Enhancement of hydrogen spillover by surface labile oxygen species on oxidized Pt/TiO_2 catalyst

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TPD, H_2–O_2 titration and TPR techniques have been used to study the effect of the surface oxygen species on hydrogen adsorption in an oxidized Pt/TiO_2 catalyst system. Oxygen desorption peaks in the temperature range of 610–730 K were observed in the O_2-TPD profiles of the Pt/TiO_2 samples oxidized in oxygen at temperatures 573, 673 and 773 K, respectively. They reveal that labile oxygen species were formed on the surfaces of these oxidized catalysts. Much more hydrogen spillover on the oxidized Pt/TiO_2 catalysts was observed at room temperature using H_2–O_2 titration. The results from TPR and H_2-TPD experiments further support the proposal that the existence of labile oxygen species enhances hydrogen spillover in the system studied.

Keywords: oxidized Pt/TiO_2 catalyst; surface labile oxygen species; hydrogen spillover

1. Introduction

Titania supported platinum catalyst in a reduced state has been extensively studied since Tauster et al. reported in 1978 that Pt/TiO_2 catalyst reduced at high temperature exhibits a strong metal–support interaction (SMSI) [1–3]. Unfortunately, relatively fewer studies have been made on the Pt/TiO_2 catalyst in an oxidized state. Belton et al. [4] have compared the capacities of adsorbing hydrogen and CO on Pt supported on fully oxidized and partially reduced TiO_2. They found that there is less chemisorption of both H_2 and CO on the reduced TiO_2 supported Pt as compared to the sample using oxidized TiO_2 as the carrier. Baker et al. [5,6] examined the effects of high temperature (873 K) oxidation on the morphology of the platinum particles in the Pt/TiO_2 system. This treatment converts Pt particles to much larger and thick hemispherical aggregates, and particularly destroys the SMSI state as evidenced by a return to normal chemisorption properties. From the point of view of basic research, the chemical features of the oxidized Pt/TiO_2 cat-

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alyst give rise to considerable scientific interest. Much attention needs to be focused on the Pt/TiO_2 catalyst in an oxidized state.

It is well known that the TiO_2 carrier will not adsorb hydrogen and be reduced in the presence of elemental hydrogen below 473 K [7–9]. But in the presence of atomic hydrogen produced by a noble metal, hydrogen adsorption on TiO_2 accompanied by reduction of Ti^{4+} to Ti^{3+} can occur even at room temperature [10]. This is due to that hydrogen dissociatively adsorbed on the noble metal can migrate onto the supporting oxide, known as hydrogen spillover (Hso) [11–14]. The phenomenon of hydrogen spillover from a noble metal to a transition metal oxide such as TiO_2, MoO_3, WO_3, V_2O_5 has been known for quite some time [15–18]. A number of studies have demonstrated that surface states involving the final metal crystallite size and morphology, adsorbed species such as water and alcohols, and residual ions from catalyst preparation on some occasions greatly influence the hydrogen spillover [11,15]. On the other hand, hydrogen spillover also plays an important role of modifying the surface states of the catalyst in H_2-treatment as well as in the reaction using hydrogen as one of the reactants [19,20]. Study of hydrogen spillover is still one of the attractive objects in heterogeneous catalysis. In the study of Pt/TiO_2 catalyst, it is also known that the TiO_2 carrier can take up significant quantities of hydrogen through hydrogen spillover in the reduction process [21–23]. However, the influence of the surface state on hydrogen spillover is not completely understood for Pt/TiO_2 catalyst. In the present study, attention has been concentrated on the oxidized Pt/TiO_2 catalyst. O_2-TPD was used to examine the surface oxygen species, and its role in hydrogen spillover is further investigated by H_2–O_2 titration, TPR and H_2-TPD techniques.

