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Enhanced Activity of Pd/TiO_2 Catalysts for the CO/H_2 Reaction in the Absence of Strong Metal–Support Interactions (SMSI)

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Pd/TiO_2 and Pd/SiO_2 catalysts have been prepared and reduced at different temperatures. The dispersion of the Pd has been determined by adsorption of H_2 and CO, and the catalytic activity has been determined for the hydrogenolysis of ethane and for the CO/H_2 reaction. It is found that the Pd/SiO_2 catalysts, and the Pd/TiO_2 catalyst reduced at low temperatures, exhibit normal chemisorption and catalytic properties. Pd/TiO_2 catalysts reduced at high temperatures have much lower capacity to adsorb H_2 or CO and much lower specific activities for the hydrogenolysis of ethane, which is consistent with the presence of a strong metal–support interaction (SMSI). For the CO/H_2 reaction it is found that all the Pd/TiO_2 catalysts have enhanced activity for the CO/H_2 reaction, irrespective of whether or not strong metal–support interactions are operative. It is concluded that the high activity of titania-supported catalysts in the CO/H_2 reaction is not due to SMSI. Instead it is proposed that the role of the support is to create new active sites at the interface between the metal and the support. These new sites have the capacity to adsorb, or assist in, the adsorption of CO. It is suggested that a similar model may account for the observed effects of other, irreducible, supports, where enhanced activity may also be obtained.

INTRODUCTION

There are now many well-documented examples of catalysts in which the chemisorption and catalytic properties of a metal are altered by changing the support (see Ref. (*1*)). Particularly dramatic effects have been observed when titania or other readily reducible oxides are used as the support (*2–6*). This has led to the suggestion that in such cases there is a strong interaction between the metal particles and the partially reduced support, possibly as a result of electron transfer between the metal and the support.

A characteristic feature of metals in the strong metal–support interaction (SMSI) state is a large decrease in the capacity to adsorb H or CO. Paradoxically, these same metals have enhanced activity for reactions involving CO and H_2. Various suggestions have been put forward to account for this apparent contradiction. In most cases the preferred explanation is in terms of a modification of the electronic properties of the metal particles due to SMSI. However, in the particular case of Ni/TiO_2 catalysts we have shown recently (*7–9*) that an enhanced activity in the CO/H_2 reaction can be obtained under conditions where SMSI are absent. In this case it was concluded that the high activity of Ni/TiO_2 catalysts cannot be due to the type of SMSI defined in the literature. It was suggested instead that the role of the titania was to create new active sites at the interface between the metal particle and the support.

The purpose of the present work is to investigate whether a similar direct intervention of the titania in the CO/H_2 reaction occurs in the case of Pd/TiO_2 catalysts. There is some evidence already in the work of Wang *et al.* (*10*) that this is indeed the case. However, Wang *et al.* appear to have overlooked the possibility that an enhanced activity may occur even in the absence of SMSI.

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EXPERIMENTAL

Catalyst preparation. Catalysts containing 2% Pd (nominal composition by weight) were prepared by wet impregnation of the supports (either silica, Davison type 57, surface area 290 m^2g^{-1}, or titania, Degussa P25, surface area 50 m^2g^{-1}) with a solution of Pd(II) chloride in water. Excess water was removed by rotary evaporation, after which the catalysts were dried in an air oven at 400 K for 16 h.

Catalyst pretreatment. Samples of the dried catalysts were calcined in flowing air *in situ* in a glass microreactor by heating for 1 h at 573 K. Subsequently, the reactor was cooled to room temperature, flushed with hydrogen, and the catalyst reduced by slowly raising the temperature (over a 0.5-h period) to the required reduction temperature, where reduction was continued for different times. The flow rate of hydrogen used for reduction was 3×10^5 cm^3 g Pd^{-1} h^{-1}.

Measurement of ethane hydrogenolysis activity. The activity of the catalysts for the hydrogenolysis of ethane was determined at 673 K. An ethane/hydrogen mixture (10% ethane, B.O.C. special gas) was passed over the heated catalyst (0.2 g) at a flow rate of ethane of 3.0×10^4 cm^3 g Pd^{-1} h^{-1}. Samples of the reaction products were removed from the outlet of the microreactor with a gas syringe after 2, 5, 10, 15, and 20 min from the start of the experiment. The products were separated by gas chromatography using a 3.5-m 20% w/w silicone fluid on Chromosorb P column fitted in a Perkin–Elmer F33 gas chromatograph. Peak areas were determined with an Infotronics 308 electronic integrator.

