Gold-Decorated Biphase α -Fe₂O₃(0001): Activation by CO-Induced Surface Reduction

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ABSTRACT: CO adsorption and oxidation on Au-covered "Opoor" biphase α -Fe₂O₃(0001) have been studied with HREELS and TDS. We found that the amount of CO that the surface can bind at room temperature increases with the CO dose, indicating that the CO–surface interaction produces new adsorption sites. Surface reduction via carbon dioxide formation was identified as the mechanism responsible for this. Reduction does probably already occur during dosing since the CO molecules detected at the surface after dosing just occupy the produced sites but are not oxidized toward CO₂. CO oxidation does not occur without the gold clusters at the surface under the given experimental conditions. According to a theoretical study by Hoh et al. [*Res. Chem. Intermed* **2015**, *41*, 9587] gold clusters weaken the bond



of oxygen at the oxide surface, which might facilitate the consumption of these atoms for CO oxidation. Spectroscopic data provide evidence that the reduction induces electron charge accumulation in the oxide near the Fermi level. The reduced surface is active for CO oxidation in a Mars-van Krevelen-type mechanism at room temperature: oxygen bound to the sample surface reacts with subsequently dosed CO toward CO_2 .

INTRODUCTION

Gold had not received much attention in catalytic studies until in the 1980s researchers reported a series of Au-catalyzed reactions, such as the hydrogenation of alkenes,^{1,2} CO oxidation,^{3,4} and hydrochlorination of ethyne,⁵ etc.⁶ The catalytic activity of nanosized Au particles supported on a metal oxide substrate has been attributed to quantum size effects,⁶⁻¹¹ low coordination numbers of nanoparticle atoms,^{12,13} and metal-support interactions.¹⁴⁻¹⁷ The perimeter between supported Au nanoparticles and the oxide support has been considered as being active for CO oxidation in many theoretical and mechanistic studies.^{12,18,19} Zhang et al. have shown that CO oxidation on Au nanoclusters supported on iron oxide is accompanied by the reduction of Fe anions.²⁰ In this process the support provides surface oxygen to react with CO adsorbed on the Au particles to form CO₂. Au nanoparticles supported on Fe₂O₃ were supposed to exhibit a higher activity toward CO oxidation than Au nanoparticles supported on TiO₂ since Fe₂O₃ is more reducible.¹³ It was also reported that Au particles supported on Fe₂O₃ are highly active for low-temperature CO oxidation in the presence of water vapor.^{5,21-23} Water was thought to prevent either the reduction or the aggregation of Au clusters.²⁴⁻²⁷

 α -Fe₂O₃ is the thermodynamically most stable iron oxide phase at standard pressure and temperature conditions. It has been widely used in heterogeneous catalysis as catalyst or support material.^{8,9,28,29} The α -Fe₂O₃(0001) surface was shown to exhibit different structures depending on the environment and the preparation parameters.³⁰⁻³² One of the observed surface terminations of α -Fe₂O₃(0001) is the biphase structure which forms at not too high oxygen pressures.³³⁻³⁶ The complex LEED pattern of this structure was first observed by Lad and Henrich who attributed the pattern to multiple scattering between a FeO_{1-x} surface layer and α -Fe₂O₃(0001) below the surface.³⁴ A later STM study by Condon et al. came to the conclusion that the surface would be terminated by an ordered array of $FeO_{1-r}(111)$ and $Fe_2O_3(0001)$ patches,³⁵ which gave the structure its name "biphase structure". Again somewhat later Lanier et al. questioned this interpretation and proposed instead that the surface would be terminated by a $Fe_3O_4(111)$ -derived layer. A similar surface structure was recently reported by Osaka et al. for an α -Fe₂O₃(0001) layer after annealing at 650 °C in ultrahigh vacuum (UHV).³⁶ Based on a combination of DFT calculations with STM and LEED Lewandowski et al.³⁷ put forward a model according to which the biphase structure consists of an ordered array of patches of ferryl-, iron-, and oxygen-terminated areas. Very recently still another model was proposed by Jelinek et al.,³⁸ mostly based on STM data. According to this model the surface would consist of an FeO₂

Special Issue: Hans-Joachim Freund and Joachim Sauer Festschrift

Received:August 31, 2018Revised:October 11, 2018Published:October 14, 2018

trilayer, i.e., an iron layer sandwiched between two oxygen layers, which would result in an oxygen-terminated surface.

