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Low temperature CO induced growth of Pd supported on a monolayer silica film

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Abstract

Nucleation, growth and sintering of Pd deposited on an ultra-thin silica film were studied by scanning tunneling microscopy and infrared reflection absorption spectroscopy. No preferential nucleation of Pd on the silica surface was observed both at 90 and 300 K deposition. When adsorbed on Pd clusters formed at 90 K, CO causes a strong sintering effect even at this temperature. The results are rationalized on the basis of a high mobility of Pd carbonyl-like species on the silica film. At a given Pd coverage, the extent of CO induced sintering cannot be achieved by annealing in vacuum. In addition, vacuum sintering, which commences above 700 K, goes simultaneously with interdiffusion of Pd and support.

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Environmental and thermal effects on the structure of metal particles are key issues in an understanding of deactivation processes over oxide supported metal catalysts. Metal sintering at elevated temperatures may play a crucial role in the stability of working catalysts. In addition, adsorption of molecules strongly interacting with metal surfaces may significantly change morphology of the particles (wetting/dewetting) [1] or even result in their redispersion [2–4].

In order to understand these effects on a molecular level, many research groups develop planar model systems where metal clusters are deposited on oxide single crystals or well ordered thin films (see reviews [5–8]).

In particular, numerous studies have been reported for Pd model catalysts [5–26], and references therein. It has been shown that the structure of Pd particles is altered upon heating. A surface restructuring (faceting) of the Pd

particles seems to occur first, before the sintering sets in. When supported on reducible oxides like TiO₂, annealing may result in an encapsulation of a Pd particle with a TiO_x layer [9,10]. Also, under certain oxidation–reduction conditions at elevated temperatures, a Pd oxide layer can be formed on the particle/support interface, which can reversibly store large amounts of oxygen, as recently shown for the Pd/Fe₃O₄ system [11].

Thermal stability of Pd particles deposited on thin oxide films has been addressed in a number of studies [12–15]. For example, we have previously shown that vacuum sintering of Pd particles on a thin alumina film commences at above 500 K [12]. At higher temperatures, Pd migration into the substrate should be also taken into account [12,15], which was most strongly manifested on an FeO(111) film [13]. Goodman and co-workers reported that Pd on the thin silica film grown on Mo(112) is stable up to 700 K, above which interdiffusion and sintering of the Pd particles takes place [17]. Note that the same group has earlier reported results for a 10-nm thick silica film (later referred

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to as amorphous) grown on Mo(110), where Pd sintering was observed at much lower temperatures according to the Pd dispersion measured by oxygen chemisorption [14].

It is generally believed that sintering occurs via an Ostwald ripening mechanism, whereby a monomer detaches from a smaller island and attaches to a larger island. However, recent DFT calculations of Pd diffusion on the MgO(100) surface [18,19] have predicted a high mobility of small Pd clusters (trimer and tetramer) which diffuse at room temperature even faster than monomers. These results indicate that nucleation, growth and sintering mechanisms on the oxide surfaces are more complex than those typically considered.

Environmental effects on the structure of the model Pd systems were studied to less extent. In our laboratory, we studied the effect of a CO ambient on the growth of Pd particles on an alumina film [15,16]. Data showed that Pd carbonyls form aggregates at 90 K, which decompose on heating above 200 K and transform into metallic Pd particles.

In this Letter, we show that post-adsorption of CO on silica supported small Pd clusters results in strong sintering at temperatures as low as 90 K. The results suggest a high mobility of Pd carbonyl-like species on the silica surface. These effects may provide a tool to vary metal dispersion and size distribution under mild conditions, which cannot be achieved by annealing in vacuum.

The experiments were carried out in an UHV chamber (base pressure below 10^{-10} mbar) equipped with scanning tunneling microscopy (STM), low energy electron diffraction, X-ray photoelectron spectroscopy (XPS) and infrared reflection absorption spectroscopy (IRAS) [20]. The preparation of the silica film on a Mo(112) substrate was described in details in Refs. [20,21]. The film consists of a “monolayer” of corner-sharing $[\text{SiO}_4]$ tetrahedra, where one oxygen is bound to the Mo substrate atoms [21]. The surface is oxygen terminated and essentially inert towards adsorption of many molecules such as CO and water.

