Reaction of CO with O Adatoms on Rutile TiO_2(110) Surfaces

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Abstract

After exposing a reduced TiO_2(110) surface to an O_2 gas, the defect state seen in the band gap for the reduced surface disappeared, while O adatoms (O_{ad}) appeared on the 5-fold Ti rows. We then dosed a CO gas onto the TiO_2(110) surface oxidized by $^{18}O_2$ exposure and measured the defect state intensity and the amount of ^{18}O by photoemission and ion scattering analyses, respectively. With increasing CO dose, the defect state intensity increases, whereas the amount of ^{18}O decreases. The results obtained clearly show the reaction of CO with O_{ad} probably to form CO_2.

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Rutile Titania (TiO_2) with the most stable (110) face ($TiO_2(110)$) has been used as a model support to investigate the chemical activities of metal clusters. It is also known that the rutile titania itself works as a catalyst. In this case, O deficiency and excess on the surface play a key role in the catalytic activities. Up to now, scanning tunneling microscopy (STM) observations have provided much information about local structures of the surfaces before and after chemical reactions including adsorption and desorption of O_2, CO, H_2O and so on[1,2]. Despite that, STM sometimes meets difficulties in identifying the species appearing on the surfaces after reactions and also in probing depth profiles. In this regard, high-resolution medium energy ion scattering (MEIS) combined with photoemission spectroscopy (PES) can be utilized complementarily to analyze the structures of surfaces before and after chemical reactions.

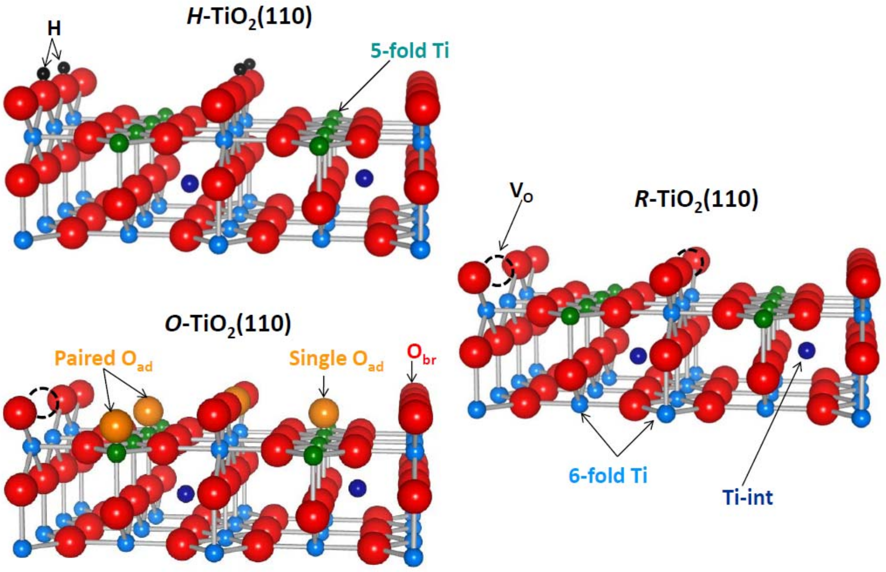


FIG. 1. Ball and stick model of *R*- and *O*-$TiO_2(110)$surfaces.

In this study, we manifest the CO oxidation kinetics quantitatively dependent on the surface structure of $TiO_2(110)$ by high-resolution MEIS coupled with PES using synchrotron-radiation (SR) light. Our concern resides in the reactivity of $TiO_2(110)$ surfaces in CO oxidation correlated with O excess on the surface. We prepared three types of clean (1×1) $TiO_2(110)$ surfaces, (i) reduced (*R*-), (ii) O-rich (*O*-), and (iii) hydroxylated (*H*-)-$TiO_2(110)$. The above three surfaces are indicated by a ball and stick model in Fig. 1. All the surfaces probably contain Ti interstitials segregated toward the surfaces to some extent. STM observations showed that exposing the *R*-$TiO_2(110)$ with bridging O (O_{br}) vacancies (V_O) to an O_2 gas led to formation of the *O*-TiO_2(110) surface which has unfilled V_O and O adatoms (O_{ad}) on the 5-fold Ti rows[2-5] and H_2O dosing onto the *R*-TiO_2(110) resulted in the *H*-TiO_2(110) with paired $O_{br}H$[6,7]. We are also interested in the finding by Haruta[8] that Au clusters become strongly active for oxidation of CO even at low temperatures, if the size ranges below 5 nm. In this respect, the role of Au nano-clusters on TiO_2(110) is investigated upon strong promotion of the rate of CO oxidation.