The results reported here have been obtained in the context of a study of "O-poor" and "O-rich" biphase-terminated α -Fe₂O₃(0001) layers.³⁹ We have used "O-poor" biphase α - $Fe_2O_3(0001)$ as the substrate for gold deposition in this study; due to time constraints a possibly interesting comparative study for "O-rich" biphase α -Fe₂O₃(0001) could not be performed. In ref 39 the preparation and some properties of both types of layers, "O-poor" and "O-rich" biphase α - $Fe_2O_3(0001)$, are described. The layers were grown on Pt(111), which is a commonly used substrate for the growth of iron oxide layers. Much knowledge about the properties of iron oxide layers on this substrate has been accumulated over the years,^{40,41} which is the reason this substrate was also used in this study. CO adsorption and oxidation as well as the modification of the sample by CO were studied with electron energy loss spectroscopy (EELS) and thermal desorption spectroscopy (TDS).

EXPERIMENTAL SECTION

All experiments were performed in a two-chamber UHV system with base pressures of $\sim 2 \times 10^{-10}$ mbar (upper chamber) and $\sim 5 \times 10^{-11}$ mbar (lower chamber). The upper chamber was used for preparation tasks. It was equipped with a system (produced by SPECS) for low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES), a quadrupole mass spectrometer (QMS) manufactured by Hiden analytical, a sputter gun, and metal evaporators (Focus) for Fe and Au. The lower chamber contained a HREELS (high-resolution EELS) spectrometer (Delta 0.5 from VSI). The Pt(111) sample $(7 \text{ mm} \times 8 \text{ mm} \times 2 \text{ mm})$ was mounted on a transferable sample plate with a K-type thermocouple spot-welded to the side of the sample. It could be cooled with liquid nitrogen down to 90 K, and heating to 1300 K was possible with electron bombardment using a tungsten filament mounted behind it.

The energy of the primary electron beam for HREELS in the vibrational spectroscopy mode was set to 8 eV with an energy resolution of 4–6 meV. Electronic excitation spectra were recorded with a primary electron energy of 46 eV and an energy resolution in the range of 15 meV. All data were taken in specular geometry with an electron incidence angle of 55° with respect to the surface normal. The vibrational spectra shown in this publication were subjected to a deconvolution procedure to remove structures due to multiple energy losses.^{42,43} It is known that this procedure works reasonably well, but it can sometimes produce spurious structures in the deconvoluted spectra near the multiple loss energies if the experimental data do not properly conform with the mathematical scenario of the deconvolution formalism.

The QMS was situated in a housing pumped by a small ion getter pump, with the volume of the housing being connected to the chamber volume only via a small opening (4 mm diameter) in front of the QMS ionizer. During TDS the sample was positioned in front of this opening at a distance of ~1 mm, which substantially reduces the contribution of gas molecules desorbing from the sample holder to the TDS spectra. The heating rate in the TDS experiments was always 1.5 K s⁻¹.

The structure of thin gold layers on biphase α -Fe₂O₃(0001)/Pt(111) has been studied recently with STM by Lewandowski et al.³⁷ Deposition of several monolayers of gold at room temperature led to gold aggregates densely

covering the surface with little free space between them. Annealing at 700 K induced condensation to gold nanocrystals with reasonably sized uncovered areas between them. A structural characterization was not performed for our samples, but we assume that the structure of the gold layers was similar to that reported by Lewandowski et al. The gold-covered samples were annealed at 600 K to induce the formation of gold nanocrystals and to produce free uncovered areas for the interaction of the oxide with adsorbates.

RESULTS AND DISCUSSION

Figure 1 shows TPD and HREELS spectra of 5 ML Au on α -Fe₂O₃(0001) exposed to different doses of carbon monoxide.



