Fluctuations and Bistabilities on Catalyst Nanoparticles

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We show that coverage fluctuations on catalyst particles can drastically alter their macroscopic catalytic behavior. Scrutinizing the occurrence of kinetic bistabilities, it is demonstrated by molecular beam experiments on model catalysts that macroscopically observable bistabilities vanish completely with decreasing particle size, as previously predicted by theory. The effect is attributed to fluctuation-induced transitions between two kinetic reaction regimes, with a transition rate controlled by both particle size and surface defects. These results suggest that fluctuation-induced effects represent a general phenomenon affecting the reaction kinetics on nanostructured surfaces.

Heterogeneous catalysts (1) have surfaces with highly specific structural and chemical properties that vary on the nanometer scale, primarily with respect to particle size, particle structure, support, and promoters. All of these aspects are carefully optimized for the reaction of interest (2). As a result, structurally and chemically complex surfaces are obtained that are extremely difficult to characterize in desired detail. Hence, molecular-level knowledge on heterogeneously catalyzed reactions is scarce, a fact which for a long time led to the depiction of heterogeneous catalysis as “black magic” (3).

In the last decade, however, enormous progress has been made toward a fundamental and detailed understanding of the underlying processes. This development has been driven by three main factors: (i) advances in experimental techniques now provide greatly improved microscopic (4–6) and in situ spectroscopic (7) information, (ii) the development of model catalysts has made available catalyst surfaces with reduced complexity and extremely well-controlled structure and composition (8–13), and (iii) the development of first-principles calculations and phenomenological simulation schemes has greatly advanced the theoretical understanding of the molecular details on catalyst surfaces.

One of the much-discussed mysteries in heterogeneous catalysis is so-called size effects, i.e., the dependence of the global reaction kinetics on the size of the active particles. Size effects are a common phenomenon and are typically taken advantage of in catalyst optimization. Unfortunately, their exact origin remains highly ambiguous in most cases. Among the most common explanations are those that have their basis in the assumption that small particles expose specific sites with modified adsorption properties (e.g., (14)). The reason for these modifications could either be of geometrical nature (e.g., edge, corner, or other irregular adsorption sites) or of electronic origin (e.g., electron confinement effects in small aggregates or interaction with the support).

However, there are other pure nanoscale effects, which exclusively arise as a consequence of the limited dimension of the active particle, i.e., without any modification of the individual adsorption site. One example are so-called communication effects originally discussed by Zhdanov and Kasemo (15). They arise from coupling of the kinetics between different nanofacets, occurring via surface diffusion, and may play a critical role for the global kinetics. Here, we focus on an even more general but widely ignored nanoscale effect, which is the influence of coverage fluctuations. As the relative amplitude of fluctuations in a confined system scales with $N^{-1/2}$ ($N$ being the number of molecules involved), a strong influence is expected on the length scale of a typical catalyst particle (a few nanometers). Fluctuations have received extensive theoretical treatment (e.g., (16)), and a substantial influence on the catalytic activity was predicted (17–19). However, there is no experimental evidence for a fluctuation-induced contribution to the reaction rate on a macroscopic catalyst. In fact, the only experimental confirmation stems from FEM (field electron microscopy) studies (18, 20) on catalytically active field-emitter tips. The reason for this apparent contradiction is simple: Experimentally, it proves to be extremely difficult to identify fluctuation-induced effects in the global reaction kinetics of a macroscopic system.

We present experimental evidence for a direct influence of fluctuations on the global kinetics of a catalytic reaction on a supported catalyst surface. We analyzed the appearance of kinetic bistabilities, i.e., the existence of two stable kinetic regimes coexisting for a given set of reaction conditions. Such bistable behavior is observed for several reaction systems on various single-crystal surfaces [e.g., (21)]. For the specific example of CO oxidation on oxide-supported Pd particles, we demonstrate by means of transient molecular beam experiments that the macroscopically observable bistable behavior vanishes with decreasing particle size. The globally monostable kinetics in the small particle limit is attributed to fluctuation-induced kinetic transitions between both kinetic regimes. Quantitative stochastic simulations show that the frequency of these transitions drastically increases in the presence of defect sites, the abundance of which typically increases with decreasing particle size. Thus, on realistic nanoparticles, the influence of fluctuation-induced effects is expected to play a larger role than predicted on the basis of their pure size, a prediction that is in full agreement with the experimental results. The results obtained in this work are expected to be valid not only for the specific reaction system under investigation but in a universal fashion for all reactions showing similar multistability effects.