Measurement of activity in the CO/H_2 reaction. Fresh samples of catalyst (0.2 g) were reduced as described above. The sample was cooled to the reaction temperature, 573 K, and the CO/H_2 mixture (25% CO, B.O.C. special gas) passed over the sample at a flow rate of CO of 3.4×10^4 cm^3 g Pd^{-1} h^{-1}. Samples of the product mixture were removed with a gas syringe, and analyzed by gas chromatography in the normal way.

Chemisorption experiments. The dispersion of the Pd catalysts was determined by measuring the amount of hydrogen or CO adsorbed. For most catalysts the amount of hydrogen adsorbed was determined using a temperature-programmed desorption procedure. The catalysts were reduced at the required temperature, and then cooled to 273 K in a 5% H_2/Ar gas mixture. The sample was heated to 370 K to desorb absorbed hydrogen (*11*), and then heated to the reduction temperature to remove adsorbed hydrogen. The heat of adsorption of hydrogen on Pd is such that even at elevated temperatures not all of the adsorbed hydrogen will desorb into a 5% H_2 stream, so these measurements will tend to underestimate the degree of dispersion to some extent. To check on whether or not this represented a serious problem, the total amount of hydrogen adsorbed on the Pd/TiO_2 catalysts was determined independently using a conventional static volumetric apparatus. Very close agreement between the two techniques indicated that only a small amount of residual hydrogen could be present on the Pd after temperature-programmed desorption.

The adsorption of CO was also measured. For this a pulse method was employed in which pulses of CO were injected over a catalyst which had previously been reduced and then cooled down in hydrogen. This technique is applicable to Pd because CO adsorbs much more strongly than hydrogen and displaces the hydrogen from the surface of the metal (*12*). It has the advantage that the adsorbed hydrogen helps to preserve the cleanliness of the metal surface during the passage of gases over the catalyst prior to the adsorption measurement. This is a potentially serious problem in the context of SMSI since there is evidence that the SMSI state (in which adsorption is suppressed) may be reversed by exposure of the metal to water vapour or oxygen.

TABLE 1

Representative Chemisorption Data for Pd Catalysts

Catalyst	H_s/Pd[a]	H_{ab}/Pd[b]	H_{ad}/Pd[c]	H_b/Pd_b[d]	CO/Pd	CO/H
Pd/Si/473(1)[e]	0.49	0.35	0.14	0.41	0.09	0.64
Pd/Si/573(1)	0.48	0.36	0.12	0.41	0.08	0.67
Pd/Si/773(1)	0.49	0.36	0.13	0.41	0.06	0.46
Pd/Ti/473(1)	0.69	0.25	0.44	0.45	0.35	0.80
Pd/Ti/573(1)	0.60 (0.64)	0.21	0.39	0.34	0.32	0.82
Pd/Ti/673(0.5)	0.53	0.20	0.33	0.30	0.27	0.82
Pd/Ti/773(1)	0.31	0.18	0.13	0.21	0.11	0.85
Pd/Ti/773(16)	0.18 (0.07)	0.10	0.08	0.11	0.08	1.00

[a] Total amount of sorbed hydrogen.

[b] Amount of absorbed hydrogen.

[c] Amount of adsorbed hydrogen.

[d] Ratio of hydrogen absorbed to the number of bulk Pd atoms.

[e] Corresponds to Pd/SiO_2 catalyst reduced at 473 K for 1 h, values in parentheses were obtained using a volumetric method.

RESULTS AND DISCUSSION

The objective of this research has been to determine whether the enhanced activity of titania-supported Pd catalysts for the CO/H_2 reaction is due to the existence of strong metal–support interactions. It has been shown previously (*7–9*) that this is not the case for titania-supported Ni catalysts. The criteria which have been adopted to test for the existence of SMSI are first, the suppression of the adsorption of hydrogen and CO, and second, the suppression of the activity of the catalyst for the hydrogenolysis of ethane.

