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Adsorption of Carbon Monoxide on Pd(111) and Palladium Model Catalysts

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The adsorption of carbon monoxide on Pd(111) and SiO_2/Si(100)-supported palladium particles, ranging in size from 1.5 to 9.5 nm, was investigated with ellipsometry. By calibrating the sensitivity of the ellipsometric parameter $\delta\Delta$ for the carbon monoxide coverage on Pd(111) with LEED, ellipsometry could be used for a quantitative analysis of the adsorption isotherms. The saturation coverage of carbon monoxide appeared to be $\approx$0.5 ML on all samples, with respect to the number of surface atoms and within the temperature (400–540 K) and pressure range (up to 1 Pa) studied. The initial isosteric heat of adsorption was 148 ± 5 kJ/mol on all samples. The heat of adsorption decreased with an increasing CO coverage. The decrease of the heat of adsorption with an increasing CO coverage occurred in a similar way on all samples. From these results we conclude that there are no particle size effects with the adsorption of CO on SiO_2/Si(100)-supported palladium particles. Since other studies on the adsorption of CO on palladium model catalysts do find a particle size effect, it is concluded that the particle size effects are dependent on the support or that the observed particle size effect is in fact a support effect. © 1997 Academic Press

1. INTRODUCTION

The adsorption of carbon monoxide on palladium and transition metals in general is one of the most studied topics in surface science. Especially the adsorption of CO on the low index planes has been studied thoroughly (1). In the past decade the adsorption of CO on small particles has also been investigated, although some early studies date back to the late 1970s (2, 3).

At room temperature and above, CO adsorbs on Pd single crystals mainly bridge-bonded. Only on the Pd(111) surface CO adsorbs initially on threefold sites, up to a coverage of 1/3, but at the saturation coverage ($\theta = 0.5$) the CO molecules are bridge-bonded (4). The saturation coverage is 0.5 ML on Pd(111) and Pd(100) and 1 ML on Pd(110) (5, 6). The initial isosteric heat of adsorption (ΔH_{ad}) varies from 142 kJ/mol for Pd(111) to 167 kJ/mol for Pd(110) (7). The initial ΔH_{ad} on other planes like the (100), (210), (112), (311), and (331), lies between the values of the (111) and (110) planes (7–9). Davies and Lambert conclude from their study of the CO adsorption and desorption on Pd(331) and thermally faceted palladium surfaces that CO adsorbs first on the step sites which have a higher binding energy toward CO (9). Only when the step sites are fully occupied does CO adsorb on the close-packed regions of the surface. The same is observed at the stepped Pd(112) surface by Ramsier *et al.* (8). On the contrary the opposite seems to occur on the Pd(510) surface: CO adsorbs initially on the terraces. Svensson *et al.* attribute this difference to the type of steps and terraces on the surfaces (10). On all planes the ΔH_{ad} decreases with increasing coverage (3, 7, 11, 12). Dissociation of carbon monoxide is never observed on palladium single crystal surfaces (1).

On supported palladium particles the adsorption of CO can be influenced by the surface morphology of the particles and the interaction of CO with the support. The adsorption of CO is studied on palladium particles supported on Al_2O_3 (3, 13–15), SiO_2 (16–19), TiO_2 (20), and MgO (14, 21–23). From these studies it is clear that on particles linearly bonded CO is present besides bridge-bonded CO. The ratio between CO in the briding mode and CO in the linear mode decreases with decreasing particle size from about 10 for a dispersion of 0.1 (particle size $\approx$15 nm) to about 2 for a dispersion of 1 (particle size $\leq$1 nm) (16). The linearly bonded CO is most likely present on the corners and edges of the particle. Zilm *et al.* conclude from the absence of motional narrowing in their ^{13}CO NMR spectra that the linearly bonded CO is less mobile and bonded more tightly than bridge-bonded CO (18). In the studies reporting linearly bonded CO the adsorption of CO was performed at room temperature (16–18). Ladas *et al.* (3) found that on small particles ($\leq$5 nm) two adsorption states of carbon monoxide exist. The first state was filled at exposures of a few Langmuirs and had a maximum coverage of 0.5 ML. This state desorbed at temperatures above 400 K. The second adsorption state was filled at higher exposures, resulting in a coverage exceeding 0.5 ML. This state, however, desorbed already at temperatures below 400 K. It is tempting to ascribe the second adsorption state reported by

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Ladas *et al.* to linearly bonded CO, although a low desorption temperature contradicts a tight bonding of this species as reported by Zilm *et al.* (18).

