2O_3

1. Introduction

Copper based catalysts find widespread use in the synthesis of methanol from $CO/CO_2/H_2$ feedstock. These contain copper and zinc oxide, often with small quantities of alumina or chromia which is supposed to inhibit sintering [1]. The Cu component in the catalyst is believed to act as a promoter in lowering the activation barrier of the reaction on ZnO. The highest catalytic activity in the Cu/ZnO system is found for compositions with a CuO : ZnO ratio of 30 : 70 [2]. There have been many studies on the characterization of the Cu/ZnO catalysts [3–11]. An earlier extended X-ray absorption fine structure investigation (EXAFS) from this laboratory [9] showed that the calcined catalyst contains Cu^{2+} in a CuO-like phase as well as in substitutional sites in the ZnO lattice. It is generally accepted in the literature that reduced Cu/ZnO catalysts contain, in addition to ZnO and metallic Cu, a significant amount of Cu^{1+} in a dispersed state. Our earlier EXAFS study

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[9] provided evidence for a Cu_2O-like phase and a Cu^{1+} species dissolved in ZnO. Some workers have associated the catalytic activity with the latter species [12]. A recent EXAFS study [10] on Cu/ZnO catalysts with low copper loading (upto 10 wt%) suggests the presence of metallic (bulk) Cu, small Cu crystallites, Cu_2O and Cu^{1+} in ZnO. These workers conclude that the active composition contains a high proportion of metallic Cu after reduction.

In view of the uncertainties regarding the nature of the active species in this important catalyst system, we considered it necessary to investigate different compositions of Cu/ZnO catalysts by employing in situ EXAFS and XANES (X-ray absorption near edge structure) measurements. Another aspect of interest was to study the effect of adding Al_2O_3 to ZnO on the surface species. We have examined Cu/ZnO and Cu/ZnO–Al_2O_3 catalysts prepared under different reduction rates in order to understand the origin of various surface species in the reduced catalysts. The present study has shown that the catalysts contain metallic Cu (both in bulk and microcrystalline forms), Cu_2O and a Cu^{1+} species dissolved in ZnO, the proportion of the last being quite significant in the catalytically active compositions.

2. Experimental

The catalyst precursors were prepared by coprecipitation from an aqueous solution of the nitrates of the metals, by the addition of sodium hydrogen carbonate at 353 K. After filtration, the precipitate was washed thoroughly with distilled water and dried at 353 K followed by calcination at 573 K. By this procedure, precursors of binary catalyst samples with Cu : Zn atomic ratios of 10 : 90, 20 : 80 and 30 : 70, and of ternary catalyst samples with Cu : Zn : Al atomic ratios of 24 : 56 : 20, 21 : 49 : 30 and 30 : 40 : 30 were prepared.

X-ray absorption spectra were recorded using a Rigaku spectrometer with a rotating anode X-ray generator (Ru-200B, Rigaku, Japan). A Ge(220) crystal was used as the monochromator with a 0.2 mm slit for EXAFS measurements while a Ge(333) monochromator with a 0.1 mm slit was employed for XANES measurements to achieve a spectral resolution of less than 2 eV. The precursor catalysts were pressed into self-supporting wafers after mixing with fine powder of boron nitride (Merck) and a drop of PVA. The thickness of the wafer was adjusted so that the edge jump (μ.d) in the EXAFS was 2.0 in every case. The wafers were mounted in a locally fabricated all-quartz in situ cell, details of which are described elsewhere [13]. Reduction was carried out in dry purified hydrogen (passed through BASF R-3-11) at atmospheric pressure. During the reduction, the temperature was gradually increased from 293 to 523 K either at a rate of 10 K/min (as normally adopted) or at a rate of 0.8 K/min (which we call, slow reduction), and was kept constant at 523 K for 3 h. After reduction, the samples were cooled to room temperature under flowing hydrogen.