When Pd has been deposited at room temperature, we do not observe by STM any preferential nucleation of Pd

on the silica film (Fig. 1). Even at very low Pd coverage (~ 0.01 ML), Pd particles are randomly dispersed on the surface, both on the step edges and terraces. At increasing Pd coverage, the cluster density scales but the average size remains nearly the same (compare profile lines shown as insets in Fig. 1). At further increasing coverage, the particles became larger (Fig. 1c).

At Pd coverage below 0.1 ML, the particles of only 2–4 Å in height were mainly observed by STM. Based on an IRAS study, showing a majority of CO adsorbing on the on-top sites [22], these particles expose a rather disordered surface, in contrast to the well-shaped crystalline Pd particles typically observed on thin alumina and iron oxide films under these conditions [8,12,24]. Room temperature STM images of the samples prepared at 90 K did not show large differences in the morphology as compared to 300 K deposition. Thus, the formation of small Pd particles on the terraces implies a relatively strong interaction with the support and a low diffusivity of Pd species across the surface. Alternatively, there must be point defects from which trapped Pd atoms cannot escape at 300 K.

Very recently, Pacchioni and co-workers have published a DFT study on adsorption of single Pd and Au atoms on this silica film [25]. Their calculations reveal a very low adsorption energy of Pd atom over Si and O sites of the silica film, ca. 0.3 eV (cf. 1.4 eV on MgO(100) [18] and ~ 3.2 eV on an $\text{Al}_2\text{O}_3/\text{Al}(111)$ film [26]), thus indicating a high mobility of the Pd ad-atoms on the silica surface. Therefore, in order to explain our STM results, we have to assume that nucleation occurs on point defects present on the film. On the other hand, STM inspection of the films prior to Pd deposition did not reveal such a high density of the irregularities of the film as one would deduce from the STM image in Fig. 1b assuming that all particles are nucleated at the point defects.

Interestingly, the DFT study mentioned above showed that a Pd atom (in contrast to Au), when placed above the hollow site between the $[\text{SiO}_4]$ tetrahedra, penetrates into the film via a non-activated process and thus become strongly (3.3 eV) bound directly to the Mo surface. This