Figure 1. Spectra of gold-covered (5 ML) biphase α -Fe₂O₃(0001) after exposure to different doses of CO. (a) TDS data with an inset showing the mean sticking coefficient (for details see text) and (b) vibrational HREELS data. The HREELS and TDS spectra were recorded sequentially for the same preparation. A flash to 600 K was performed before the experiments in order to break up the dense packing of Au nanocrystals, uncovering reasonably large areas between them (see Lewandowski et al.³⁷). The TDS data were actually measured up to 600 K, but only the relevant part up to 500 K is shown (there is no signal above 500 K).

HREELS and TPD spectra were measured sequentially from the same preparation with the sequence dosing \rightarrow HREELS \rightarrow TDS. Dosing was performed at 300 K, which was also the temperature at which the HREELS spectra were recorded. The TDS spectra show the presence of reasonably strongly bound CO species with a desorption maximum at ~370 K, which corresponds to a binding energy of ~ 1 eV calculated with the first-order Redhead equation,⁴⁴ using an attempt frequency of 10^{13} s⁻¹. A plot of $\Delta A/\Delta D$ is shown in the inset of Figure 1(a), with ΔA being the increase of the TDS peak area between two successive spectra and ΔD the increase of the CO dose. This number is proportional to the CO sticking coefficient averaged over the CO dose range between two successive spectra. The graph reveals that the CO sticking probability did not vanish even after a dose of 2000 L, which might be compatible with a very low sticking coefficient but also with a process where CO adsorption sites are produced by CO dosing. Sites with a low sticking coefficient would not lead to a sticking coefficient curve with a maximum [see inset in Figure 1(a)], which gives support to the other explanation, the production of adsorption sites by CO dosing. A process responsible for such a site production would be the reduction of the surface via CO oxidation. Later we will provide additional evidence for this process. Other information contained in the inset in Figure 1(a) is that the sticking probability starts to decrease above

1000 L, indicating that the coverage approaches saturation. We have estimated the CO coverage at the surface after exposure to 4000 L of CO by calibrating the area under the TDS peak in Figure 1(a) (top spectrum) with the area under the CO desorption peak of $c(4 \times 2)CO$ on Pt(111), which has a CO coverage of 0.5 with respect to the surface Pt atoms. Using this we found that the CO surface coverage is ~0.2 with respect to the oxygen atoms in a quasi-hexagonal α -Fe₂O₃(0001) oxygen layer.

The peaks at 1903 and 2039 cm⁻¹ in the HREELS data [Figure 1(b)] are attributed to C–O stretching vibrations of molecular CO. Their intensities are in line with the intensities in the TPD spectra in that the peaks still grow larger after a dose of 2000 L of CO. We suppose that the broad TPD peaks in Figure 1(a) are composed of two unresolved structures for doses larger than 500 L, where the HREELS data exhibit two C–O stretching vibration losses.

In addition to the two C–O stretching vibration losses there are two losses at lower energies, at ~1020 and ~1260 cm⁻¹. We identified two different possible explanations for them:

(1) They are remnants of the deconvolution procedure. The two most intense Fuchs-Kliewer losses of the oxide [see Figure 2] are at $\nu_1 \sim 639 \text{ cm}^{-1}$ and $\nu_2 \sim 392 \text{ cm}^{-1}$. Therefore,



Figure 2. HREELS spectrum of the Fuchs–Kliewer polaritons of biphase α -Fe₂O₃(0001).

the most intense double loss peaks would be at $2 \times \nu_1 = 1278$ cm⁻¹ and $\nu_1 + \nu_2 = 1031$ cm⁻¹. The deconvolution procedure should remove multiple loss intensities from the spectra, but quite often some structures do remain near the multiple loss positions. As can be seen from a comparison of the numbers, the double loss energies are not much different from the energies of the two low-energy loss peaks in Figure 1(b).

(2) They are due to a surface carbonate. The energies of the two losses are in the range of vibrational energies observed for carbonate-related surface species.^{45–47} Loss energies determined for carbonate on oxygen-covered Ag(110) and carbonate on CaO(001)^{48,49} are not much different from the ones observed here. The carbonate surface species might be a transition species in the CO oxidation process, or it may result from a reaction of CO₂ with surface defects resulting from a preceding CO oxidation step. Carbonate formation has not yet been observed on α -Fe₂O₃(0001), but there are observations for noncrystalline samples.⁵⁰ In the present case it might be possible that the gold at the surface changes the chemistry such that carbonate formation does also occur on biphase α -Fe₂O₃(0001).