This higher binding energy of linearly bonded CO could be the reason for the particle size effects observed in the adsorption energy of CO. Henry *et al.* reported a rapid increase of the initial ΔH_{ad} with a decrease of the particle size with particles smaller than 4 nm supported on MgO single crystals (22, 23). Chou and Vannice measured the ΔH_{ad} of CO on palladium particles on several catalyst supports (24). They also found an increase of the ΔH_{ad} with particles smaller than ≈4 nm. But we find their graph of ΔH_{ad} versus the particle size somewhat suggestive since the particle size effect disappears if one only compares the results of one support at the time. Ladas *et al.* have measured the ΔH_{ad} on palladium particles supported on α-Al_2O_3, but they did not find a particle size effect in the range of 1.5 to 8 nm, besides the low-temperature adsorption state described earlier (3). In the study presented here we examined palladium particles ranging in size from 1.5 to 9.5 nm at temperatures from 400 to 540 K. Particle size effects were not observed.

Matolín and co-workers concluded from static secondary ion mass spectrometry and temperature-programmed desorption (TPD) measurements that disproportionation of CO takes place on small palladium particles (14, 15, 25). Disproportionation is also reported by Ichikawa *et al.* after CO adsorption at 50 kPa (26). Doering *et al.* observed dissociation of CO during repeated TPD measurements (27). Henry *et al.* attribute these findings to defect sites created by the ion bombardment and the preparation method used (22). Dissociation or disproportionation of CO on palladium particles is not reported by other authors nor found in the work presented here. On smoothly shaped particles the adsorption of CO seems to be completely reversible just as on single crystals.

Another feature of supported particles is the possibility of spillover of CO between the particles and physisorption of CO on the support. The importance of the latter process is demonstrated by Henry *et al.* in a study on CO adsorption on palladium particles supported on MgO (21). Eriksson *et al.* have studied the adsorption and oxidation of CO on palladium supported on SiO_2 (19). They found a sticking coefficient for CO larger than unity on large palladium particles. This was explained by adsorption of CO on the SiO_2 substrate.

The preceding paragraphs show that in the past decade the adsorption of carbon monoxide on supported palladium particles has become a reasonably well-studied topic, but that quantitative measurements of the CO coverage *during* the adsorption are absent. This paper presents an ellipsometry study of the adsorption of CO on palladium particles supported on SiO_2/Si(100). Ellipsometry is an optical technique which makes it possible to monitor processes at the surface in principle at any pressure regime and without the possibility of beam damage or interaction. This makes ellipsometry a very useful technique to study adsorption and reaction kinetics at surfaces.

With ellipsometry the change in the state of polarization of a reflected laser beam is measured. This results in two parameters, called Δ and Ψ. When a species, e.g., CO, is adsorbed on the surface, the optical properties of the surface change and so do Δ and Ψ. The changes in Δ and Ψ are normally denoted as $\delta\Delta$ and $\delta\Psi$, respectively. Calibration experiments on the interaction of several organic and inorganic molecules on metals have shown that especially $\delta\Delta$ is linearly dependent on the coverage of the adsorbing species, even at submonolayer coverages (28, 29). Changes in Ψ are usually small with respect to those of Δ during adsorption experiments and not necessarily linearly dependent on coverage on the surface (28). If the optical constants of a species are known, it is possible to calculate the changes of Δ and Ψ as a function of the coverage. The optical constants of CO adsorbed on metals are not known. Therefore, we must calibrate the sensitivity of Δ and Ψ for the coverage of CO. This is straightforward since the saturation coverage of CO on palladium single crystals is known. This method has successfully been used in studies on the adsorption of CO on Fe(110) (30), Cu(100)–Fe (31), and Ni(111)–Fe (32). The penetration depth of light in metals is several hundred angstrom, much larger than the escape depth of the electrons used in electron spectroscopies. Therefore, ellipsometry can be used to probe a large depth range, but submonolayer sensitivity is also readily obtained (28, 33).