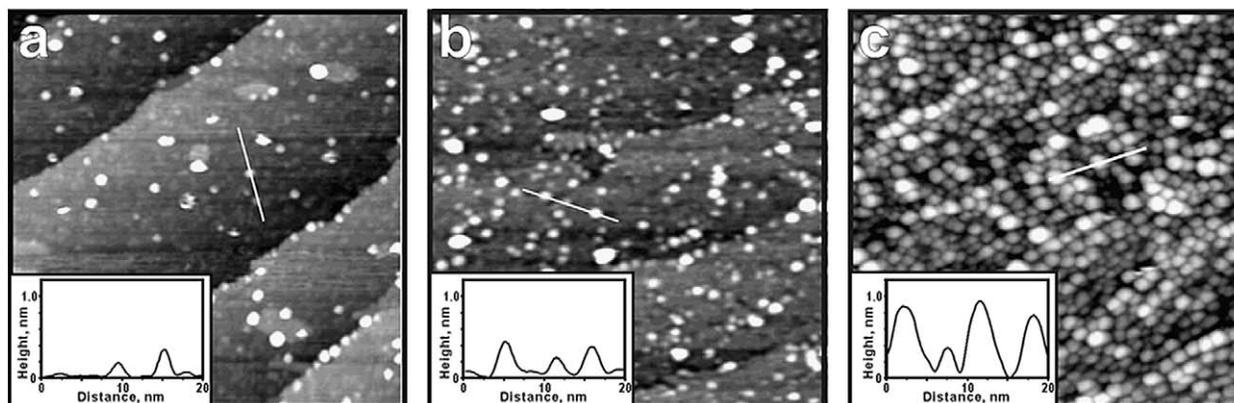


Fig. 1. $80 \times 80 \text{ nm}^2$ STM images of 0.01 ML (a), 0.1 ML (b) and 1 ML (c) of Pd deposited on a silica film at 300 K. Insets show the topography profile along the white lines. Tunneling parameters: $V_s = 2 \text{ V}$, $I = 0.24 \text{ nA}$ (a); $V_s = 4 \text{ V}$, $I = 0.2 \text{ nA}$ (b); $V_s = 2 \text{ V}$, $I = 0.23 \text{ nA}$ (c).

finding brought the authors to the conclusion that Pd nucleation on defect-poor silica films is rather homogeneous. At present, our room temperature STM results cannot verify this mechanism, further STM studies particularly at low temperatures are necessary to prove it.

Adsorption of CO on Pd/silica samples prepared at 300 K did not result in any structural changes detectable by STM or IRAS. The situation changed dramatically when CO was exposed to Pd deposited at 90 K.

Fig. 2 presents STM images of two samples both possessing 0.3 ML of Pd. The sample (a) was prepared at 300 K in vacuum. (Note that the same morphology was observed for the sample prepared at 90 K and heated to 300 K). The sample (b) was prepared at 90 K, then exposed to 20 L CO at 90 K and heated to 300 K (for STM measurements). It is clear that the CO treated Pd particles are much larger (diam = 6 nm and height = 2 nm (b) vs. 3 nm and 0.6 nm (a), respectively) and apparently exhibit a narrower particle size distribution.

In order to monitor the structural changes induced by CO we have employed IRAS. Fig. 3 shows two series of CO IRAS spectra taken for two Pd samples of different coverage (0.01 and 0.3 ML) prepared at 90 K as a function of CO exposure. (It should be mentioned that, in order to better resolve signals coming from the adsorbed molecules, it is convenient in IRAS spectroscopy to present the spectra, which are referenced to a spectrum measured immediately prior to gas exposure). Surprisingly, the CO IRAS spectra (referenced to a clean Pd/silica) revealed not only the signals in the CO stretching region, 1800–2200 cm^{-1} , but also in the low frequency region, 1024 cm^{-1} (in a) and 1046 cm^{-1} (in b), which increase with CO exposure. The latter (low frequency) signals were never observed upon CO adsorption on the samples either prepared at 300 K or prepared at 90 K and then heated to 300 K prior to adsorption at 90 K. Therefore, the effect must be definitely associated with the structure of Pd clusters formed at 90 K.

In order to understand the origin of the low frequency signal, we have to recall that this is the phonon region of the silica film. Fig. 3c shows the IRAS spectra of the clean

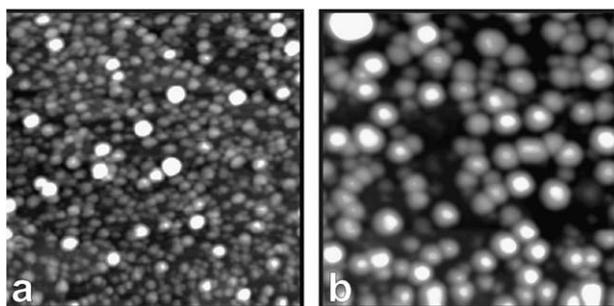


Fig. 2. Room temperature STM images of 0.3 ML Pd deposited on a silica film at 300 K (a) and at 90 K following adsorption of 20 L CO at 90 K (b). (Image size is $80 \times 80 \text{ nm}^2$, $V_s = 1 \text{ V}$, $I = 0.36 \text{ nA}$ (a); $V_s = 3.6 \text{ V}$, $I = 0.11 \text{ nA}$ (b)).