**Supported model catalysts and molecular beam setup.** The main prerequisite for the present study was the preparation of well-defined supported model catalyst surfaces spanning a very large range of particle sizes. For this reason, two types of preparation methods were combined (Fig. 1, A to C). Both methods use planar model supports, which are compatible with the molecular beam approach described below (22).

1) Small particles in the range of a few nanometers in diameter were prepared by metal evaporation and growth of Pd on a well-defined alumina film on a NiAl(110) single-crystal substrate. The full preparation procedure was carried out in situ in the ultrahigh vacuum (UHV) molecular beam apparatus [Fritz Haber Institute (FHI), Berlin] (23). The corresponding model systems were previously characterized in great detail with respect to their structure and adsorption properties (24, 25). Moreover, the
CO oxidation kinetics were investigated by means of systematic molecular beam experiments (26). Although the deposition and growth method yields chemically clean and structurally well-defined model surfaces, there are limitations with respect to the preparation of larger particles. This is because of the intrinsically high nucleation density on the oxide model support.

2) In order to obtain larger particle sizes, model catalysts were prepared by means of electron beam lithography (EBL). The method has been established previously for various noble metals and allows the fabrication of samples consisting of particles of well-defined size and variable aspect ratio in a perfectly regular array (27). Here, we used Pd particles with an aspect ratio of 1, arranged in a hexagonal array, and supported on a silica film on Si(100). The samples were prepared at Chalmers University (Göteborg, Sweden), Microtechnology Laboratory MC2, and transported to FHI, where the reactivity measurements were performed.

Fig. 1. Overview of the supported model catalysts used in this work. (A) Scanning electron microscopy (SEM) image of large Pd particles prepared by EBL on a SiO$_2$ film on Si(100) (for model system I, particle diameter of 500 nm; Pd surface atoms per particle, 6 × 10$^{12}$; and particle density, 5.1 × 10$^{20}$ cm$^{-3}$). (B and C) Smaller particles were prepared by in situ evaporation and growth of Pd on a Al$_2$O$_3$ film on NiAl(110) [scanning tunneling microscopy (STM) image from (24, 25)] (for model system II) (B), particle diameter, 6 nm; Pd surface atoms per particle, 540; and particle density, 1 × 10$^{12}$ cm$^{-2}$. For model system III (C), particle diameter, 1.8 nm; Pd surface atoms per particle, 60; and particle density, 6.5 × 10$^{12}$ cm$^{-2}$). (D) Schematic representation of the UHV molecular beam setup: Modulated CO and O$_2$ beams of variable intensity are crossed on the sample surface, while the integrated reaction rate is measured by a non-line-of-sight quadrupole mass spectrometer. For details on the setup and general experimental procedures, see (23, 26).

An overview of the supported model catalysts used in this work is given in Fig. 1, A to C. The particles span a diameter range from 2 to 500 nm. For simplicity, we denote the samples as model systems I to III. Model I (500 nm) represents a reference case for the limit of large particle sizes. Models II and III (6 nm and 1.8 nm) correspond to the range of particle sizes typically used in real supported noble metal catalysts.

The reactivity experiments were performed in a UHV molecular beam system at FHI described previously (23). The setup is displayed schematically in Fig. 1D. The reactants, CO and O$_2$, were supplied via two high-intensity effusive beam sources. For the following discussion, we define the intensity ratio of the beam fluxes as $F_{CO} = F_{CO}(F_{CO} + F_{O2})$, with $F_{CO}$ and $F_{O2}$ representing the impinging CO and O$_2$ flux densities, respectively. The total flux was typically kept constant in all experiments.

Kinetic bistabilities on supported nanoparticles. The steady state reaction rate was determined systematically as a function of the CO flux ratio, $x_{CO}$, and the surface temperature for the type I model catalyst (Fig. 2A). We find the typical features of the CO oxidation system, an O-rich regime with first-order dependence of the reaction rate on the CO flux and a CO-rich regime of negative order in the CO flux and positive order in the O$_2$ flux (28).