Adsorption Experiments

Table 1 summarizes some typical adsorption data for the Pd/SiO_2 and Pd/TiO_2 catalysts after reduction at different temperatures and for different lengths of time. For the Pd/SiO_2 catalysts the results show that the dispersion of the Pd is hardly affected by increasing the reduction temperature from 473 to 773 K. Both the hydrogen and the CO adsorption data indicate a fairly low dispersion (about 12%). This is rather less than would normally be expected for Pd/SiO_2 catalysts, and may be due to the method of preparation. In fact, in the present context it is an advantage to have a fairly low dispersion because it is less likely that the data for the silica-supported catalysts will be affected by the support, or by particle size effects, etc. Therefore, these catalysts should give a reliable indication of the properties which are to be expected of a typical metallic Pd catalyst.

The quantity of hydrogen absorbed by the Pd, after correction for surface adsorption, corresponds to the composition $PdH_{0.41}$. Although this value is lower than the value obtained for massive samples of Pd ($PdH_{0.59}$), it is sufficiently close to indicate that the Pd particles on the silica support have typical bulk properties.

For the titania-supported catalysts reduced at temperatures below 673 K, Table 1 shows that the adsorption of hydrogen and CO is high, indicating a well-dispersed catalyst. The quantity of absorbed hydrogen after reduction at 473 K is consistent with the value obtained for the Pd/SiO_2 catalysts. However, as the reduction temperature is increased the quantity of absorbed hydrogen decreases more or less in parallel with the decrease in the dispersion. Since increasing the reduction temperature is unlikely to result in a decrease in the average particle size of the Pd particles the loss of capacity for the absorption of hydrogen cannot be due to a particle size effect. (The presence of adsorbed hydrogen on the surface of a very small Pd particle causes the quantity of absorbed hydrogen to be reduced.) It is possible that the loss of absorption capacity, and the loss of adsorption capacity as the reduction temperature is increased to 773 K (see Table 1) for the titania-supported catalysts are both due to SMSI. Whether this SMSI originates in an electronic interaction with the support or as a result of partial poisoning of the Pd particles by the titania is an open question. However, for our purposes it is sufficient to observe that after reduction at 773 K the Pd/TiO_2 catalysts adsorb only a small amount of hydrogen or CO, and that they have a much lower capacity for absorbing hydrogen. These results are consistent with literature data on the suppression of adsorption, so we assume, therefore, that after high-temperature reduction our catalysts are in the "SMSI-state."

Included also in Table 1 are two results on the adsorption of hydrogen on a Pd/TiO_2 catalyst, measured in a static volumetric apparatus. These experiments were performed for two reasons. First, as a check on the temperature-programmed desorption technique, and second to eliminate possible problems of contamination of the catalyst by small amounts of water or oxygen in the gas streams used in the TPD experiments. The results show that after reduction at 573 K the total amount of hydrogen adsorbed is essentially the same in both cases. However, after reduction at 773 K, the amount of hydrogen adsorbed in the static experiment was significantly lower than in the TPD experiment (0.18 as compared with 0.07).

We believe that this difference is due to the fact that SMSI is reversible. Thus, in a separate experiment, the Pd/TiO_2 catalyst was first reduced at 473 K, cooled in hydrogen, and CO adsorbed using the pulse technique. The same catalyst was then reduced at 773 K for 2 h, cooled in hydrogen, and CO adsorbed. Finally, this catalyst was reheated in hydrogen to 573 K (chosen because this is the temperature at which the CO/H_2 reaction was performed) and 5×2 μl pulses of water were injected over the catalyst. The catalyst was cooled down and the amount of CO adsorbed was determined. Taking the quantity of CO adsorbed by the fresh catalyst reduced at 473 K as 1.00, the quantity of CO adsorbed after reduction at 773 K was 0.36, and after partial regeneration with water vapor at 573 K was 0.64. It would appear that the capacity of the Pd to adsorb CO can be partially restored if the catalyst is exposed to water vapor at the temperature of the CO/H_2 reaction. A similar effect has been noted in the case of ruthenium catalysts (*13*). These results have obvious implications when the role of SMSI in the CO/H_2 reaction is considered.