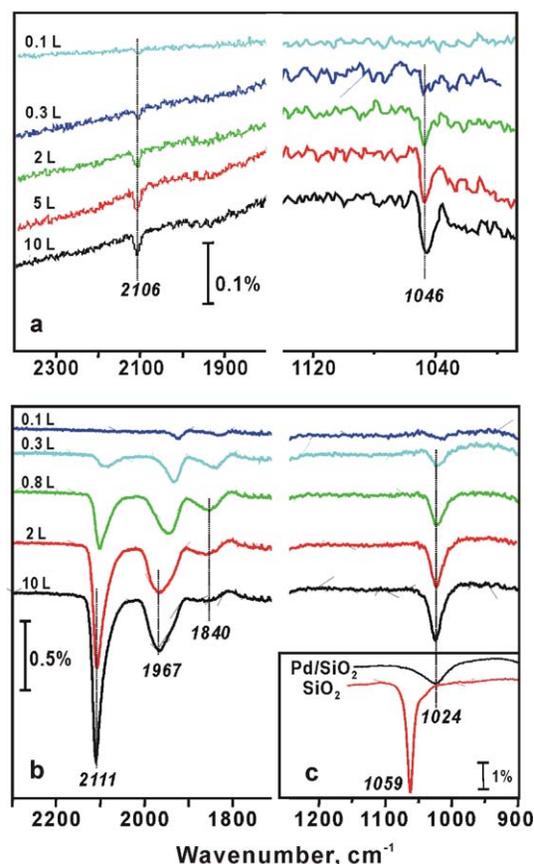


Fig. 3. CO IRAS spectra for two Pd/silica samples of 0.01 ML (a) and 0.3 ML (b) of Pd deposited at 90 K (referenced to a clean Pd/silica). CO was adsorbed at 90 K in amounts as indicated. (c) IRAS spectra of the pristine silica film and of 0.3 ML Pd/silica measured in vacuum and referenced to a clean Mo(112) substrate.

silica and Pd/silica films when referenced to a Mo(112) substrate. The sharp peak at 1059 cm^{-1} has previously been assigned to asymmetric Si–O–Mo vibrations [21]. Metal deposition results in a red-shift of the silica phonon (depending on coverage, to 1024 cm^{-1} in this case) with simultaneous signal broadening. And this is the signal that grows upon CO adsorption, which is more clearly seen in the spectra referenced to a clean Pd/silica as shown in Fig. 3b. Therefore, CO adsorbed on Pd species formed at 90 K actually increases the phonon intensity of the Pd/silica system.

The effects of metal particles on vibrational properties of thin oxide films have been systematically studied by Frank et al. [27]. In particular, Pd deposited on alumina films reduces (non-linearly) the integral intensity, causes a red-shift and broadens the oxide phonon signal at increasing Pd coverage. The analysis performed for different metals (Pd, Rh, Ir, V, Al) and deposition conditions (90 K vs. 300 K) revealed that two properties of the metal overlayer govern the phonon intensity: its reactivity (in other words, the strength of metal-support interaction) mainly at low metal coverage, and its metallicity. Accordingly, CO may partially lift the phonon damping due to weakening of the metal-oxide interaction and thus increase the phonon

intensity. In addition, strong adsorption of CO on Pd reduces the number of conduction electrons and hence metallic screening, which again increases the phonon intensity of the oxide film.

In principle, this approach can be applied to our case, too. However, the CO induced increase of the signal intensity observed in Fig. 3b is about 30% of its original value, i.e., much larger than $\sim 5\%$ observed for Pd on alumina at the same experimental conditions [27]. Note again, that the above effect of CO on Pd/silica is observed only when Pd has been deposited at 90 K and not for the samples prepared at or heated to 300 K. These findings strongly suggest that the effect is inherent to Pd species formed at low temperatures. Therefore, we conclude that vibrational changes must be associated with morphology changes upon CO adsorption as revealed by STM at room temperature (see Fig. 2). It should be mentioned that a two-dimensional metal overlayer must attenuate the substrate modes more efficiently than three-dimensional aggregates. Therefore, sintering of highly dispersed Pd species into the large particles should increase phonon intensity as observed.

