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# Poisoning of the adsorption of CO, $O_2$ and $D_2$ on Pt(111) by preadsorbed $H_2O$

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We have measured the influence of adsorbed $H_2O$ on the sticking coefficients and saturation coverages of CO, $O_2$ and $D_2$ on Pt(111) at $\sim$100 K. Strong poisoning is observed for all three gases. For $O_2$ and $D_2$, the surface is essentially totally poisoned at 1 monolayer (ML) water coverage. For CO, the effect is weaker, with some CO adsorption still occurring at 2–3 ML $H_2O$. The influence of these results on the kinetics of the CO and $H_2$ oxidation reactions are discussed briefly. It is concluded that the influence of water must be included in kinetics simulations, at least at low temperatures, when significant humidity levels are present in inlet gas mixtures, or produced by the reactions themselves.

**Keywords:** poisoning, water, CO, $D_2$, $O_2$, saturation coverage, sticking coefficient

## 1. Introduction

Simulations of the kinetics of heterogeneous catalytic reactions is a central subfield of catalysis, motivated both by its purely scientific importance and by its role as a tool in practical catalysis. A central ingredient in the simulations is the coverage dependencies of the sticking coefficients of the relevant participating gas-phase species. Ideally, the latter are only the reactants in the feed gas. In some other, less controlled cases additional gas components, which are unintentionally or inevitably present, may interfere with the ideal reaction kinetics, and/or readsorption of reacting products must be considered. A prominent and important example of the latter is car exhaust cleaning and, more generally, vehicle and industrial emission cleaning by catalytic means, where the oxidizing inlet gas is usually air taken from the ambient, and where the overall feed gas composition is a function of a time varying combustion process.

The specific question, related to the above general problem, that we address experimentally in this letter is how the presence of water vapor, i.e., the humidity of, e.g., inlet air, may affect the kinetics of simple, important catalytic reactions via the influence of water surface coverage on the sticking coefficients of important reactants. The lack of detailed studies of how $H_2O$ influences the kinetics of standard model reactions like CO and $H_2$ oxidation and NO reduction is quite surprising since $H_2O$ is a common gas in reactant gas mixtures. A simple Langmuir-type numerical estimate shows that an inlet gas at 1 atm with 50% humidity at room temperature corresponds to about 15 Torr or 2% $H_2O$, which on a Pt catalyst would produce an (adsorption–desorption) equilibrium surface coverage of $H_2O$ very near unity, i.e., considerable surface poisoning effects may be expected. Another relevant estimate is to use the $H_2O$ concentration in a fully combusted, stoichiometric ($\lambda = 1$) air–fuel mixture, which is about 100 Torr $H_2O$ for a typical gasoline fuel. Also, in the latter case, a catalyst would be exposed to potentially poisoning amounts of $H_2O$, even if entirely dry air were used in the inlet. Obviously, the risk of $H_2O$ interference is successively higher the lower the temperature, since thermal desorption counteracts the self-poisoning. In order to elucidate this problem, we have measured how the sticking coefficients and saturation uptakes of CO, $O_2$ and $H_2$ vary as functions of $H_2O$ coverage on Pt(111). These data demonstrate strong poisoning effects by $H_2O$ both for the sticking coefficients and for the saturation coverages of these gases. They provide important input for future realistic simulations of catalytic reactions involving $H_2O$ in the reactant gas mixtures.

## 2. Experimental

The experiments were performed by thermal desorption spectroscopy in a system described elsewhere [1]. Briefly, the experiments were performed by first dosing the Pt(111) surface with a given amount of $H_2O$, at $T = 110$–150 K (for details, see captions of figures 1–3). The surface coverage of $H_2O$ was determined using the distinct monolayer peak for $H_2O$ on Pt(111) [2], containing $1 \times 10^{15}$ molecules $\mathrm{cm}^{-2}$ at saturation. After the $H_2O$ dosing, the surface was exposed to the gas, X, to be studied (X = CO, $O_2$ or $D_2$). Two different constant doses (exposures) of the X gas were used for each gas (1 and 100 L for CO, 20 and 300 L for $D_2$, and 8 and 300 L for $O_2$). In this way the *relative change* in sticking coefficient versus $H_2O$ coverage was obtained, i.e., the sticking coefficients at different $H_2O$ coverage, normalized to the clean surface value.