We cannot assign the two losses definitely. There is a good chance that they are just remnants of the deconvolution procedure since their energies are not too much different from the multiple loss energies, but we cannot definitely rule out that they are due to a CO_2 -related surface species like carbonate. Infrared spectroscopy would be required to finally resolve this issue.

Surface reduction by CO oxidation produces oxygen vacancies. A theoretical study of Hoh et al.⁵¹ proposes that the presence of gold lowers the energy for formation of an oxygen vacancy near or below the gold clusters, which would lead to an enhanced probability for CO oxidation via reduction of the oxide. Following this, one would expect that CO_2 desorption is detectable in TDS spectra. A set of spectra are shown in Figure 3. Apparently, there is no clearly detectable



Figure 3. TPD spectra (mass 28: CO and mass 44: CO₂) of 4000 L of CO on "O-poor" biphase α -Fe₂O₃(0001). The mass 28 spectrum is the top spectrum in Figure 1(a), and the mass 44 spectrum is the corresponding carbon dioxide desorption trace.

 $\rm CO_2$ signal, which leads us to the conclusion that the adsorbed CO molecules desorb molecularly without being oxidized (acually, for every CO TDS spectrum shown in Figure 1(a) a corresponding CO₂ spectrum was measured, but in none of the spectra a CO₂ partial pressure signal could be detected). This result shows that the CO molecules which are detected in the TPD and HREELS spectra are not the ones which reduce the surface—these molecules just bind to already existing adsorption sites and desorb without being oxidized. The CO molecules which had reduced the surface had already done this before the spectra were recorded, possibly already during dosing. The resulting CO₂ molecules did probably desorb directly after production.

The modification of the iron oxide surface by Au clusters and CO adsorption is clearly visible in EELS spectra in the range of the electronic valence band excitations [see Figure 4(a)]. At the bottom (A) a spectrum of "O-rich" biphase α - $Fe_2O_3(0001)$ is shown. "O-rich" means that this layer has not been flashed to 1000 K. The flat area extending up to \sim 2 eV is part of the α -Fe₂O₃ band gap.³⁹ No excitations are expected in this energy range for an ideal nonreduced Fe₂O₃ crystal, and therefore this region is rather flat. However, intensity attributed to Fe²⁺ ions shows up in the gap region when the "O-poor" layer is produced by annealing (B).³⁹ Two ML of gold leads to an even more intense feature (C) with the maximum shifted to somewhat lower energy. Exposing the sample to different doses of CO (D-F) produces an even more intense feature, which shifts to 0.67 eV for the highest dose. For comparison a spectrum of bilayer FeO(111) on Pt(111) is included, which also has an intense feature at 0.67 eV. This indicates that CO reduces the sample so much that the oxide stoichiometry gets near to that of FeO.



Figure 4. (a) HREELS data with loss energies in the range of valence level electronic excitations. The surfaces were prepared sequentially at 300 K (from A to F). The top curve (G) is a spectrum of a FeO(111) bilayer, which consists of a hexagonal iron layer and a terminating hexagonal oxygen layer.^{52–54} (b) Electronic excitation spectra of 2 ML Au on "O-poor" biphase α -Fe₂O₃(0001) recorded after flashing to the indicated temperatures. For details see the labels in the figures.

Recent theoretical studies by Pabisiak et al.^{55,56} indicate that small gold particles (Au_1-Au_4) may be positively charged on α -Fe₂O₃(0001), while Hoh et al.⁵¹ found that the charge distribution is not strongly affected by the deposition of Au_{10} gold clusters on defect-free α -Fe₂O₃(0001). Spectrum C in Figure 4(a) would be well compatible with a reduction of iron atoms by gold, i.e., with an electron transfer from the gold clusters to the oxide, which would lead to a positive charge on the gold clusters. According to Hoh et al.,⁵¹ charge goes to a gold cluster (Au₁₀ in the paper of Hoh et al.) if oxygen is removed from the oxide below the cluster, while it goes to iron when oxygen is removed from a site near a cluster. Our results [Figure 4(a), D–F] would be compatible with a removal of oxygen from sites near the clusters if we consider the results of Hoh et al.