Even though we have no STM images of Pd deposits formed at 90 K, it is plausible that these Pd clusters are very small and relatively strongly bound to the silica surface. Since CO is known to strongly adsorb on Pd, it may significantly reduce the interaction with the silica support and thus make the Pd species highly mobile. The diffusing species may sinter upon collisions and form larger aggregates, or they stick to larger particles (particularly, at high Pd coverage) as schematically shown in Fig. 4. As a result, the silica phonon signal attenuated by the highly dispersed Pd species will be partially restored. This mechanism is supported by a good correlation observed between the intensity of the signal at 2106 cm^{-1} , characteristic for metal carbonyls, and the phonon signal at 1046 cm^{-1} as shown in Fig. 3a. Interestingly, no carbonyl-like species are observed in the first CO IRAS spectrum for the 0.3 ML Pd sample while the changes in phonon region already emerge (see Fig. 3b). Instead, CO is found to adsorb on multi-coordinated sites giving rise to the signals between 1900 and 1800 cm^{-1} . This indicates that the growth may also occur via larger clusters like tetramer (trigonal pyramid) on which CO presumably adsorbs in threefold hollow sites. However, further DFT studies remain to be done to elucidate the diffusion mechanism.

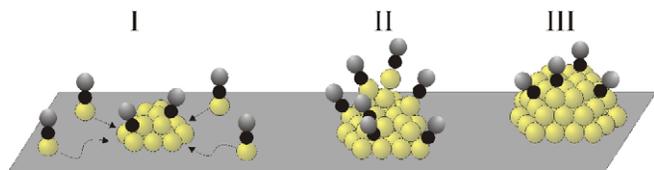


Fig. 4. Schematic of a CO induced growth of Pd particles at 90 K. (I) CO adsorption on Pd species and diffusion of Pd carbonyls, which stick together or to a large immobile particle. (II) Formation of Pd-carbonyls agglomerates, which decompose upon heating to 200 K and transform into metallic Pd particles at 300 K with CO residing in multi-coordinated sites.

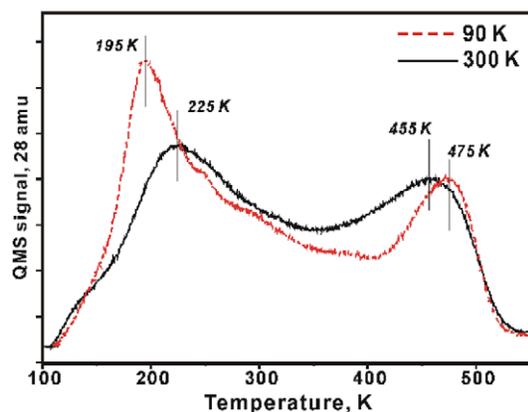


Fig. 5. TPD spectra of 2 L of CO exposed at 90 K to 0.3 ML of Pd deposited on silica film at 90 K and 300 K as indicated. Heating rate is 3 K/s.

Fig. 5 show two CO TPD spectra observed for 0.3 ML of Pd deposited on silica at 90 and 300 K, respectively. The spectra are similar and both show significant amounts of CO desorbing at temperatures below 300 K, that is in line with the IRAS results showing the majority of CO species adsorbing on on-top sites (Fig. 3). The TPD spectrum for Pd deposited at 90 K exhibits a higher intensity at 195 K, which is consistent with the formation of Pd carbonyl agglomerates as suggested above. Indeed, a very strong desorption peak centred at 190 K was previously observed for Pd grown on alumina at 90 K in CO atmosphere in a wide range of Pd coverage [15]. Based on combined TPD, PES and IRAS results [15,16], this desorption peak was assigned to the decomposition of Pd carbonyl agglomerates. Interestingly, in those IRAS experiments, the alumina phonon signal (at 858 cm^{-1}) was strongly attenuated following CO desorption upon heating above 200 K [16]. The effect has been explained by the screening of the alumina phonon upon formation of the large metallic Pd particles due to the decomposition of strongly branched CO saturated Pd-carbonyl like aggregates at 90 K. In contrast to Pd/alumina, the phonon region of the spectra shown on Fig. 3b for the Pd/silica system did not undergo significant changes after heating to 300 K. Therefore, all CO induced morphological changes must have occurred at 90 K during CO exposure.