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Surface cleanness was controlled by inspection of the TDS spectra for all the gases when adsorbed to completed monolayer coverage. When the TD spectra for all these molecules were highly reproducible and consistent with previously reported desorption studies [2–5], it was concluded that the surface was clean. In addition, the sample had been originally cleaned in a separate system by heating–sputtering cycles and XPS control.

## 3. Results

The results are presented in the following way. The saturation uptake of the studied X gas (Co, $H_2$ or $O_2$) is plotted as a function of water precoverage on Pt(111). The saturation coverage was measured at a constant large exposure, where additional exposure did not change the uptake. In the same graph, the uptake at a constant, much lower X gas exposure is displayed, corresponding to $<50\%$ of the saturation coverage. The former data is a measure of the total density of available adsorption sites for gas X versus water coverage. The latter data is a measure of how the sticking coefficient, averaged over the measured coverage range, varies with water precoverage.

Such results are displayed for CO, $H_2$ and $O_2$ in figures 1–3, respectively. One monolayer of water is defined as corresponding to the saturation of the monolayer peak on Pt(111) ($1 \times 10^{15}$ molecules $\mathrm{cm}^{-2}$) [2].

### *3.1. CO*

The results for CO are shown in figure 1. The decline in the saturation coverage ($\theta_{\mathrm{CO}}^{\mathrm{Sat}}$, closed circles) and average sticking coefficient ($S_{\mathrm{CO}}$, open circles), with increasing $H_2O$ coverage ($\theta_{H_2O}$) are generally strong and monotonic. However, up to about half a monolayer the effect is weak, and then $\theta_{\mathrm{CO}}^{\mathrm{Sat}}$ and $S_{\mathrm{CO}}$ decreases rapidly in the range 0.5–1.5 ML of $H_2O$. In contrast to $H_2$ and $O_2$ (see below), CO poisoning is not complete at 1 ML $H_2O$. The functional form of the decline of $\theta_{\mathrm{CO}}^{\mathrm{Sat}}$ and $S_{\mathrm{CO}}$ with the $\theta_{H_2O}$ suggests that CO may perform an extrinsic precursor motion (i.e., on top of the $H_2O$ monolayer) at low coverage of $H_2O$ before desorbing or finding an unoccupied chemisorption site.

### *3.2. $H_2$ ($D_2$)*

To obtain optimal sensitivity $D_2$ was used in these experiments. The influence of $\theta_{H_2O}$ on $D_2$ adsorption is stronger than for CO. The decreases in $\theta_{D_2}^{\mathrm{Sat}}$ (figure 2, closed circles) and $S_{D_2}$ (figure 2, open circles) with $\theta_{H_2O}$ are nearly linear, with a slightly slower rate at low $\theta_{H_2O}$. At $\theta_{H_2O} = 0.9$ ML, $S_{D_2}$ is not measurable and less than 7% of the clean surface value, and $\theta_{D_2}^{\mathrm{Sat}}$ has decreased nearly an order of magnitude. It appears that 1 ML of $H_2O$ totally poisons the surface with respect to $D_2$ adsorption. The dependence of $S_{D_2}$ on $\theta_{H_2O}$ indicates site blocking by $H_2O$ for $D_2$ adsorption, with a slight indication of an extrinsic precursor-mediated adsorption at low coverage, where the distance between empty sites is not too large.

Since $D_2$ was used in combination with a $H_2O$-covered surface, some information was also obtained about the H–D exchange between the chemisorbed (dissociated) D atoms and water molecules. The total amount of adsorbed $D_2$ deduced from the sum of the integrated areas of the M4 ($D_2$) and M3 (HD) peaks in the TDS mass spectrometer signals. (The M2 ($H_2$) signal was negligibly small.)

