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An examination of praseodymia as an oxygen-storage component in three-way catalysts

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The redox properties of praseodymia have been compared to those of ceria using temperature-programmed desorption (TPD) of O_2 from films prepared by vapor deposition onto an α-Al_2O_3(0001) support, in order to assess the potential for praseodymia as an oxygen-storage component in three-way catalysts. Desorption of O_2 was observed between 700 and 1000 K, and diffraction measurements confirmed that the films change from Pr_6O_{11} to Pr_2O_3 in this temperature range. However, once reduced, the films could not be reoxidized by exposures to O_2 in the vacuum system. Evidence was found for oxygen transfer from Pr_6O_{11} to supported Rh particles. Following CO adsorption on Rh particles deposited onto Pr_6O_{11} film, significant amounts of CO_2 were observed in TPD until the film was completely reduced to Pr_2O_3. Following deposition of Rh particles onto Pr_6O_{11}, the oxygen desorption curves became identical to those normally observed for Rh. These results are compared with similar measurements performed on ceria films and the implications for automotive, emission-control catalysis are discussed.

Keywords: oxygen-storage capacity, praseodymia, ceria, Pd, Rh, O_2 desorption, temperature-programmed desorption, CO oxidation

1. Introduction

An oxygen-storage component is crucial for optimal performance of a three-way, emissions-control catalyst. This component controls the ratio of oxidants and reductants in the exhaust, so that CO and hydrocarbons can be oxidized while NO_x is simultaneously reduced. The reducible oxide used for oxygen storage is always ceria, and it is generally agreed that ceria must also be in contact with a precious-metal catalyst for facile reduction to occur [1,2]. Deactivation of the oxygen-storage component is a problem, since the redox properties of ceria appear to be very sensitive to the structure of the oxide [3,4]. Stabilization of ceria can be accomplished by mixing it with zirconia [5–11]. Recently, thermally stable, high-surface-area ceria–zirconia has been introduced as a direct support for the precious metal component, providing higher oxygen-storage capacity and greater durability compared with pure ceria.

There are clearly many other reducible oxides which are not used, but would seem to have similar properties to that of ceria. For example, praseodymium is next to cerium in the Periodic Table and also has multiple stable oxidation states, yet praseodymia does not appear to be an effective replacement for ceria as an oxygen-storage component. One major reason for this has to do with the drastic difference in the reactivities of ceria and praseodymia with alumina. Praseodymia, due to its relatively low stability, reacts with alumina at temperatures above 600 °C in air and forms inert aluminates, whereas ceria remains stable to at least 1100 °C. The advent of zirconia stabilization, however, raises the possibility that this particular problem for praseodymia may be avoided, and thermally stable, high-surface-area praseodymia–zirconia and ceria–praseodymia–zirconia materials are under evaluation. Here, some other fundamental questions regarding the relative suitability of praseodymia and ceria for oxygen storage are considered, with the hope that new insight into the reasons for ceria deactivation may also be gained.

In our past studies of the properties of ceria, we have developed relatively simple methods to characterize oxygen-storage properties. First, in TPD studies of the reaction CO on catalytic metals (e.g., Pt, Pd, or Rh) deposited onto ceria films, a substantial fraction of the adsorbed CO reacts to CO_2 on active forms of ceria, while negligible amounts of CO_2 are formed when the ceria had been deactivated by high-temperature calcination [3]. Second, in TPD studies of O_2 from ceria films, we observed a low-temperature desorption state, between 800 and 1100 K, which was not observed for a CeO_2(111) single crystal [15]. The oxygen from this state corresponds to that which reacts with CO adsorbed on supported Rh particles. Third, we observed a ceria-mediated process for steady-state CO oxidation in excess CO over ceria-supported metals [12]. This reaction involves oxidation of CO adsorbed on the metal by oxygen supplied from the ceria, and its rate is zeroth order in CO. This process is not observed for ceria-supported metals if the ceria has been deactivated prior to the addition of the metal [3].

