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Journal of Catalysis 226 (2004) 382–392

JOURNAL OF CATALYSIS

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Study of the origin of the deactivation of a Pt/CeO$_2$ catalyst during reverse water gas shift (RWGS) reaction

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Received 8 March 2004; revised 4 June 2004; accepted 8 June 2004

Abstract

The effect of carbon deposition in the deactivation of a 2% Pt/CeO$_2$ under RWGS conditions was investigated via an accelerated ageing procedure consisting of measuring the catalyst activity (under 1% CO$_2$, 4% H$_2$, 300 °C) before and after exposure to CO, CO$_2$, H$_2$, or CH$_4$ at 400 °C. Exposure to CO led to severe deactivation while exposure to CO$_2$, CH$_4$, or H$_2$ led to moderate or no deactivation. Additional activity measurements performed before and after exposure to CO followed by subsequent temperature-programmed oxidation (TPO) showed that exposure to increasing amounts of CO led to increased deposits of carbon and deactivation. No evidence for metal sintering was found. Additional TPO following catalyst exposure to RWGS conditions evidenced the deposition of carbonaceous deposits under the RWGS reactant mix.

Keywords: Deactivation; Ceria; Reverse water gas shift; Pt; Temperature-programmed oxidation; Carbon deposition; Active site

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1. Introduction

In the past few years, much research has been devoted to the development of fuel-cell power generation for transportation applications. A main focus of the research has been on providing the necessary hydrogen feedstock for the fuel cell. Technical solutions range from liquid H$_2$ tanks, high-pressure H$_2$ storage, medium-pressure H$_2$ storage on hydrides or nanostructured carbons to on-board H$_2$ production. Among the technical solutions offered, the on-board reforming of hydrogen-rich fuels such as natural gas, gasoline, or methanol has the most potential [1–4].

Nevertheless, this solution also presents a challenging drawback coming from the fact that the reformate gas always contains a fraction of carbon monoxide. This CO needs to be removed as it is both a pollutant and a poison for the platinum electrodes of the fuel cell.

To meet this goal, a water gas shift (WGS) converter, including a high- and a low-temperature stage, is added after the reformer to convert carbon monoxide with water to hydrogen and CO$_2$. The WGS converter is generally followed by an additional preferential oxidation stage to reduce the CO level to about 10 ppm [5].

This new interest in the application of the WGS reaction to fuel-cell applications has led to extensive research on improved catalysts for the kinetically limited low-temperature part of the WGS reaction. Among all the areas of research investigated, one solution came from earlier work on three-way catalysts and the observation of the effect of the addition of ceria to these catalysts. As a matter of fact, when used with platinum group metals, it was observed that ceria greatly promotes the WGS reaction [6–12].

Consequently, several metal/ceria catalysts were investigated and some of them (e.g., Pt/CeO$_2$) showed activity ex-

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doi:10.1016/j.jcat.2004.06.011

ceeding that of conventional Cu/ZnO shift catalysts [5–17]. However, these investigations also revealed that the activity and stability of these catalysts were closely linked to their preparation conditions [12,18,19]. These observations underlined the fact that a clear understanding of the reaction mechanism taking place on these catalysts was compulsory in order to develop improved ceria-based catalysts.

To achieve this, several mechanistic studies were undertaken and two possible mechanisms were proposed. Gorte and co-workers [12,13,18,19] and Li and co-workers [20] proposed a redox mechanism mainly based on kinetic studies.

In another approach, Shido and Iwasawa [7] performed infrared and TPD studies on ceria-supported Rh. These authors observed the formation of several surface species under reaction conditions (formates, carbonyls, and carbonates) and proposed that terminal hydroxyl groups on reduced ceria react with CO to produce adsorbed bidentate formate species. In the presence of water, these formates decompose to produce, in a first step, H_2 and unidentate carbonates. In a second step, unidentate carbonates decompose to CO_2 and a hydroxyl group is regenerated. The rate-determining step is proposed to be the decomposition of this formate to H_2 and a unidentate carbonate. In this mechanism it seems that the function of the metal is to facilitate the reduction of the ceria and the production of surface hydroxyl groups. This mechanism was supported by recent work performed by Jacobs and co-workers [21,22].

More recently, Fu and co-workers [23] published an interesting study that brought new insight into the effective role played by the metal in these ceria-supported catalysts. These authors removed most of the metal from ceria-supported gold and platinum catalysts (to the point of removing all the TEM observable particles) and showed that this treatment did not affect the activity of the catalyst compared to the untreated ones. Fu and co-workers proposed that part of the metal, in the form of ions, diffused into the ceria and anchored to surface defects. These ions were proposed to be responsible for the increase in the reducibility of the support. The remaining part of the metal in the form of nanoparticles was considered to be unimportant in the WGS reaction.

Fu and co-workers advocated a mechanism similar to the “normal-support activation” effect summarized by Golunski and co-workers [24]. In this effect, the insertion of a metal into a reducible support leads to a modification of the reducibility of this support through the so-called “junction effect”, that was first proposed by Frost [25] for methanol synthesis catalysts. The most striking effect observed with the NSA is a reversal of the normal roles of the metal oxide and the precious metal through an encouragement of the formation of highly active sites on the phase that normally acts as the support.

In addition to the reaction mechanism insight, a better understanding of the mechanisms responsible for the catalyst deactivation is also compulsory for further catalyst improvement.