Ethane Hydrogenolysis Reaction

The hydrogenolysis reaction is very sensitive to small changes in the properties of a catalyst so it is an excellent reaction with which to probe metal–support interactions. Table 2 summarizes our data on the hydrogenolysis of ethane over Pd catalysts at 673

TABLE 2

Activity of Pd Catalysts for the Hydrogenolysis of Ethane at 673 K

Catalyst	Conversion[a] (%)	Specific activity[b]
Pd/Si/673(0.5)	3.62	11.9
Pd/Si/773(3)	3.10	9.44
Pd/Si/773(16)	3.82	11.6
Pd/Ti/673(0.5)	3.85	5.86
Pd/Ti/773(3)	0.15	0.46
Pd/Ti/773(16)	0.07	0.35

[a] Defined as the % ethane converted into methane.

[b] Units are $10^3 \times$ molecules/s/surface Pd atom.

TABLE 3

Activity and Selectivity of Pd Catalysts in the CO/H_2 Reaction at 573 K

Catalyst	Conversion[a] (%)	Specific activity[b]	N_{C1}[c]	Selectivity			
				C1	C2	C3	C4
Pd/Si/573(1)	0.20	1.24	0.89	71.8	11.3	11.1	5.8
Pd/Si/773(3)	0.16	0.91	0.69	75.3	13.4	8.4	2.9
Pd/Ti/473(0.5)	3.38	5.71	5.54	97.1	2.3	0.2	0.2
Pd/Ti/573(1)	3.26	6.20	6.05	97.5	2.1	0.2	0.1
Pd/Ti/773(3)	1.10	6.28	5.82	92.6	6.5	0.8	0.1

[a] Defined as the % of CO converted into all products.

[b] Units are $10^3 \times$ molecules/s/surface Pd atom.

[c] Specific activity for the formation of methane.

K. Because Pd has a low specific activity for hydrogenolysis it was necessary to use a fairly high reaction temperature, and so it was not possible to use very low reduction temperatures with the Pd/TiO_2 catalysts. Nevertheless, the data in Table 2 show that when a Pd/TiO_2 catalyst is reduced for 0.5 h at 673 K it has a specific activity within a factor of 2 of the specific activity of the Pd/SiO_2 catalysts. Sinfelt (*14*) has reported a specific activity for Pd/SiO_2 for the hydrogenolysis of ethane, which when converted into the same units, and when account is taken of the different partial pressures of hydrogen and ethane, corresponds to about 0.025 molecules/s/Pd atom, which agrees well with our value of about 0.012 molecules/s/Pd atom. We conclude that both our Pd/SiO_2 catalysts and our Pd/TiO_2 catalyst reduced at 673 K contain Pd in a normal metallic state, devoid of metal–support interactions.

When the Pd/TiO_2 catalyst is reduced at 773 K, however, there is a marked decrease in activity (see Table 2). Since this loss of activity parallels a loss of chemisorption capacity it seems clear that in both cases this reflects the onset of SMSI when the reduction temperature is raised to 773 K.

CO/H_2 Reaction

Table 3 summarizes our results for the CO/H_2 reaction over Pd catalysts at 573 K. The silica-supported catalysts are significantly less active than the titania-supported catalysts, in agreement with published data. Indeed the agreement with literature data is very close. For our Pd/SiO_2 catalysts we obtain a specific activity for the formation of methane of 0.69–0.89 $\times 10^{-3}$ molecules/s/Pd atom, which may be compared with the range of values of 0.33–1.02 $\times 10^{-3}$ molecules/s/Pd atom calculated from the data of Vannice (*15*). Similarly, our activity data for Pd/TiO_2 lie in the range 5.54–6.05 $\times 10^{-3}$ molecules/s/Pd atom, which compares very favorably with the data obtained by Wang *et al.* (*10*) for Pd/TiO_2 catalysts in the non-SMSI state (9.9–10.5 $\times 10^{-3}$) or in the SMSI state (7.2–10.7 $\times 10^{-3}$ molecules/s/Pd atom). These specific activities are based on the amount of hydrogen adsorbed on fresh samples. Slightly higher activities were obtained by Wang *et al.* when calculations were based on the amount of hydrogen adsorbed on used catalysts.

