Catalysis Letters Vol. 98, Nos. 2–3, November 2004 (© 2004)

CO spillover and oxidation on Pt/TiO_2

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Received 9 July 2004; accepted 20 July 2004

The adsorption of CO has been measured on a 2.5 wt% Pt/TiO_2 catalyst using TPD. A somewhat surprising observation is that (i) CO_2 is produced, even though oxygen is not dosed into the system, (ii) repeated experiments result in the same amount of CO_2 desorption. The results appear to be due to a combination of factors–(i) is due to spillover of CO from the Pt to the TiO_2 support, while (ii) is due to the diffusion of Ti^{3+} into the bulk of the TiO_2 crystallite, which effectively removes the surface non-stoichiometry which might otherwise be expected.

KEY WORDS: carbon monoxide; CO adsorption; CO oxidation; metal-support interactions; Pt-TiO2; spillover; TPD.

1. Introduction

An important aspect of reactivity in heterogeneous catalysis is the nature of the interaction between the metal particle and the support, since most metal particles are supported on an oxidic material in order to stabilise them and to reduce sintering, and such types of catalyst are widely used in industry and academia. Interactions can be of a number of types, as illustrated in Figure 1, and these can be summarised as follows.

1. *Weak metal-support interactions*. In this case, there is essentially little modification of the inherent reactivity of the metal particle from that which might be expected if it was in the gas phase. However, the mere location of the metal and support adjacent to each other induces several possible new effects

   (a) Periphery Sites. Here the active site is a combined one, that is, the reaction requires both the metal function and the oxide function. Examples of this kind of catalysis are the bifunctional catalysis of alkane reforming [1], which requires the dehydrogenation facility of the metal, combined with the acidity of the alumina support, and photocatalysis where the oxide plays the role of light energy absorber/convertor [2].

   (b) Adsorbate spillover. The rate of a catalytic reaction might be enhanced by spillover of the reactant from one phase to another. A nice example of this is the higher-than-expected reactivity of Pd/Al_2O_3 catalysts highlighted by Boudart, occurring due to the spillover of CO from the support to the metal (often called reverse spillover) [3,4]. This was further highlighted recently for model catalysts of Pd/TiO_2(110), where it was shown that the sticking probability of CO on the catalyst was significantly higher than expected, due to the diffusion of weakly held CO across the support to the metal [5]. Indeed, as a result, the sticking probability of CO on the catalyst was enhanced from the expected value, that is, the cross section for reaction of CO was significantly greater than that of the size of the Pd nanoparticles. It is more common to report spillover from the metal component to the support, and the alkane reforming described above may be a case of this. Very recently this phenomenon has been directly observed *in-situ* at high temperature for the case of oxygen adsorption and spillover on a Pd/TiO_2(110) model catalyst [6]. Note, however, and notwithstanding the previous references in this section, that the vast majority of publications on spillover concern hydrogen mobility [7].

2. *Strong metal-support interactions*. In this case the reactivity of the metal particle is strongly modified by the presence of the support. This can occur in a number of ways, as follows

   (a) Electronic interaction can result in charging of the particle. It must be noted, however, that the extent of charging of a small particle can only be very limited. Nonetheless, such small interactions can result in significant electronic structure modifications. For instance for Pd, which has a nearly filled *d*-band, small increases in electron density can result in much reduced reactivity if the *d*-band becomes completely filled. Further, there can be polarisation of charge within the particle when it is placed on a charge surface and this can strongly affect the reactive properties.

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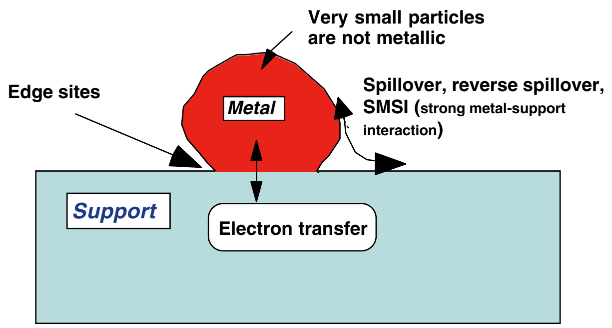

Figure 1. Schematic diagram illustrating the interactions between a metal nanoparticle and a support. All of the effects shown are enhanced as the particle size gets smaller since (i) the number of atoms in the particle is reduced and (ii) there are relatively more atoms at the surface and at the periphery between the support and the metal compared with the total number of metal atoms.