2. Experimental

2.1. CATALYSTS

The 1.0 wt% Pt/TiO_2 catalyst was prepared by the photodeposition method [24,25]. 5.00 g TiO_2 powder (S_{BET} = 10.6 m^2/g) was impregnated in the solution of $H_2PtCl_6 \cdot 6H_2O$, with subsequent addition of 10 ml ethanol (99%) as the reducing agent. A photo-induced reaction was carried out by a 400 W mercury lamp for 45 min. During this procedure, the brown solution changed to colourless, while the white TiO_2 changed to grey, indicating reduction of Pt ions in the complex contained in the solution to metal supported on TiO_2. Then the resultant Pt/TiO_2 powder was washed by deionized water until the Cl^- ions could not be detected by the $AgNO_3$ solution. The fresh catalyst was obtained by drying of the wet catalyst at 393 K overnight without further calcination. Under different pretreatments, two kinds of Pt/TiO_2 catalyst samples were prepared, denoted as PA and PB, respectively. PA is obtained by oxidation of the fresh Pt/TiO_2 catalyst in oxygen at 573 K for 1 h; and PB is obtained by a TPD run of the PA sample in argon to 673 K,

then maintained at this temperature for 5 min. Also pure TiO_2 and a mechanical mixture of Pt-black and TiO_2 were illuminated in the same way as Pt/TiO_2 without introduction of the $H_2PtCl_6 \cdot 6H_2O$ solution.

2.2. TPD AND TPR

A series of experiments such as temperature-programmed desorption (TPD) and temperature-programmed reduction (TPR) were carried out in a multiple function gas handling system. 0.500 g fresh catalyst sieved between 0.9 and 1.5 mm was used in each experiment. Ar and 5% H_2–Ar were chosen as the carrier gases with gas flow of 25 cm^3/min in both TPD and TPR experiments. In the case of TPD, the thermal conductivity detector (TCD) signal observed is due to appearance of oxygen or hydrogen in the Ar flow, which was analyzed by another TCD equipped with a column filled with 5A molecular sieve. In TPR, a positive TCD signal will be attributed to a decrease of hydrogen content in the H_2–Ar gas flow and a negative TCD signal to an increase of hydrogen content. Between the reactor and thermal conductivity detector, a cold trap immersed in a paste of ethanol and solid CO_2 was used to remove H_2O. The temperature program was controlled to a linear rate of 10 K/min for both TPD and TPR procedures.

2.3. H_2–O_2 TITRATION

H_2–O_2 titration was measured on a flow apparatus with Ar as the carrier gas at a flow rate of 25 cm^3/min. 0.500–1.000 g fresh catalyst was oxidized in flowing oxygen at different temperatures for 1 h, then cooled to room temperature in flowing oxygen. The oxidized catalyst was purged with argon at 298 K for 1 h, then the hydrogen and oxygen uptakes were made by the addition, at 2.5 min intervals, of hydrogen or oxygen in the amount of 0.134 cm^3 (STP) into the carrier gas just upstream of the catalyst. The hydrogen or oxygen signal was monitored by a thermal conductivity detector. Saturation of the catalyst was indicated when the effluent H_2 or O_2 peaks increased to a constant size, and the total uptake was calculated. A few hydrogen–oxygen cycles at room temperature smoothed or homogenized the surface and reproducible results in the titration were obtained similar to the previous study reported by Menon and his coworkers [26,27]. In the present study, only the hydrogen and oxygen uptakes in the first and final cycles (denoted as HT_1, OT_1, HT_f, and OT_f, respectively) are listed in the tables.

2.4. GASES

Commercial Ar, H_2 and 5% H_2–Ar gases were further purified by allowing the gases to flow over two cartridges filled with 5A molecular sieve and 401-deoxygen catalyst respectively. Commercial oxygen was further purified by passing through at Pd/TiO_2 catalyst and 5A molecular sieve.