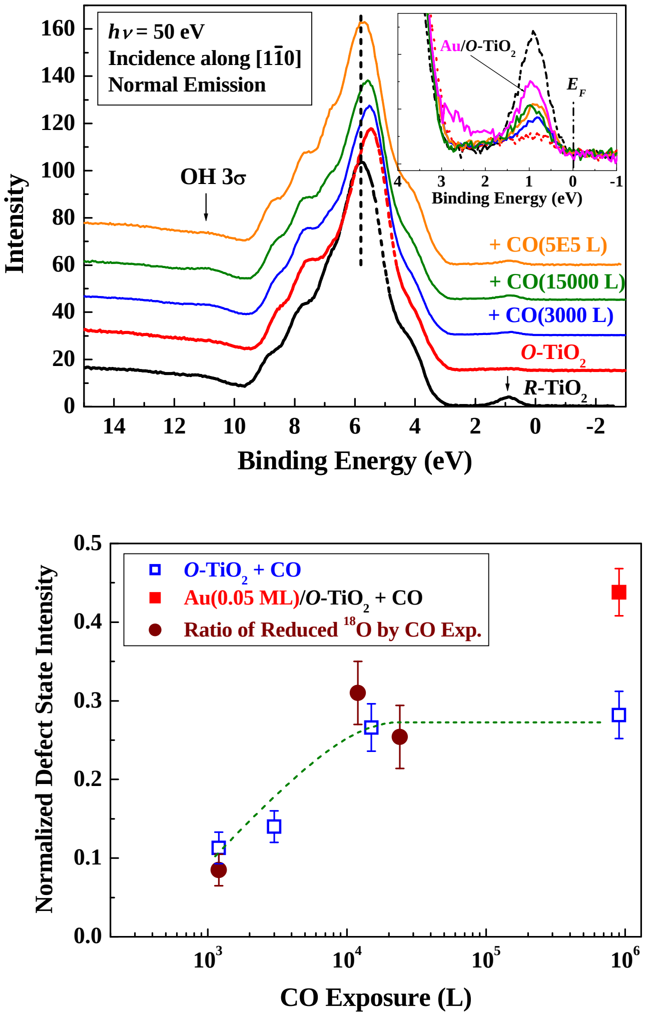


FIG. 2. (a) UPS spectra observed for *R*- and *O*- TiO_2(110) and *O*-TiO_2(110) exposed to CO. The spectra were taken at photon energy of 50 eV at the $[1\bar{1}0]$-azimuth. Inset indicates magnified spectra from Ti 3d defect state. (b) Defect state intensities (open squares) for *O*-TiO_2(110) after CO exposure normalized by that for *R*-TiO_2(110) as a function of CO dose. The normalized defect state intensity for Au(0.05 ML)/*O*-TiO_2(110) after CO exposure of 9×10^5 L is denoted by full square. Full circles indicate reduction rate of ^{18}O after CO exposure.