(b) Chemical Exchange. This occurs when atoms exchange between the two materials, especially in the well-known case of SMSI (the strong metal-support interaction) for precious metals on reducible supports. This is reviewed elsewhere [8] and, although several proposals have been put forward to explain the phenomenon, it is widely accepted that cations transfer from the support to the metal and thereby reduce its reactivity. This, in turn, can be viewed as a kind of reverse spillover process–reduced support material decorating the metal particle.

It is obvious that such effects may be crucial in many aspects of heterogeneous catalysis. In this work we report some results for TPD experiments on a Pt-TiO$_2$ catalyst which show that, indeed, the oxygen from the support can certainly participate in CO$_2$ formation via spillover of CO from the Pt to the support.

2. Experimental

TPD was carried out on the catalyst sample held within a UHV chamber. A diffusion pump and a rotary pump evacuated the system to give a base pressure of $< 10^{-9}$. The desorption was monitored with a quadrupole mass spectrometer. The catalyst was made by incipient wetness impregnation, using an aqueous solution of chloroplatinic acid which was impregnated into P25 titania, giving a Pt loading of 2.5 wt%. The solid sample was ground in a mortar, which was thoroughly cleaned before use. The grinding was done slowly to minimise heat induced chemical changes at the newly created surfaces. Approximately 0.1 g of ground catalyst was pressed on to a stainless steel mesh using a mechanical press. The mesh measured 20 mm by 15 mm, with an aperture size of 0.41 mm. Two stainless steel legs were spot welded to two sides of the mesh and this allowed the mesh to be supported at the head of the manipulator arm, which was used to guide the catalyst between the preparation chamber and the main chamber. A thermocouple of cromel–alumel wire was spot welded to the centre of the mesh and a tungsten filament ($é = 0.25$ mm, 99.98% purity) was secured ~2 mm behind the sample to provide the heat source and the heating was carried out using a programmable power supply. Once the catalyst was in the preparation chamber the whole apparatus was baked for 24 h to assist with the lowering of the base pressure after which the sample was heated it to 650 K for 30 min. Such cleaning was repeated before each TPD experiment. The gases used were usually CO (99.9%, Argo) and O$_2$ (99.9% Argo), but an isotopic mixture was used for some experiments, which consisted of 43% $^{16}O_2$ and the remainder is $^{18}O_2$.

3. Results and discussion

Figure 2 shows the desorption results after CO adsorption on Pt/TiO$_2$. CO desorption is fairly broad, but evolves in the approximate temperature range expected for nanoparticles of Pt [9]. Note that no desorption was observed from TiO$_2$ in the absence of the Pt, due to the fact that CO is only bound very weakly on TiO$_2$ (at ~25 kJ mol^{-1} [10]). The breadth of the peak in figure 2 is related to the well-known fact that CO exhibits a broad range of heat of adsorption which is strongly coverage-dependent. From single crystal studies on Pt surfaces this heat varies from ~160 kJ mol^{-1} at low coverage to ~80 kJ mol^{-1} at high coverage [11]. However, what is of more significance in figure 2 is the evolution of CO$_2$ with a peak at ~570 K. This is somewhat surprising since only CO was dosed. Therefore the only possible source of this oxygen is the

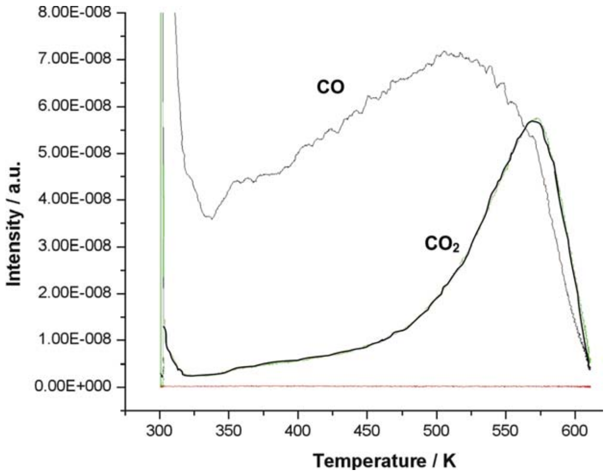

Figure 2. The results of an experiment measuring the product desorption after dosing CO onto the Pt/alumina catalyst surface at ambient temperature. The externally measured CO dose was 0.068 Torr s. The sharp peak observed at the start of the experiment is due to desorption from the heating filament.