One point which is immediately obvious, both from the present work and from published data, is that for the CO/H_2 reaction there is little difference between the activity of Pd/TiO_2 catalysts whether they are reduced at low or at high-temperatures. Consequently, unless SMSI is becoming operative even after reduction at low temperatures, it is not correct to attribute the enhanced activity of titania-supported catalysts to strong metal–support interactions.

The chemisorption data and the activity data for the hydrogenolysis of ethane obtained in this work show that when the reduction temperature is maintained below about 673 K the Pd retains characteristic metallic properties. There is no evidence to suggest that the Pd is modified by interaction with the titania support. Moreover, in many other cases, there is general agreement that SMSI do not become apparent until the reduction temperature is raised above the temperature at which titania itself begins to reduce, i.e., above 573 K. Thus, the fact that our Pd/TiO_2 catalyst reduced for 0.5 h at 473 K already shows enhanced activity for the CO/H_2 reaction, while at the same time exhibiting normal adsorption and hydrogenolysis properties, shows that the enhanced activity cannot be attributed to a strong metal–support interaction. Some form of interaction with the support cannot, of course, be ruled out, but this cannot be of the type suggested in the literature. A weak metal–support interaction may operate and this may be sufficient to affect the activity of Pd for the CO/H_2 reaction but not affect either the adsorption or hydrogenolysis properties. However, it would seem more reasonable to conclude that the metal is not altered at all by interaction with the support. In this case the titania may be directly involved in the catalytic reaction. Some ways in which this could happen are considered below.

The Role of Titania in the CO/H_2 Reaction

The intense recent interest in titania-supported catalysts has tended to disguise the fact that enhanced activity in the CO/H_2 reaction over Pd catalysts is observed with other supports, some of which are not reducible. For example, when Al_2O_3 (*16*), ZrO_2 (*17*), La_2O_3 (*17*), or Nd_2O_3 (*18*) are used as supports the activity is significantly larger than when SiO_2 is used or when Pd is used in an unsupported form. Consequently, when examining the role of titania in the CO/H_2 reaction it is important to consider whether a common explanation may be devised which will apply also to these other supports. Most recently, workers have assumed that the metal catalyzes the reduction of the titania, and that this is followed by a strong, direct interaction between metal particles and exposed Ti^{3+} ions in the surface of the support. The alteration in the catalytic and chemisorptive properties of the metal are assumed to be due to electronic interactions in which electrons are transferred from the Ti^{3+} to the metal.

The results obtained in the present work for Pd/TiO_2 catalysts, and previously for Ni/TiO_2 catalysts (*7–9*), cast doubt on the validity of this particular interpretation. Our data show that the enhanced activity in the CO/H_2 reaction can occur under conditions where the titania is not reduced, and where there is no evidence for the existence of SMSI. Consequently, it is necessary to consider alternative ways in which the titania, and also other supports, may affect catalytic activity.

In the case of Ni/TiO_2 catalysts we have suggested previously (*7–9*) that the enhanced activity for the CO/H_2 reaction may arise because of the creation of new active sites at the interface between the metal and the reduced support. These interfacial metal–support interactions (IMSI) do not require that the properties of the metallic particles are in any way different from those of normal particles. Instead, the proposal is that the support acts directly in the catalytic process by adsorbing, or assisting in the adsorption, of CO. The active site in the case of titania is assumed to be a Ti^{3+} cation exposed in the surface of the support, adjacent to a normal metal particle.

Recently Poels *et al.* (*18, 19*) have suggested that in Pd/SiO_2 catalysts the formation of methanol may involve Pd ions stabilised in the surface of the silica. Actually Pd black also can produce methanol with high selectivity (*17*), so Pd ions may not be essential for methanol synthesis. Nevertheless, the work of Poels *et al.* indicates a possibility that metal ions can contribute to the activity of catalysts for the CO/H_2 reaction. We would differ from Poels *et al.* only in suggesting that, when oxides such as titania are used, it is the ions of the support itself rather than ions from the metal which are involved.

