Isotope-Resolved Transient Analysis of Formate Turnover on Reducible Oxide–Copper Interfaces

Authors

Oliver Bennett[1*], Emily Carter[2]

Affiliations

Department of Chemical Engineering, Faculty of Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom.

***Corresponding author:** Bennett@imperial.ac.uk

Abstract

Surface formate is widely observed during catalytic CO_2 conversion, but its kinetic role remains debated because steady-state spectra alone cannot distinguish spectator species from reactive intermediates. Herein, isotope-resolved transient analysis was used to quantify formate turnover on reducible oxide–copper interfaces under methanol-forming conditions. Oxide-modified Cu catalysts containing Zr, Ce, and Zn surface domains were prepared by sequential wet impregnation and reduced at 300 °C before reaction. Transient switching experiments using $^{13}CO_2/H_2$, $^{12}CO_2/D_2$, and $^{13}CO_2/D_2$ were conducted at 230–260 °C and 3.0 MPa, combined with operando DRIFTS, online mass spectrometry, and kinetic isotope effect analysis. Among the tested catalysts, the Zr-modified Cu sample showed the fastest ^{13}C incorporation into methanol, reaching 90% isotopic exchange within 11.6 min, compared with 24.8 min for Zn-modified Cu and 19.3 min for Ce-modified Cu. The apparent formate consumption rate on Zr–Cu interfacial sites was 2.7 times higher than that on unmodified Cu, while the surface formate lifetime decreased from 41.2 to 15.4 s. Deuterium substitution reduced the methanol formation rate by a factor of 2.4, confirming that hydrogen addition to formate-derived intermediates is kinetically significant. Operando spectra showed that reactive bidentate formate bands at 1588 and 1372 cm^{-1} decayed synchronously with the appearance of $^{13}CH_3OH$, whereas strongly bound carbonate species remained largely unchanged during isotope switching. These results demonstrate that only a fraction of the observed formate pool participates directly in methanol formation and that reducible oxide–copper interfaces accelerate the turnover of this reactive formate fraction. The findings offer kinetic evidence for the ensemble-site mechanism of oxide-promoted copper catalysts.

Keywords: formate turnover; isotope transient analysis; reducible oxide; copper catalyst; operando DRIFTS; kinetic isotope effect; methanol formation

1. Introduction

CO_2 hydrogenation to methanol provides a promising route for coupling captured carbon with renewable H_2 to produce fuels and value-added chemicals. Methanol is widely used as a

chemical feedstock, liquid fuel, energy carrier, and intermediate for the synthesis of olefins and other carbon-based products. Its production from CO_2 can therefore contribute to both carbon utilization and renewable-energy storage. Nevertheless, the high thermodynamic stability of CO_2 and the multiple proton- and electron-transfer steps required for methanol formation impose substantial kinetic limitations. Methanol synthesis also competes with the reverse water–gas shift reaction, which generates CO and can reduce carbon efficiency and methanol selectivity. Cu-based catalysts remain among the most widely investigated systems because Cu can activate H_2 and hydrogenate adsorbed carbon-containing intermediates under relatively mild conditions. Their catalytic behavior, however, cannot be described solely by the amount of exposed Cu. Cu particle size, oxidation state, local coordination, surface reconstruction, and interaction with neighboring oxide phases can all alter CO_2 adsorption, hydrogen activation, intermediate stabilization, and product desorption [1,2]. Operando studies further demonstrate that Cu–oxide interfaces may restructure in response to temperature, pressure, and reactant composition, meaning that the catalytically relevant surface can differ substantially from the structure observed before or after reaction [3,4]. Recent atomistic modeling of inverse ZrO_2/Cu catalysts has reinforced this view by showing that catalytic activity is distributed across an ensemble of interfacial configurations rather than a single static active site. Only a limited fraction of accessible configurations remain highly active throughout the reaction pathway, while the stability of methoxy-containing states and structural evolution of the interface can strongly influence turnover and deactivation [5]. These findings emphasize that the identity, population, and dynamics of oxide–Cu interfacial sites must be considered when interpreting methanol synthesis kinetics.