support TiO_2. Experiments with titania alone in this machine, or in a reactor, did not produce CO_2 when in the presence of CO in this temperature range. Note that, even though oxygen was not added to the system, the desorption from the Pt/TiO_2 catalyst, upon repeated experiments, remained essentially the same. This is also surprising since the TiO_2 surface is being reduced. However experiments with single crystals have shown that oxygen vacancies do not remain trapped at the surface [12–15] after thermal treatment. The defects exist, in principle, as an oxygen vacancy and two Ti^{3+} ions, but single crystal work has shown that upon annealing, TiO_2 surfaces return to close to stoichiometry and this has been shown to be due to the loss of Ti^{3+} to the bulk of the crystal. Oxygen vacancies appear to first form at step sites and are lost during the overall process of reduction and thermal treatment by the loss of Ti^{3+} to the bulk which is manifested by step retreat [12]. This leaves a near stoichiometric surface, as evidenced by XPS and ion-scattering studies [13,14]. Presumably, if a sufficient number of TPD experiments were carried out, the support TiO_2 would eventually become significantly depleted of oxygen in the bulk, such that the properties of the system would change. However, the overall reduction for the limited number of experiments carried out here was insufficient to cause such an effect; even after 100 desorption experiments of this type, we estimate that only ~0.2% of the oxygen atoms in the titania would have been removed.

It is interesting to note that very high exposures of gas are needed to obtain saturation of the Pt surface with CO (around 0.1 Torr s), compared with that for a Pt single crystal surface, which requires exposures of only ~10^{-5} Torr s [11]. The reasons for this are related to the very different nature of adsorption on a porous catalyst sample, compared to a single crystal, and not to the inherent properties of Pt nanoparticles. Basically the pores of the high area catalyst act as mini-reactors and the gas exposure down the pore is very different from that expected from the measured external pressure, whereas a single crystal experiences the externally-measured pressure. At the beginning of the exposure to gas the internal ends of the pores see no CO because the Pt at the front of the pores have mopped it up by adsorption. This is treated in more detail elsewhere [16], but figure 3 shows examples of what is to be expected. Effectively the pores acts as individual plug-flow reactors, and it takes some considerable time for the plug of gas to reach the ends of the pores. Thus the average exposure to gas within the pore is much lower than the expected exposure determined from the external pressure.