EXAFS and XANES spectra of the reference compounds, CuO, Cu_2O and Cu metal were recorded under similar conditions. The structural parameters of the reference compounds are listed in table 1. Fourier transforms (FT) of the EXAFS data were obtained with $k_{\min} \approx 2.4$ and $k_{\max} \approx 11.4$ Å^{-1} after weighting the data by k^3. EXAFS data were treated using the multiphasic model involving the additive relationship of EXAFS function [14].

3. Results and discussion

3.1. EXAFS STUDIES

We first investigated binary Cu/ZnO catalysts with Cu : Zn atomic ratios of 10 : 90, 20 : 80 and 30 : 70 reduced in hydrogen at 523 K by employing a heating rate of 10 K/min (normal reduction). In fig. 1a, we show the FTs of Cu K-EXAFS of these catalyst samples along with that of Cu metal. FTs of the catalysts exhibit a first peak around 1.44 Å probably due to oxygen coordination and a second peak around 2.16 Å due to Cu–Cu coordination of metallic Cu. Both the peaks grow in intensity with increasing Cu concentration. The peak around 2.16 Å shows a slight asymmetry on the higher r-side. The features in the 3–5.5 Å range closely resemble those of the bulk Cu metal. We have carried out a detailed curve-fitting analysis involving the residual FT method in order to evaluate the multiphasic nature of the catalysts.

Curve-fitting of the first peak around 1.44 Å employing Cu–O parameters from Cu_2O gave coordination numbers of 1.5, 2.2 and 2.4 at distances of 1.86, 1.87 and 1.89 Å for the 10 : 90, 20 : 80 and 30 : 70 catalysts, respectively. This indicates the presence of a Cu_2O-like phase, probably in a multiphasic environment (table 1). Inverse-transformed data from the second peak (r-window: 1.96–2.36 Å) using Cu–Cu parameters from Cu metal gave a good fit with an interatomic distance in the range 2.53–2.56 Å. The observed reduction in the average Cu–Cu distance implies the presence of Cu microclusters (~ 10 Å) in admixture with the bulk metal [15]. Coordination numbers of 4.5, 6.3 and 7 are obtained for the 10 : 90, 20 : 80 and 30 : 70 catalysts respectively, suggesting an increasing proportion of bulk Cu.

Table 1
Structural parameters for the reference compounds

	Atom pair	N	R(Å)
Cu metal	Cu–Cu	12	2.56
CuO	Cu–O	4	1.96
	Cu–Cu	4	3.00
Cu_2O	Cu–O	2	1.84
	Cu–Cu	12	3.02
ZnO	Zn–O	4	1.99
	Zn–Zn	12	3.23

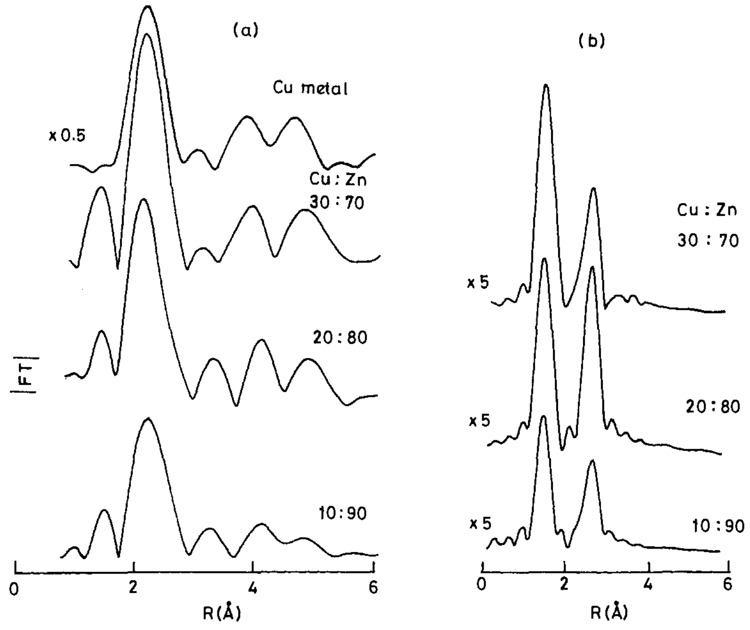

Fig. 1. (a) Fourier transforms (FT) of the Cu K-EXAFS of binary Cu/ZnO catalysts with Cu : Zn ratios of 10 : 90, 20 : 80 and 30 : 70, after reduction in hydrogen at 523 K using a heating rate of 10 K/min (normal reduction) along with the FT of the Cu metal; (b) residual FTs of the same obtained after subtracting the metal contribution.