With the aim of probing the existence of kinetic bistabilities, we superimposed two sets of experiments starting from CO- and O-rich conditions, respectively, and subsequently switching on the complementary reactant beam. Within a well-defined temperature and $x_{CO}$ interval, both reactive states were perfectly stable for a given set of conditions on a time scale of at least 30 min and more. A corresponding bistability diagram showing the monostable and bistable regions is displayed in Fig. 2B.

The reaction scheme in Fig. 2 illustrates the origin of the two reactive regions and the occurrence of two stable kinetic states. Under conditions of high O$_2$ flux, the surface of the Pd particles is largely covered by adsorbed O. Because the influence of O on the sticking probability of CO ($S_{CO}$) is moderate, the reaction rate is high and nearly proportional to the CO flux. CO, and the surface coverage.

Within a well-defined temperature and $x_{CO}$ range, two stable reactive regions coexist. The arrows indicate the direction of the hysteresis loop. The total flux of CO and O$_2$ beams at the sample position was equivalent to a local pressure of 10$^{-4}$ Pa, whereas the fraction of CO in the total flux $x_{CO}$ was varied systematically. (B) Bistability diagram for the CO oxidation on the model catalyst. The origin of the bistable kinetics is related to the coverage dependencies of CO and O$_2$ sticking probabilities (see reaction diagram and text). At high temperatures, the bistability vanishes because of the increasing CO desorption rate.
the bistability window). Coupling of this type of kinetics to surface diffusion opens up the possibility for the formation of chemical waves [e.g., (30)]. Transitions from one kinetic regime to the other are actually initiated by the nucleation and propagation of such waves (29, 30), and the corresponding phenomena are well understood both theoretically and experimentally [e.g., (21, 29)].

The results in Fig. 2, for supported nanoparticles under low-pressure or UHV conditions, are fully consistent with the experimentally and theoretically expected behavior for typical single-crystal surfaces [e.g., (29, 31)]. Moreover, bistabilities in the ambient pressure range were recently observed and extensively analyzed for a similar reaction system (32). These results suggest that, on sufficiently large supported nanoparticles, the occurrence of kinetic bistabilities can be regarded as a common phenomenon that qualitatively resembles the single-crystal case. This result raises the question: At what relevant length scale might deviations be expected from the single-crystal behavior? For the more typical particle size range of a few nanometers, reports on multistability phenomena are extremely rare. This difference in reactivity may be in line with theoretical predictions that suggest the disappearance of the bistability regime for sufficiently small particles (19).

**Size-dependent kinetic bistabilities.** In the next step, we scrutinize the size-dependent behavior of the kinetic bistability. In particular, we investigate the transient behavior in the region where the transition from the O-rich to the CO-rich regime occurs and where hysteresis is expected.

Starting with the large particles of the model system I, typical transients observed within the bistable region are shown in Fig. 3D. As discussed in the previous section, the two different reactive states are obtained by preparing the surface either in an O or CO precovered state and by subsequently admitting the complementary reactant beam. After an initial transient region, both reactive states are perfectly stable within the experimental accuracy on a time scale of 10³ s and above.

When we proceed to the smaller particles of the model system II (6 nm), we make the unexpected observation that, although different reaction rates are initially established by either starting from O- or CO-rich conditions, these differences vanish slowly but completely on a typical time scale of 10³ s. A thorough inspection of the transient behavior as a function of \( x_{CO} \) indicates that this is not only the case for the specific set of conditions in Fig. 3E, but a similar time-dependent behavior was observed for other \( x_{CO} \) values (Fig. 3B) and surface temperatures as well.

Also, for the smallest particles of model system III (Fig. 3C), a common steady-state rate is reached, independent of whether the reaction starts from CO- or O-rich conditions. The time scale on which the common state is reached becomes extremely short, however. Typically, the rates are identical within the experimental accuracy after significantly less than 10² s.