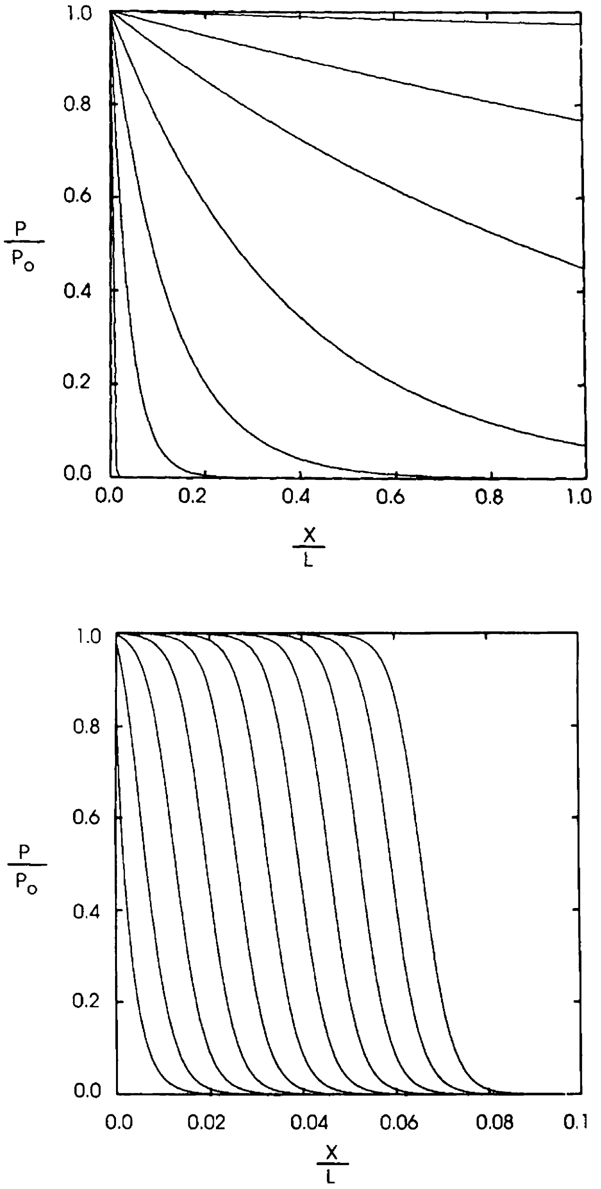

Figure 3. Upper panel: a plot of the pressure drop down the pore length of a catalyst, the pressure is normalised to the external pressure Po, and the position in the pore is normalised to the total pore length. The parameter here is the sticking probability of CO on the active phase (the metal nanoparticles) within the pore. The fraction of the active phase within the pore is 10%, and the input sticking probabilities are (from the lowest curve to the top) 0.17, 0.05, 0.013, 0.004, 0.0013, 0.00013, 0.000013; the important message is, if the sticking probability is high, the pressure drop down the pore is very large. Lower panel: the variation of the pressure down the pore with time of exposure to the gas, the time varying from 0 s for the left curve to 100 s for the right curcve, with steps of 10 s in between and at a pressure Po of 10 Torr. This shows the advance of the plug of gas down the pore as the active phase becomes saturated with adsorbate at the high pressure end of the pore.

Some experiments were carried out using sequential dosing of oxygen and CO, and the results are typified by those shown in figure 4. The CO desorption was very similar in shape to that shown in figure 2, except with somewhat reduced intensity. The CO_2 desorption now looks different from that in figure 1 with significant CO_2 evolution at low temperature. This is typical of what might be expected for *the reduction of oxygen which is adsorbed on Pt*, by adsorbed CO. Although the high temperature CO_2 state is little affected by the amount of

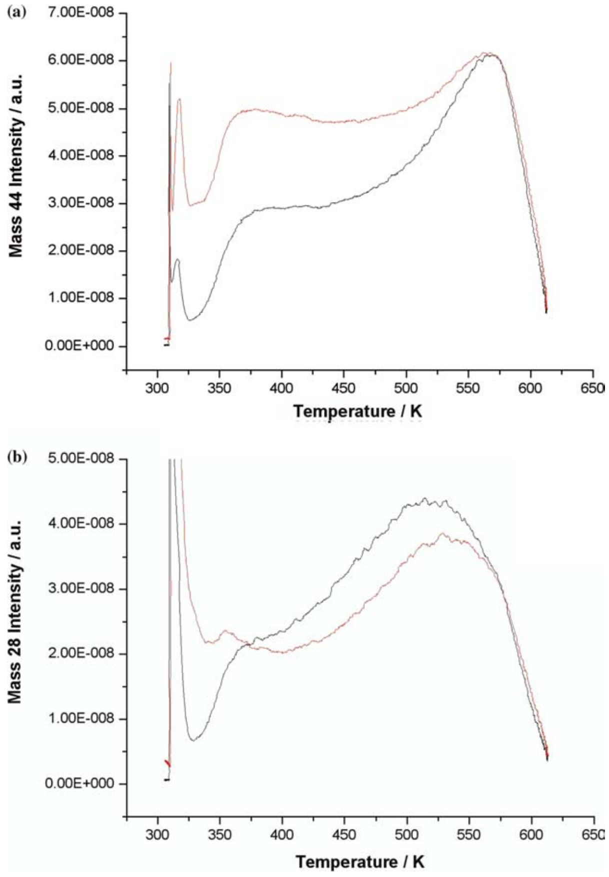

Figure 4. a) CO_2 desorption after dosing 0.068 Torr s of CO onto the catalyst surface for two different pre-exposures to O_2 of 0.011 Torr s and 0.023 Torr s. (b) CO desorption for the same experiments as in figure 4a.