In a previous study of praseodymia-supported Pd [13], no evidence was found for a zeroth-order CO oxidation

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mechanism under reducing conditions. This suggests that oxygen from praseodymia is not utilized under reaction conditions in the same way as that from ceria. In this study, we examined the adsorption–desorption characteristics for O_2 from praseodymia films in order to determine why this is the case. We also examined the ability of praseodymia to provide oxygen to the surface of catalytic metals for reaction with CO. Based on our findings, we conclude that praseodymia appears to exhibit some of the desirable properties required by an oxygen-storage component, although the rate of reoxidation of reduced praseodymia, probably in the form of Pr_2O_3, may be too slow for its effective use in its pure form.

2. Experimental techniques

The experimental setup used in this study has been described previously [14]. It consisted of an ion-pumped vacuum chamber with a cylindrical-mirror analyzer for Auger electron spectroscopy (AES) and a quadrupole mass spectrometer for temperature-programmed desorption (TPD). To improve sensitivity for the detection of desorbing species during TPD experiments, the quadrupole mass analyzer was mounted in a stainless-steel cone with a small aperture, in front of which the sample could be placed. Samples were exposed to the adsorbates using directed beam dosers in order to maintain a low base pressure. The pressure in front of the dosers has been estimated to be approximately 20 times higher than the background chamber pressure during dosing, and quoted exposures were calculated using this factor. TPD measurements were carried out with a linear heating rate of 12 K/s.

The substrate consisted of a circular disk of α-Al_2O_3 (0001), 3 mm in diameter, mounted on a Ta foil that could be resistively heated to 1400 K. The temperature was monitored using a thermocouple attached to the back surface of the crystal using ceramic adhesive (Aremco 516). After cleaning the α-Al_2O_3(0001) substrate by Ar^+ ion bombardment and subsequent oxidation and annealing, a praseodymia film was vapor deposited onto its surface. The film was prepared by evaporating Pr metal (Johnson Matthey, 99.9%) onto the crystal, held at 570 K, in the presence of 10^{-7} Torr of O_2. The flux from the Pr source was determined using a quartz-crystal, film-thickness monitor, allowing the film thickness to be determined within approximately 10%. Following deposition, the sample was further oxidized in 10^{-7} Torr of O_2 for 15 min at 570 K. In those experiments requiring the presence of a catalytic metal, Rh was subsequently vapor deposited onto the substrate at 300 K. Following Rh deposition, the sample was heated to 600 K to promote Rh particle formation.

3. Results

The initial experiments examined O_2 desorption from praseodymia films. TPD curves obtained following deposition of 1×10^{15} and 1×10^{16} PrO_x/cm^2 onto the α-Al_2O_3(0001) substrate are shown in figure 1. These coverages correspond to average film thicknesses of approximately 0.4 and 4.0 nm, respectively, assuming the film density is the same as that for bulk Pr_6O_{11}. For both coverages of praseodymia, O_2 desorption is observed between 700 and 1100 K. Using a calibration factor determined in previous work with Rh films [15], the amount of O_2 which desorbed from each praseodymia film corresponded well to that which would be expected for reduction of Pr_6O_{11} to Pr_2O_3. Consistent with this, we observe about 10 times more O_2 from the thicker film, which also implies that the praseodymia in contact with the sapphire crystal is similar to the bulk film.