3. Results and discussion

3.1. O_2-TPD

TPD profiles of the Pt/TiO_2 samples oxidized in oxygen at 573, 673 and 773 K, separately, are shown in fig. 1. One desorption peak was observed at 630, 668 and 710 K respectively, and identified to be molecular oxygen by analyzing the effluent gas. These results indicate that some oxygen species are present on these oxidized catalysts, and labile in the sense that each species was desorbed at a different temperature when the catalyst samples were oxidized at different temperatures. The peak intensity of the desorbed oxygen for the oxidized Pt/TiO_2 sample at 673 K is the largest, and the peak position shifts upwards with the oxidation temperature.

In order to find out how these labile oxygen species were formed, complementary experiments were done. Herein, two reference samples of pure TiO_2 and a $Pt + TiO_2$ mixture oxidized at 573 K were used. Much smaller peaks of oxygen desorption were found in their O_2-TPD profiles (fig. 1, d, e) compared with the results of fig. 1 a, b and c. So the formation of the labile oxygen species as detected in fig. 1 a, b and c cannot be ascribed to Pt and TiO_2 individually. Rather, it seems that the formation of the labile oxygen species depends on the mutual function of Pt and TiO_2 in the Pt/TiO_2 catalysts. In addition, when the PA sample (the fresh Pt/TiO_2 sample oxidized at 573 K for 1 h) proceeded a TPD to 673 K, and maintained at this temperature for 5 min (the resultant sample is designated as PB), no oxygen desorption was observed in the subsequent TPD run indicating that the

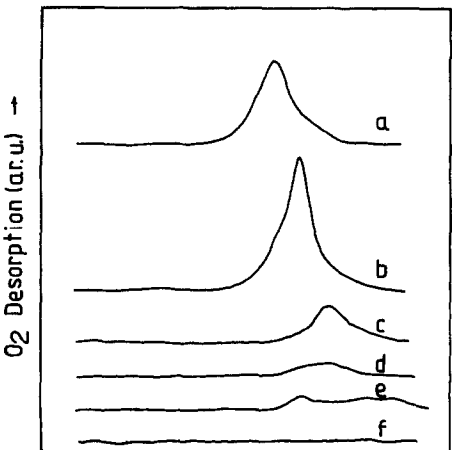

Fig. 1. O_2-TPD profiles of the Pt/TiO_2 samples pretreated in oxygen at (a) 573 K (PA sample), (b) 673 K and (c) 773 K for 1 h respectively; (d) TiO_2, (e) a mechanical mixture of Pt-black and TiO_2 and (f) the PB sample oxidized at 573 K for 1 h.

labile oxygen species or its precursor has been completely removed from the PB sample. If the PB sample was further reoxidized in oxygen at 573 K for 1 h, its TPD profile showed hardly any oxygen desorption as depicted in fig. 1 f. This demonstrates that the labile oxygen species desorbed in the TPD run could not be restored by reoxidation.

From the above facts, it appeals that the labile oxygen species is closely related to the procedures of catalyst preparation and oxidation. It is well known that the Pt/TiO_2 catalyst is a good catalyst for photo-decomposition of water to produce active hydrogen and oxygen species (H_a and O_a) adsorbed on the surface [28]. If the amount of adsorbed hydrogen is more than $2O_a$, the TCD signal will give hydrogen desorption during the TPD run. Indeed, we have seen that a large amount of hydrogen desorbs from the fresh catalyst in a H_2-TPD experiment. Whereas, when the fresh catalyst was oxidized at or above 573 K, the strongly adsorbed hydrogen formed in water decomposition will react with oxygen in stages. There are apparently at least three kinds of strongly adsorbed hydrogen remained in the Pt/TiO_2 system studied. Oxygen would react with each one of them in succession as the oxidation temperature is raised and leave one species of labile oxygen on the site where the residual strongly adsorbed hydrogen was held. Upon desorption from samples oxidized at different temperatures, the TPD profiles would thus give three different desorption peaks at different temperatures, one for each sample oxidized at 573, 673 and 773 K, respectively, as shown in fig. 1 a, b and c. The peaks observed in fig. 1 b and c are presumably associated with TiO_2 in view of the fact that these two peaks are also present in fig. 1 d and e although in much smaller magnitude. As for fig. 1 f, in which no labile oxygen was found on PB upon oxidation, it is probably caused by loss of residual strongly adsorbed hydrogen and sintering as seen below.