**Microkinetic simulations and discussion.** In general, there are two possible effects that may lead to a vanishing bistability in the small particle limit. The first one is related to the presence of defect sites. The density of such defects, such as edges, steps, corners, interface sites, or other irregularities, increases with decreasing particle size. As a result of the differences in chemisorption energy at such sites, their presence should result in an increased dependence of the adsorption energies on coverage. Such an effect has been verified experimentally for CO adsorption and oxidation on the model catalyst used in this work (24, 26). With respect to the bistability behavior, Zhdanov and Kasemo have shown that an increasing coverage dependence of the CO desorption energy leads to a decreasing extension of the bistability region (29), but up to now there had been no experimental verification of such an effect. We show that the high-defect density on small particles is likely to generate a cover-

age dependence of the CO adsorption energy, which in turn potentially may lead to a quenching of the kinetic bistability.

Coverage fluctuations on small particles must also be considered. In the limit of negligible surface diffusion via the oxide support, which interacts only weakly with the reactants (33), the particles act like isolated nanoreactors. On their confined surface area, the amplitude of coverage fluctuations increases with decreasing particle size. We expect an increasing probability for fluctuation-induced transitions between the two kinetic regimes as the particles become smaller. Similar fluctuation-related confinement effects are expected in cases of limited adsorbate mobility (34). Experimentally, fluctuation-induced transitions have been observed for CO oxidation on a Pt field-emitter tip, exhibiting facets in the size range of a few nanometers, and the results could be theoretically reproduced by means of hybrid Monte Carlo mean field simulations (18, 20, 35, 36). In the case of a macroscopic catalyst sample, fluctuation-induced spontaneous kinetic transitions should eventually result in the formation of a dynamic equilibrium between both reactive states and, thus, in a macroscopically monostable kinetics. Indeed, disappearance of bistability and hysteresis effects on facets expos-
ing substantially less than $10^2$ adsorption sites was recently predicted on the basis of Monte Carlo simulations (19). We speculate that the rarity of reported bistability effects on supported catalysts and model catalysts may be the result of such fluctuation-induced transitions.

We examined the effect of surface defects by using a mean-field model based on kinetic rate equations (KRE), which has previously been successfully used to describe the transient and steady-state behavior of CO oxidation on Pd particles (37). As a first step, the model was fitted to quantitatively reproduce reactivity data for the model system I (500-nm particles) as a function of $x_{\text{CO}}$ and surface temperature. A typical result of the simulation is plotted in the topmost diagram in Fig. 4B. The model provides a good description of both the dependence of the rate on the reaction parameters and the width and temperature range of the bistability region. Some minor deviations remain, in particular on the CO-rich side, which most likely are related to differences in the local reactant fluxes on the three-dimensional particles.

We have previously shown that the reactivity changes observed in the transient and steady-state behavior on small Pd particles are mainly related to the presence of defect sites, which are characterized by a weaker chemisorption of CO (26, 37). In order to explore the influence of these sites on the bistability, we simulate the kinetics as a function of the fraction of weakly adsorbing CO sites (Fig. 4B) (see (37) for details of the model). As expected on the basis of previous work (29), the width of the bistable region rapidly decreased with increasing defect density (Fig. 4C).

In spite of the pronounced influence of surface defects on the nature of the bistability region, a thorough inspection of the transient behavior shows that there is no indication for a fundamentally modified transient behavior. In particular, the appearance of an unusually slow transient kinetics, as observed experimentally in the case of the model system II (6 nm), cannot be explained by the influence of defects. Thus, we conclude that the particle size–dependent bistability effect cannot be attributed to the presence of defects alone.

In order to explore the role of fluctuations, we used a stochastic mean-field model. The CO oxidation is described by a Markovian process based on a master equation (ME) approach, as has been previously used in studies on Pt surfaces (20, 36). The probability factors for the master equation are directly extracted from the fitted KRE model. Similar to the KRE model, the ME approach allows us to quantitatively reproduce the experimental results, but in addition the latter takes into account the role of fluctuations in a confined system (38).

Some representative results are displayed in Fig. 5. In contrast to the KRE model, in which the O-rich and CO-rich steady states are represented by a single point in coverage space, the stochastic ME model describes the same situation as a probability distribution of finite width. With increasing particle size (Fig. 5A), the widths of the probability maxima become more narrow and the reaction rates asymptotically approach the KRE limit. Under these conditions, no transitions between the CO- and the O-rich states occur (Fig. 5A, inset).

