Single stage water gas shift conversion over Pt/TiO₂—Problem of catalyst deactivation

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Abstract

Pt/TiO₂ is an active and selective catalyst for single stage water gas shift reaction. However, the catalyst deactivated with time on stream. Detailed studies of fresh, used, and reactivated Pt/TiO₂ catalysts were carried out using kinetic (steady state and transient) and *in situ* IR spectroscopic methods in order to understand the mechanism of deactivation. The loss of Pt surface area was the cause of Pt/TiO₂ deactivation, exclusively. Pt sintering occurred mainly due to the presence of traces of formaldehyde formed under WGS reaction conditions by reaction of H_2 and CO. Details concerning the deactivation behavior are discussed.
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1. Introduction

Water gas shift (WGS) conversion, $CO + H_2O \leftrightarrow CO_2 + H_2$, $\Delta H = -41.1$ kJ/mol, is a key reaction in the production of hydrogen for fuel cell applications. This reaction increases the hydrogen content from synthesis gas produced during steam reforming or partial oxidation of hydrocarbons. There has been much interest in the use of noble metal (*e.g.* Pt) based WGS catalysts for *in situ* hydrogen generation in the auto-mobile fuel cell applications because of the limitations and complexity of the current two stage commercial WGS technology. We reported earlier [1] that Pt/TiO₂ promoted with Re, which contains very low contents of Pt and Re (<0.5 wt% each), showed an excellent activity, stability, and selectivity to WGS at moderate temperature (300 °C). These characteristics of the catalyst make it very promising single stage WGS catalyst that can be used in a hydrogen selective catalytic membrane reactor for hydrogen generation for auto-mobile applications.

Pt/CeO₂ is one of the most studied catalysts [1–11]. In general, Pt based catalysts are reported to be bifunctional [1,3,11,12], in which the noble metal and the oxide support sorbs/activates CO and H_2O, respectively. We have shown recently [1] that the oxide support not only determines activity of Pt based catalysts but also influence their stability.

Pt/CeO₂ is usually cited as a promising WGS catalyst to make hydrogen, *in situ*, for fuel cell applications [2–4,6,9], but this catalyst deactivates with time on stream. Since Pt-based catalysts are bifunctional [1,3,11,12], the deactivation of Pt/CeO₂ during WGS can involve Pt and/or CeO₂ [5–7,11]. Wang et al. [5] reported the reason for the deactivation of Pt/ CeO₂ and Pd/CeO₂ due to the loss of active metal surface area. Zalc et al. [11], on the other hand, attributed deactivation of Pt/CeO₂ catalyst (WGS, 250 °C) to the irreversible "over"-reduction of ceria by H_2. Still differently, Kim and Thompson [7] claimed that the formation of carbonate and/or formate on ceria surface was the reason for the deactivation of Au/CeO₂ catalyst. The most plausible explanation in our view is given by Farrauto and co-workers [6] who found that, during startup and shutdown cycles in WGS reaction, stable carbonate build up on ceria surface led to catalyst deactivation. They [6] indicated that the catalyst could be regenerated by heating it in air to 430 °C. We have shown [1,13], using H_2 chemisorptions, *in situ* FTIR and transient kinetic studies that carbonate build up on CeO₂ surface indeed caused the deactivation of Pt/CeO₂ catalyst, in agreement with Farrauto and co-workers [6]. We found that

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these carbonates were stable at the reaction temperature (300 °C) and decomposed only above 430 °C. Accordingly, the catalyst could be completely regenerated by heating it in air to 450 °C. However, this will be problem for single stage WGS catalysts operated at lower temperatures (300 °C) because the reactor feed from the hydrocarbon conversion step contains significant amounts of CO_2 (2–15% depending on the route to syngas production, *i.e.*, catalytic partial oxidation or steam reforming) as well as the fact that CO_2 is produced during WGS conversion. In order to overcome this, it is essential that carbonates are not stable at the reaction conditions. TiO_2 or ZrO_2 have the advantage over CeO_2 as support because surface carbonates are unstable on TiO_2 and ZrO_2 at 300 °C [1,13,14]. Accordingly, Pt/ZrO_2 catalyst [1] showed excellent stability during WGS; however, it showed very low activity. Interestingly, Pt/TiO_2 was even more active than Pt/CeO_2, but deactivated with time on stream.