Surprisingly, only a few studies have been aimed at addressing this crucial question for ceria-supported catalysts. The extent of this issue led Zalc and co-workers [5] to claim that ceria-supported metal catalysts may not be practical for the WGS reaction because of their high rate of deactivation. Based on a study performed with Pt-based catalysts, Zalc and co-workers proposed that the deactivation is due to irreversible overreduction of ceria by H_2. Gorte and co-workers [17] performed an accelerated aging study of Pd/ceria and Pt/ceria and stated that deactivation was due to the growth of the metal particles under a CO-containing atmosphere and discarded deactivation by overreduction. Gorte and co-workers also proposed that the recovery of part of the activity after reoxidation could be the consequence of the redispersion of the metal under oxygen thermal treatment. In the present study of the reverse water gas shift reaction, the contribution of carbon deposition to the deactivation of a Pt/CeO_2 catalyst has been investigated. Carbon deposition through the decomposition of CO (the Boudouard reaction) is well known with platinum group metals and we will present results that indicate that this could be an important factor under our experimental conditions:

$$2CO \rightarrow C + CO_2, \quad \Delta H^0 = 86.0\ \mathrm{kJ\,mol^{-1}}.$$

The results obtained are discussed in terms of both the mechanism responsible for the catalyst deactivation and its influence on the RWGS mechanism. The effect of carbonaceous deposits on the activity of the Pt/ceria catalyst for the WGS reaction will be reported in a subsequent paper.

2. Experimental

The catalyst used in this study was a 2% Pt/CeO_2 provided by Johnson Matthey p.l.c. The specific surface area was measured by BET (Micromeretics ASAP 2010) and was found to be 180 $m^2\,g^{-1}$. The Pt dispersion was measured by H_2 chemisorption (Micromeretics Autochem 2910) and was found to be 17%. Note that the dispersion measurements were performed at −80 °C to minimize the potential spillover of H_2 onto the support [26]. For all the experiments described below, the gases (H_2, He, CO_2, CO, and CH_4) were >99.9% purity and were supplied by BOC.

2.1. Study of the ageing under CO, CO_2, CH_4, and H_2

The deactivation of the 2% Pt/CeO_2 catalyst was a slow process under our typical reaction conditions (see Table 1).

Table 1
Conversion of CO_2 as a function of time for 40 mg of 2% Pt/CeO_2 under RWGS reaction conditions: 290 °C with 1% CO_2 and 4% H_2, balance He at 200 $cm^3\,min^{-1}$

Time (h)	0	20	40
CO_2 conversion (%)	21.7	20.6	19.1

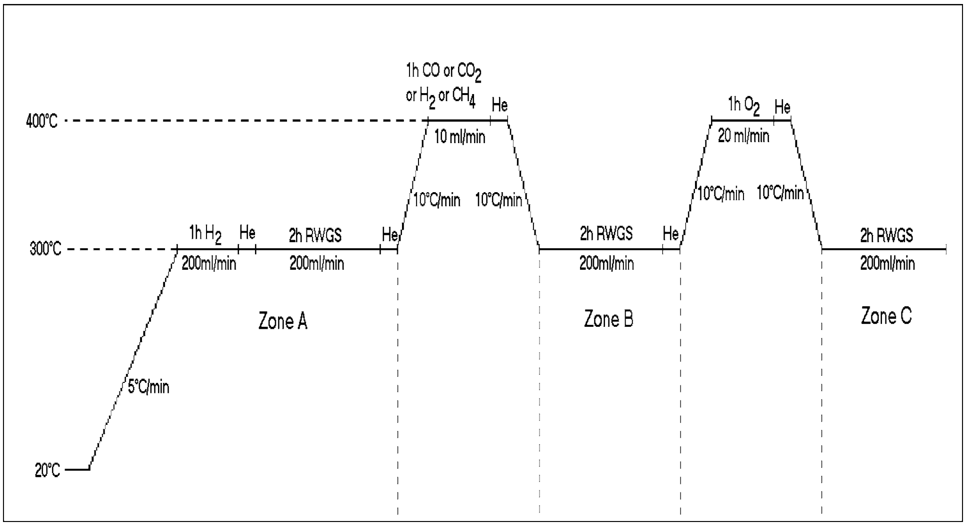

Fig. 1. Typical experimental cycle for ageing investigations of 2% Pt/CeO_2 for the RWGS reaction.

Therefore, we decided to apply an accelerated ageing procedure inspired by the one developed by Gorte and co-workers [14].

The principle of our procedure consisted of measuring the catalyst activity before and after exposure to pure CO, CO_2, H_2, or CH_4. After the second activity test the catalyst was reoxidized and a third activity test was performed. This third test was performed to investigate possible recovery of the activity.

Typically, 20 mg of catalyst (2% Pt/CeO_2) was placed in a $\frac{1}{4}$-inch tubular reactor and reduced at 300 °C under H_2 (200 $cm^3\,min^{-1}$) for 1 h. The catalyst was then exposed to the RWGS reaction mixture (1% CO_2 + 4% H_2, balance He, 200 $cm^3\,min^{-1}$) for 2 h at 300 °C. Following this step, the temperature was increased to 400 °C and the catalyst was exposed to either pure CO, H_2, CH_4, or CO_2 for 1 h. After the exposure, the temperature was brought back to 300 °C and a new catalytic test was performed under the RWGS conditions. Following this test, the catalyst was reoxidized at 400 °C under 20% O_2/Ar and then tested again at 300 °C under RWGS conditions (see Fig. 1 for details).

The concentrations of the reactants and products were determined using an on-line gas chromatograph (Perkin-Elmer 8700), equipped with a Hayesep Q column and a FID, fitted with a methanator to allow the detection of CO and CO_2.

2.2. Temperature-programmed oxidation (TPO) investigations

2.2.1. TPO with DRIFT

A first TPO of the 2% Pt/CeO_2 previously exposed to the RWGS reaction mixture (1% CO_2 + 4% H_2) was performed in a DRIFT apparatus. This experiment allowed us to determine the temperature range over which IR-sensitive surface species were desorbed/decomposed under the TPO conditions.