2. METHODS

The experiments were performed in an UHV system equipped with Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), ellipsometry, and an electron beam evaporation source loaded with palladium with a purity of 99.97% (Balzers).

The palladium particles were prepared by evaporating palladium at room temperature onto a commercial Si(100) wafer, followed by calcination in air for 1 h at 773 K, and finally the palladium oxide particles were reduced in 10^{-3} Pa CO at 470 K. The native SiO_2 layer on this wafer is about 2.5 nm thick (34). During the deposition of the palladium the background pressure was kept below 10^{-5} Pa. The flux of palladium was determined using a microbalance thickness monitor. The size of the particles is determined by the amount of palladium evaporated. The shape of the particles is more or less spherical (34), which is expected for metal particles under UHV conditions: the anisotropy in the surface energy for fcc metals is only of the order of a few percent (35). In this study we calculated the particle

TABLE 1

The Particle Sizes as Determined with AES and Some Calculated Characteristics of Such Particles

Pd loading ($\times 10^{15}$ at/cm^2)	d (nm)	Number of particles (μm^{-2})	Number of atoms	Surface atoms	Dispersion
1.3	1.5	97,690	135	92	0.68
2.7	3.0	27,912	959	404	0.42
3.5	3.8	18,026	1,961	684	0.35
5.0	5.4	8,974	5,642	1446	0.26
10	9.5	3,319	30,817	4686	0.15

Note. The characteristics were calculated using bulk lattice positions. A surface atom is defined as an atom with less than 12 neighbors (37).

sizes from AES intensities in a similar way to the particle size can be calculated from XPS intensities. This method has proven to be reliable (34). Five SiO_2/Si(100)-supported samples were used. The palladium loadings and particle sizes as determined with AES are listed in Table 1. The smallest particles studied were 1.5 nm. Smaller particles could only be prepared using very low palladium loadings. Such low palladium loadings do not give enough signal for useful ellipsometry or AES measurements. Therefore, particles smaller than 1.5 nm were not studied.

The Pd(111) single crystal (diameter 5 mm, thickness ≈1 mm) was prepared by routine methods. The crystal was cleaned by exposure to 10^{-3} Pa oxygen at 770 K and Ar ion bombardment. The crystal cleanliness was checked by AES and LEED (36). Of course, exposing the palladium particles to Ar ion bombardment and high temperatures would destroy the particles. Therefore, the particles were cleaned by exposing them to 10^{-3} Pa oxygen at 570 K. The oxygen was removed by means of carbon monoxide exposure. Since the particles do not have a "bulk reservoir" with contaminations this treatment is assumed to be sufficient.

AES and LEED were performed by means of a four-grid retarding field analyzer with an on-axis electron gun. The Auger electron spectra were obtained with a primary beam energy of 2.5 keV and a beam current of 1–3 μA. The spot size was about 0.1 mm. A lock-in-amplifier was used to record the direct spectrum $N(E)$ versus E.

The interaction of carbon monoxide with the samples was monitored during the exposure by means of an ellipsometer using a rotating analyzer. The laser had a wavelength of 632.8 nm and an angle of incidence of 68.25°. Since the sample had to be moved for each type of measurement the Δ and Ψ values scattered with tenths of degrees. However, the changes in Δ and Ψ which occurred when performing ellipsometry with a fixed sample position could be determined with two orders of magnitude greater accuracy. For this reason $\delta\Delta$ and $\delta\Psi$ are used. $\delta\Delta$ and $\delta\Psi$ represent $\Delta^0 - \Delta$ and $\Psi^0 - \Psi$, respectively, where Δ^0 and Ψ^0 are the Δ and Ψ of a clean palladium surface.

The CO isotherms were recorded in the temperature range of 400 to 540 K and with pressures up to 1 Pa. At temperatures above 540 K pressures higher than 1 Pa are needed to measure adsorption isotherms. This could not be performed in our system. At temperatures below 400 K the adsorption CO is very fast and the desorption is very slow. Our ellipsometry setup is not suited for such measurements.

The system was pumped by means of a turbo molecular pump, an ion getter pump, and a titanium sublimation pump. The base pressure of the system was better than 10^{-8} Pa.