To our knowledge, there is no detailed study on the causes of deactivation of Pt/TiO_2 catalyst during WGS reaction. Obviously, a better understanding of the deactivation mechanism of Pt/TiO_2 may allow design of efficient and stable catalyst. In this manuscript, we report on a detailed study on fresh, deactivated, and regenerated oxide supported Pt catalysts and analyze the reasons for deactivation.

2. Experimental

2.1. Catalyst preparation

Pt/TiO_2 catalyst was prepared by wet impregnation of TiO_2 (P25, Degussa) with aqueous solution of H_2PtCl_6 (Aldrich). TiO_2 was brought in contact with a solution containing the required concentration of H_2PtCl_6 for 1 h at room temperature to yield catalysts with 0.5 wt%. The catalyst was then dried at 75 °C for 2 h under vacuum in a rotary evaporator and subsequently calcined at 450 °C for 4 h (heating rate 10 °C min^{-1}).

2.2. Characterization

Surface areas of the catalysts were measured by the BET method using ASAP 2400 (Micromeritics). Pt dispersions were measured by H_2 chemisorption [13] at room temperature using Chemisorb 2750 (Micromeritics). About 50 mg sample was used for each measurement. Prior to measuring H_2 uptake, the samples were oxidized in air at 450 °C, reduced in pure H_2 (99.9%) after cooling down to 300 °C, flushed with Ar at 425 °C for 1 h and then cooled to room temperature (25 °C) in Ar. The H_2 uptake measurements were conducted at room temperature by injecting a series of pulses containing 1 ml of H_2 into Ar stream flowing over the sample at a rate of 25 ml/min and measuring the amount of H_2 adsorbed per pulse.

FTIR spectra were recorded using a Bruker Vector 22 with MCT detector under flow conditions (50% CO and 50% H_2) at the same temperature used in the catalytic activity measurements (300 °C).

2.3. Catalytic tests

Catalytic tests for WGS reaction were carried out in a fixed bed quartz tubular reactor (i.d. 3 mm). Details of the kinetic setup are described elsewhere [1,13]. The total flow rate of the feed gas into the reactor was 350 ml/min. The feed gas mixture was 3 vol.% CO, 7.5% H_2O and N_2 balance (N_2 is used as internal standard).

Pulse transient experiments were performed at 300 °C, at atmospheric pressure using also a fixed-bed reactor. A 14 mg catalyst was placed between two quartz plugs in a quartz tubular reactor ($d = 2$ mm). The reactor was then filled with quartz particles ($d = 0.25–0.3$ mm in size) to reduce the volume of reactor system. The gases (He, H_2, CO) used were of >99.9% purity. The catalyst was first reduced at 300 °C in 10 vol.% H_2/He, 20 ml/min flow for 1 h. After this, the catalyst was flushed with He at 300 °C (20 ml/min) for 30 min. The catalyst was then contacted with pulses of CO/H_2 mixture at 300 °C using He as carrier gas (13.4 μmol each pulse, CO/H_2 ratio of 1:1) in order to investigate the catalysts deactivation.

In order to simulate deactivation, Pt/TiO_2 catalyst was first reduced in H_2 at 300 °C for 1 h then pre-treated for 20 h in pure gas or 50% each in case of binary mixtures of reactants, intermediates and products. Details are discussed in the manuscript, wherever relevant.

3. Results and discussions

We have shown earlier [1] that Pt/TiO_2 catalyst has excellent activity in WGS (TOF of 10 s^{-1} at 300 °C) and was even more active than Pt/CeO_2 (TOF of 5 s^{-1}). The stability of the catalyst is a critical issue for catalyst application in WGS, especially for the auto-mobile use because of the severe conditions that exist during startup and shutdown cycles [6].