Making use of these results, we have subtracted the metal contribution from the inverse-transformed data of a wider window (1.2–2.84 Å) in order to obtain the residual FT. In the case of the 10 : 90 catalyst, we obtain a residual peak at 2.62 Å which shifts to a lower r-value by 0.05 Å with the increase in Cu concentration (fig. 1b). Curve-fitting of this peak using Cu–Cu parameters gave a distance of 3.11 Å and a high Debye–Waller factor ($\sim$ 0.001 Å^2). This is rather surprising since neither the oxides nor the metal contain such a Cu–Cu distance. Furthermore, this distance decreases (3.08 Å) with the increase in the Cu content, approaching the Cu–Cu distance in Cu_2O. This may be reconciled if one considers the presence of an additional Cu^{1+} species with a higher Cu–Cu distance such as Cu^{1+} dissolved in ZnO, besides Cu_2O. Such a species would give rise to a Cu–Zn distance of $\sim$ 3.23 Å (table 1). This assignment is consistent with the fact that the EXAFS parameters of Cu and Zn do not differ much.

We have calculated the proportions of the Cu_2O-like and the Cu^{1+}/ZnO species, equating the observed distance to a weighted average value. In the absence of information about sizes of the metal particles, a rough estimate of the proportion of metallic Cu is obtained by treating the Cu–Cu coordination number (at $\sim$ 2.56 Å) from curve-fitting analysis as a fraction of the bulk coordination number. The proportions of different species are listed in table 2. The 10 : 90 catalyst

Table 2
Proportions of copper in different species

Catalyst composition	Normal reduction			Slow reduction		
	metallic[a] Cu	Cu^{1+} phase		metallic[a] Cu	Cu^{1+} phase	
		Cu_2O-like	Cu^{1+} in ZnO		Cu_2O-like	Cu^{1+} in ZnO
binary						
Cu : Zn						
10 : 90	38	35	37	41	36	23
20 : 80	52	35	13	53	24	23
30 : 70	58	30	12	22	44	34
ternary						
Cu : Zn : Al						
26 : 54 : 20	–	–	–	24	14	62
21 : 49 : 30	39	49	12	16[b]	28	56
30 : 40 : 30	–	–	–	58	37	5

[a] Partly in bulk form and partly in microcrystalline form. We are unable to provide the relative proportions of the two quantitatively.

[b] Cu is mostly in the microcrystalline form.

comprises nearly 38% of metallic Cu, 35% of Cu_2O-like species and 27% of Cu^{1+}/ZnO. The proportions of the different species are comparable with those reported by Kau et al. [10] for the same composition. As the Cu content increases, the proportion of metallic Cu exceeds 50% while the proportions of Cu^{1+} species decrease, indicating saturation of the ZnO surface-sites and increased segregation. We have further examined on this aspect by varying the rate of reduction.

In fig. 2a, we show the FTs of Cu/ZnO catalysts with Cu : Zn atomic ratios of 10 : 90, 20 : 80 and 30 : 70 reduced at 523 K with a heating rate of 0.8 K/min (slow reduction). We notice that the intensity of the features increases when the Cu content changes from 10 to 20% similar to the case of normal reduction (fig. 1a), but decreases drastically when the Cu content reaches 30%. We also observe that the relative intensity of the first peak in the 30 : 70 catalyst, is quite high and that the second peak is considerably broader implying the dispersed nature of the catalysts. Curve-fitting analysis followed by residual FT method was carried out in all the cases and the residual FTs are shown in fig. 2b. In the case of the 10 : 90 and 20 : 80 catalysts (*r*-window: 1.2–2.8 Å), there is a residual peak around 2.62 Å which on curve-fitting gives a Cu–Cu distance of 3.1 and 3.12 Å, respectively. A wider *r*-window of 1.2–3.3 Å was employed in the case of the 30 : 70 catalyst since the features due to the second coordination of metallic Cu overlap with the region of interest. The residual FT (fig. 2b) exhibits two peaks at 2.58 and 3.14 Å where the latter is considered to be due to the second coordination of the metallic Cu species. The peak at 2.58 Å was analysed for the proportions of the Cu^{1+} species. The