The experimental setup consisted of an in situ high-temperature diffuse–reflectance IR cell (from Spectra-Tech) fitted with ZnSe windows. The cell was connected to H_2, Ar, and CO_2 gas cylinders through low-volume stainless-steel lines. The gas flows were controlled by Aera mass-flow controllers, which were regularly calibrated. The DRIFTS cell was installed in a Bruker Equinox 55 spectrometer, operating at a resolution of 4 cm^{-1}.

The amount of 2% Pt/CeO_2 catalyst used was about 30 mg (particle diameter $<$150 μm). Typically, the catalyst was placed in a ceramic crucible and reduced in situ at 300 °C in pure H_2. Following this step, the sample was submitted to the reaction mixture (1% CO_2 + 4% H_2, 50 $cm^3\,min^{-1}$) for 2 h at 300 °C. After 2 h, the reactor was cooled down to room temperature, the flowing gas was switched from the reaction mixture to a flow of 20% O_2/Ar, and the temperature was increased to 600 °C at a rate of 5 °C min^{-1}. During the temperature ramp, an IR spectrum was recorded every 3 min.

2.2.2. TPO after exposure to increasing amounts of CO

These experiments had a structure similar to the ones described in Fig. 1. The difference came from the fact that a TPO step experiment was added between the zones B and C instead of a simple reoxidation.

Typically, the catalyst activity was measured before and after exposure to various amounts of CO (controlled by varying the percentage of CO in the gas mix (1, 10, or 100%) as well as the time of exposure (5 to 1440 min)). Then, TPO experiments were performed by ramping from room temperature up to 400 °C (5 °C min^{-1}) under 1% O_2/He. The concentrations of CO and CO_2 formed were followed by gas chromatography with a point recorded every 2 min. The TPO experiments were followed by a third activity test in order to investigate possible activity recovery.

Two additional experiments were performed with a 2% Pt/SiO_2 catalyst and a pure CeO_2 as references. They allowed us to investigate the decoupled behavior of the metallic phase (silica is an inert support) and the ceria support. These catalysts were submitted to the same experimental cycle as that described for the ceria-supported platinum catalyst. The exposure to CO was performed using 10% CO/He for 120 min. These conditions were chosen because they corresponded to the conditions under which the 2% Pt/CeO_2 displayed the maximum loss of activity.

2.2.3. *TPO after exposure to increasing time in the RWGS mixture*

TPO experiments were performed after various times of exposure of the 2% Pt/CeO_2 to the RWGS reactant mixture (1% CO_2, 4% H_2). These experiments were performed in order to investigate the buildup of carbonaceous deposits under true RWGS reaction conditions.

Typically, 40 mg of catalyst was placed in a 5 mm (i.d.) tubular reactor, reduced at 300 °C for 1 h under H_2, and then exposed to the RWGS reaction mixture for 5, 24, 72, or 96 h at 300 °C. Then, the reactor was cooled down to room temperature, the reaction mixture was switched to a flow of 1% O_2/He, and the temperature was increased to 500 °C at 5 °C min^{-1}. The CO and CO_2 concentrations were followed at the outlet of the reactor with a quadrupole mass spectrometer (VG Gaslab300).

It is worth noting that the deactivation under these conditions was very slow. Therefore, the aim of these experiments was only to investigate the formation of carbonaceous deposits under reaction conditions. No attempt was made to evaluate the extent of deactivation as it was too small to be accurately measured.

3. Results

3.1. *Study of the ageing under CO, CO_2, CH_4, and H_2*

For all the experiments, the initial CO_2 conversion of the fresh catalyst (zone A) was always close to 19%. Table 2 reports the percentage of deactivation between the fresh catalyst and the catalyst exposed to CO, CO_2, H_2, or CH_4 (zone A/zone B) as well as between the fresh catalyst and the reoxidized catalyst (zone A/zone C). These percentages of deactivation were calculated with the following formula:

$$\%\ \text{Deactivation} = 100 - \left(100 \times \frac{\text{Conv.}_{\text{zone B or C}}}{\text{Conv.}_{\text{zone A}}}\right).$$

Note that the reoxidation step was performed under 20% O_2/Ar for all experiments except for the experiment involving the exposure to CH_4 where it was carried out under 1% O_2/Ar.

Table 2
Percentage deactivation of the 2% Pt/CeO_2 catalyst for the RWGS reaction (1% CO_2 + 4% H_2, balance He, 200 $cm^3\ min^{-1}$) at 300 °C, before and after exposure to pure CO, H_2, CH_4, or CO_2 for 1 h at 400 °C and after reoxidation at 400 °C under 20% O_2/Ar

Species used for ageing before zone B	% Deactivation between zone A and zone B	% Deactivation between zone A and zone C
CO	86.0	27.9
CO_2	11.6	3.0
H_2	2.4	4.7
CH_4	19.8	−11.5

It can be seen that an exposure to pure CO led to a severe deactivation (86%) and that a subsequent reoxidation allowed only a partial recovery of the activity. An exposure to either pure CO_2 or pure CH_4 led to a moderate loss of activity and subsequent reoxidation led to a total recovery of the initial activity. An exposure to pure H_2 had almost no impact on the catalyst activity. Neither had the subsequent reoxidation.

3.2. *Temperature-programmed oxidation investigations*

3.2.1. *TPO with DRIFT*

Several IR bands were readily observed following the introduction of the (1% CO_2 + 4% H_2) reaction mixture over the 2% Pt/CeO_2 sample. The bands formed were characteristic of surface formates (e.g., 2950 and 2830 cm^{-1}), carbonates (e.g., 866 and 851 cm^{-1}), and carbonyls (e.g., 2065 cm^{-1}) as already described in detail by Shido and co-workers [7], Li and co-workers [27,28], Binet and co-workers [29], and Bourane and co-workers [30]. The intensity of all the IR bands reached a steady-state value within 10–20 min on stream.