3.2. H_2–O_2 TITRATION

On the pure TiO_2 oxidized at 573 K for 1 h, no capacity for hydrogen or oxygen adsorption was seen. This demonstrates that H_2–O_2 titration cannot be carried out on TiO_2. After Pt metal was introduced to TiO_2, the Pt/TiO_2 sample shows a very high capacity of hydrogen adsorption, and subsequent oxygen titration can be made. We carried out the H_2–O_2 titration in cycles as reported by Menon et al. [26,27], similar findings were obtained. Usually, the values of the first hydrogen and oxygen titers (designated as HT_1 and OT_1 respectively) are different from those in the subsequent titration cycles. After several H_2–O_2 titration cycles, reproducible hydrogen and oxygen titers were obtained and designated as HT_f and OT_f, respectively. From comparison of HT_1, OT_1 with HT_f and OT_f, some useful information can be extracted.

The hydrogen and oxygen titers in the first and final titration cycles of the Pt/TiO_2 catalysts oxidized in the temperature range of 393–773 K are listed in table 1. For these samples, HT_1 is always larger than HT_f, while OT_1 is about the same as

Table 1
Hydrogen–oxygen titration on oxidized Pt/TiO_2 catalysts. (Values in 10^{-6} mol g^{-1})

Oxidization temp. (K)	HT_1	OT_1	HT_f	OT_f	Hso[a]
393	29.54	5.94	11.98	5.46	17.56
473	33.78	6.97	13.87	6.48	19.91
573	45.24	6.33	13.23	6.32	32.01
673	14.56	3.74	9.14	3.93	5.38
773	12.82	3.40	8.30	3.51	4.52

[a] Amount of hydrogen spillover in HT_1 calculated from ($HT_1 - HT_f$).

OT_f. The fact that $2OT_1$ is much smaller than HT_1 indicates that there is a large portion of the consumed hydrogen in HT_1 that was not titrable in the subsequent oxygen titration at room temperature. This can be understood that HT_1 contains hydrogen consumption by both Pt and TiO_2, and HT_f contains principally Pt consuming hydrogen. Therefore, the difference of HT_1 and HT_f, which is inert to O_2 titration, can be ascribed to the adsorbed hydrogen on TiO_2, brought about by hydrogen spillover (Hso).

One may ask whether the Hso can represent the total amount of spillover hydrogen, the answer is no. Hydrogen spillover has been recognized as a reversible process [29,30]. The spillover hydrogen formed at room temperature can be divided into two forms: (a) the weakly adsorbed hydrogen species which is easily purged out by argon in back spillover; (b) the strongly adsorbed hydrogen species, some of which can desorb at a relatively high temperature as shown by the TPR and H_2-TPD runs described below. It is very hard to set a clear demarkation between the weakly and strongly adsorbed hydrogen on TiO_2. Transformation between these two species depends on the existing experimental conditions. Hso is assumed to be predominantly the amount of strongly adsorbed hydrogen species in the present paper.

Oxidation temperature exhibits a strong influence on the Hso as well as the H_2 and O_2 titers. For the catalysts oxidized at 393, 473 and 573 K, the first hydrogen titer increases with temperature, and the final hydrogen and oxygen titers are not significantly changed. And the amount of Hso is the largest for the sample treated at 573 K. These findings can be understood by the TPD determinations. When the fresh sample was oxidized at 393 K, its TPD profiles showed predominantly hydrogen desorption; and for the sample oxidized at 473 K, the residual hydrogen not oxidized at this temperature was found to desorb at a high temperature (>673 K) in the TPD run. Only when the fresh sample was oxidized at 573 K, did the TPD run show oxygen desorption, as seen in fig. 1 a. So the increase of HT_1 and Hso can be attributed to the presence of the labile oxygen species on the sample. Furthermore, the HT_f and OT_f values obtained on these samples are comparable, indicating that the Pt particle size was not much changed for these samples. These facts imply that the phenomenon of hydrogen spillover is closely related to the labile oxygen species. However, when the Pt/TiO_2 was oxidized at temperatures above