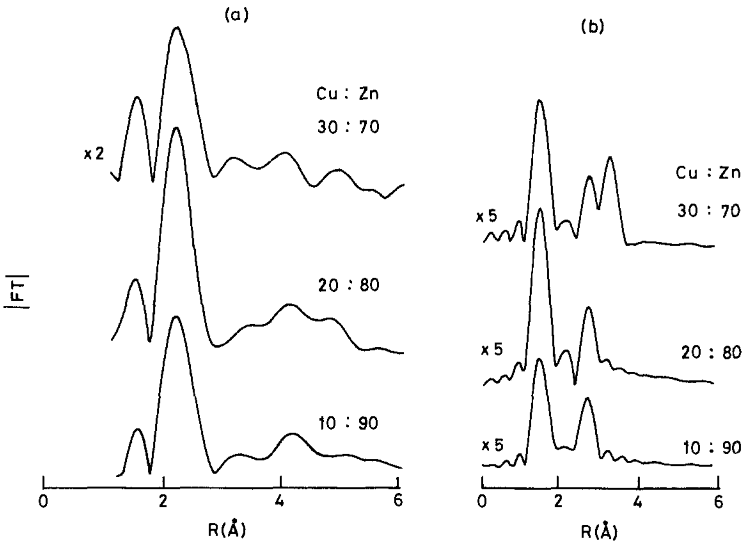

Fig. 2. (a) Fourier transforms (FT) of the Cu K-EXAFS of binary Cu/ZnO catalysts with Cu : Zn ratios of 10 : 90, 20 : 80 and 30 : 70, after reduction in hydrogen at 523 K using a heating rate of 0.8 K/min; (b) residual FTs of the same obtained after subtracting the metal contribution.

results of the analysis are given in table 2. It is interesting that in case of the 10 : 90 catalyst the proportions of various species remain nearly the same irrespective of the rate of reduction. For a relatively low metal loading of 10%, one would not expect the dispersion to alter with the rate of reduction. In case of the 20 : 80 catalyst, however, the proportion of the Cu^{1+}/ZnO species increases by about 10% compared to normal reduction, although the percentage of the metallic species remains the same. The proportion of Cu^{1+}/ZnO is highest (34%) in case of the 30 : 70 catalyst while the metallic Cu species is only 22%. Clearly, the rate of heating has a marked effect on the kinetics of reduction. Based on this study, we would expect more Cu^{1+} species to form even with a normal reduction rate, provided a milder reducing atmosphere is adopted. We have indeed found such an enhancement of the Cu^{1+} species in case of the 30 : 70 catalyst when the reduction was carried out in an atmosphere at 1%H_2 + 99%Ar (instead of pure H_2) using a heating rate of 10 K/min.

Another aspect of our work has been to study the effect of adding alumina on the nature of the active species in Cu/ZnO catalysts. In fig. 3a, we show the FT of a ternary catalyst with 30% Al concentration and an internal Cu : Zn atomic ratio of 30 : 70, after normal reduction in hydrogen. The features due to oxygen and metal coordinations are seen, the latter having a distinct asymmetry on the higher r-side. The proportions of the different species estimated from the residual FT (fig. 3b) are given in table 2. The percentage of metallic Cu decreases considerably with a simultaneous increase in the Cu_2O-like phase, compared to the correspond-