With respect to the role of the particle size, we quantitatively investigate two systems, the sizes of which are chosen in order to correspond to the particle surface areas of model systems II [540 Pd surface atoms (40)] and III [60 Pd surface atoms (40)]. Decreasing particle size increased the width of the probability distribution (Fig. 5, B and D). As a result, the probability of finding the system in the transition region between both regimes increases, and spontaneous transitions between both kinetic states become more frequent.

In order to answer the question of whether the experimental results are fully described by the fluctuation-induced transition rate on a homogeneous surface, we simulate the global transient response by propagating the probability distributions starting from fully CO- and O-saturated surfaces, respectively. The results (Fig. 5F) indicate that on the basis of a defect-free surface model the fluctuation-induced transitions are considerably slower than those observed experimentally.

Consequently, we take into account the combined effect of defects and fluctuations in the ME model, using adsorption, desorption, and reaction probabilities according to the heterogeneous KRE model described in Fig. 4. Indeed, a semiquantitative agreement between the calculated and the experimental transients is obtained only after adding a substantial fraction of defect sites (Fig. 5F).

In the case of the KRE model, the introduction of weakly CO-adsorbing defects shifts the CO- and O-rich states to lower CO and O coverage, respectively, thus effectively
reducing the distance between both states in coverage space (Fig. 4D). The same effect is observed in the stochastic ME model. Here, however, it has the additional effect of dramatically enhancing the transition probability between the two kinetic regimes (Fig. 5, C and E). Although the system remains microscopically bistable as indicated by the existence of two probability maxima at high-O and high-CO coverage, the chance of finding the system in the transition regime is greatly enhanced, leading to a strongly shortened lifetime and thus to a fast dynamic equilibrium between both kinetic states.

Conclusions and outlook. The results we reported should likely hold not only for the specific case we studied but also for other reactions exhibiting similar kinetic multi-stabilities. In general, the frequency of fluctuation-induced transitions should sensitively depend on modifications of the adsorption properties and on the presence of specific adsorption sites, with both effects naturally playing an increasing role with decreasing particle size. Moreover, the presence of coverage fluctuations on nanoscale particles should influence the global reaction kinetics even in the absence of kinetic phase transitions. Thus, general deviations from a rate equation–based description are predicted, although these effects can be subtle and may be difficult to identify experimentally.

As a last point concerning the origin of size and structure effects in heterogeneous catalysis, the present work supports the idea that in many cases it might not be possible to assign a kinetic phenomenon to a single geometric, electronic, or confinement effect. Instead, we should expect a strong coupling between different effects, leading to synergistic or antisynergistic contributions once a specific property of a complex surface is modified. This point might be one of the reasons for the difficulties in deriving a quantitative understanding of reaction kinetics in heterogeneous catalysis. For future studies, it underlines the necessity of developing model systems and microkinetic descriptions that do not only focus on a single structural or electronic effect but simultaneously take into account multiple degrees of complexity (40).

Fig. 5. Stochastic mean field simulations, illustrating the combined effect of limited particle size and surface defects on the kinetic bistability. Because of the increasing amplitude of fluctuations, the width of the probability distributions in coverage space increases with decreasing particle size (A, B, and D), and spontaneous transitions between both reaction regimes become more frequent (insets show the reaction rate on an individual particle). For an ensemble of particles, this results in a dynamic equilibrium being established between both reactive states. Upon modifying the adsorption and reaction probabilities according to the defect model in Fig. 4, the probability maxima approach each other [(C) versus (B) and (E) versus (D)] and the transition rate between both states increases drastically (insets). (F) By integrating over an ensemble of particles, the transient response predicted by the stochastic model can be compared with the experimental data for model system II (Fig. 3). A substantial fraction of defects has to be added in order to reproduce the experimentally observed relaxation times. [All probability factors for the elementary processes in the stochastic model were derived from the kinetic rate equation approach described in Fig. 4. \( T_{\text{surface}} = 415 \, \text{K} \); for (A), \( x_{\text{CO}} = 0.48 \) and 0% defects; for (B), \( x_{\text{CO}} = 0.49 \) and 0% defects; for (C), \( x_{\text{CO}} = 0.52 \) and 10% defects; for (D), \( x_{\text{CO}} = 0.46 \) and 0% defects; and for (E), \( x_{\text{CO}} = 0.50 \) and 20% defects. All parameters were chosen according to the model in Fig. 4 and in (37).]
Phospholipid Metabolism Regulated by a Transcription Factor Sensing Phosphatidic Acid