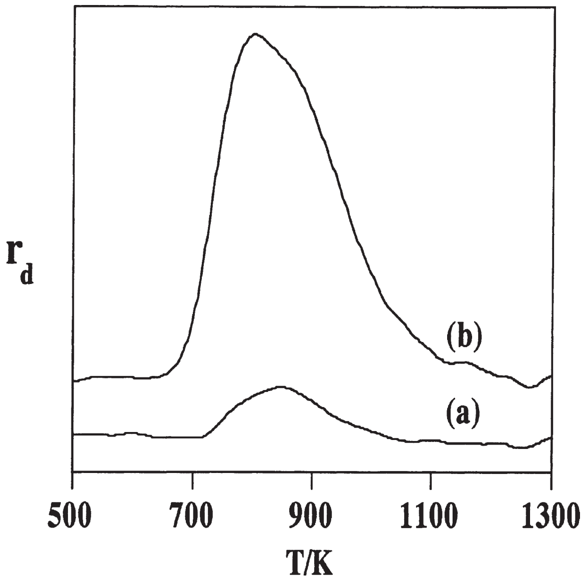


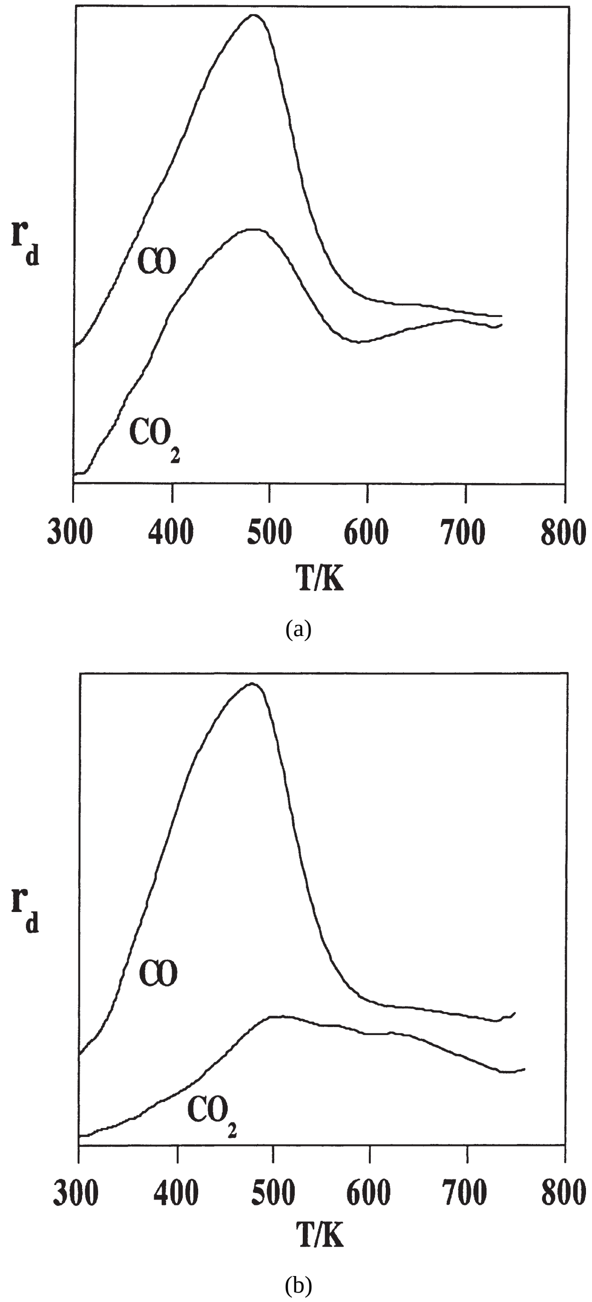
Figure 1. TPD curves for O_2 from praseodymia films having (a) 1×10^{15} and (b) 1×10^{16} PrO_x/cm^2.

The results for O_2 desorption from the praseodymia films on α-Al_2O_3(0001) exhibit some similarities to those observed for ceria films. One similarity is that O_2 desorption from both films occurs over the same temperature range. From the peak desorption temperature of 800 K, assuming second-order kinetics and a pre-exponential factor of 0.01 cm^2/s, the activation energy for desorption is calculated to be 60 kcal/mol. This is a reasonable value for praseodymia, given that the ΔH for the reaction $4PrO_2 \rightarrow 2Pr_2O_3 + O_2$ is 45 kcal/mol at this temperature, especially since adsorption is activated. In the case of ceria, ΔH for the reaction $4CeO_2 \rightarrow 2Ce_2O_3 + O_2$ is 178 kcal/mol, so that the correspondence between the enthalpy change and the desorption activation energy is less obvious.

In order to provide an independent measure of the oxidation state of Pr in the films, two 0.1 μm thick praseodymia films were prepared. Following film deposition, one sample was heated to 700 K and the other to 1100 K in vacuum. They were then carried in air to an X-ray diffractometer. For the sample heated to only 700 K, the primary oxide phase in the film was cubic Pr_6O_{11}. The peaks which could be associated with hexagonal Pr_2O_3 were very small. For the sample heated to 1100 K, the major peaks were those associated with Pr_2O_3. Because we observed oxidation of the Pr_2O_3 with time in the X-ray beam and because some reoxidation may have occurred upon exposure to air, we did not attempt to quantify these results. However, they do confirm that the deposited films are Pr_6O_{11} and are completely reduced to Pr_2O_3 by heating.