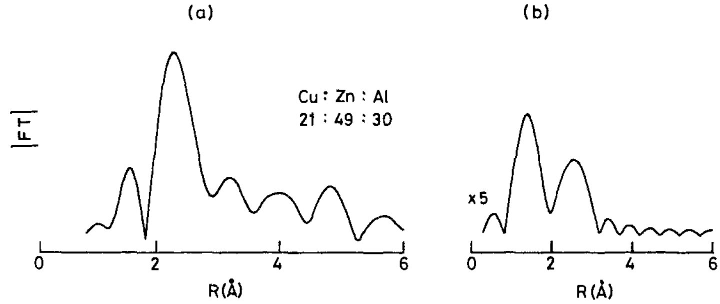

Fig. 3. (a) Fourier transform (FT) of the ternary catalyst with Cu : Zn : Al ratio of 21 : 49 : 30, after reduction in hydrogen at 523 K using a heating rate of 10 K/min (normal reduction); (b) residual FT obtained after subtracting the metal contribution.

ing binary system. Clearly, the addition of alumina helps in achieving a better dispersion in the catalyst.

We have carried out similar measurements on different ternary catalysts using the slow reduction procedure. In fig. 4a, we show FTs of the reduced Cu/ZnO–Al_2O_3 catalysts with 20 and 30% Al concentrations, having an internal Cu : Zn atomic ratio of 30 : 70. The relative intensity of the first peak arising from Cu^{1+}–O coordination increases with the Al concentration and is quite comparable to that of the metal peak. We find some differences in that the first peak in case of the 20% Al catalyst is shifted to a higher *r*-value (1.52 Å) whereas the metal peak in the

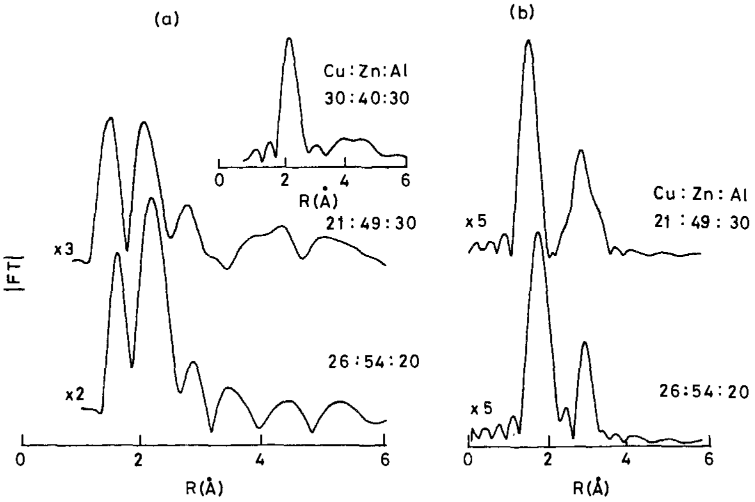

Fig. 4. (a) Fourier transforms (FT) of the Cu K-EXAFS of ternary Cu/ZnO–Al_2O_3 catalysts with Cu : Zn : Al ratios of 26 : 54 : 20 and 21 : 49 : 30, after reduction in hydrogen at 523 K using a heating rate of 0.8 K/min. The inset shows FT of a ternary catalyst with Cu : Zn : Al ratio of 30 : 40 : 30 after reduction; (b) residual FTs obtained after subtracting the metal contribution.

30% Al catalyst occurs at a lower r-value of 2.04 Å. Accordingly, curve-fitting analysis gives a Cu^{1+}–O distance of 1.94 Å and a Cu–Cu distance of 2.49 Å in the above cases. A Cu–Cu distance of 2.49 Å provides a definitive evidence for the presence of Cu microclusters on the surface of the 30% Al catalyst. Unlike the binary catalyst samples, the ternary catalysts show a well-resolved peak arising from the Cu^{1+} phases at an unusually high r-value of $\sim$ 2.72 Å. The phase compositions calculated from the analysis of the residual FTs (fig. 4b) are listed in table 2. The proportion of the Cu^{1+}/ZnO species in the ternary catalysts is strikingly high ($\sim$ 60%) in contrast to that in the binary catalysts, but the metal fraction remains the same. The occurrence of a longer Cu^{1+}–O distance of 1.94 Å, which is close to the Zn–O distance in ZnO (see table 1), strengthens this assignment.