As-supplied $TiO_2(110)$ surfaces were annealed at 1070 K for 60 min in UHV after several cycles of sputtering by 0.75 keV Ar^+ and annealing at 870 K for 10 min in UHV. As a result, the specimens changed the color from transparency to blue due to creation of O-vacancies in the bulk acting as an F-center and simultaneously became conductive (n-type semiconductor) caused by Ti-interstitials (Ti-int) as an electron donor. The clean (1×1) surfaces without Ti-rich oxide clusters on the surfaces were checked by reflection high-energy electron diffraction (RHEED) combined with medium energy ion scattering (MEIS) analysis using 80 keV He^+ ions. Indeed, if such Ti-rich clusters exist on the surface, the MEIS spectra from Ti and O have the surface peaks with low energy tails compared with the simulated spectrum assuming a stoichioemtric surface. The R-$TiO_2(110)$ surface was prepared by annealing at 870 K in UHV for 10 min and the O-$TiO_2(110)$ was obtained by exposing the reduced surface to O_2 at RT (1000 – 2000 L, 1 L = 10^{-6} Torr s). STM observations[4,5] showed that there are two O adsorption channels; (i) an O_2 molecule dissociates at a V_O site, with one O atom healing the vacancy and another O atom bonding at the neighboring Ti site as a single adatom and (ii) direct adsorption of O_2 on the 5-fold Ti rows to form paired O_{ad}. The adsorption of O_2 on R-$TiO_2(110)$ at RT is saturated at O_2 exposure above 200 L[4]. We also prepared the hydroxylated surface, H-$TiO_2(110)$ by dosing H_2O onto the R-$TiO_2(110)$ surface at 330 K (5 - 10 L). The amount of H was measured by elastic recoil detection (ERD) using 147 keV Ne^+ ions[9], corresponding to twice that of V_O, which ranged from 0.10 to 0.14 ML (1 ML = 5.2×10^{14} atoms/cm^2) under the present preparation condition. The density of adsorbed O on the R-$TiO_2(110)$ is 20 – 30 % as large as that of V_O and about half of V_O vacancies are unfilled. It is difficult to obtain a stoichiometric surface and also to confirm that because the amounts of O_{ad} atoms and Ti interstitials cannot be detected directly. In spite of that, we tried to grow a nearly stoichiometric (S*-) surface by annealing at 820 K for 5 min in O_2 ambience (1×10^{-6} Torr), which showed a clear 1×1 RHEED pattern and no significant defect state intensity. The S*-$TiO_2(110)$ surface has probably smaller amounts of V_O and O_{ad} compared with the O-$TiO_2(110)$ surface. Actually, the amount of V_O was small less than ~0.02 ML estimated from ERD by exposing the sample to H_2O but the latter cannot be detected by our instrumentation. We employed high purity gases of $^{16}O_2$ (99.999 %), CO (99.999 %) and $^{18}O_2$ ($^{18}O/^{16}O$ = 95/5) and monitored the partial pressures in the sample preparation chamber by a quadrupole mass filter (QMAS). During O_2 and CO exposure the partial pressure of

H_2O was four orders of magnitude lower than that of O_2 and CO. All the experiments were performed *in situ* under UHV conditions (~2×10^{-10} Torr)[10,11].

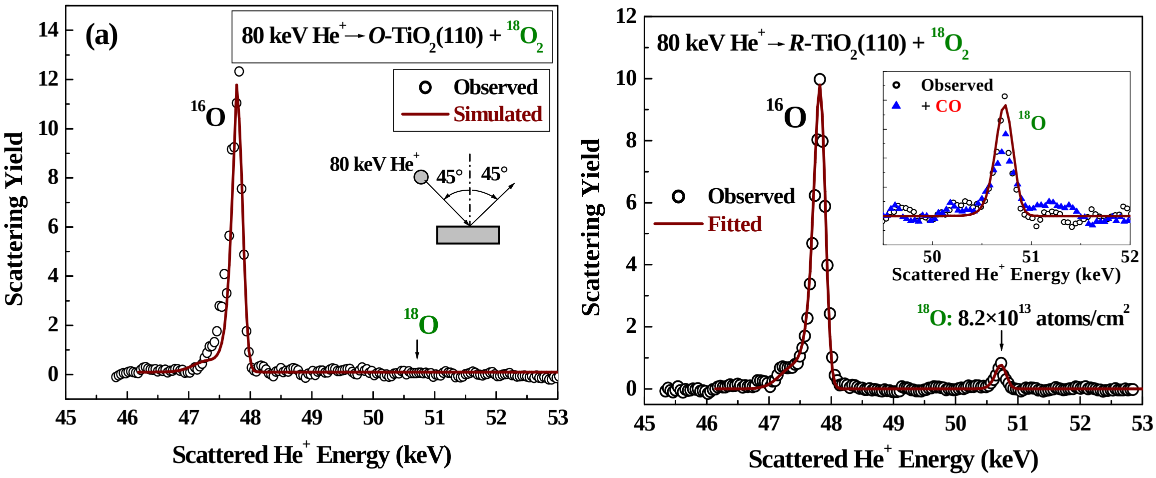
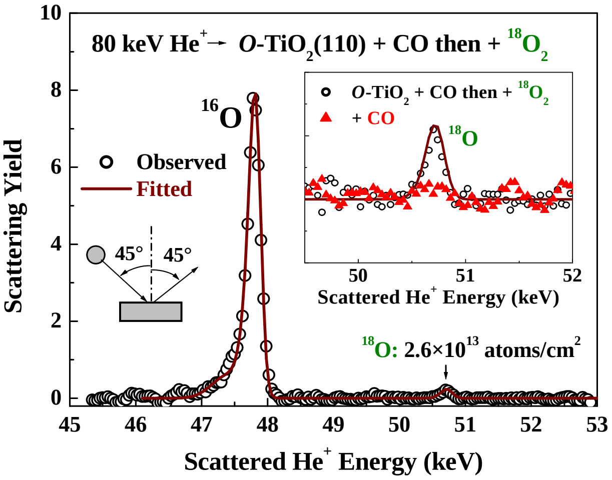