573 K, the values of hydrogen and oxygen titers decline significantly compared to the samples oxidized at low temperatures. Meanwhile, the amount of Hso is also decreased. These facts imply that the great changes in the Pt/TiO_2 samples were caused by oxidation at high temperatures. For the sample oxidized at 673 K, the hydrogen and oxygen titers and Hso are smaller than those of the sample oxidized at 573 K. This is inconsistent with the result of O_2-TPD, in which the amount of the desorbed oxygen is larger than that of the sample oxidized at 573 K. This implies that other factors will also influence the H_2–O_2 titration results besides the labile oxygen species. A possible cause is the increase in Pt particle size, i.e., some sintering has taken place. In the early works, Baker et al. [5,6] have reported that Pt particles supported on TiO_2 tend to increase in size during oxidation at 873 K. On the other hand, oxidation at high temperature will also induce a closer contact between Pt and TiO_2 [15]. The former factor will decrease hydrogen spillover, whereas the latter increases it [12,13]. The present results demonstrate that the effect from the latter factor cannot compensate the effect from the former. This means that the particle size plays an important role in the H_2–O_2 titration when the oxidation temperature was raised to above 573 K. Oxidation at 773 K significantly removed the residual hydrogen and caused the labile oxygen species to decrease greatly, while the amount of Hso detected by H_2–O_2 titration also decreased. These results obtained from the catalysts oxidized at 673 and 773 K suggest that the effects of oxidation temperature on the hydrogen adsorptivity for these Pt/TiO_2 catalysts are due to two factors: surface labile oxygen species and Pt particle size.

To further illustrate the effect of the labile oxygen species on Hso, complementary H_2–O_2 titration experiments are designed using the PA sample purged with argon at different temperatures. Purging induces marked effects on the hydrogen–oxygen titration as displayed in table 2. It is clearly observed that the HT_1 value decreases sharply with the increase of purging temperature. For the sample purged at 573 K, the fact that $HT_1 > HT_f$ is similar to those in table 1, indicating that hydrogen spillover is still in operation. In contrast, for the sample purged at 673 K, Hso cannot be detected because HT_f is now slightly larger than HT_1. For these two samples, the OT_1 values are nearly equal to OT_f. It is worth noting that when the sample was purged at 773 K, OT_1 is larger than OT_f; in this case it is suggested that reduced Ti ions or oxygen vacancies were produced on the sample to consume more oxygen in the first oxygen titer. This finding is consistent with those reported in the literature [31–33], in which evacuation or argon bombardment at high temperatures causes reduction of TiO_2 to occur to some extent. The big difference of

Table 2
Effect of Ar purging on hydrogen–oxygen titration for sample PA. (Values in 10^{-6} mol g^{-1})

Purging temp. (K)	HT_1	OT_1	HT_f	OT_f
573	6.15	2.47	5.03	2.49
673	4.35	2.25	4.63	2.33
773	0.38	1.43	2.10	1.02

the hydrogen/oxygen titers between the samples purged at 673 and 773 K suggests that a slight reduction of the carrier decreases greatly the capacity of adsorbing hydrogen by Pt. Of cause, sintering also plays a role here. The extremely low value of HT_1 for the sample purged at 773 K strongly suggests that significant sintering has taken place in this sample. Since it is known that the labile oxygen species can be totally removed by purging with argon at 673 K, and in view of the fact that the value of Hso found for this sample was negligible, it is reasonable to propose that the phenomenon of enhancing hydrogen spillover found in the system studied is closely related to the presence of the labile oxygen species.