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Cells regulate the biophysical properties of their membranes by coordinated synthesis of different classes of lipids. Here, we identified a highly dynamic feedback mechanism by which the budding yeast Saccharomyces cerevisiae can regulate phospholipid biosynthesis. Phosphatidic acid on the endoplasmic reticulum directly bound to the soluble transcriptional repressor Opi1p to maintain it as inactive inside the nucleus. After the addition of the lipid precursor inositol, this phosphatidic acid was rapidly consumed, releasing Opi1p from the endoplasmic reticulum and allowing its nuclear translocation and repression of target genes. Thus, phosphatidic acid appears to be both an essential ubiquitous metabolic intermediate and a signaling lipid.

Lipid synthesis in widely divergent organisms is coordinately regulated by transcriptional feedback loops (1–4). An important class of transcription factors that regulate lipid metabolism have inactive precursors anchored in the endoplasmic reticulum (ER) (1–3). Although it is clear that these transcription factors respond to changes in lipid concentrations by being released from the ER and translocating to the nucleus, it is not known precisely how such transcription factors are coupled to changes in the lipid composition of the ER membrane.

In yeast, a high proportion of genes involved in phospholipid metabolism are regulated by the same set of three transcription factors (Fig. 1A) (5, 6). A cis-acting inositol-sensitive upstream activating sequence (UAS INP) common to these genes is activated by a pair of transcription factors, Ino2p and Ino4p, that in turn are repressed by Opi1p (7). Inositol is a master regulator of this pathway; it activates Opi1p, thereby creating a negative feedback loop because the most highly regulated gene in the pathway is INO1, which codes for the rate-limiting enzyme in inositol synthesis (Fig. 1A). Thus, deletion of OPI1 leads to unregulated overproduction of inositol (hence called “opi”). Opi1p is a cytoplasmic protein that contains two phenylalanines in an acidic tract (a FFAT motif) that binds the integral ER membrane protein Sec2p and thus targets it to the ER (8). However, both the signal generated by inositol and the mechanism by which the signal is sensed by Opi1p are not known.

Results. In log-phase cells growing without inositol, green fluorescent protein (GFP–Opi1p) was targeted to the ER, which in yeast consists of a peripheral network beneath the plasma membrane, the nuclear envelope (NE) on which GFP–Opi1p was slightly enriched, and occasional linking strands (Fig. 1B) (8). To study the regulation of Opi1p by inositol, we visualized GFP–Opi1p after the addition of inositol. Within 5 min GFP–Opi1p relocated away from the cell periphery to the nucleus (Fig. 1B). The increase in soluble nuclear Opi1p slightly preceded accumulation on the NE (fig. S1, A to D), indicating that Opi1p is not constitutively recycling from ER to nucleus. In contrast, complete inhibition of nucelocytoplasmic traffic reduced the enrichment of GFP–Opi1p on the NE and prevented its translocation in response to inositol (Fig. 1C). Thus, inositol appeared to activate nuclear import of Opi1p, possibly after it had been displaced from the ER into the cytoplasm, and the enrichment of GFP–Opi1p seen on the NE was likely to be intranuclear (i.e., on the inner NE). The time course of inositol-mediated repression is not known (10, 11), so we examined the short-term effects of inositol on transcription of INO1. After addition of inositol, INO1 mRNA amounts declined, with little initial lag time (Fig. 1D). Thus, nuclear translocation by GFP–Opi1p had the same kinetics as inositol-mediated gene repression, suggesting the physiological relevance of the translocation.

We next set out to identify the signal sensed by Opi1p. First, we tested whether Opi1p sensed inositol directly with the use of cells carrying a mutant phosphatidylinositol (PI) synthase gene that limits incorporation of inositol into PI (12). Translocation of GFP–Opi1p was slow and partial (Fig. 2A), indicating that the inositol-derived signal required production of PI. Downstream of PI, yeast synthesize four PI phosphates (PIP2s); however, we found that production of PIP2s was not required for Opi1p translocation (Fig. 2A). Alternatively, the signal detected by Opi1p might be the production of PI or the cytidylylphosphatidylglycerol (CDP-DAG), biosynthetic intermediates
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