A similar effect may operate in the case of alumina. Thus, Palazov *et al.* (*20*) have shown by infrared spectroscopy that methoxy and formate-type groups are adsorbed on pure alumina after exposure to a CO/H_2 mixture. These adsorbed species were formed even in the absence of Pd; when Pd was present similar adsorbed species were observed, but they could be formed at lower temperatures. Palazov *et al.* suggested that at low temperatures CH_xO species were formed on the Pd metal particles and then spilled over to the support where they were trapped. On raising the temperature they observed a decrease in the intensity of the infrared bands which they took to be indicative of reverse spillover from alumina to Pd, where decomposition to form methane took place.

In summary, the evidence presently available suggests that a number of different supports can be directly involved in the CO/H_2 reaction. Providing the support has exposed cations which are able to adsorb CH_xO species, then such oxygenated species may be formed as intermediates either in the formation of methanol or of methane. Whether CH_xO species are formed first on the metal and then transferred to the support, or are formed initially on the support and transferred to the metal, is an open question. In any case it would seem likely that the relative stability of CH_xO adsorbed species on the support or on the Pd would be very sensitive to the temperature of the experiment. When methane is formed as the major product it is not clear whether this would be formed by hydrogenation of CH_xO species on the Pd, or by decomposition of CH_3OH on the support. The latter possibility has been noted by Ryndin *et al.* (*17*) who have pointed out that there is evidence that CH_3OH will decompose over the rutile form of titania at 523 K to give methane and coke (*21*). In the presence of Pd, which could provide spillover hydrogen, it is easy to envisage that the coke would be hydrogenated to methane.

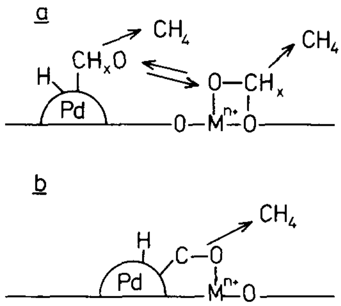

FIG. 1. Proposed reaction scheme for the formation of methane over supported Pd catalysts.

Fajula *et al.* (*22*) have presented evidence also that the support may be directly involved in the formation of methane over Pd/SiO_2 catalysts. Thus, they have observed that the rate of formation of methane is related to the acidity of the support, and have postulated that methanation mainly proceeds through direct hydrogenation of CO adsorbed on acidic sites on the support. In view of the work of Poels *et al.* (*18, 19*) on Pd/SiO_2 catalysts, which suggested that the active ions were Pd ions, it is possible that the acidity effect observed by Fajula *et al.* may arise because of a tendency for the Pd to interact to different extents with different types of silica.

Figure 1 shows a reaction scheme which would appear to account for the information presently available on the role of different supports in the CO/H_2 reaction over Pd catalysts. A similar idea has been suggested by Bell (*23*) and by Ichikawa (*24*). In Fig. 1, M^{n+} represents a metal ion which depending on circumstances and on the nature of the support could be an ion of the support (e.g., Al^{3+}, Ti^{3+}, Zr^{4+}, Si^{4+}, etc.) or an ion from the active metal (Pd^{n+}). The only criterion which the "active" ion must satisfy is that it is capable either of adsorbing or assisting in the adsorption of CO or of a CH_xO intermediate. For obvious practical reasons it would be anticipated that ions in the support adjacent to a metal particle would contribute most to any dual site process. Thus, just as previously suggested for Ni/TiO_2 catalysts (*7–9*), we propose that much of the enhanced activity of supported metal catalysts for the CO/H_2 reaction originates in the creation of new active sites at the interface between the metal and the support. Figure 1b indicates a possible situation in which the metal and support act in concert to dissociate the CO molecule. At present there is no way of differentiating between the possible processes indicated in Figs. 1a and b. As an extension of this basic idea, it would be very interesting to know whether supports, which had been deliberately doped with metal ions which are known to have some tendency to adsorb CO or CH_xO species, would exhibit high activity in the CO/H_2 reaction. Work on this subject is currently being undertaken in this laboratory.

CONCLUSIONS

The main conclusions of this work are as follows.

1. The enhanced activity of titania-supported Pd catalysts is not due to SMSI. High specific activity can be observed in catalysts for which there is no evidence that SMSI exist.

2. The main role of the support is to present active sites which can adsorb, or assist in the adsorption, of CO or CH_xO intermediates. For practical reasons, it is suggested that the interface between the metal particles and the support should be a region of special catalytic significance.

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