Fig. 2a reports the spectra recorded during the temperature ramp of the TPO experiment. Note that the first and the second spectra were recorded at room temperature before and after the admission of the 20% O_2/Ar onto the catalyst, respectively. Fig. 2b reports a plot of the area of bands associated with surface formates (2830 cm^{-1}) and carbonates (866 and 851 cm^{-1}) as a function of the reactor temperature.

The band representative of the carbonyl species (2065 cm^{-1}) disappeared as soon as the 20% O_2/Ar was admitted to the reactor at room temperature. It is worth noting that a temperature increase of 50 °C was observed in the catalyst bed when switching to 20% O_2/Ar even though the reactor temperature was set at room temperature. This is likely to be due to the exothermic oxidation reaction of the CO adsorbed on Pt. In Figs. 2a and 2b, it can be clearly seen that formate (2830 cm^{-1}) and carbonate band (866 and 851 cm^{-1}) intensities decrease rapidly with increasing temperature; 95% of the bands attributed to the carbonate and formate species has disappeared before 250 °C. Note that small negative bands were observed in the carbonate region at higher temperatures. These bands probably correspond to carbonates on strong basic sites.

3.2.2. *TPO after exposure to increasing amounts of CO*

Fig. 3 reports the activities obtained during a typical experimental cycle (see Fig. 1). In this example, the catalyst

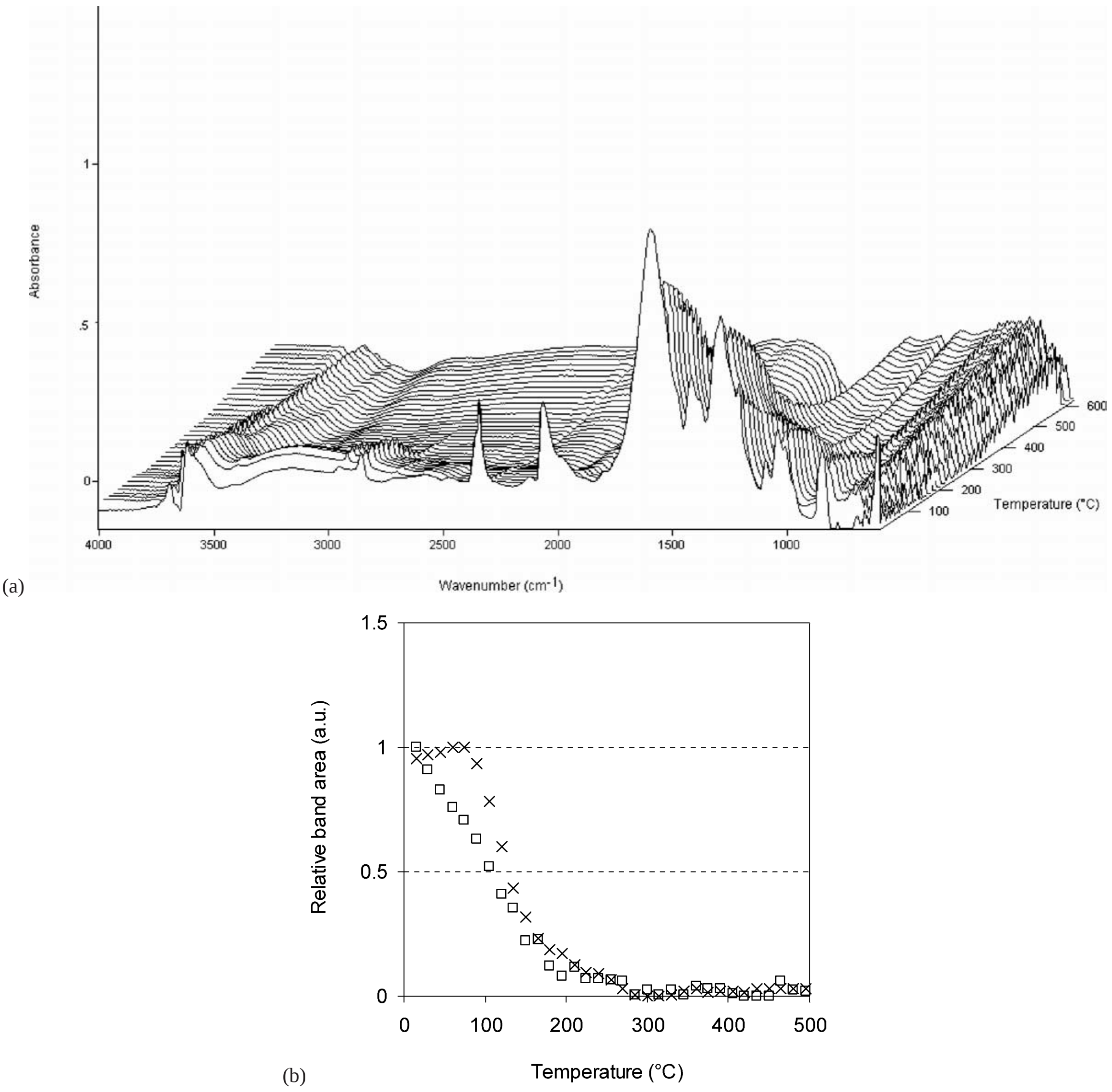

Fig. 2. (a) 3D plot of the spectra recorded during the temperature ramp of the TPO experiment. (b) Plot of the area of the bands representative of surface (×) formates (2830 cm^{-1}) and (□) carbonates (866 and 851 cm^{-1}) as a function of the reactor temperature during the TPO performed in the DRIFT apparatus.