The energies of the CO stretching vibrations in Figure 1(a), 1903 and 2039 cm^{-1} , are significantly smaller than the corresponding value for gas-phase CO (2143 cm^{-157}). In the Blyholder picture of CO adsorption,⁵⁸ charge is transferred into the antibonding CO 2π orbital, which is unoccupied in gas-phase CO. The charge weakens the C-O bond and consequently lowers the energy of the CO stretching vibration. Thus, the observed CO stretching vibration redshift may be viewed as an indicator for the presence of charge which can be transferred to the CO 2π level. Oxide reduction leaves the charge of the removed oxygen atoms in the oxide, making it available for such a transfer. The two C–O stretching vibration losses might be assigned to CO molecules on iron oxide surface sites with different degrees of reduction, with the loss at 1903 cm⁻¹ being due to CO on more strongly reduced sites since here more charge would be available.

Figure 4(b) shows that EELS spectra of gold-coated "Opoor" biphase α -Fe₂O₃(0001) do not change very much when the sample is annealed to temperatures up to 700 K. This proves that substantial changes do not occur when the sample is annealed without CO being involved.

To answer the question whether the reduced samples are able to catalyze CO oxidation if both reaction partners are supplied from the gas phase, we have performed an experiment where the CO_2 partial pressure was recorded in situ during CO or O_2 dosage to a sample surface covered with the respective

other reactant (O_2 for a CO adsorbate or CO for an oxygen adsorbate). All experimental steps following the initial sample preparation were performed at room temperature. In these experiments the sample was positioned in front of the QMS housing with a small gap between the sample and the opening in the QMS housing. The respective gases were dosed with the doser having its tube end positioned near to the small space between the sample surface and the QMS housing (see Figure 5). With this setup we could expose the sample to gas from the



Figure 5. Schematic drawing of the experimental geometry in the in situ TDS experiment.

doser, while the QMS could record the partial pressure of the dosed gas and gases desorbing from the sample. Panel (b) of Figure 6 shows the partial pressure of different CO_2 isotopic



Figure 6. Partial pressures as a function of time of several gases measured in front of a biphase α -Fe₂O₃(0001) layer covered with 2 ML gold and total pressures measured with the ion gauge in the measuring chamber. (a) and (b) Mixture of ${}^{13}C{}^{16}O$ (90%) and ${}^{13}C{}^{18}O$ (10%) is dosed to a sample pre-exposed to ${}^{16}O_2$. Before this the sample was reduced by exposure to 10000 L of CO, followed by a flash to 450 K to remove the adsorbed CO. (c) and (d) ${}^{16}O_2$ is dosed onto a sample pre-exposed to 5000 L of ${}^{12}C{}^{16}O$. We note that the QMS sensitivity was not calibrated relative to that of the ion gauge. For details of the experimental setup see text.

gases while dosing an isotopic CO mixture (90% $^{13}C^{16}O + 10\% \,^{13}C^{18}O$) to a sample predosed with $^{16}O_2$. O_2 does not adsorb on regular α -Fe₂O₃, but in the case discussed here the surface was reduced, which leads to a stronger interaction. From the composition of the isotopic CO mixture and the mass of the dosed oxygen atoms one would expect the formation of CO₂ with masses 45 and 47, if the CO molecules react with the oxygen at the surface. Panel (b) shows that such CO₂ molecules indeed form with approximately the expected intensity ratio I(mass 45)/I(mass 47) = 9 and an approximately exponential time profile as one might expect

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for this reaction due to the limited reservoir of oxygen at the surface. From these data we conclude that CO reacts with predosed oxygen. Likewise, panel (d) shows the formation of a large amount of CO₂, while ¹⁶O₂ was dosed to a sample preexposed to ¹²C¹⁶O. However, in this case there is no exponentially decaying time profile. Instead it appears that the CO_2 desorption rate is steadily increasing. This is a hint that in this case the origin of the desorbing CO_2 is not the sample surface but the chamber wall surfaces, especially the inner surface of the mass spectrometer housing and the surface of the QMS. The latter surfaces are named here since the detection probability is higher for gases desorbing from them than for gases desorbing from the chamber walls due to the construction of the TDS setup. If part of the comparatively large reservoir of ¹²C¹⁶O molecules adsorbed on the walls reacts with the ¹⁶O₂, then ¹²C¹⁶O₂ may form without a recognizably decaying profile. The mass 28 (CO) time profile in panel (d) seems to consist of two components: an exponentially decaying profile plus a profile similar to that of CO₂. Our interpretation is that the exponentially decaying part of the profile is due to CO desorption from the sample, possibly by a reaction where oxygen replaces CO. This conclusion is based on the observation that the integrated area of the exponential part of the CO partial pressure time profile is not much different from that of the sum of the CO₂ time profiles in panel (b). The nondecaying part of the CO desorption time profile is probably again due to a reaction occurring at the surfaces of the QMS and the QMS housing.