Reducible and amphoteric oxides can modify Cu through several complementary effects. ZrO_2 provides acid–base pairs, surface oxygen atoms, hydroxyl groups, and interfacial sites capable of stabilizing oxygenated carbon species. CeO_2 introduces oxygen vacancies together with the reversible Ce^{4+}/Ce^{3+} redox couple, which can modify CO_2 adsorption and facilitate hydrogen and oxygen transfer. Zn-containing oxides can alter the electronic and geometric environment of Cu and generate interfacial structures that differ from those present on unsupported Cu. Studies of Cu/ZrO_2, ZrO_x/Cu, Cu–CeO_x, and CuZn/ZnZrO_x systems have consistently shown that methanol productivity and selectivity are strongly affected by the nature and extent of oxide–Cu contact rather than by Cu surface area alone. Changes in oxide dispersion, defect density, hydroxyl coverage, Cu oxidation state, and boundary structure can shift the relative stability of formate, carbonate, methoxy, and CO-derived intermediates [6,7]. The oxide component therefore does not act simply as an inert support. Instead, it participates in the creation of chemically distinct reaction environments in which CO_2-derived species can be stabilized and subsequently hydrogenated. This interfacial sensitivity also makes direct comparison among promoted Cu catalysts difficult because changes in oxide composition are often accompanied by changes in Cu size, reduction degree, surface area, or metal–oxide contact [8,9]. Formate species are among the most frequently observed surface intermediates during CO_2 hydrogenation over Cu-based catalysts and are

commonly associated with the pathway toward methanol. Their presence in infrared spectra, however, does not establish that every adsorbed formate species participates directly in catalytic turnover. A highly populated intermediate may accumulate because it is strongly bound or slowly converted, whereas a less abundant species may account for a larger fraction of the actual reaction flux. Time-resolved DRIFTS measurements on Cu/ZrO_2 have revealed kinetically distinct formate populations with markedly different disappearance rates, with only the more rapidly responding population showing a clear relationship with subsequent methoxy formation [10,11]. This distinction is important because conventional steady-state spectra mainly report surface coverage and cannot directly determine the fraction of an adsorbate that proceeds to methanol. Product-based measurements alone are also insufficient for assigning elementary pathways, particularly when secondary methanol reactions become significant as CO_2 conversion increases [12]. Additional studies on $Cu–CeO_x$ and $Cu–ZrO_2$ catalysts have shown that surface hydroxyls, adsorbed water, oxide structure, and interfacial hydrogen transfer can influence both the formation and subsequent hydrogenation of formate species [13,14]. H_2/D_2 switching experiments over promoted Cu catalysts have likewise identified formate populations with different hydrogenation kinetics, further indicating that spectroscopically similar species can possess substantially different reactivities [15,16]. Taken together, these observations highlight a fundamental mechanistic problem: the dominant species observed on the catalyst surface is not necessarily the species that dominates methanol production. Isotopic transient methods provide a direct means of addressing this problem because they introduce time as an additional mechanistic dimension. Switching from $^{12}CO_2$ to $^{13}CO_2$ allows the exchange and replacement of surface carbon-containing species to be followed independently of their steady-state concentration. H_2/D_2 switching can probe the involvement of hydrogen-transfer steps and reveal whether the conversion of a particular intermediate exhibits a measurable kinetic isotope effect. Combined $^{13}CO_2$ and D_2 experiments can further distinguish carbon exchange from hydrogenation kinetics. When isotope switching is coupled with operando DRIFTS and sufficiently rapid online mass spectrometry, the temporal evolution of formate, carbonate, and methoxy bands can be compared directly with the appearance of isotopically labelled methanol. Such measurements provide information on intermediate lifetime, exchange rate, surface residence time, and the relationship between adsorbate consumption and product formation that cannot be obtained from steady-state spectra alone. Recent work has also indicated that reaction pressure and surface basicity can substantially alter the measurable formate reservoir and modify the apparent route toward methanol [17,18]. Mechanistic conclusions obtained at low pressure therefore cannot always be transferred directly to technically relevant methanol-synthesis conditions. Despite these advances, a quantitative connection between surface formate dynamics and methanol formation under elevated pressure remains insufficiently established. Many spectroscopic studies characterize the total population of adsorbed species without determining what fraction of that population is kinetically coupled to product formation. Transient investigations frequently monitor either the infrared response or the

