# Heats of Adsorption of $H_2$ and CO on a Pd/TiO₂ 'S.M.S.I.' (Strong Metal–Support Interaction) Catalyst

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CO and $H_2$ heats of adsorption on Pd/TiO₂ are comparable to or higher than those for typical Pd catalysts indicating that suppressed chemisorption capacity in the strong metal–support interaction state is not because of weakened adsorbate–metal bonds.

We report here what we believe to be the first measurement of heats of adsorption on a catalyst after it is in the 'S.M.S.I.' state, which is obtained after a high temperature reduction in $H_2$.[1]

Since the first reports of suppressed $H_2$ and CO chemisorption on titania-supported group 8 metals[1] and their enhanced specific activity for CO hydrogenation,[2,3] metal/TiO₂ catalysts have received much attention.[4] This suppression of chemisorption has been attributed to a strong metal–support interaction (S.M.S.I.) involving electron transfer from the support to the metal;[5] however, other explanations have since been proposed.[4] This reduced chemisorption capacity has been attributed to a weakened adsorbate–metal interaction,[5] and it has subsequently been assumed that heats of adsorption of $H_2$ and CO are lower on TiO₂-supported metals after such a metal–support interaction. This interpretation, however, has not led to a ready explanation of the higher CO hydrogenation activities which are obtained.

A decrease in chemisorption capacity can be due to either a decrease in the heat of adsorption or a decrease in the number of adsorption sites, or both. Therefore, we embarked on an experimental study to measure directly integral heats of adsorption of CO and $H_2$ on a family of well characterized Pd catalysts which had been shown to exhibit more than a 100-fold variation in methanation turnover frequency.[6]

The 'typical' Pd catalysts (Pd/η-Al₂O₃, Pd/SiO₂, and Pd/SiO₂–Al₂O₃) were given a standard pretreatment involving 1 h reduction in flowing $H_2$ at 673 K whereas the Pd/TiO₂ catalysts were given both a low temperature reduction (L.T.R.) at 448 K and a high temperature reduction (H.T.R.) at 773 K in a flowing gas mixture of 20% $H_2$ and 80% He following the procedure of Tauster *et al.*[1] Energy changes were measured using a modified Perkin-Elmer DSC-2C differential scanning calorimeter, and gas uptakes were measured in a volumetric adsorption system which provided a vacuum of $<1.3 \times 10^{-4}$ Pa. Details of the calorimeter and adsorption systems

and the high purity gases are given elsewhere.[7] For Pd/η-Al₂O₃, Pd/SiO₂ and Pd/SiO₂–Al₂O₃, reduction either at 618 K in flowing $H_2$ or at 673 K in a flowing mixture of 20% $H_2$ and 80% Ar in the calorimeter gave virtually the same results. The reduced and calcined Pd/TiO₂ (L.T.R.) catalyst was treated in 20% $O_2$ at 573 K for 1 h after each CO heat of adsorption measurement to stabilize the sample and to facilitate complete CO removal. The sharp decrease in chemisorption after the H.T.R. step verifies the presence of the 'S.M.S.I.' state. The results are listed in Table 1. Correction has been made for bulk Pd hydride formation in all cases.

Under ultra-high vacuum conditions on Pd films and single crystal surfaces, initial heats of adsorption for $H_2$ have varied from 84 to 147 kJ mol⁻¹ while $\Delta H_{ad}$ values for CO on Pd have normally ranged between 105 and 167 kJ mol⁻¹.[8] The integral $\Delta H_{ad}$ values measured on the typical supported Pd catalysts are very reasonable compared to this range of adsorption enthalpies. The $\Delta H_{ad}$ values for $H_2$ are quite consistent and vary between 88 and 113 kJ mol⁻¹, with the exception of the (L.T.R.) Pd/TiO₂. The higher value for this catalyst may possibly be associated with adsorption on special sites on the titanium or at the Pd–TiO₂ interface. The CO heats of adsorption show less variation and range from 67 to 100 kJ mol⁻¹.

The most important result of this study is that the very low $H_2$ and CO uptakes on TiO₂-supported Pd cannot be associated with weak surface bonding states. Although $\Delta H_{ad}$ values for CO adsorption on the (H.T.R.) Pd/TiO₂ catalyst are somewhat lower, they are comparable to values on Pd dispersed on Al₂O₃ and SiO₂–Al₂O₃, while such $\Delta H_{ad}$ values for $H_2$ are even higher than average. Therefore, the assumption that low heats of adsorption are responsible for low adsorption capacity does not appear justified for Pd/TiO₂ catalysts. These results also indicate that the supports can, to some extent, affect the bonding strengths of chemisorbed $H_2$ and CO. It is not known at this time whether this is due to

**Table 1.** Chemisorption and differential scanning calorimetry (D.S.C.) results for 'typical' Pd catalysts (Pd/η-Al₂O₃, Pd/SiO₂ and Pd/SiO₂–Al₂O₃) and Pd/TiO₂.

| | Chemisorption | | | | | D.S.C. | | | |
| | Pretreatment | | Gas uptake[a] (μmol/g cat.) | | Pd crystallite | Pretreatment | | Heat of adsorption[a] $\Delta H_{ad}$/kJ mol⁻¹ | |
| Catalyst | $T_R$/K | % $H_2$ | $H_2$ | CO | size/nm | $T_R$/K | % $H_2$ | $H_2$ | CO |
|---|---|---|---|---|---|---|---|---|---|
| 1.71% Pd/SiO₂ | 673 | 100 | 10 | 19 | 9.4 | 618 | 100 | 88 | 96 |
| ,, | 673 | 100 | 10 | 19 | 9.4 | 673 | 20 | 113 | 100 |
| 1.95% Pd/SiO₂–Al₂O₃ | 673 | 100 | 28 | 53 | 3.9 | 618 | 100 | 88 | 71 |
| ,, | 673 | 100 | 28 | 53 | 3.9 | 673 | 20 | 92 | 67 |
| 2.0% Pd/Al₂O₃ | 673 | 100 | 26 | 51.1 | 4.1 | 673 | 20 | 105 | 71 |
| 2.03% Pd/TiO₂ (L.T.R.) | 448 | 20 | 28.5 | — | 3.4 | 448 | 20 | 138 | — |
| ,, | 448[b] | 20 | 30 | 64.4 | 3.4 | 448[b] | 20 | 138 | 100 |
| ,,        (H.T.R.) | 773 | 20 | 0.8 | 3.2 | — | 773 | 20 | 109 | 71 |

[a] Determined at an equilibrium pressure of 75 Torr (10 kPa) and 300 K. [b] Calcined in 20% $O_2$ at 573 K prior to reduction.

stabilization of different crystallite planes, creation of different metal–support interface sites, or other causes. However, with these average crystallite sizes, it does not appear to be attributable to alteration of the Fermi level of Pd because of electron transfer. Therefore, we conclude that heats of $H_2$ and CO adsorption are not decreased on $TiO_2$-supported Pd, and that the observed 'S.M.S.I' behaviour, i.e. decreased chemisorption, is principally due to Pd site blockage by migrating $TiO_n$ species[9] rather than any electronic effect.

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