3. RESULTS AND DISCUSSION

In Fig. 1 a typical ellipsometry measurement of the interaction of carbon monoxide with Pd(111) is shown. As can be seen the values of $\delta\Delta$ and $\delta\Psi$ are dependent on the CO pressure, i.e., the CO coverage. $\delta\Delta$ increases with increasing CO coverage, while $\delta\Psi$ decreases a little with increasing CO coverage. Measurements on the particles are similar to measurements on the single crystal with one typical difference: $\delta\Psi$ remains almost zero during the adsorption. When the carbon monoxide is evacuated from the system $\delta\Delta$ and $\delta\Psi$ return to zero; the adsorption is completely reversible and dissociation of CO was never observed on any of the samples studied. Measurements on a SiO_2/Si(100) wafer without palladium showed no significant change in $\delta\Delta$ and/or $\delta\Psi$ during CO exposure. It could be possible that $\delta\Delta$ and $\delta\Psi$ are very insensitive for CO adsorbed on SiO_2, but it is more likely that barely any CO adsorbs on the oxide surface at the applied temperatures and pressures.

At a certain pressure the saturation coverage is reached; $\delta\Delta$ and $\delta\Psi$ no longer change with increasing CO pressure. As shown in Table 2 the saturation value of $\delta\Delta$ on the single

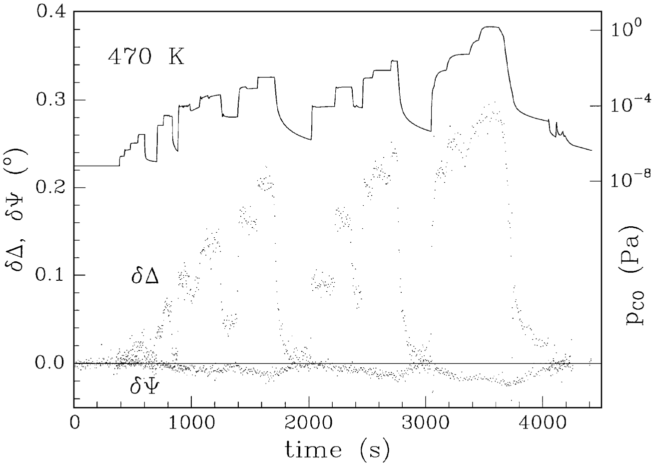

FIG. 1. Ellipsometry measurement of the interaction of carbon monoxide with Pd(111) at 470 K. The CO pressure is given by the solid line. Measurements on the particles are similar except that $\delta\Psi$ remains almost zero during the adsorption.

TABLE 2

The Measured Saturation Values of $\delta\Delta$ for the Different Samples and the Calculated Saturation Values Based on the Number of Surface Atoms and the Surface Areas

d (nm)	$\delta\Delta_{\mathrm{sat}}$	$\delta\Delta_{\mathrm{atoms}}$	$\delta\Delta_{\mathrm{area}}$
1.5	0.16	0.17	0.21
3.0	0.21	0.21	0.23
3.8	0.22	0.23	0.24
5.4	0.29	0.25	0.24
9.5	0.31	0.29	0.27
Pd(111)	0.29	—	—

crystal is ≈0.29° LEED performed during the adsorption of CO on the single crystal showed initially the expected $(\sqrt{3}\times\sqrt{3})$R30° pattern, followed by a weak $c(4\times 2)$ pattern at higher exposures. The latter structure corresponds to a coverage of $\theta = 0.5$ (1). From this it follows that on the single crystal $\delta\Delta = 0.29°$ corresponds with $\theta = 0.5 \equiv 0.765\times 10^{15}$ molecules CO cm^{-2}.