gas-phase isotope response, making it difficult to establish whether the disappearance of a particular surface species occurs on the same timescale as labelled methanol production. Comparisons among Zr-, Ce-, and Zn-modified Cu catalysts are further complicated by differences in synthesis route, promoter loading, Cu particle size, reduction history, and measurement conditions. Isotope experiments are also commonly performed over restricted temperature windows or at pressures substantially below those relevant to practical CO_2 hydrogenation. In addition, gas holdup, transport delay, and reactor dead volume can broaden isotope transients and create apparent residence times that do not represent intrinsic surface kinetics. A controlled comparison that combines catalyst preparation, high-pressure isotope switching, surface spectroscopy, and product-resolved isotope detection is therefore required to determine whether the formate species accumulated on different oxide–Cu interfaces are reactive intermediates or predominantly spectator reservoirs.

In this study, Zr-, Ce-, and Zn-modified Cu catalysts were prepared using the same synthesis protocol and subjected to identical reduction procedures to minimize variations unrelated to promoter identity. Isotopic switching experiments using $^{13}CO_2/H_2$, $^{12}CO_2/D_2$, and $^{13}CO_2/D_2$ were performed at 230–260 °C and 3.0 MPa, conditions selected to probe surface kinetics under an elevated-pressure methanol-synthesis environment. Operando DRIFTS was employed to resolve the temporal evolution of formate, carbonate, and methoxy species, while online mass spectrometry simultaneously monitored isotopically labelled methanol and gas-phase switching responses. The analysis focuses on formate lifetime, carbon exchange time, consumption kinetics, and kinetic isotope effects, allowing surface coverage to be distinguished from catalytic turnover. Particular attention is given to whether rapidly exchanging or rapidly consumed formate populations correlate with methanol formation and whether this relationship changes with the identity of the oxide promoter. By comparing Zr-, Ce-, and Zn-containing interfaces within a common experimental framework, the study seeks to identify how oxide chemistry changes the size and reactivity of the surface formate reservoir, the coupling between carbon exchange and hydrogen addition, and the progression from formate-derived species to methoxy and methanol. The broader objective is to establish a kinetic criterion for distinguishing reactive formate intermediates from strongly bound stored species and to clarify how oxide–Cu interfacial environments regulate the fraction of adsorbed carbon that enters productive methanol synthesis. Establishing this relationship is important for moving beyond assignments based primarily on steady-state band intensity and toward a mechanistic description based on measurable surface turnover. The resulting insight provides a basis for understanding why different oxide promoters can produce markedly different methanol activities even when comparable Cu surfaces are present, and offers guidance for designing Cu–oxide interfaces that favor rapid productive intermediate conversion rather than the accumulation of kinetically inactive surface carbon.

2. Materials and Methods

2.1. Catalyst Samples and Reaction Conditions

Four Cu-based catalysts were prepared: unmodified Cu, Zr-modified Cu, Ce-modified Cu, and Zn-modified Cu. The promoter content was fixed at 6 wt% for all modified samples. Copper nitrate was used as the Cu source. Zirconium nitrate, cerium nitrate, and zinc nitrate were used as promoter precursors. The catalysts were prepared by sequential wet impregnation. The solids were dried at 90 °C for 12 h, calcined in air at 350 °C for 4 h, and reduced in 10 vol% H_2/N_2 at 300 °C for 2 h. CO_2 hydrogenation was tested in a stainless-steel fixed-bed reactor at 230–260 °C and 3.0 MPa. The feed contained H_2, CO_2, and N_2 at a molar ratio of 72:24:4. The total flow rate was 70 mL min^{-1}, and 180 mg of catalyst was used in each test. Each catalyst was prepared in two separate batches. Each reaction condition was tested three times.

2.2. Experimental Design and Control Tests

The catalyst groups were used to compare the effects of Zr, Ce, and Zn surface domains on formate conversion. Unmodified Cu served as the main control. All modified catalysts had the same promoter loading and received the same drying, calcination, and reduction treatments. This design reduced differences caused by sample preparation. Blank tests were conducted without a catalyst and with each promoter oxide alone. These tests checked gas-phase reactions and the activity of the oxide itself. Steady-state tests were first carried out under $^{12}CO_2/H_2$. Isotope-switching tests were then conducted using $^{13}CO_2/H_2$, $^{12}CO_2/D_2$, and $^{13}CO_2/D_2$. The total pressure, flow rate, and CO_2 concentration were kept constant during each switch. A bypass test without catalyst was used to measure the gas delay caused by the reactor and transfer lines.