Fig. 1 shows CO conversion for Pt/TiO_2 catalyst, during WGS, plotted as a function of time on stream. It can be seen that activity decreased by more than 35% of the initial value during
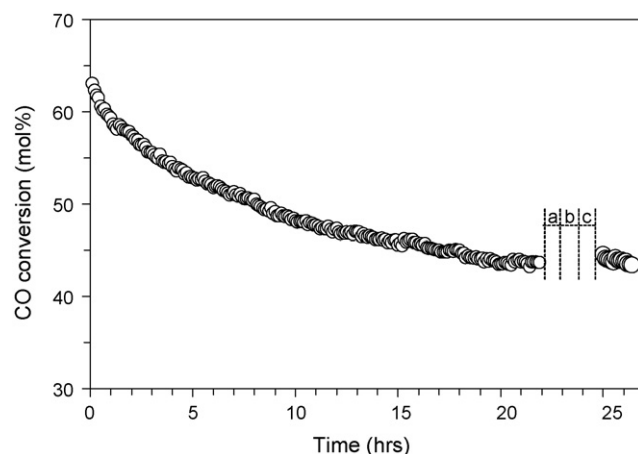

Fig. 1. WGS CO conversion for Pt/TiO_2 with time on stream at 300 °C. After 22 h tests, the catalyst subjected to the following treatment for 1 h each: (a) O_2 at 450 °C, (b) H_2 at 300 °C, (c) N_2 at 300 °C, then tested in WGS. Testing conditions: $p_{CO} = 60$ mbar, $p_{H_2O} = 150$ mbar, $P = 2$ bar, and GHSV = 410,000 h^{-1}, $m_{cat} = 51$ mg.

22 h on stream. Since both Pt and TiO_2 have catalytic functions during WGS (bi-functional catalyst), deactivation may be occurring through Pt, TiO_2, or both. In an attempt to regenerate the catalyst after this 22 h testing, it was heated to 450 °C in oxygen for 1 h (Fig. 1, stage a). This was done to burn off any coke formed or remove any stable carbonates/formates species present. The catalyst was then reduced in H_2 at 300 °C (stage b) for 1 h. Subsequently, the catalyst was flushed with N_2 at 300 °C for 1 h (stage c) prior to the second cycle of activity test (Fig. 1). It can be seen from the figure that this regeneration/oxidation treatment did not help to regain catalyst activity.

Fig. 2(a) shows the IR spectra of the catalyst in He, *in situ*, after reduction in H_2 at 300 °C. After exposure to CO at 300 °C (Fig. 2(b)), the bands appearing at 2071 and 2060 cm^{-1} represent linearly adsorbed CO on Pt [13,15,16]. In the case of *in situ* IR during WGS reaction (Fig. 2(c)), an extra band appeared at 1612 cm^{-1} corresponding to (weakly) adsorbed H_2O on titania [17]. It can be seen from Fig. 2 that oxygenate species (carbonate/formate, region of 1200–1600 cm^{-1}), are not stable on Pt/TiO_2 at 300 °C. Such species could clearly be seen for Pt/CeO_2 with *in situ* IR at WGS conditions (inset in Fig. 2). Therefore, in contrast to Pt/CeO_2 [1], we exclude the role of any stable oxygenate intermediates on catalyst deactivation, in agreement with the regeneration experiments discussed earlier in Fig. 1.

In addition, to check if traces of carbon deposition played any significant role in the catalyst deactivation, we performed O_2 pulse titration experiments over Pt/TiO_2 catalyst after
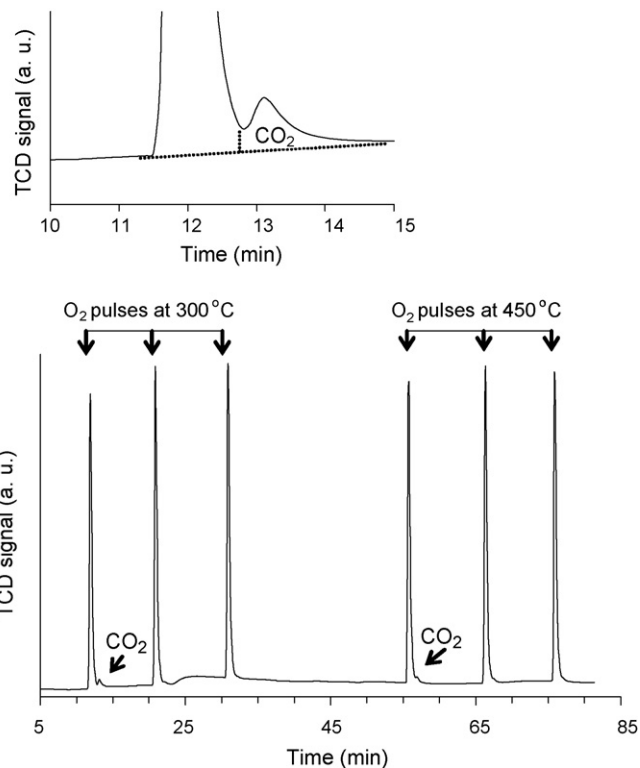
Fig. 3. CO_2 response using TCD observed from the successive pulses of O_2 at 300 and 450 °C on Pt/TiO_2 catalyst after 20 h testing on the stream.