The M3 signal provided a measure of the amount of H–D exchange taking place prior to the desorption of the

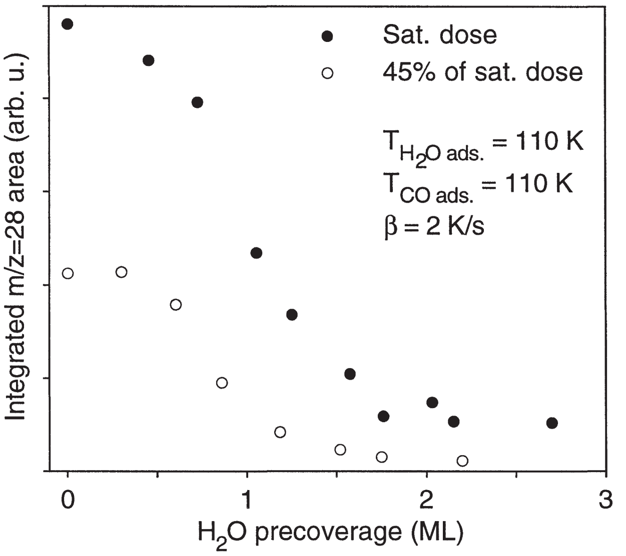

Figure 1. Integrated desorption peak areas (TDS) for CO adsorption on water-precovered Pt(111) as a function of water coverage. CO exposures correspond to saturation coverage (•) and to 45% of saturation coverage (○) on the clean Pt surface. Note the different $H_2O$ coverage scale compared to figures 2 and 3.

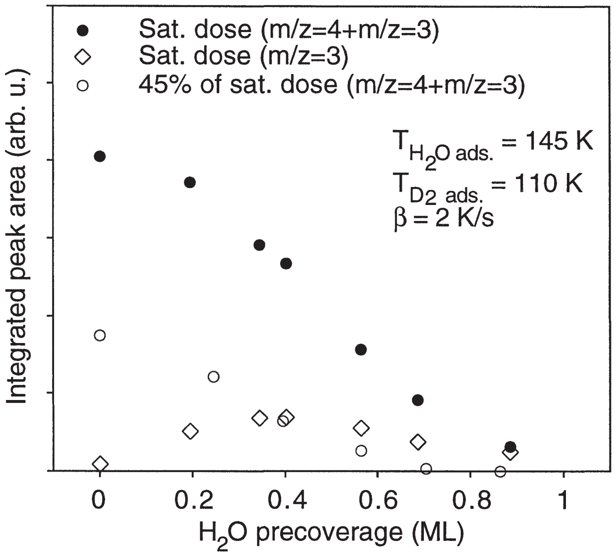

Figure 2. Similar plot as in figure 1 for $D_2$ adsorption on water-precovered Pt(111). The plot shows the result for two different $D_2$ exposures that correspond to saturation coverage (•) and to 45% of saturation coverage (○) on the clean Pt surface. (◇) display the amount of HD adsorption versus $\theta_{H_2O}$ in the experiment corresponding to saturation dose of $D_2$.

water at 150–160 K. (Note that $D_2$ adsorption is fully dissociative on Pt(111) at the present temperatures.) These data are presented by the open diamonds in figure 2, showing the amount of HD desorbing after saturation exposure. At $\theta_{H_2O} = 0$, no HD desorbs, as expected, since there is no $H_2O$ available for H–D exchange. As the water precoverage increases, the absolute amount of desorbing HD increases to a maximum at $\theta_{H_2O} \approx 0.4$ ML and then decreases again. The maximum occurs because the HD production is essentially reflecting the product $\theta_{H_2O}\theta_{D_2}^{Sat}$. The data demonstrate efficient isotopic mixing. No attempt was made to quantify this further.

### 3.3. $O_2$

Before inspecting the $O_2$ results it is important to remind that $O_2$ adsorption on clean Pt(111) at $T < 100$ K is molecular, i.e., non-dissociative. Upon heating the adsorbed $O_2$ molecules undergo a branching reaction, where a certain fraction desorbs molecularly at 150 K, while the remaining fraction dissociates at the same temperature and forms chemisorbed oxygen atoms [3]. The latter desorb associatively around 700 K. The branching ratio, amount of molecular desorption (150 K)/amount of dissociation, depends on the initial oxygen coverage [3]. At saturation coverage, the branching ratio is about 2.4 (i.e., dominating molecular desorption at 150 K). At coverages $\ll$1 ML, the corresponding branching ratio is $<$0.1, i.e., the dissociation channel dominates at low initial $O_2$ coverage.