2.3. Measurement Methods and Quality Control

Crystal phases were identified by X-ray diffraction using Cu Kα radiation. Particle size and promoter distribution were examined by transmission electron microscopy and energy-dispersive X-ray mapping. The surface states of Cu, Zr, Ce, Zn, and O were measured by X-ray photoelectron spectroscopy. Surface formate, carbonate, methoxy, and adsorbed CO species were monitored by operando diffuse reflectance infrared Fourier-transform spectroscopy. Spectra were collected every 2 s during isotope switching. Gas products and isotope-labelled species were measured by online mass spectrometry. Methanol, CO, CO_2, and labelled carbon products were identified from calibrated mass-to-charge signals. Gas chromatography was used to confirm product concentrations under steady-state conditions. Certified gas mixtures and liquid methanol standards were used for calibration. Data were accepted when the carbon balance was between 95% and 105%. The reactor temperature was kept within ±1 °C, and the variation among repeated tests was below 5%.

2.4. Data Processing and Kinetic Calculations

The mass-spectrometry signals were corrected using the bypass response. This correction removed the effects of reactor dead volume and gas holdup. The fraction of labelled methanol was calculated as

$$f_{^{13}CH_3OH}(t)=\frac{I_{^{13}CH_3OH}(t)}{I_{^{12}CH_3OH}(t)+I_{^{13}CH_3OH}(t)},$$

where $I_{^{12}CH_3OH}$ and $I_{^{13}CH_3OH}$ are the corrected signals of unlabelled and labelled methanol, respectively. The average lifetime of surface formate was calculated from the decrease in the normalized DRIFTS band area:

$$\frac{A_t}{A_0}=\exp\left(-\frac{t}{\tau_f}\right),$$

where A_0 is the initial formate band area, A_t is the band area at time t, and τ_f is the average formate lifetime. The apparent formate consumption rate was obtained from the initial slope of the band-area decrease and corrected by catalyst mass. The kinetic isotope effect was calculated by dividing the methanol formation rate under H_2 by that under D_2. Results are reported as mean values with standard deviations. Differences among catalysts were tested by one-way analysis of variance followed by Tukey's test. A value of $p<0.05$ was considered significant.

2.5. Isotope-Switching and Surface Turnover Tests

Each catalyst was first reduced in the DRIFTS cell and then exposed to $^{12}CO_2/H_2$ at 240 °C and 3.0 MPa. The test continued until the surface bands and outlet products became stable. The feed was then switched to $^{13}CO_2/H_2$ to measure carbon exchange between surface species and methanol. A second switch from $^{12}CO_2/H_2$ to $^{12}CO_2/D_2$ was used to measure the effect of hydrogen substitution. A $^{13}CO_2/D_2$ switch was also conducted to separate carbon exchange from hydrogen-transfer effects. The time required for labelled methanol to reach 90% of its final value was recorded for each catalyst. The decrease in the bidentate formate bands at 1588 and 1372 cm^{-1} was compared with the increase in labelled methanol. Carbonate bands that changed by less than 5% during switching were treated as strongly bound surface species. The reactive formate fraction was estimated from the part of the formate signal that decreased together with the rise in labelled methanol.

3. Results and Discussion

3.1. Effect of Oxide Promoters on Carbon Exchange

The oxide promoter changed the rate at which surface carbon was converted into methanol. Zr-modified Cu reached 90% ^13C incorporation into methanol within 11.6 min. The exchange times were 19.3 min for Ce-modified Cu and 24.8 min for Zn-modified Cu. Unmodified Cu showed the slowest response. The short exchange time of Zr-modified Cu reflects faster replacement of surface carbon species rather than greater CO_2 uptake alone. CeO_x adsorbed CO_2 through its redox sites, but part of the adsorbed carbon remained as carbonate. ZnO_x also

interacted with Cu, although carbon exchange was slower under the tested conditions. Methanol production and normalized isotope responses are shown in Fig. 1. Liang et al. (2025) also found that CO_2 conversion and methanol selectivity depended on the type and amount of oxide in Cu-based catalysts.