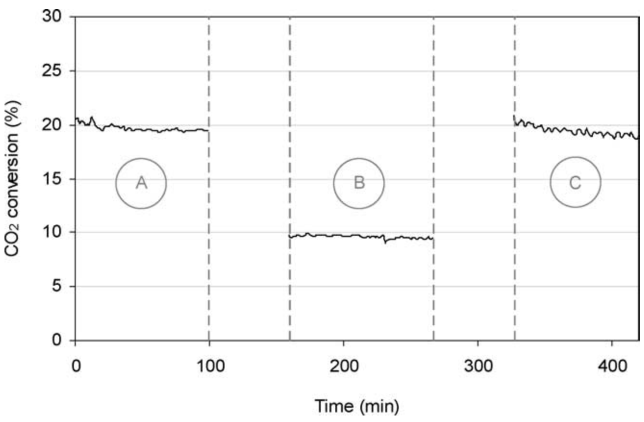

Fig. 3. Conversion of CO_2 for 2% Pt/CeO_2 at 300 °C for 1% CO_2, 4% H_2. In this example, the catalyst was exposed to 10% CO/He during 45 min between zones A and B.

was exposed to 10% CO/He for 45 min between zones A and B. Table 3 summarizes the results of all the experiments performed. This table reports the percentage of deactivation between the fresh catalyst and the catalyst exposed to different amounts of CO (zone A/zone B) as well as the percentage of deactivation between the fresh catalyst and the reoxidized catalyst (zone A/zone C).

It was seen that an exposure to CO always led to a noticeable deactivation of the catalyst. Increasing the amount of CO introduced to the catalyst led to increased deactivation. The subsequent reoxidation under 1% O_2/He always led to an almost total recovery of the initial activity. Note that the extent of the recovery of the activities was different from the one reported in Table 2 where only partial recovery was observed. This difference was apparently due to the different reoxidation conditions used in each experiment. This difference will be discussed later.

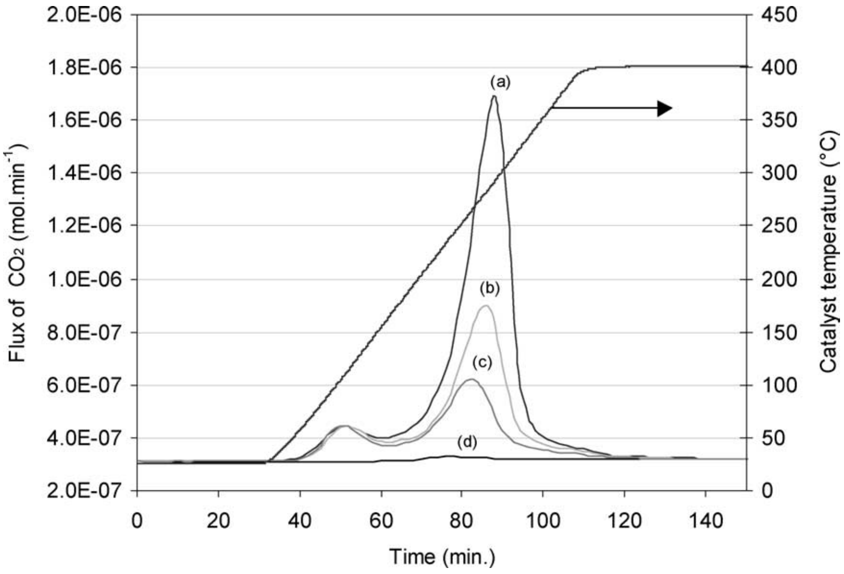

Fig. 4. TPO profiles for the 2% Pt/CeO$_2$ exposed to 10% CO for (a) 126 min, (b) 45 min, (c) 15 min, and (d) blank experiment (no catalyst and flowing of 10% CO for 60 min between zones A and B).

Table 3
Percentage of deactivation of the 2% Pt/CeO$_2$ catalyst for the RWGS reaction as a function of the amount of CO introduced to the catalyst

Time of exposure (min)	% of CO of the gas mixture	% Deactivation between zone A and zone B	% Deactivation between zone A and zone C
300	1	13	2.5
840	1	10	1.6
1440	1	16	3.0
10	10	24	0.1
15	10	42	0.1
20	10	54	3.3
45	10	51	2.6
126	10	78	5.0
5	100	77	3.9
15	100	70	7.1
30	100	74	−10.2

Fig. 4 reports an example of the profiles of the CO$_2$ concentration recorded during the TPO step of the experiment cycles. Note that no CO was detected in any of the TPO performed. The example given in Fig. 4 corresponds to results obtained with the catalyst exposed to 10% CO for 15, 45, and 126 min.

The profiles of all the TPO experiments were similar to the ones reported in Fig. 4. They consisted of two peaks at 100–110 and 260–290 °C, respectively.

The peak at 100–110 °C was identical in shape and intensity for all the TPO experiments. Therefore, this peak corresponds to species that are not affected by prolonged exposure to CO and associated with the deactivation. These species are probably formates and carbonates. This attribution was further confirmed by the TPO performed with the DRIFT apparatus. Indeed, the range of temperature during which formates and the carbonates desorbed/decomposed (between room temperature and 250 °C) corresponded well with the temperature range of the peak obtained with the TPO.

The second peak at 260–290 °C was attributed to the oxidation of carbon deposits because: (1) the temperature of the maximum of this peak was above the temperature of desorption/decomposition of the carbonyl, formates, and carbonates (see Figs. 2a and 2b), (2) the intensity of this peak varied substantially with the time of exposure to CO, indicating an accumulation of an oxidizable form of carbon.

This attribution was further confirmed by the result of a TPO following exposure of the catalyst at 400 °C to CH$_4$ instead of CO. This TPO showed a large peak of CO$_2$ at 250–280 °C (Fig. 5) that is located at the exact same position as the second peak observed during the TPO of the catalyst exposed to CO. These results corresponded well with the fact that an exposure of PGM catalysts to CO or CH$_4$ leads to carbon deposition through CO disproportionation or CH$_4$ cracking.