FIG. 3. (a) MEIS spectrum (open circles) measured for 80 keV He^+ ions incident along the [100]-axis and backscattered from ^{16}O and ^{18}O to the [010] direction of *O*-TiO_2(110) exposed to $^{18}O_2$ (1000 L). (b) MEIS spectrum (open circles) observed for *R*-TiO_2(110) exposed to $^{18}O_2$ (2000 L). The solid curve is fitted one to guide the eyes. Inset indicates the magnified spectrum around the scattering component from ^{18}O. After CO exposure of 12000 L, the ^{18}O intensity is reduced, as shown in the inset (full triangles).



(c) MEIS spectrum (open circles) observed for *O*-TiO_2(110) after CO exposure (12000 L) and then $^{18}O_2$ dose (2000 L). The ^{18}O signal completely disappears after the same CO exposure (12000 L), as shown in the inset (full triangles).

We observed the UPS spectra for *R*- and *O*-TiO_2(110) and *O*-TiO_2(110) exposed to CO at RT, as shown in Fig. 2(a). The small peaks seen ~0.8 and ~11 eV below the Fermi level (E_F) originate from the Ti 3d defect state and from OH 3σ[4] (hybridization of H 1s and O $2p_z$ orbitals), respectively. It is widely accepted that the above gap state comes from the Ti^{3+} state which corresponds to a Ti^{4+} core binding one *3d* electron[12-14] but the primary source of the gap state is still a debatable issue[4,15]. The inset is the magnified spectra of the defect state. The defect state signal almost disappears by exposing the *R*-$TiO_2(110)$ to $O_2(1200$ L), indicating that the initially introduced subsurface excess charge is withdrawn by filling partly the V_O vacancies and to create O_{ad} atoms[4,5]. Obviously, with increasing the CO dose the defect state intensity increases and reaches saturation at 15,000 L. The saturated intensity is about 1/3 that for the *R*-$TiO_2(110)$. This means that about 1/3 of the initially introduced subsurface excess charge is regained by exposing the *O*-$TiO_2(110)$ to a CO gas. The defect state intensity normalized by that for *R*-$TiO_2(110)$ is shown in Fig. 2(b), as a function of CO exposure. Interestingly, the defect state intensity is strongly enhanced for Au(0.05 ML) deposited *O*-$TiO_2(110)$ surface. Here, 1 ML means 1.39×10^{15} atoms/cm^2, corresponding to the areal density of Au(111). In this case, the deposited Au occupies a surface area of ~7 % and takes a form of 2D islands with average diameter of ~2.0 nm and two-atomic layer height, which was determined by high-resolution MEIS[16]. It is also seen that the O 2p peak as well as valence band edge shift to higher binding energies with increasing CO exposure compared with the *O*-$TiO_2(110)$ surface. In contrast, we observed no significant change in the UPS spectra for *S**-$TiO_2(110)$ and Au(0.05 ML)/*S**-$TiO_2(110)$ before and after CO exposure (not shown here).