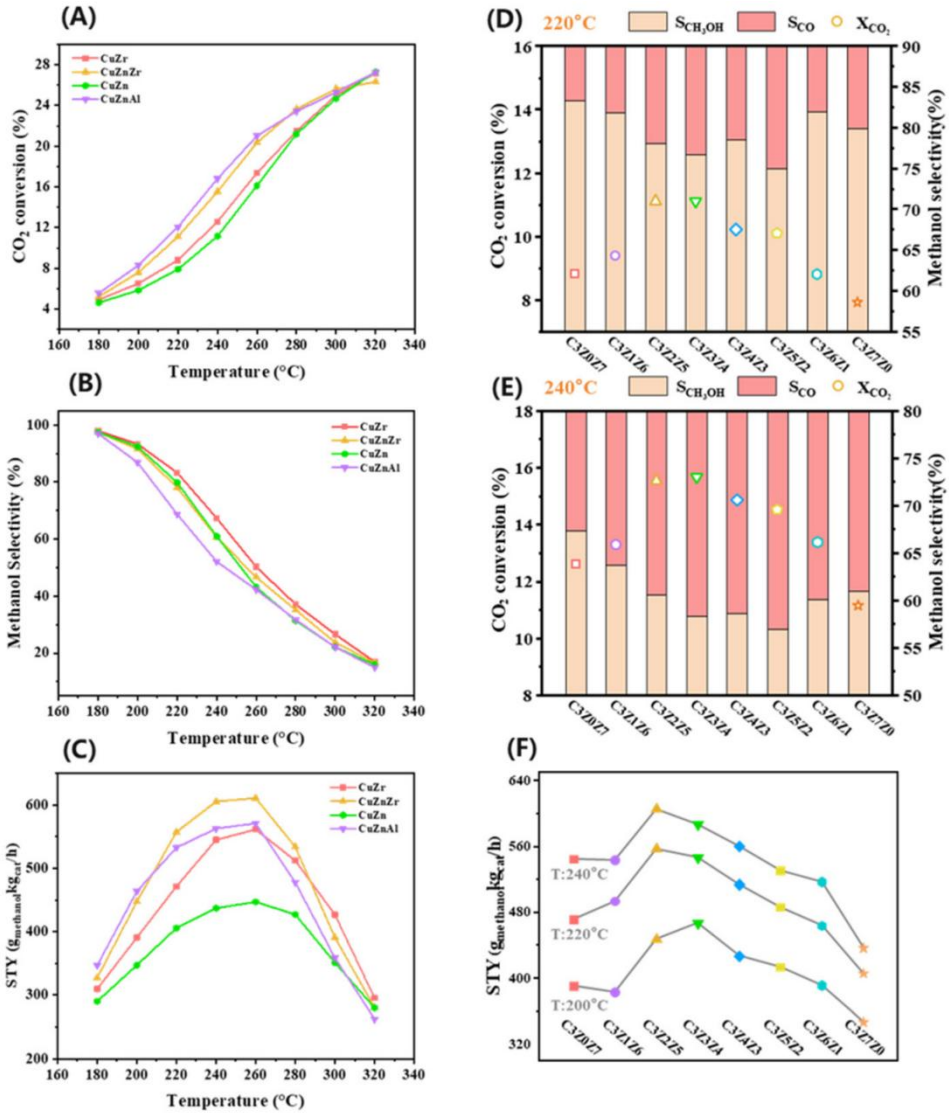

Fig. 1. Methanol formation and ^13C exchange over unmodified and oxide-modified Cu catalysts.

3.2. Formate Lifetime and Reaction Rate

The steady-state formate band intensity did not directly follow the methanol formation rate. On Zr-modified Cu, the apparent formate consumption rate was 2.7 times higher than that on unmodified Cu. The average formate lifetime decreased from 41.2 to 15.4 s. Thus, formate was formed and consumed rapidly at Zr–Cu interfaces. Ce-modified Cu showed an intermediate lifetime, while formate remained longer on Zn-modified Cu. A strong formate band may therefore arise from either an active intermediate or a slowly reacting surface species. Dharmalingam et al. (2025) also observed formate species with different exchange rates during high-pressure isotope

switching over Cu–Zn catalysts. Their results showed that formate reactivity depended on its position near Cu and ZnO sites [19,20].