running the catalytic test for 20 h (Fig. 3). To determine the O_2 consumption and product formation, the outlet of the reactor was directly connected to a Porapak column (5 m, 100 °C, to separate O_2 and CO_2) and TCD detector. Downstream to the TCD detector, gases were analyzed by an online mass spectrometer.

For the used Pt/TiO_2 sample (Fig. 3) three O_2 pulses were introduced consequently at 300 °C. After that, the temperature was increased to 450 °C and three additional O_2 pulses were introduced. The total amount of CO_2 released from the catalyst during O_2 pulses at 300 and 450 °C was 2.8 ± 0.1 μmoles/g_{cat}. To recall, the catalyst contained 14 μmoles/g_{cat} accessible Pt. Thus, the CO_2 formed can originate from the oxidation of CO adsorbed on Pt, and/or carbonaceous specie present on catalyst. The amount of CO_2 observed corresponded to about 20% of all the accessible Pt sites covered with CO (IR shows that CO is present on Pt at these temperatures, see Fig. 2). Thus very little or no coke type species are present on the catalyst. Accordingly, we exclude blockage by coke species to be the reason for catalyst deactivation since an oxidative regeneration also did not result in regaining catalyst activity (Fig. 1).

In the case of Pt/TiO_2 catalyst, the phenomenon of strong metal support interaction (SMSI) can also be of critical importance [18–20]. This phenomenon occurs when the catalyst is reduced (*e.g.* in H_2 or CO) at higher temperatures (>300 °C) resulting in covering (blockage) of metal Pt by partially reduced titania (TiO_{2-x}) species [18–20]. SMSI, if present, can thus affect the catalytic activity. For Pt/TiO_2, SMSI is usually observed when the reduction temperature is above
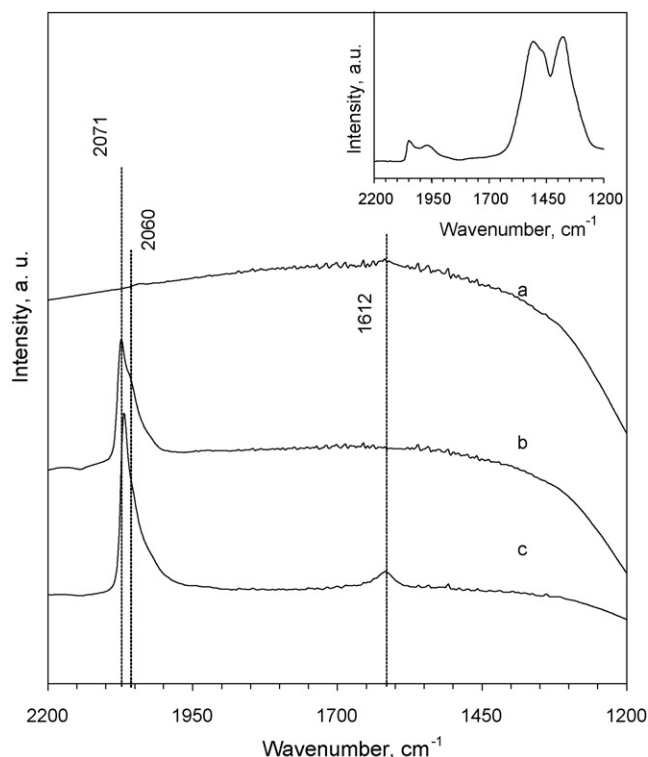

Fig. 2. *In situ* FTIR spectra at 300 °C of Pt/TiO_2 catalyst: (a) reduced in H_2 (10%)/He flow; (b) during CO flow; (c) *in situ* WGS conditions. Inset figure is the *in situ* IR spectra of Pt/CeO_2 under WGS shift conditions showing presence of carbonate.