Fig. 6 reports the plot of the percentage of deactivation (reported in Table 3) against the area of the peak at 260–290 °C obtained during the TPO step of each experiment cycle.

It can be seen that the percentage of deactivation increased almost linearly with the amount of carbon deposited during the first 60–70% of deactivation. Above this value, a slope break was observed and the extent of deactivation decreased more slowly with the amount of carbon. This result indicates a correlation between deactivation and carbon deposition.

Regarding the results obtained with 2% Pt/SiO$_2$ and the CeO$_2$ support, the catalytic tests showed that these catalysts had poor activity for the RWGS reaction under the conditions explored. The conversions of CO$_2$ obtained in zone A (fresh catalyst reduced at 300 °C) were $\leqslant$1% for the ceria and $\leqslant$2% for the 2% Pt/SiO$_2$.

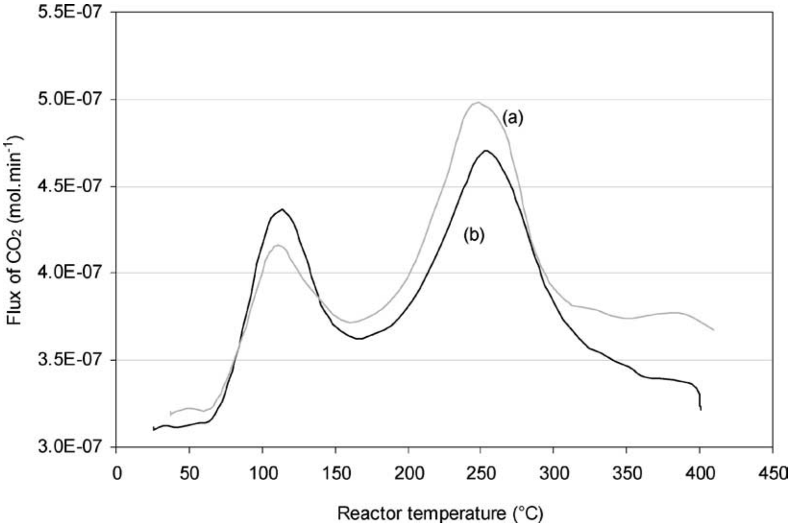

Fig. 5. TPO experiments obtained after exposure of the 2% Pt/CeO$_2$ to (a) pure CH$_4$ for 60 min or (b) 10% CO/He for 10 min at 400 °C between zones A and B.

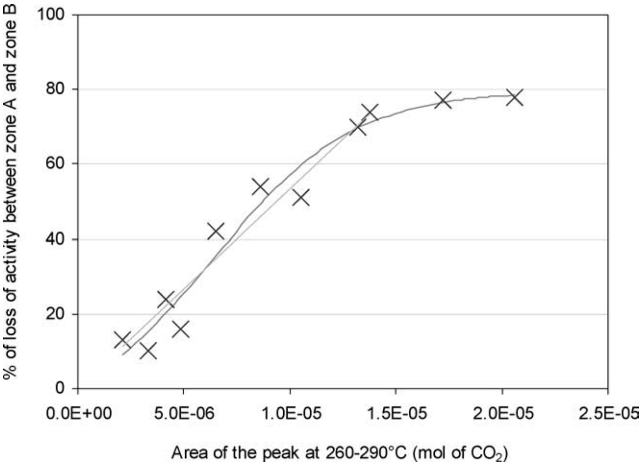

Fig. 6. Percentage of deactivation between zones A and B against the amount of carbon deposited on the 2% Pt/CeO$_2$ surface (area of the peak at 260–290 °C).

Fig. 7 reports the TPO profiles obtained for 2% Pt/SiO$_2$ and CeO$_2$ after exposure to 10% CO for 126 min. The profile obtained with the 2% Pt/CeO$_2$ is included for comparison. This profile was truncated for clarity purpose (for full scale see Fig. 4). The profile obtained with the ceria presented two peaks: one at 100–110 °C, similar to the one observed for 2% Pt/CeO$_2$ and a second peak, very small and very broad in the range 260–290 °C. The profile obtained with the 2% Pt/SiO$_2$ showed a small and poorly defined peak that seemed to extend between 50 and 300 °C. We estimated that the C/Pt ratio is about 0.5 which is what would be expected for carbon deposition on Pt.

3.2.3. TPO after exposure to increasing time in the RWGS mixture

Fig. 8 reports a typical result obtained during the TPO experiments after the exposure of the catalyst to the RWGS reactant mixture (72 h exposure at 300 °C). Note that only

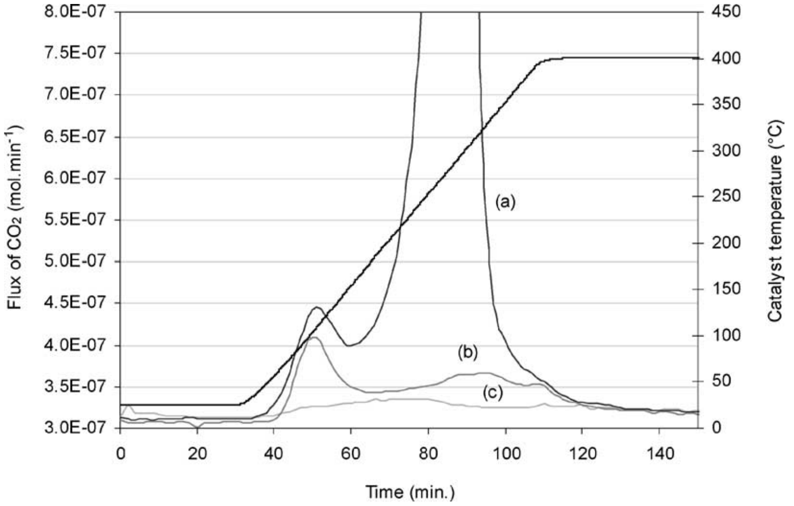

Fig. 7. TPO experiments obtained after exposure to 10% CO for 126 min for (a) 2% Pt/CeO$_2$, (b) CeO$_2$, and (c) 2% Pt/SiO$_2$.