The TPD spectra presented in Fig. 5 also revealed a significant CO desorption at $\sim 460\text{ K}$ for both samples, typically assigned to CO adsorbing on multi-coordinated sites. This is consistent with our scheme shown in Fig. 4 in that mobile Pd carbonyls species stick to the larger particles, pre-formed during deposition in vacuum at high Pd coverage, rather than form “pure” carbonyls-like aggregates, which would be expected to behave similarly to Pd prepared on alumina in CO ambient, where the signal at 450 K was negligible.

Finally, it should be mentioned that such a strong sintering of Pd observed with CO could not be achieved by annealing in vacuum. Fig. 6 shows STM images of the same

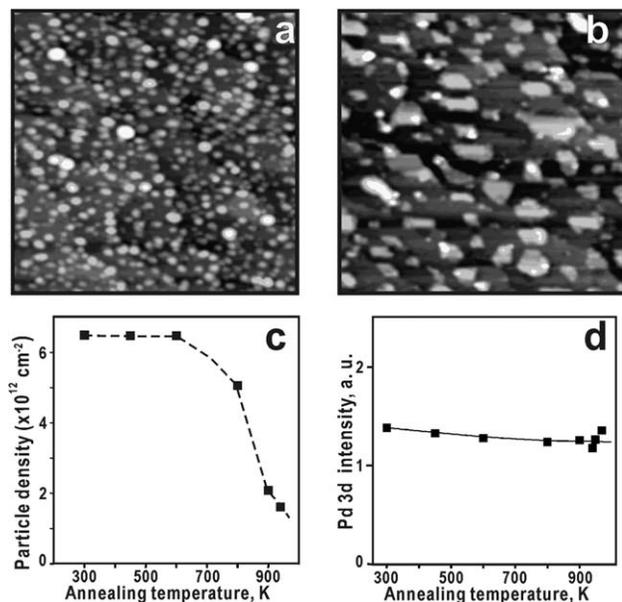


Fig. 6. Room temperature STM images of the same sample imaged in Fig. 2a after vacuum annealing to 600 K (a) and 950 K (b). Particle density (c) and integral area of Pd 3d level in XPS spectra (d) measured upon stepwise heating are shown as a function of annealing temperature.

sample as shown in Fig. 2a annealed to 600 (a) and 950 K (b), respectively. The morphological changes have been observed only above 700 K where the particles become larger and irregularly shaped, while particle density significantly decreases (Fig. 6c). The particles grew up in lateral dimensions without significant increase of particle height, which is still below 1 nm. Since the escape depth of Pd 3d photoelectrons is about 1 nm, the morphology changes do not affect the integral XPS signal (see Fig. 6d). The XPS results also show that Pd remains in the surface region upon high temperature annealing.

However, CO TPD and IRAS experiments revealed a significant drop of CO adsorption capacity, remarkable changes in IRAS spectra, and simultaneous shift of CO desorption maximum from 470 K, typical for the clean Pd surfaces, to ~ 275 K for the samples annealed above 700 K (not shown here). Lowering of CO desorption temperature is well documented for Pd bimetallic surfaces (e.g., see review [28]). In principle, these findings support the conclusion previously reached by Goodman's group on interdiffusion of Pd and silica at elevated temperatures [17]. The nature of this inter-diffusion is not well understood. Note only, that our XPS spectra of Si 2p and Pd 3d core levels did not show any evidence for the formation of Pd-silicides.

In summary, we have observed that CO post-adsorption on small Pd clusters formed at 90 K on ultra-thin silica film induces a strong sintering effect, which occurs at temperatures as low as 90 K. The extent of Pd sintering induced by CO could not be achieved by annealing in vacuum, which in addition causes interdiffusion of Pd and support at elevated temperatures.

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