Table 1
Effect of reduction temperature (T_R) on H_2 chemisorption capacity (H/Pt) of Pt/TiO$_2$ catalyst (SMSI effect)

T_R (°C)	H/Pt (%)
200	55
250	54
300	54
350	42
400	34
450	15[a]

[a] The H/Pt increased to 56% when this sample re-oxidized in O_2 at 450 °C and reduced in H_2 at 300 °C.

300 °C [18–20]. The criterion for the presence of SMSI state is the loss of hydrogen or CO adsorption capacity without significant enlargement of Pt particle size. An oxidation treatment usually reverses the SMSI state [18].

In order to check the relevance of SMSI, the influence of reduction temperature on Pt metal dispersion was studied. Table 1 shows the effect of reduction temperature (T_R) on hydrogen chemisorption capacity for Pt/TiO$_2$ catalyst. Indeed, reduction at temperatures higher than 300 °C seemingly induced SMSI. The chemisorption capacity (H/Pt) dropped from 55% to 15% when the reduction temperature increased from 300 to 450 °C. When the last catalyst (i.e., reduced at 450 °C) was re-oxidized in O_2 at 450 °C (followed by standard pre-reduction in H_2 at 300 °C), the hydrogen chemisorption capacity was completely recovered. It increased from 15% to 56% indicating return to pre-SMSI state as well as absence of any Pt particles sintering.

To check if SMSI influenced Pt/TiO$_2$ deactivation, samples were reduced in pure hydrogen stream at three different temperatures (i.e. 300, 350 and 400 °C) prior to catalytic testing. Fig. 4 shows the influence of reduction temperature on WGS CO conversion. For the samples reduced at 350 and 400 °C (where SMSI can occur) initial CO conversions were
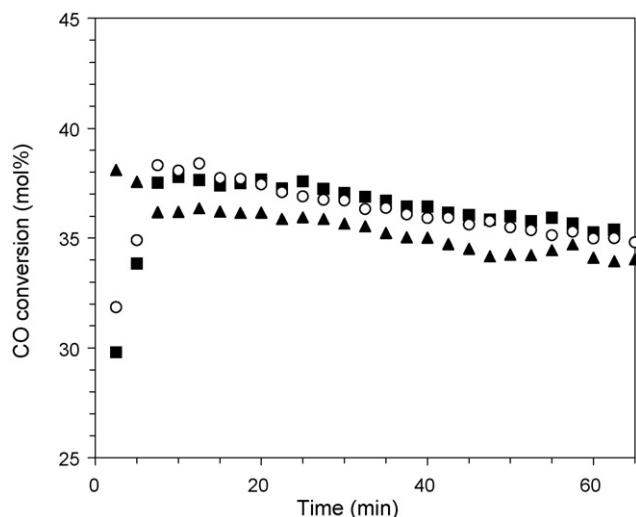
32% and 30%, respectively. However, CO conversions increased to 38% after 4 min time on stream indicating that the catalyst activity was completely recovered. After this all catalysts followed the same trend in deactivation. This means that the SMSI effect, if present, was almost immediately reversed under WGS reaction conditions. Our observations are in agreement with those of Haller and Resasco [18] who proposed that presence of H_2O is able to reverse the SMSI state. We can conclude therefore that any influence of SMSI on catalyst deactivation can be excluded during WGS conditions used in our study.

Further, it is possible that, TiO$_2$ support is susceptible to reduction due to the presence of CO and H_2 during WGS. This might lead to loss of support surface area and probably affect catalyst activity, as was observed for ceria [11]. BET surface area measurements before and after 20 h catalytic testing showed no change in the catalyst surface area (48 ± 1 m^2/g). Moreover, results shown in Fig. 4 also indicate no irreversible deactivation when the catalyst was reduced in pure H_2 at higher temperature (e.g. 400 °C).