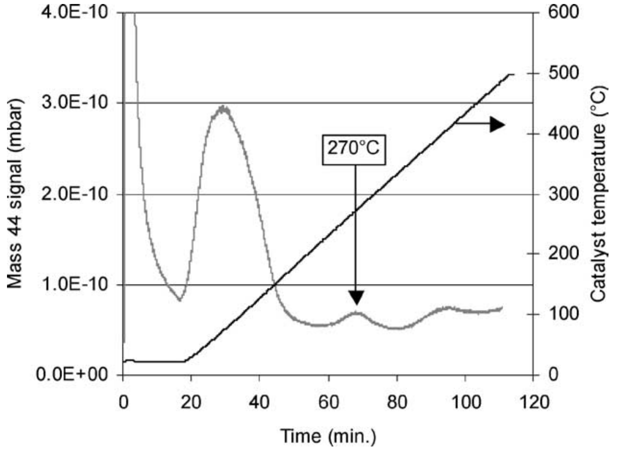

Fig. 8. TPO experiment following 72 h exposure of the 2% Pt/CeO_2 to the RWGS reactant mixture at 300 °C (1% CO_2, 4% H_2).

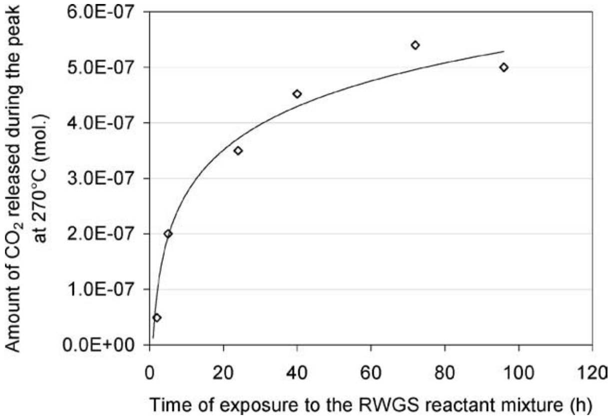

Fig. 9. Amount of CO_2 released during the peak at 270 °C against the length of exposure of the 2% Pt/CeO_2 to the RWGS reactant mixture at 300 °C (1% CO_2, 4% H_2).

the mass 44 representative of CO_2 is reported. No contribution for CO was observed.

All the TPO profiles (entailing 5, 24, 72, or 96 h exposure at 300 °C to the RWGS reaction mixture) displayed similar features: a first very sharp peak at room temperature, a second large and broad peak centered around 100 °C, and a third peak around 270 °C. It was possible to attribute the different peaks observed by comparing these results to the results provided by the DRIFT experiment and the results of the TPO following CO exposure.

The first very sharp peak corresponds to the oxidation of the carbonyl (note that, in Fig. 8, this peak was truncated for clarity). The second large and broad peak (at 100 °C) is attributed to the decomposition of the formate and carbonate species. The third peak around 270 °C, that appeared to increase in intensity with time of exposure to the RWGS reaction mixture, was attributed to carbonaceous deposits.

It is worth noting that an additional broad peak located at about 410 °C was also observed. This peak did not increase in intensity with time on stream. It is possible that this peak corresponds to carbonates on strong basic sites. This feature could therefore correspond to the small negative bands that were observed above 350 °C during the DRIFT experiment.

Fig. 9 reports the amount of CO_2 released during the peak at 270 °C against the length of exposure of the catalyst to the RWGS reactant mixture. This result clearly shows that the “intensity” of this peak increases with the time of exposure of the catalyst to the RWGS reactant mixture. Therefore it can be concluded that during the course of the RWGS on the 2% Pt/CeO_2, deposition of carbonaceous species occurs.

4. Discussion

The results of these experiments highlight the potential role played by carbon deposition in the deactivation of the 2% Pt/CeO_2 catalyst under RWGS reaction conditions. As a matter of fact, the catalytic tests and the TPO experiments showed that exposing the catalyst to increasing amounts of CO led to increasing deposits of carbon and increasing deactivation of the 2% Pt/CeO_2.

The plot of the percentage of deactivation against the area of the peak characteristic of the carbon deposits clearly showed that there is a correlation between the amount of carbon deposited on the surface of the catalyst and its deactivation. This correlation was almost linear for deactivation up to 60–70%. Above this value, a change of slope could be observed.

The results of the experiments performed with unpromoted ceria and 2% Pt/SiO_2 seem to indicate that the carbon deposition is located on the support (ceria) and not only the platinum. As a matter of fact the TPO performed with the pure ceria exhibited a small but significant peak at about 260–290 °C characteristic of carbon deposits. Under the same conditions, the TPO of the 2% Pt/SiO_2 showed a small and broad peak. The amount of carbon deposited was estimated from the dispersion of the Pt (30%) to correspond to a C/Pt ratio of about 0.5, assuming that no carbon is deposited on the silica.

Additional evidence for the fact that the carbon is deposited on the surface of the ceria was given by the amount of carbon deposited on the 2% Pt/CeO_2 during exposure to 10% of CO for 126 min. The carbon to surface platinum ratio was calculated knowing the platinum dispersion of the catalyst (17%) and was found to be ca. $C/Pt_s = 60$. This value, far above unity, indicates that the carbon could not be located only on the platinum and therefore was mainly located on the ceria surface.