3.3. TPR AND H_2-TPD

TPR patterns of Pt/TiO_2 and TiO_2 samples are shown in fig. 2. To facilitate the description, the TPR pattern of the oxidized Pt/TiO_2 sample (PA) is divided into three temperature regions: in region 1, 300–500 K, a reverse peak is seen, which is associated with hydrogen desorption; in region 2, 500–673 K, hydrogen consumption increases; in region 3, >673 K, the rate of hydrogen consumption rises sharply with temperature. After the PA sample was purged with Ar to remove the residual strongly adsorbed hydrogen and labile oxygen species, the TPR run of the sample (PB) showed two hydrogen consumption peaks at 390 and 460 K, respectively, ascribed to hydrogen adsorption in region 1 (see fig. 2b). In region 2, no pronounced phenomenon of hydrogen consumption is observed, while in region 3 hydrogen consumption increases with increasing temperature. Also included is a TPR pattern of the TiO_2 support after oxidation in oxygen at 573 K for 1 h as shown in fig. 2c. For the TiO_2 support, a small amount of hydrogen is consumed in region 2 and hydrogen consumption continues to increase in region 3.

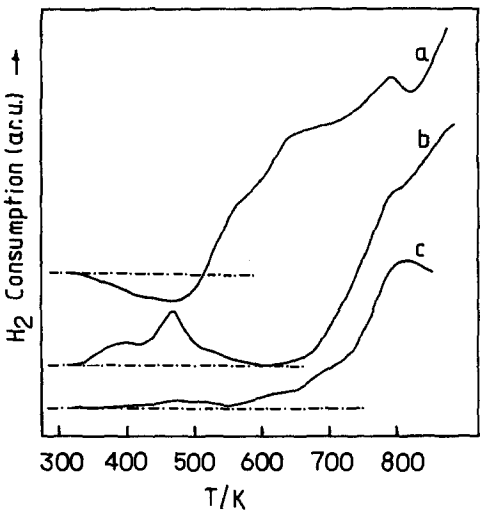

Fig. 2. TPR profiles of (a) the PA sample, (b) the PB sample, and (c) the TiO_2 support.

From comparison of these TPR profiles, it can be seen that reduction of the labile oxygen species of the oxidized catalyst occurs significantly in region 2, and the continuous hydrogen consumption above 673 K for all the samples can be ascribed to further reduction of the surface and/or the bulk of TiO_2 [6–8]. Higher quantities of hydrogen consumption on the Pt/TiO_2 samples (PA and PB) than that on TiO_2 indicate that Pt promotes reduction of the support. It is of particular interest to discuss the reverse peak appearing in the low temperature range of 300–500 K. A similar phenomenon was also reported by Menon, Kuninori et al. for the reduced Pt/TiO_2 catalysts [27,34]. From the H_2–O_2 titration results, it has been revealed that a large fraction of the adsorbed hydrogen is held by TiO_2 through hydrogen spillover. As the temperature is raised, a fraction of the adsorbed hydrogen on the TiO_2 support desorbs again by way of a reverse spillover. This fact indicates that a competition between hydrogen consumption (adsorption and reaction) and desorption exists in the TPR procedure of the Pt/TiO_2 catalyst. Interestingly, the reverse peak corresponding to hydrogen desorption was only observed on the Pt/TiO_2 catalyst oxidized at 573 K (PA) with the labile oxygen species. There remain still considerable amounts of residual strongly adsorbed hydrogen in this Pt/TiO_2 sample which can only be driven out by treatment at higher temperatures. As the residual hydrogen and the labile oxygen species were purged out with argon at 673 K, this appears to be why the PB sample did not show the reverse peak. So the appearance of the reverse peak is an evident indication that the adsorbed hydrogen on the sample with the labile oxygen species has high mobility.