Fig. 5 shows the Pt dispersions for Pt/TiO$_2$ catalysts measured after various stages of catalyst testing. Pt dispersion was 55% (1.9 nm Pt particle size) for fresh catalyst (Fig. 5(a)); however, it dropped to 34% (Fig. 5(b)) after 20 h time on stream. Catalyst deactivation during this period can thus be related to the loss of Pt metal surface. TEM results [1] confirmed the growth of Pt particles after WGS tests, in which average Pt particle size increased from 1.2 ± 0.2 to 2.7 ± 0.4 nm after 20 h testing. Therefore, based on the above results, we conclude that Pt sintering is exclusively the cause of Pt/TiO$_2$ deactivation during WGS reaction.

In order to understand what causes Pt sintering and the related deactivation, we performed a set of experiments where the catalyst was pre-treated with reactants, intermediates or products prior to catalytic testing. The WGS CO conversions following the pre-treatments are illustrated in Fig. 6. The choice of HCOOH is based on the fact that surface formate is a possible intermediate over Pt/TiO$_2$ during WGS [1]. Fig. 6 shows that there is no evidence for the deactivation due to the
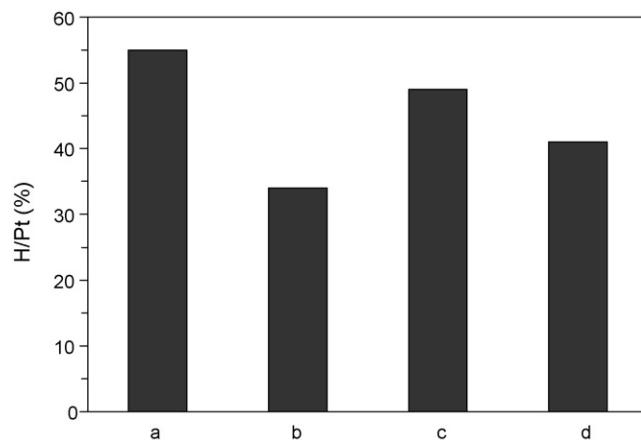

Fig. 4. Effect of reduction temperature in WGS CO conversion over Pt/TiO$_2$. Conditions: $p_{CO} = 60$ mbar, $p_{H_2O} = 150$ mbar, $T_{rxn} = 300$ °C, $P = 2$ bar, HSGV = 1,050,000 h^{-1}. Reduced in H_2 at (▲) 300 °C; (○) 350 °C; (■) 400 °C.

Fig. 5. Pt dispersion of Pt/TiO$_2$ using H_2 chemisorption: (a) before test, (b) after 20 h WGS catalytic test after (c) 20 h pre-treatment in H_2O, (d) after 20 h pre-treatment in a mixture of CO/H_2.
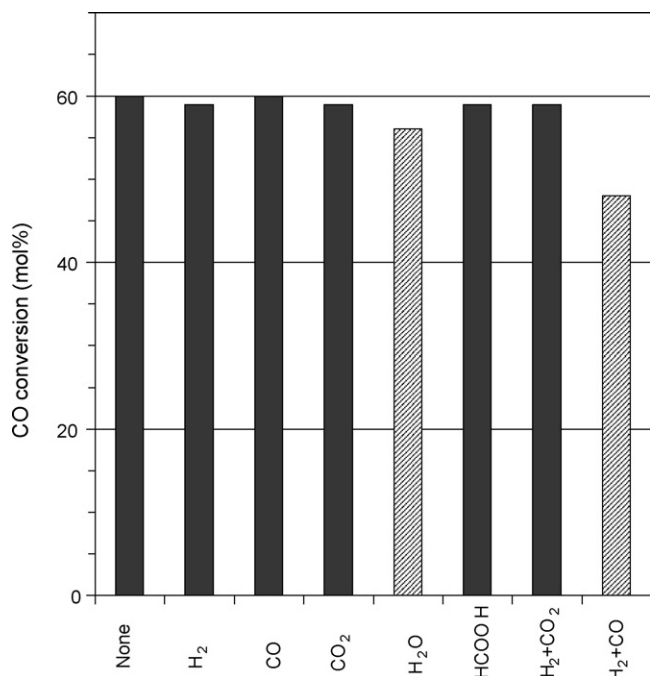
Fig. 6. Initial WGS CO conversions for Pt/TiO$_2$ catalyst following pre-treatment in gas(es) at 300 °C for 20 h. Conditions: p_{CO} = 60 mbar, p_{H_2O} = 150 mbar, T_{rxn} = 300 °C, P = 2 bar, and GHSV = 410,000 h^{-1}.

presence of H$_2$, CO, CO$_2$, HCOOH or a mixture of H$_2$/CO$_2$. H$_2$O had a smaller effect on the catalyst, the CO conversion dropped from 60% (no pre-treatment) to 55% after 20-h pre-treatment in H$_2$O at 300 °C. Pre-treating the catalyst with H$_2$/CO mixture caused the most significant deactivation, CO conversion dropped to 47%, following the pre-treatment, i.e., the catalyst lost about 22% (relatively) of its initial activity.