Next we measured by MEIS the absolute amounts of ^{18}O for the ^{16}*O*-$TiO_2(110)$ exposed to CO and then dosed with an $^{18}O_2$ gas and also for the ^{18}*O*-$TiO_2(110)$ before and after CO exposure. The detail of how to estimate the amount of ^{18}O in MEIS spectra was described elsewhere[17]. Figure 3 (a) shows the MEIS spectrum observed for 80 keV He^+ ions incident along the [100]-axis and scattered to the [010]-direction from O atoms of the *O*-$TiO_2(110)$ after $^{18}O_2$ exposure (1000 L). Obviously there is no scattering signal from ^{18}O. Here, the solid curve is drawn to guide the eyes. Then we observed the MEIS spectrum for the *R*-$TiO_2(110)$ exposed to $^{18}O_2$ ($\rightarrow$ ^{18}*O*-$TiO_2(110)$), which is shown in Fig. 3(b). The amount of ^{18}O was determined to be $8.6\pm0.3\times10^{13}$ atoms/cm^2 after correction of the isotopic ratio of $^{18}O/^{16}O = 95/5$, corresponding to 0.16 ML. Note that the amount of adsorbed O is significantly larger than that of V_O[4,5]. Then dosing the surface to CO (12000 L) led to reduction of the ^{18}O from the above value to $5.9\pm0.3\times10^{13}$ atoms/cm^2. The reduction ratio $(8.6-5.9)/8.6 = 0.31$ coincides with the normalized defect state intensity, as shown in Fig. 2(b). This correlation clearly indicates that the excess charge created by CO exposure allows for O adsorption.

According to STM observations[18], CO molecules are dominantly adsorbed on the 5-fold Ti and diffuse along the Ti rows at a low temperature. However, the adsorption of CO on the 5-fold Ti does not produce an electronic excess charge. The most probable candidate giving the excess charge is a reaction of CO with electronegative atomic species such as O_{br} and O_{ad} resulting in formation of neutral CO_2 molecules, which escape from the surface. Note that the 2-fold O_{br} and O_{ad} atoms are relatively weakly bonded to underlying Ti atoms and thus they work as active sites on the surface.

In order to clarify which O atoms reacts with CO, we first measured the amounts of ^{18}O for the ^{16}O-TiO_2(110) which was exposed to CO and then dosed with $^{18}O_2$ (2000 L) and after that we exposed again the surface to CO. Figure 3 (c) shows the scattering components from ^{16}O and ^{18}O in the MEIS spectrum observed for the ^{16}O-TiO_2(110) surface which was exposed to CO(12000 L) and then dosed with $^{18}O_2$ (1000 L). The amount of ^{18}O was estimated to be $2.7\pm0.3\times10^{13}$ atoms/cm^2 (0.052 ML). After the same CO exposure again, the ^{18}O signal almost disappeared in the MEIS spectrum, as shown in the inset of Fig. 3(c). This fact clearly shows that the O_{ad} atoms react with CO molecules, because if the O_{br} atoms react with CO to create V_O, the reduction of ^{18}O after the same CO exposure should be much smaller than the initial amount of ^{18}O, because the amount of observed ^{18}O is about 0.05 ML corresponding to 5 % of O_{br}. It must be noted that the reaction is completed after CO exposure of ~10000 L, as mentioned before (see Fig. 2(b)). The amount of the ^{18}O observed for the ^{16}O-TiO_2(110) which was exposed to CO and then dosed with $^{18}O_2$ is compatible with the reduction of ^{18}O measured for the *R*-TiO_2(110) which was oxidized by $^{18}O_2$ at RT and then exposed to CO. Here, if we assume a simple model that a CO molecule crosses over an activation barrier of E_a to migrate on the surface and finally reacts with an O_{ad}, the E_a value is estimated to be 0.30±0.02 eV, which is compatible with the CO adsorption energy (0.38 eV) and diffusion barrier (0.32-0.35 eV)[18]. As expected from the UPS analysis for Au(0.05 ML)/*O*-TiO_2(110) exposed to CO, it was found that the amount of ^{18}O for the above surface exposed to CO and then dosed with $^{18}O_2$ is almost twice that for the *O*-TiO_2(110). In addition, quite consistent with the UPS result for the *S**-TiO_2(110) and Au(0.05 ML)/*S**-TiO_2(110), we found no significant ^{18}O signal in the MEIS spectra observed for the above surfaces after exposure of CO and then $^{18}O_2$ dose. Further detailed discussion about the strong enhancement of CO oxidation on Au/*O*-TiO_2(110) is out of the scope of this paper.