The saturation value of $\delta\Delta$ is dependent on the palladium surface area, as shown in Table 2. The third ($\delta\Delta_{\mathrm{atoms}}$) and fourth ($\delta\Delta_{\mathrm{area}}$) column of Table 2 are calculated saturation values of $\delta\Delta$ using the saturation value of $\delta\Delta$ on Pd(111) as reference and assuming uniformly sized spherical particles with characteristics as listed in Table 1. The $\delta\Delta_{\mathrm{area}}$ values are calculated on the ground of the palladium surface areas relative to the surface area of the single crystal:

$$\delta\Delta_{\mathrm{area}} = 4\pi r^2 \frac{N}{A}\delta\Delta_{\mathrm{sat,Pd(111)}}. \qquad [1]$$

In this equation N represents the number of particles per unit area A of the support and r represents the particle radius. The values calculated with this equation deviate about 10 to 25% from the measured saturation values. This is expected since the particles consist of a rather limited number of atoms and therefore the particles cannot be smooth spheres. Good agreement is obtained when the saturation values are calculated on the ground of the number of surface atoms per particle, as shown in the third column of Table 2. Only the $\delta\Delta_{\mathrm{sat}}$ of the sample with an average particle size of 5.4 nm deviates more than 10% of the calculated value. The reason might be a larger size distribution on this sample.

In the calculation of the saturation coverage we neglected the surface atoms at the particle–support interface, but even with the smallest particles studied ($d = 1.5$ nm) these interface atoms make up less than 10% of the total number of surface atoms. Furthermore, we tacitly made the assumption that the sensitivity of $\delta\Delta$ for the coverage of CO on palladium is independent of the nature of palladium (i.e., single crystal versus supported particles). The good agreement, however, of the calculated values of $\delta\Delta_{\mathrm{sat}}$ with the measured saturation values of $\delta\Delta$ gives confidence in the correctness of this assumption. In addition we should mention that Den Daas *et al.* (33) have shown that the roughness of a thin layer has no influence on the Δ and Ψ of the layer. So we may conclude that on the palladium particles the saturation coverage of carbon monoxide is ≈0.5 ML with respect to the number of surface atoms and within the temperature and pressure range studied. This finding is consistent with the results of Ladas *et al.* (3). They studied the adsorption of CO on palladium particles supported on α-Al$_2$O$_3$ and found at temperatures above 400 K a saturation coverage of ≈0.5 ML on particles with sizes similar to ours.

In Fig. 2 the adsorption isotherms are shown of the sample with an average particle size of 9.5 nm. The isotherms of the single crystal and the other model catalysts are similar to those in Fig. 2. From the adsorption isotherms the isosteric heat of adsorption (ΔH_{ad}) can be determined. The initial ΔH_{ad} is about the same on all samples: 148 ± 5 kJ/mol. The ΔH_{ad} as a function of the coverage is shown in Fig. 3. It seems as if the ΔH_{ad} initially remains constant on the samples with an average particle size of 3.0, 3.8, and 9.5 nm, while on the single crystal and the sample with an average particle size of 5.4 nm ΔH_{ad} starts decreasing directly with increasing coverage. Within the experimental error (±12 kJ/mol), however, the behavior of ΔH_{ad} as a function of coverage is the same for all samples studied.

The almost linear decrease of ΔH_{ad} with the coverage of CO on Pd(111) is not consistent with the results of Conrad *et al.* (7). They found with work function ($\Delta\phi$) measurements on Pd(111) that the ΔH_{ad} remained constant up to a coverage of 0.33 ML, assuming the coverage to be linearly proportional with the work function. Their experimental conditions are not very different from ours and at a first

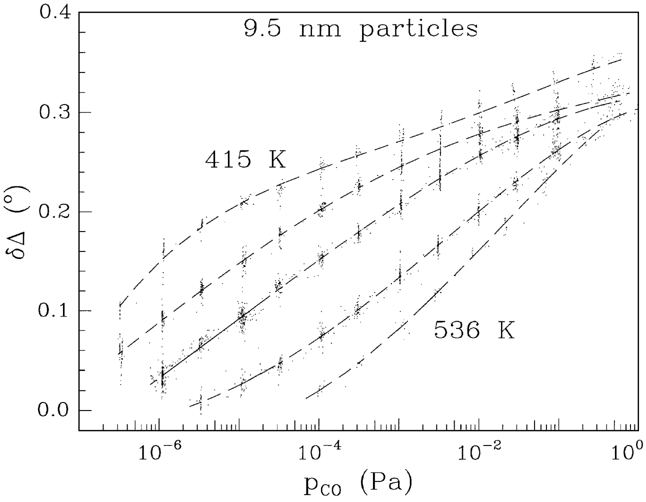

FIG. 2. Adsorption isotherms on the sample with 9.5-nm particles as a function of the CO pressure at different temperatures.