The measurements of Pt dispersions (Fig. 5) confirmed the effect of pre-treatments in H$_2$O or mixture of CO/H$_2$ on catalyst deactivation. To recall, during WGS test Pt dispersion of the catalyst was 55% to start with and it dropped to 34% after 20 h

time on stream. In the case of pre-treatment of the catalyst in H$_2$O for 20 h, Pt dispersion dropped from 55% to 49%. However, it dropped to 41% when pre-treated in a mixture CO/H$_2$. These results imply that both H$_2$O (to a smaller extent) and a CO/H$_2$ mixture contributed to the loss of platinum surface area (Pt sintering).

As shown above, the decrease in activity when pre-treated with H$_2$O does not completely mimic the deactivation behavior after 20 h catalytic testing (35% relative loss in CO conversion). A significant influence on catalyst deactivation was observed when the catalyst pre-treated with CO/H$_2$ mixture. Therefore, the major cause of deactivation may be related more to the presence of the mixture of CO/H$_2$ or surface species formed from it. Kim and Thompson [7] also reported deactivation of Au/CeO$_2$ catalyst in WGS due to the presence of CO/H$_2$. They [7] attributed this to the formation of carbonate on CeO$_2$ surface. It is important to emphasize here that carbonates are unstable on Pt/TiO$_2$ catalyst at 300 °C (Figs. 2 and 3). Moreover, we showed in Fig. 1 that treating the spent catalyst in oxygen at 450 °C (conditions under which carbonate can be completely removed) did not help in regenerating the catalyst. Therefore, carbonates are ruled out as significant in our case.

In our attempts to understand the role of CO/H$_2$ on catalyst deactivation (Pt sintering), we led CO/H$_2$ (50% each) at 300 °C over Pt/TiO$_2$ and followed all possible mass fragmentations by Mass Spectroscopy. Only traces of CH$_4$ was detected implying CO hydrogenation reaction to methane. Fig. 7 shows in situ FTIR spectra obtained during the pre-treatments of Pt/TiO$_2$ catalyst with CO/H$_2$ mixture (50% each) at 300 °C. In addition to gaseous CO (2143 cm^{-1}), we observed three bands at 2071, 2830, 3015, and a broad band from 2915 to 2960 cm^{-1}.

The band at 2071 cm^{-1} corresponds to adsorbed CO on platinum (CO–Pt) [13,15,16]. It is clearly seen that the intensity of this CO–Pt band decreased with time on stream. This decrease in its intensity (2071 cm^{-1}) implies that Pt surface area was lost with time and bigger particles (Pt sintering) were
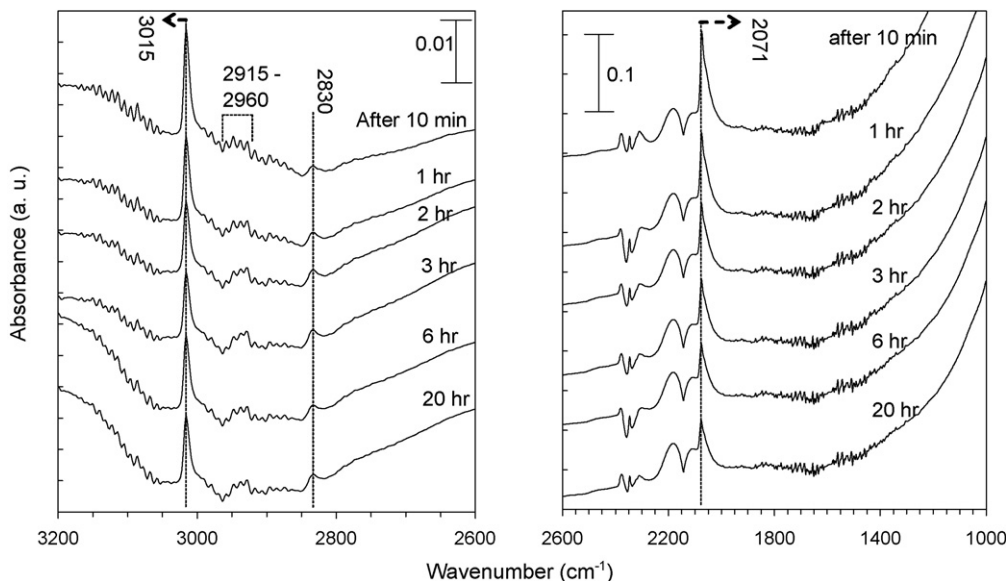