The results for $O_2$ are shown in figure 3 (a) and (b). From figure 3(a) we conclude that $H_2O$ very effectively poisons both the $O_2$ sticking, $S_{O_2}$ (open circles), and the saturation coverage, $\theta_{O_2}^{Sat}$ (closed circles). The poisoning is in both cases linear with water coverage. At 1 ML $H_2O$, the surface is totally poisoned. The linear poisoning effect indicates a simple site blocking, $S_{O_2} \sim (1 - \theta_{H_2O})$ and $\theta_{O_2}^{Sat}(\theta_{H_2O}) \sim \theta_{O_2}^{Sat}(0)(1 - \theta_{H_2O})$. In contrast to CO and $H_2$, there is no indication of a second layer (extrinsic) precursor channel for adsorption.

Figure 3(b) shows how the water coverage affects the above mentioned branching ratio between molecular desorption and dissociation of $O_2$ at 150 K. The closed circles in figure 3(b) are the same as the closed circles in figure 3(a), i.e., they display the total amount of adsorbed (desorbed) $O_2$, i.e., the sum of direct molecular desorption at 150 K and dissociation followed by desorption at 700 K. The open symbols in figure 3(b) display the two components of $O_2$: the open diamonds correspond to direct molecular desorption and the open triangles to dissociation followed by high-temperature desorption. At low water coverage, molecular desorption dominates. As the water coverage increases and the saturation $O_2$ coverage decreases, the branching ratio changes and the dissociation channel becomes dominating at $\theta_{H_2O} > 0.2$ ML. For the smallest $\theta_{O_2}^{Sat}$ (largest $\theta_{H_2O}$), the branching ratio is 0.2, i.e., close to the branching ratio of $O_2$ on the clean surface, at similar oxygen coverages.