A comment on the formation of Cu^{1+} in the ZnO lattice would be in order. ZnO occurs in the wurtzite structure with Zn^{2+} ions occupying tetrahedral sites. Diffusion of Cu^{1+} ion would creat a charge imbalance in the lattice, restricting the formation of the Cu^{1+}/ZnO species. A simultaneous doping of Al^{3+} into ZnO lattice like in the case of ternary catalysts brings about overall charge balance thereby favouring the formation of the Cu^{1+}/ZnO species.

We have studied a ternary catalyst wherein the internal Cu : Zn ratio is different from 30 : 70 (Cu : Zn : Al = 30 : 40 : 30). Interestingly, this catalyst sample on slow reduction, mainly gives the metallic Cu species (see the inset of fig. 4a). A decrease in the relative Zn content has obviously caused more Cu to spread over the surface of alumina resulting in a higher degree of reduction since alumina has negligible interaction with Cu [13]. This is reflected in the relative proportions of Cu^{1+} species (with the Cu^{1+}/ZnO phase being as low as 5%).

3.2. XANES STUDIES

We have performed XANES measurements on a reduced ternary catalyst in order to unambiguously establish the oxidation state of Cu. In fig. 5, we show normalized Cu K-near edge spectra of the ternary catalyst with Cu : Zn : Al atomic ratio of 21 : 49 : 30 before and after reduction along with the spectra of the reference compounds, CuO, Cu_2O and Cu metal. The presence of a weak feature around 8.987 keV and the main peak at 8.997 keV in the calcined precursor suggest that Cu is predominantly in the 2+ state. On slow reduction, the main peak shifts to lower energy with a well-defined mid-edge feature at 8.983 keV characteristic of Cu^{1+}. This supports the observation from EXAFS studies that the unreduced Cu is present as a Cu_2O-like species and as Cu^{1+} in ZnO. Interestingly, the calcined precursor after a normal reduction displays features characteristic of Cu metal.

4. Conclusions

(1) In the reduced binary Cu/ZnO and ternary Cu/ZnO–Al_2O_3 catalysts stu-

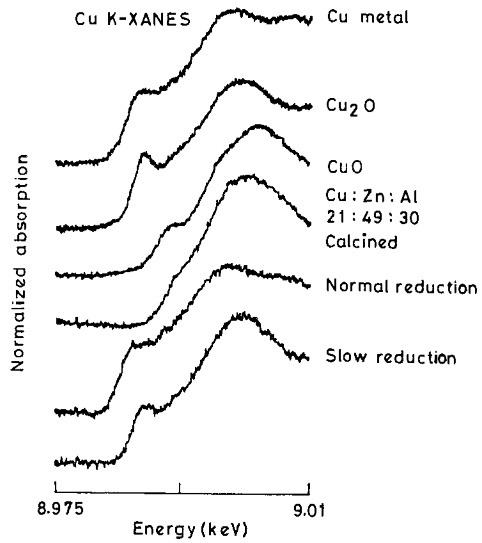

Fig. 5. Normalized Cu K-edge spectra of the ternary catalyst with Cu : Zn : Al ratio of 21 : 49 : 30 in the calcined state and after reduction. The spectra of the reference compounds CuO, Cu_2O and Cu metal are also shown.

died, copper is present in four phases. Metallic Cu and Cu microclusters are the completely reduced forms while Cu_2O-like phase and Cu^{1+} ions dissolved in ZnO constitute partially reduced fraction.

(2) A comparitive study with different rates of reduction has shown that a slower rate of reduction (0.8 K/min) in general, enhances the proportion of Cu^{1+} containing phases whereas a normal reduction (10 K/min) results in mostly metallic forms of copper.

(3) Addition of alumina to the binary catalysts, significantly increases the proportion of Cu^{1+}/ZnO species apart form providing a good dispersion.

Acknowledgement

The authors thank the Department of Science and Technology and the University Grants Commission for support of this research. One of the authors (TA) thanks the Council for Scientific and Industrial Research for a fellowship.

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