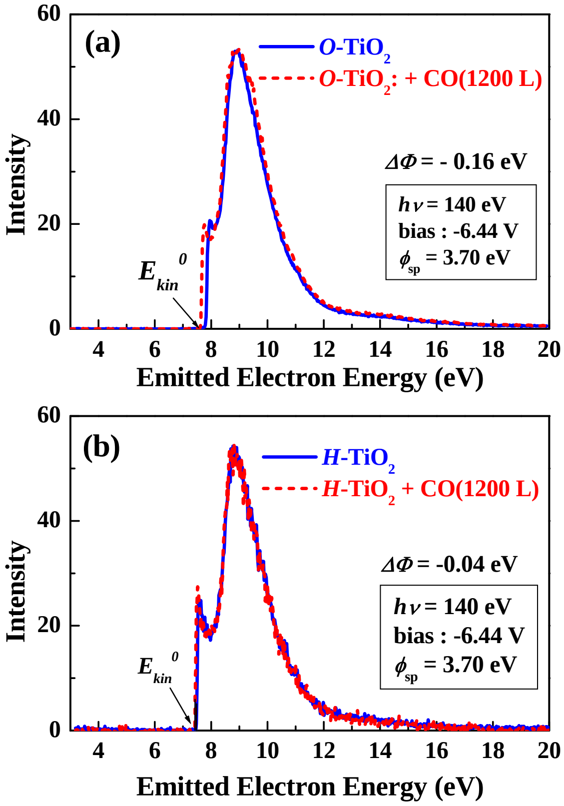


FIG. 4. Secondary electron emission spectra observed at photon energy of 140 eV for *O*-TiO$_2$(110) before and after CO exposure (1200 L) (top) and for *H*-TiO$_2$(110) surface before and after CO exposure (1200 L) (bottom), where samples were negatively biased (–6.44 V).

As another evidence for the reaction of CO molecules with O$_{ad}$ atoms, we measured the work functions for the *O*-TiO$_2$(110) and *H*-TiO$_2$(110) surfaces before and after CO exposure. The latter *H*-TiO$_2$(110) surface has no V$_O$ vacancies and O$_{ad}$ atoms (see Fig.1). Figure 4 shows the secondary electrons emission spectra measured for the *O*-TiO$_2$(110) (top) and *H*-TiO$_2$(110) (bottom) surfaces before and after CO exposure. Here, the samples were negatively biased at −6.44 eV. From the energy position E^0_{kin} where the secondary electrons yield abruptly rises, the work function Φ is deduced to be $E^0_{kin} + \Phi_{SP} - 6.44$ [eV], where Φ_{SP} is the work function of the spectrometer (3.70 eV). It is clearly seen that the work function for the *O*-TiO$_2$(110) was reduced by 0.16±0.04 eV after CO exposure (1200 L), while only a slight reduction (0.04±0.04 eV) was observed for the *H*-TiO$_2$(110). The reduction of the work function is well correlated with the higher binding energy shifts of O 2p line and valence band edge for the *O*-TiO$_2$(110) after CO exposure (see Fig. 2(a)). This is ascribed to elimination of the electronegative adsorbate O_{ad} on top of the surface resulting in lowering the surface dipole with a negative polarity on the vacuum side, which gives an upward band bending.

In summary, we have revealed unambiguously the fact that the O_{ad} atoms on the 5-fold Ti rows react with CO molecules probably to form CO_2 on the *O*-TiO_2(110) surfaces by means of high-resolution MEIS combined with UPS analysis including work function measurement. Indeed, Du et al.[19] showed the higher reactivity of O_{ad} than O_{br} in H_2O dissociation and proton transfer processes. With increasing the CO dose onto the *O*-TiO_2(110) surface, the defect state intensity increases and reaches a saturated value of ~1/3 that for the *R*-TiO_2(110). This indicates that ~1/3 of the initially introduced subsurface excess charge by annealing in UHV which makes the gap state is left on the surface by eliminating O_{ad} atoms (electronegative adsobate) via CO oxidation. In addition, presence of Au nano-clusters on *O*-TiO_2(110) strongly enhances the reaction between O_{ad} and CO. This may be due to an electronic charge transfer from Au to the *O*-TiO_2(110) support, as predicted by Wang and Hammer[20].

Acknowledgements

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