Fig. 7. In situ FTIR spectra for the Pt/TiO$_2$ catalyst following treatment in CO/H$_2$ with time.

formed. This is in agreement with our observations from catalytic testing and Pt dispersion measurements.

The bands at 2830, 2915–2960, 3015 cm^{-1} correspond to the C–H stretching of aldehyde [21,22], surface formate species [23,24], and gaseous CH_4 [25], respectively. The pre-treatment of Pt/TiO$_2$ catalyst with formic acid (this will generate formate species on TiO$_2$ surface) did not influence the catalyst stability (Fig. 6), therefore, we rule out the role of surface formate on Pt sintering. The other two possibilities, CH_4 or aldehyde (*e.g.* formaldehyde), imply a reaction of CO with H_2 (CO hydrogenation reaction). However, we did not observe any formation of gaseous methane during WGS reaction conditions (the detection limit of the Micro-GC used was 10 ppm) [1,13]. Therefore, we rule out any role of CH_4 in causing Pt sintering.

To check if there is any role of formaldehyde on Pt sintering, we pre-treated a fresh Pt/TiO$_2$ catalyst (Pt dispersion of 55%) with gaseous formaldehyde for 20 h. The catalyst was first reduced in 10% H_2/N_2 at 300 °C for 1 h then flushed with N_2 for another 1 h. Gaseous formaldehyde was provided to the catalyst by heating a vessel containing paraformaldehyde and flushed with N_2 stream (50 ml/min) at 60 °C. After 20 h pre-treatments, the catalyst was heated in oxygen at 450 °C to burn off any carbon deposited on the catalyst prior to Pt dispersion measurements. Indeed a decrease in Pt dispersion from 55% to 30% was observed. This indicates a strong influence of formaldehyde, either in gaseous phase or as adsorbed species, on the sintering of small Pt particles on TiO$_2$ surface. It is known that formaldehyde type species can be formed during WGS reaction, from the contact of CO and H_2 on Pt [26].

No information relevant to our studies could be traced in published literature regarding sintering of Pt particles assisted by oxygenate species. Trimm [27] reported, while converting methane to formaldehyde, that further oxidation of formaldehyde to carbon oxides can result in Pt sintering due to the exothermicity of the reaction. This is highly unlikely in our case as the ambient is more reducing than oxidizing during water gas shift reaction. We speculate, from our consistent observations that the presence of formaldehyde probably in combination with the presence of defect titania, enhances Pt mobility on TiO$_2$ and cause Pt sintering. More studies are necessary to pinpoint the exact steps involved.

The results discussed above and our earlier work [1] showed that Pt/TiO$_2$ deactivates with time on stream during WGS reaction. The deactivation is caused from the loss of Pt surface area exclusively. We have shown [1] that addition of Re to Pt/TiO$_2$ catalyst can prevent Pt sintering and allows significant improvement on catalyst stability. The details of the influence of Re on Pt/TiO$_2$ stability (characterization) is a subject for further study.

4. Conclusions

Growth of Pt metal particles during WGS reaction is the cause of Pt/TiO$_2$ deactivation, exclusively. We exclude any influence of SMSI state, carbon deposition or ''over''-reduction of TiO$_2$ as reasons for catalyst deactivation. At the experimental conditions of this work, Pt particles grow because of their contacts with a mixture of CO/H_2 during WGS; in addition, H_2O has small effect on Pt sintering. We speculate that the formation of traces of CH_2O on Pt surface enhances Pt mobility on TiO$_2$ and causes Pt sintering.

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