Our previous work with ceria films on α-Al_2O_3(0001) also exhibits two major differences from that obtained in the present study of praseodymia. First, the amount of oxygen that desorbed from ceria films at temperatures below 1100 K was only 20% of that from praseodymia films of the same thickness. While ceria films on zirconia could be completely reduced and gave a similar amount of oxygen as with praseodymia on alumina [16], only a fraction of the ceria on α-Al_2O_3(0001) could be reduced by simply heating. This appears to be due to structure sensitivity in the reducibility of ceria [3,4]. Second, with praseodymia, the oxygen desorption feature could not be restored by exposure to O_2 in the vacuum chamber. Even with heating to 570 K, the rate of adsorption was apparently too slow to measure using the exposures possible in our system. By contrast, adsorption on ceria was completely reversible and we were able to use this fact to study isotope exchange in ceria films [16].

We next examined whether the oxygen from the praseodymia film could be utilized by supported metals to oxidize adsorbed CO. First, a film with 1×10^{16} PrO_x/cm^2 was deposited onto the α-Al_2O_3 crystal as before. After heating the sample to 700 K in vacuum, a temperature below the onset of oxygen desorption, 1×10^{15} Rh/cm^2 was deposited. The TPD results obtained for this sample following the first saturation exposure to CO at room temperature are shown in figure 2(a). The TPD curves show desorption of significant amounts of both CO and CO_2, from room temperature to 600 K. There is also additional desorption of CO_2 above 600 K, since the baseline does not return to its original value. This high-temperature CO_2 may imply carbonate formation at lower temperatures, with decomposition above 600 K. This is similar to what has been observed in studies with lanthana [17]. It should be noted that CO does not adsorb on PrO_x in the absence of a precious metal and that CO_2 was not formed in TPD studies of CO-dosed Rh/α-Al_2O_3 in the absence of PrO_x. Therefore, the results in figure 2 demonstrate that CO adsorbed on Rh can react with lattice oxygen from PrO_x, similar to what has been observed with ceria [18]. In subsequent CO TPD measurements, additional amounts of CO_2 were formed, as shown in figure 2(b), the second TPD curve from this same sample. The ratio of CO to CO_2 increased with each TPD cycle until essentially no CO_2 was observed.

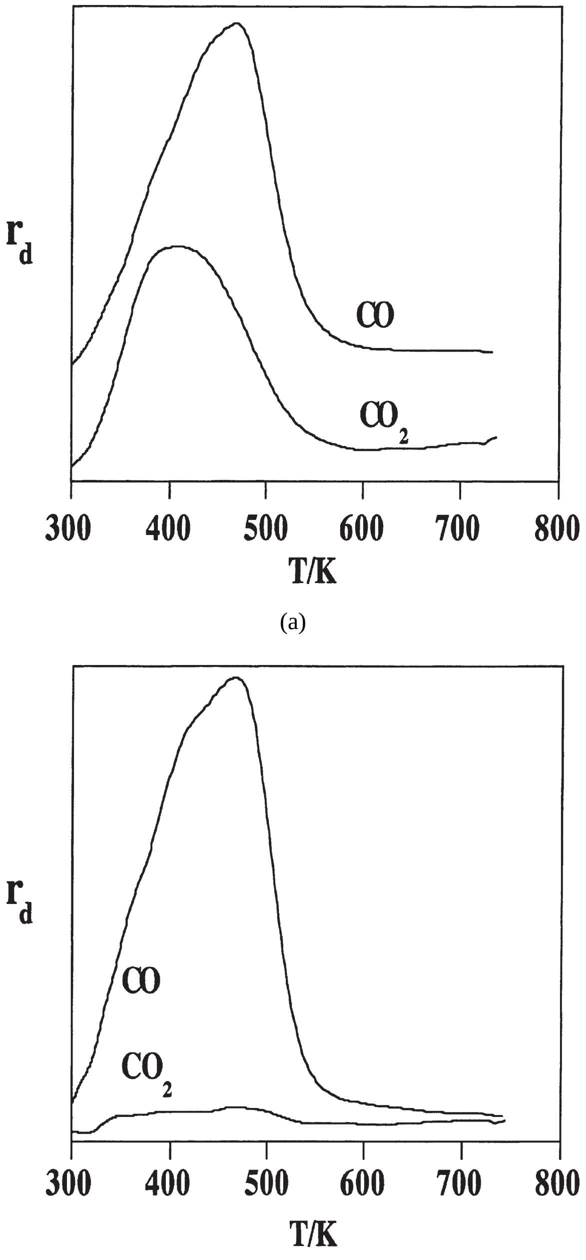


(a)