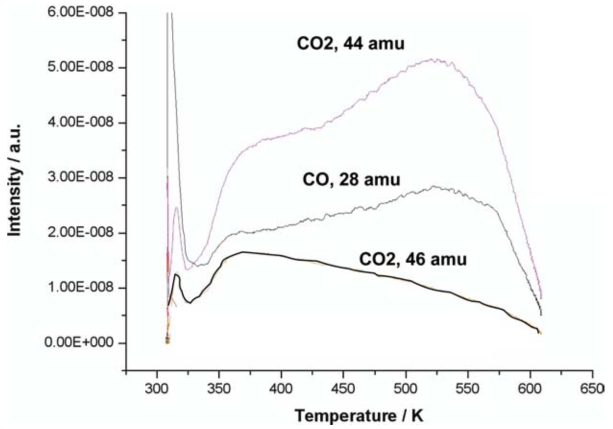

Figure 5. Products during TPD after dosing 0.068 Torr s of CO onto a surface predosed with 0.068 Torr s of the isotopically labelled oxygen mixture.

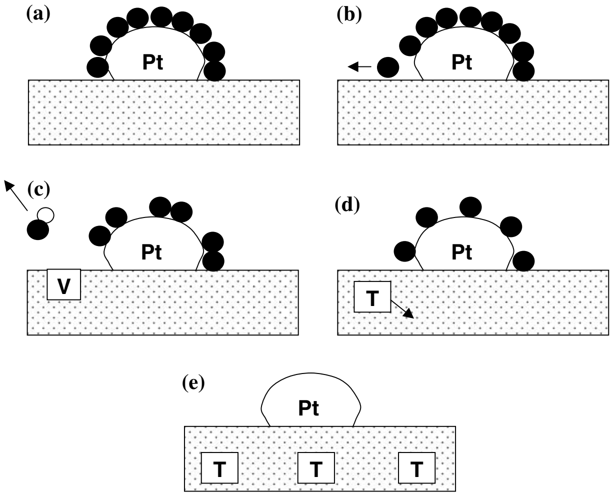

Figure 6. A schematic model of the CO spillover oxidation reaction. Filled circles represent CO, open circles are oxygen atoms. (a) CO is adsorbed on the Pt surface at 320 K, (b) upon heating CO diffuses onto the support and desorbs, (c) upon further heating CO spills onto the support and removes oxygen from the lattice to produce gas phase CO_2, leaving anion vacancies at the surface (labelled V in the figure), (d) the anion vacancies are unstable at the surface due to (i) formation of two Ti^{3+} ions (ii) Ti^{3+} ion diffusion sub-surface, leaving a stoichiometric surface (Ti^{3+} is labelled T in the figure), (e) the final state of the catalyst after TPD.

oxygen which is predosed, the low temperature state increases with the oxygen predose. This again shows that the high temperature state is due to reaction of CO with support oxygen, whereas the low temperature states are due to reaction on the Pt nanoparticles themselves. Experiments with CO predosing merely resulted in much less low temperature CO_2 production because of the well-known effect of CO on poisoning oxygen adsorption on Pt; the results were thus similar to those in figure 2.

Several experiments were carried out with predosing the labelled oxygen mixture described above, and the results of these are shown in figure 5. This shows that the main products from the surface were normal CO, together with unlabelled and labelled CO_2. The unlabelled CO_2 mainly appeared in the high temperature state, while the labelled CO_2 was at low temperatures. This confirms that dosed oxygen adsorbs on the Pt and is reacted off at low temperature, whereas the high temperature state results from reaction with the support. It should be noted however, that labelled CO_2 persists up to the highest temperature, although at much reduced intensity. This could be due to carbonate formation by readsorption of labelled CO_2 produced at low temperature on either Pt or TiO_2 to form a carbonate, which can then decompose again to produce both unlabelled and singly-labelled CO_2.

A summarising model of the reaction is given in figure 6. CO oxidation occurs by spillover of CO, which results in anion vacancy formation on the titania. The electrons are not localised in this hole, but result in Ti^{3+} formation and these diffuse subsurface, probably into interstitial sites, provided the temperature is high enough (higher than $\sim$ 600 K). This reforms the active surface, which can produce CO_2 again in a subsequent dose/TPD experiment.

4. Conclusions

Simple experiments with CO dosing on Pt/TiO$_2$ catalysts have shown that there is a strong reactive interaction between the metal nanoparticles and the support. This results in spillover of CO from the particles onto the support itself where reaction takes place to yield CO$_2$ in the gas phase at high temperatures. Although, in principle, this results in the formation of anion vacancies at the surface of the titania, these are eliminated by the formation of Ti^{3+}, which diffuses into the subsurface region, and leaves a stoichiometric surface which therefore still shows the spillover CO oxidation reaction in subsequent TPD experiments.

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