3.3. Reactive Formate and Stable Carbonate Species

The isotope tests separated reactive formate from stable carbon species. During the switch from ^12CO_2/H_2 to ^13CO_2/H_2, the bidentate formate bands at 1588 and 1372 cm^{-1} decreased as ^13CH_3OH appeared in the outlet gas. These matched changes link part of the formate pool directly to methanol formation. In contrast, the main carbonate bands changed by less than 5% during the same period. These carbonate species remained on the surface and did not form methanol within the measured time [21,22]. The surface bands and gas signals are shown in Fig. 2. Yang et al. (2026) also reported a delay between CO_2 exchange and labelled methanol formation. Their time-resolved infrared spectra showed the replacement of ^12C-formate by ^13C-formate during isotope switching.

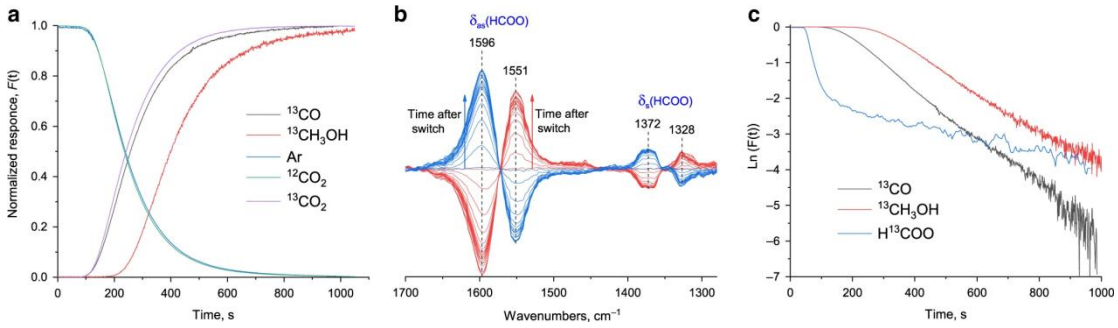

Fig. 2. Changes in formate, carbonate, and labelled methanol during isotope switching.

3.4. Hydrogen Addition at Oxide–Cu Interfaces

Replacing H_2 with D_2 reduced the methanol formation rate by a factor of 2.4. This isotope effect shows that hydrogen addition to formate-derived species affects the reaction rate. However, CO_2 adsorption, hydrogen transfer, and methoxy conversion may also contribute. The results suggest a two-site reaction route. CO_2 adsorbs near the oxide phase, while H_2 dissociates on Cu. Surface hydrogen then moves to the oxide–Cu interface and converts reactive formate into methoxy and methanol. ZrO_x gave the fastest formate turnover and methanol labelling. CeO_x retained more carbonate species, while ZnO_x showed slower exchange of surface formate. Similar oxide effects have been reported for Cu–ZrO_2, Cu–ZnO, and Cu–ZnO–ZrO_2 catalysts [23,24]. However, this study tested only one promoter loading and a narrow temperature range. The infrared response may also differ among oxide surfaces. Further studies should examine more promoter contents, measure interface-site density, and compare rates based on the number of active sites.

4. Conclusion

Isotope transient tests showed that only part of the surface formate was converted into methanol. Zr-modified Cu gave the fastest carbon exchange and formate turnover among the tested catalysts. It reached 90% ^13C incorporation into methanol within 11.6 min. Its formate consumption rate was 2.7 times that of unmodified Cu, while the average formate lifetime decreased from 41.2 to 15.4 s. Operando DRIFTS showed that the bidentate formate bands at 1588 and 1372 cm^{-1} decreased as $^{13}CH_3OH$ formed. The carbonate bands changed little during isotope switching, which shows that most carbonate species remained on the surface. Replacing H_2 with D_2 lowered the methanol formation rate by a factor of 2.4. This result confirms that hydrogen addition to formate-derived species affects the reaction rate. This study directly connects surface-band decay, isotope exchange, and labelled methanol formation under working conditions. The results show that oxide promoters improve methanol production by increasing formate turnover rather than only increasing formate coverage. This method can also be used to study active intermediates in other CO_2 hydrogenation catalysts. However, only one promoter loading and a narrow temperature range were tested. Further work should examine more oxide contents, longer reaction times, and rates based on the measured number of oxide–Cu interface sites.

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