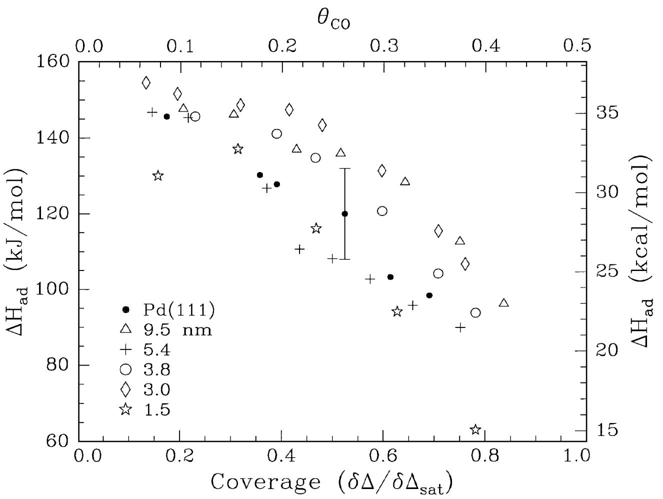

FIG. 3. The isosteric heat of adsorption on the different samples as a function of the CO coverage. The error bar indicates an error of 12 kJ/mol.

glance their adsorption isotherms look no different from ours. On the other hand Kuhn *et al.* found a ΔH_{ad} versus coverage plot identical to ours (11, 12). Probably small amounts of contamination are the cause of such differences in behavior. In addition we believe that if the differences in the dependence of ΔH_{ad} on the coverage between our samples are significant they are probably caused by small, undetectable amounts of contamination. For example, after long exposure to high temperatures it was found occasionally that some sulfur, probably originating from the sample holder, was present on the sample. This resulted only in small changes in the adsorption isotherms and a somewhat lower $\delta\Delta_{sat}$.

One may wonder whether all the differences in the studies on the adsorption of carbon monoxide on palladium surfaces are caused by small contaminations, varying from sample to sample. We believe that this certainly must be taken into account when reviewing the results of Chou and Vannice (24). As stated in the Introduction we do not find the particle size effect as reported by Chou and Vannice convincing . On the other hand the particle size effect in the ΔH_{ad} of CO on Pd/MgO model catalysts as reported by Henry *et al.* does not leave much room for discussion (22). In comparison with our study they measured a "more initial" ΔH_{ad}, i.e., at coverages of ≈ 0. The initial ΔH_{ad} we report is actually the ΔH_{ad} as measured at a CO coverage of about 0.05 to 0.1 ML. The results presented in Fig. 3, however, give no indication of a particle size effect at $\theta = 0$. So if Pd/MgO model catalysts do show a particle size effect and our Pd/SiO_2/Si(100) model catalysts and the Pd/α-Al_2O_3 catalysts of Ladas *et al.* (3) do not, under similar conditions, it is more appropriate to speak of a support effect instead of a particle size effect. Clearly the influence of the support on the adsorption of CO will increase with a decreasing particle size.

4. CONCLUSIONS

Ellipsometry was successfully used to quantitatively study the adsorption of carbon monoxide on Pd(111) and palladium model catalysts. The known saturation coverage of carbon monoxide on Pd(111) was used to calibrate the sensitivity of the ellipsometric parameter $\delta\Delta$ for the amount of adsorbed carbon monoxide on the palladium. The good agreement of the measured saturation coverages on the model catalysts with the calculated saturation coverages supports the assumption that the sensitivity of $\delta\Delta$ for CO on palladium is independent of the morphology of the palladium and the presence of a support, i.e., SiO_2/Si(100).

The initial isosteric heat of adsorption ΔH_{ad} was 148 ± 5 kJ/mol on all samples, decreasing with increasing coverage. There was also no significant difference between the samples, including the single crystal, in the relation between ΔH_{ad} and the carbon monoxide coverage. This leads to the conclusion that there are no particle size effects on the adsorption of CO on SiO_2/Si(100)-supported palladium particles in the particle size range studied. Because other studies of the adsorption of CO on supported palladium particles do find a particle size effect in the heat of adsorption, it is concluded that particle size effects of the adsorption of CO on palladium is dependent on the support or that the observed particle size effect is in fact a support effect solely.

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