(b)

Figure 2. TPD results following CO adsorption onto 1×10^{15} Rh/cm^2, which had been deposited onto a film with 1×10^{16} PrO_x/cm^2. The praseodymia film had been heated to only 700 K prior to addition of Rh. The first TPD is shown in (a) and the second in (b).

A similar set of TPD experiments was carried out using a sample in which the PrO_x film was reduced prior to the deposition of Rh by heating to 1100 K in vacuum. The desorption results for CO and CO_2 in the first and second cycles are shown in figure 3. The first set of TPD curves from this sample is shown in figure 3(a). Based on peak areas, approximately one-third of the CO again reacts to CO_2 during the temperature ramp, with the main difference from the non-reduced sample being that there is no desorption of CO_2 above 550 K. The second CO TPD experiment for the reduced sample, shown in figure 3(b), gave very little reaction to CO_2, in agreement with the expectation that most of the oxygen from the PrO_x film was removed by heating to 1100 K. The reaction observed in the first TPD run suggests that the film is not completely reduced by simply flashing to 1100 K.



(a)

(b)

Figure 3. TPD results following CO adsorption onto 1×10^{15} Rh/cm^2, which had been deposited onto a film with 1×10^{16} PrO$_x$/cm^2. The praseodymia film had been heated to 1100 K prior to addition of Rh. The first TPD is shown in (a) and the second in (b).

Because the temperature at which CO_2 is formed in figures 2 and 3 is similar to what one would observe for coadsorption of CO and oxygen on Rh, it is possible to conclude from these results that Rh is oxidized by the PrO$_x$ film. To determine whether transfer of oxygen from PrO$_x$ to Rh is possible, a sample in which 1×10^{15} Rh/cm^2 was deposited onto a fresh 4 nm thick PrO$_x$ film. An O_2 TPD measurement was then performed, as shown in figure 4. While a small amount of O_2 desorbs between 700 and 900 K, the majority of the oxygen now desorbs above 1000 K, and the shape of the TPD curve is similar to what is observed for desorption from Rh particles [15]. The total amount of O_2 leaving the sample used in the experiment in figure 4 is about half that of the sample used in the experiment in figure 1, suggesting that the praseodymia film may have been partially reduced by the addition of Rh or by heating the film to 700 K prior to the addition of the Rh. The overall conclusion is that oxidation of Rh occurred simultaneously with the reduction of Pr_6O_{11}, thus providing a mechanism for the formation of CO_2 in the results shown in figures 2 and 3.

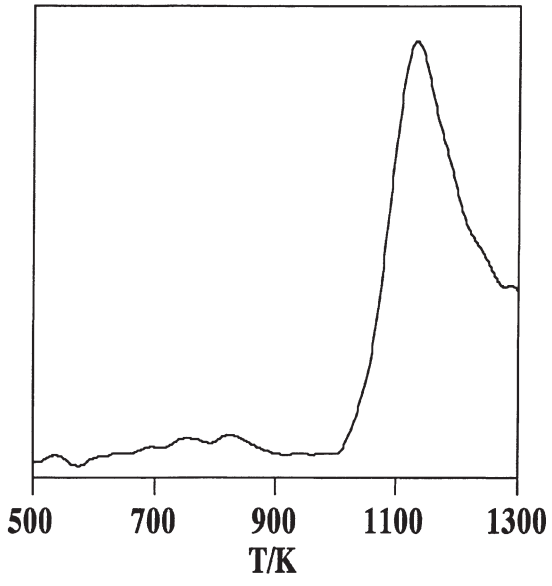


Figure 4. TPD results for O_2 following deposition of 1×10^{15} Rh/cm^2 onto a film with 1×10^{16} PrO$_x$/cm^2. The praseodymia film had been heated to only 700 K prior to the addition of Rh.