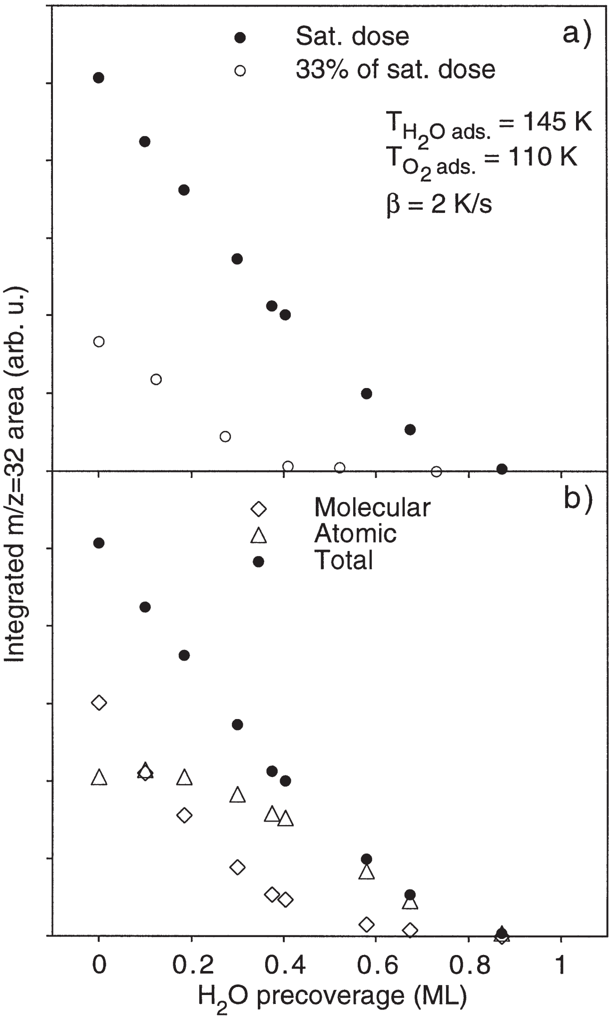

Figure 3. (a) Integrated desorption peak areas for adsorbed $O_2$ on water-covered Pt(111) versus water coverage for two different $O_2$ exposures. The two oxygen exposures correspond to saturation coverage (●) and to 33% of saturation coverage (○) of $O_2$ on the clean Pt surface. (b) The separate contributions from the molecular (◇) and recombinative (△) desorption for the higher $O_2$ dose in (a). This plot also shows the sum of the molecular and recombinative contributions (●) (which is the same result as in (a)).

## 4. Discussion and conclusions

The most interesting and important result is that adsorbed $H_2O$ molecules have a strong influence on both the sticking coefficients and on the saturation coverage of all three studied gases, CO, $D_2$ and $O_2$. Consequently, strong influences by $H_2O$ are expected on the kinetics of reactions involving these gases, when the water coverage on the surface is non-negligible. The present measurements provide quantitative data that can be used in simulations taking such effects into account.

The poisoning effect is largest for $O_2$, almost as strong for $H_2$, and weaker for CO. In the $H_2$ and $O_2$ cases, essentially complete poisoning occurs both for the sticking coefficient and for the saturation coverage at 1 ML $H_2O$ coverage. The saturation coverage of CO is, in contrast, only reduced by about 50% at $\theta_{H_2O} = 1$ ML compared to the clean surface coverage. The sticking coefficient is reduced 4–5 times at the same coverage. Even with 2–3 ML of $H_2O$ there is a significant CO coverage at saturation, but the sticking coefficient is then very low.

This difference between CO and $O_2$, with respect to how $H_2O$ poisons their sticking coefficients, is quite important from a kinetics point of view. The $CO + (1/2)O_2 \rightarrow CO_2$ reaction on Pt(111) is known to be poisoned by CO, which effectively blocks $O_2$ adsorption [6], but $O_2$ does not poison CO adsorption. This and other special features of this reaction gives rise to kinetic phase transitions and bistability with one high-reactive and one low-reactive (CO-poisoned) state [6]. Based on the present results one can predict that significant water coverage will strongly affect these kinetic properties, due to the different influence of $H_2O$ on CO and $O_2$ sticking. Since $O_2$ is more sensitive to $H_2O$ coverage than CO is, one can predict that an $H_2O$ coverage will shift the kinetic phase transitions and bistability regimes to even lower $CO/O_2$ ratios than for pure $CO/O_2$ mixtures. A similar but not so strong influence is expected for the $H_2/O_2$ reaction [6], which will also shift the bistability regime to lower $H_2/O_2$ ratios.

Since the poisoning effect of water is strongest at low temperatures, it will be important for catalytic ignition [7] and light-off in catalytic converters. The influence of $H_2O$ coverage on catalytic ignition will be subject to simulations in a forthcoming publication [8].

One could argue that the present results, obtained at $\sim$100 K, with irreversibly adsorbed $H_2O$ adlayers, are not representative for the situation at catalytic reaction conditions at, say, 300–500 K, where the $H_2O$ adsorption is reversible and essentially represented by an adsorption–desorption equilibrium. Admittedly, there may be some quantitative differences both in the properties of the $H_2O$ adlayer, due to the rapid exchange, and in, e.g., the $O_2$ adsorption behavior, since the latter is exclusively dissociative at these temperatures.

However, the main effects are expected to remain since the water adlayers are still expected to be dominated by H-bonded networks, even at these higher temperatures, just as for the 100 K adlayers. Note that it would be much more difficult to measure the $H_2$, $O_2$, CO sticking coefficients versus $\theta_{H_2O}$ at the 300–500 K conditions, where $H_2O$ partial pressures in the range 1–100 Torr would be required to obtain significant coverages $\sim$0.1–1 ML.

In summary, we have demonstrated strong poisoning effects by $H_2O$ on Pt(111) on the sticking coefficients and saturation coverages of $H_2$, $O_2$ and CO.

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