Furthermore, H_2-TPD runs of the two different Pt/TiO_2 catalysts (PA and PB) treated in hydrogen at RT were carried out and shown in fig. 3 a and b. The PA sample, that has the residual hydrogen (which cannot account for the desorbed hydrogen in the H_2-TPD run) and the labile oxygen species, shows a pronounced hydrogen desorption in the temperature range of 350–600 K. While the PB sample without the residual hydrogen and the labile oxygen species shows much less hydrogen desorption. From the comparison of the H_2-TPD curves of the two samples of PA and PB, it can also be seen that the labile oxygen species enhances hydrogen spillover at

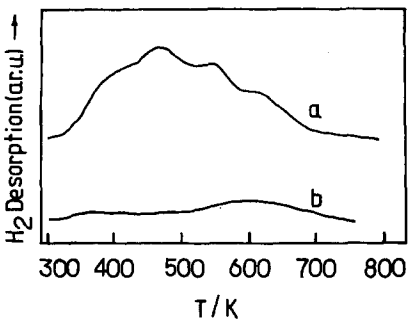

Fig. 3. H_2-TPD profiles of the samples of (a) PA and (b) PB treated in flowing hydrogen at room temperature for 1 h.

room temperature resulting in more hydrogen adsorbed on PA than on PB, which is consistent with the results obtained by H_2–O_2 titration and TPR experiments. Therefore, the high quantities of hydrogen desorption in the H_2-TPD run of the PA sample may be ascribed to a back spillover of hydrogen held by TiO_2.

Finally, it is worth speculating on the interaction of hydrogen with the oxidized Pt/TiO_2 catalyst in the different temperature regions. According to the results of TPR and H_2-TPD experiments, the behaviours of hydrogen on the Pt/TiO_2 catalyst in the different temperature regions could be visualized, perhaps greatly simplified, as follows:

$$\underset{\text{Pt- -TiO}_2}{[O_L]} + \tfrac{1}{2}H_2 \rightleftarrows \underset{\text{PtH- -TiO}_2}{[O_L]} \rightleftarrows \underset{\text{Pt- -TiO}_2}{[O_L H]} \rightleftarrows \underset{\text{Pt- -TiO}_2\text{H}}{[O_L]} \quad \text{RT–500 K} \quad \text{(on surface)} \qquad (1)$$

$$\underset{\text{Pt- -TiO}_2}{[O_L]} + H_2 \longrightarrow \text{Pt- -TiO}_2 + H_2O \quad 500\text{–}673\ \text{K} \quad \text{(on surface)} \qquad (2)$$

$$\text{Pt- -TiO}_2 + H_2 \longrightarrow \text{Pt- -TiO}[O_V] + H_2O \quad > 673\ \text{K} \quad \text{(on surface or/and in bulk)} \qquad (3)$$

where $[O_L]$ denotes labile oxygen species; $[O_V]$ denotes oxygen vacancy.

(1) In the low temperature range of RT–500 K, hydrogen adsorption and desorption equilibrium plays a dominant role in the Pt/TiO_2 sample. Hydrogen adsorption–desorption on/from TiO_2 is clearly seen to be enhanced by the presence of the labile oxygen species through spillover or back-spillover.

(2) In the medium temperature range of 500–673 K, reduction of the labile oxygen species can occur as observed in the TPR run. As a matter of fact, if the PA sample was reduced at 573 K for a long time, the labile oxygen species can be completely removed as reported in the previous studies [35,36].

(3) As the temperature was further increased to above 673 K, the TiO_2 carrier was strongly reduced to produce oxygen vacancies on the surface or/and in the sublayer and bulk. In this case, it is also known that a large quantity of hydrogen can diffuse from the surface into the bulk to form the strongly held hydrogen species as reported in the literature [21,22].

4. Conclusions

Labile oxygen species are formed on oxidized photo-deposited Pt/TiO_2 catalysts and characterized by O_2-TPD. A large quantity of hydrogen spillover from Pt onto TiO_2 has taken place as revealed by H_2–O_2 titrations. Experimental data from the H_2–O_2 titrations, TPR and H_2-TPD measurements are consistent with the

proposal that the hydrogen spillover is greatly enhanced by the labile oxygen species present in the Pt/TiO_2 system studied.

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