4. Discussion

Although the actual evaluation of praseodymia for oxygen storage still needs to be performed under realistic, redox conditions, praseodymia will probably not provide a direct replacement for ceria in three-way, automotive catalysts. In previous work, the oxidation of CO over Pd/praseodymia catalysts [13] did not exhibit the enhanced rates or any evidence for an oxide-mediated process, similar to what is found with Pd/ceria or Pd/ceria–zirconia. Based on the results in the present study, a possible difficulty with praseodymia may be that reoxidation of the pure oxide may be too slow to provide the necessary oxygen-storage properties under steady-state, warmed-up conditions when the air-to-fuel ratio switches from rich to lean. However, although we were unable to reoxidize reduced praseodymia films in our present study, previous workers have found that 50 Torr of O_2 at 575 K can easily re-oxide praseodymia which has been heated in vacuum at temperatures between 875 and 1025 K [19,20]. In this case, the reduced praseodymia is more likely to be $PrO_{1.7}$ rather than Pr_2O_3, so that it is not clear whether the difference in starting material or the difference in O_2 pressure is the more important factor affecting reoxidation. It may be that the structural changes required for oxidation from the hexagonal Pr_2O_3 to the cubic Pr_6O_{11} form makes this oxidation a highly activated process after complete reduction. In any case, formation of mixed oxides of praseodymia, similar to that of zirconia with ceria, could well result in the necessary modifications for practical utilization of this material.

More interesting is the question why partially reduced ceria is relatively easy to reoxidize, even though it undergoes structural changes upon oxidation and reduction similar to those of praseodymia. The answer may provide important insights into why ceria reducibility is structure sensitive and why zirconia stabilizes ceria reducibility. One possible explanation is that the structural changes, from cubic to hexagonal, do not occur upon reduction of the active form of ceria. Incomplete reduction of ceria to CeO_{2-x}, having the cubic form, is known and it seems likely that reduction to the hexagonal form does not occur under reaction conditions. Several observations are consistent with this scenario.

First, ΔH for the reaction $4CeO_2 \rightarrow 2Ce_2O_3 + O_2$ is 178 kcal/mol, which is simply too large for one to expect O_2 desorption to occur between 800 and 1000 K, as is observed [15]. As discussed above, 60 kcal/mol is a more reasonable estimate for the binding energy for oxygen based on our TPD peak temperatures. This energy difference between the activation energy and ΔH may well be that required for the structural change to the hexagonal form. Possibly, praseodymia does not form the same types of intermediate structures as does ceria.

Second, the structure sensitivity of ceria [3,4] and the promotional effects of zirconia [16], which maintains the oxygen-storage properties of ceria after high-temperature calcination, strongly argue for the importance of structure in the reduction process. Calculations have shown that ultra-small ceria particles do not have crystallographic structures identical to that of bulk ceria [21]. This may be especially true for the surface of small particles [15]. In the case of ceria–zirconia, the most recent evidence suggests that solid solutions are not the active species and that zirconia promotion is likely the result of structure-directing properties for zirconia on ceria [22]. For example, one possibility is that zirconia maintains ceria in its cubic form, therefore avoiding the energy change associated with formation of hexagonal Ce_2O_3.

Although praseodymia (or stabilized, praseodymia-based mixed oxides) may indeed prove to be unsuitable as a direct replacement for ceria-based, oxygen-storage materials, its ability to release large amounts of O_2 at relatively low temperature could make it useful in formulating rapid light-off catalysts for lowering cold-start emissions. In any case, based on the correspondence between the activation energy for O_2 desorption and ΔH for the reaction, praseodymia would not be expected to undergo the sort of deactivation observed for ceria after high-temperature calcination. Work is currently under way to evaluate the potential application of praseodymia.

5. Summary

Comparison of the properties of praseodymia and ceria films for O_2 desorption and for oxidation of CO over metals supported on these two oxides demonstrate that praseodymia may be suitable as an oxygen-storage component in three-way, emissions-control catalysts under certain conditions. The O_2 desorption temperatures for Pr_6O_{11} are similar to that for the catalytically active form of ceria, and the oxide is capable of transferring its oxygen to supported metals; however, adsorption of O_2 onto Pr_2O_3 is relatively slow, probably due to the structural changes required for reoxidation.

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