The CO₂ evolution time profile in Figure 6(b) differs from that of the initial sample reduction: in Figure 6(b) the highest CO₂ formation rate is observed directly at the beginning of the exposure, while the initial sample reduction process starts slowly [see Figure 1(b)]. This shows that the surface produced by O₂ dosing is different from the as-prepared surface and that the initial sample reduction represents a catalytic activation step.

Our data do not give a clue toward the reaction mechanism, but there are indications for the CO adsorption site. Typical C-O stretching vibration losses of CO adsorbed on gold crystals and not-too-small gold aggregates are roughly in the range of 2100 cm^{-1, 26,59–64} while for CO on gold atoms and small clusters smaller energies such as $\sim 2000 \text{ cm}^{-1}$ for dimers and trimers on MgO(100) and ~1850 cm⁻¹ for gold atoms on MgO(100) were reported.^{63,64} Thus, the observed C–O stretching vibration energies of 1903 and 2039 cm⁻¹ [Figure 1(b)] are not easily compatible with CO on extended gold aggregates such as the ones on biphase α -Fe₂O₃(0001), making reduced sites on the iron oxide surface, possibly with contact to the gold clusters, the more likely CO adsorption sites. However, the presence of gold atoms and small aggregates at the iron oxide surface cannot be ruled out definitely due to the lack of a thorough structural surface characterization. CO on such aggregates might have C-O stretching vibrations with energies compatible with the ones observed in the HREELS spectra [Figure 1(b)]. The observation of CO replacement by oxygen seems to indicate that both gases compete for the same adsorption sites, which would mean that the above discussion does also apply to oxygen. We note that for gold supported on an iron oxide precipitate it was reported that CO oxidation occurs via a Mars-van Krevelen mechanism where the oxygen is supplied by the oxide and CO is adsorbed on nearby gold structures.²⁰

According to Lewandowski et al.,³⁷ the gold nanocrystals would be located on the oxygen-covered areas of the film, which would leave only little oxygen-terminated area for surface reduction. However, we note that there is surface-near oxygen even in the case of the metal-terminated surface. Such an issue would not exist if the surface is oxygen terminated as proposed by Jelinek et al.³⁸

CONCLUSIONS

We have studied the adsorption and the oxidation of CO as well as the modification of the substrate by CO for a golddecorated "O-poor" biphase α -Fe₂O₃(0001) thin-film model catalyst. HREELS and TDS (including a variant where the desorption of products was measured while an educt gas was dosed) were used for the studies. At room temperature CO reduces the surface through CO oxidation to CO₂. The newly produced sites bind CO rather strongly with a TDS desorption rate maximum at ~370 K, corresponding to an activation energy for desorption of ~ 1 eV calculated with the first-order Redhead equation.⁴⁴ Gold deposition and even more the surface reduction by CO induce a significant buildup of electron density near the Fermi edge as shown by EELS spectra which exhibit intense losses in the region of the α -Fe₂O₃ band gap. This charge is probably mostly located on the reduced iron atoms. The CO stretching vibration shifts to lower energy probably due to a transfer of part of this charge into the unoccupied CO 2π levels. The reduction by CO activates the surface toward CO oxidation at room temperature: CO from the gas phase can react toward CO2 with oxygen at the surface, while O₂ dosed to a CO covered sample just leads to CO desorption without oxidation.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was funded by the Deutsche Forschungsgemeinschaft (DFG) through their Sonderforschungsbereich 546 "Transition Metal Oxide Aggregates" and the Cluster of Excellence "UniCat".

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