It is interesting to note that the amount of carbon deposited on the 2% Pt/CeO_2 was larger than the quantity deposited on the unpromoted ceria under the same conditions. This result tends to indicate that the platinum is involved in the formation of the carbon deposited on the ceria support. A possible explanation of this observation is that the Pt increases the reducibility of the ceria. TPR results showed that the addition of a noble metal to the ceria led to an easier reduction of the ceria [31,32]. Moreover, some related work showed that CO disproportionation took place on partially reduced ceria [33,34]. Therefore, when platinum is added to the ceria, a larger fraction of the support would be in a reduced state as compared to the pure ceria, leading to increased carbon deposition. Another possible explanation is that the Pt increases the CO disproportionation rate and that the carbon is easily transferred from the metal to the support.

Either or both of these effects are likely to be responsible for the increased amount of carbon deposition on the 2% Pt/CeO_2 compared to the unpromoted ceria.

In the present study of the RWGS reaction, carbon deposition could be solely responsible for the deactivation. No metal sintering seemed to occur for our Pt/ceria catalyst. This absence of sintering was evidenced by the fact that a total recovery of the initial activity was obtained after reoxidation of the catalyst exposed to CO (see Table 3). Note that the total recovery of the activity was only obtained when the reoxidation was performed under “soft” conditions, that is, 1% O_2/Ar with a slow increase of the temperature from room temperature to 400 °C.

When the reoxidation was performed under “hard” conditions with admission of 20% O_2/Ar directly at 400 °C, the recovery of the activity was only partial (see Table 2). This result indicates that the conditions under which the reoxidation was performed were crucial for the recovery of the activity of our Pt/ceria catalyst. It is proposed that, when the reoxidation was performed under hard conditions at 400 °C, the instantaneous oxidation of the adsorbed CO and carbon deposits induced a strong local temperature increase that probably led to sintering of the platinum and therefore to irreversible deactivation. When the reoxidation was performed under soft conditions, the oxidation of the adsorbed CO and the carbon deposits took place at a lower temperature and the sintering did not take place. The fact that a total recovery of the activity was obtained under our reoxidation conditions and that many studies stressed that exposing supported platinum to oxidizing conditions leads to sintering and not to redispersion [35,36] seems to indicate that the activity recovery of our Pt/ceria was due to removal of carbon deposits from the surface and not to redispersion of a sintered metallic phase.

Concerning the deactivation by overreduction proposed by Zalc and co-workers [5], the result of the artificial ageing under H_2 (see Table 2) seems to indicate that this phenomenon is not taking place under our conditions. Nevertheless, our ageing experiments were performed on a short time scale (1 h) and it is possible that the conditions used were not severe enough to fully create overreduction. Therefore, overreduction cannot be completely discarded and a more extensive study is necessary to fully address this question.

The role of carbon deposition in the deactivation of the catalyst was further supported by the TPO experiments following exposure of the catalyst to our “standard” RWGS reaction conditions. These results clearly showed that carbon deposition was indeed taking place under our normal RWGS reaction conditions, as it did to a larger extent during the harsher accelerated ageing conditions reported above. It was clearly demonstrated that the rate of deposition was slow under our standard conditions which would explain the slow deactivation rate that was observed for the 2% Pt/CeO_2 under these normal reaction conditions. Furthermore, the fact that the TPO peak attributed to the oxidation of carbonaceous species deposited under RWGS reaction conditions is located in a similar temperature range (260–290 °C) as the peak due to the oxidation of the carbon deposited during the accelerated ageing in CO suggests that the two carbon deposits are of a similar type.

Another interesting piece of information could be extracted from the quantification of the amount of carbon deposited on the catalyst. As a matter of fact, after an exposure to 10% of CO for 126 min, the amount of carbon deposited on the catalyst was 2.1×10^{-5} mol, which led to 78% deactivation of the catalyst (see Fig. 6). Assuming that the carbon atomic radius was 77 pm and that the carbon was deposited as a monolayer, this amount of carbon deposit would only cover 6.5% of the total surface of the CeO_2 support (the BET surface area of the 2% Pt/CeO_2 was 180 $m^2\ g^{-1}$). Therefore, a coverage of only 6.5% of the total surface area of the support led to almost 80% of deactivation of the catalyst. This result indicates that the fraction of the support involved in the mechanism of the RWGS reaction is very small.

Moreover, although the critical size of the platinum particles involved in the RWGS reaction mechanism is not clear [23], the average radius of the platinum particles in our sample was calculated from the platinum dispersion (i.e., 17%), and found to be ca. 3.0 nm. From this average radius and assuming that the carbon was depositing around the platinum particles, it is possible to calculate the radius of the “ring” of carbon deposit surrounding each metal particle (see Fig. 10, R_1 for Pt particle radius, R_2 for radius of the carbon ring; the Pt particles were considered to be hemispherical).

The calculation gave a value of R_2 equal to 12 nm, which corresponds to only 4 times the radius of the platinum particle (note that in the hypothesis of particles equally spaced on the surface of the support, the distance between 2 particles would be ∼150 nm). This result would mean that the “active part” of the support would correspond only to the part that is very close to the platinum particles.

This hypothesis would therefore explain why the activity of the unpromoted ceria is so low for the RWGS reaction. As was noted before, TPR results showed that the addition of a noble metal to the ceria led to an easier reduction of the latter. This effect was explained by the fact that the oxygen was diffusing from the support to the metallic surface, easing the reaction with the reductant (H_2 or CO) adsorbed on the metallic surface. It is therefore possible to envisage that the portion of the support close to the metal particle could be in a highly reduced state (a gradient is created between the vicinity of the metal particles and rest of the surface of the support) and would correspond to the active part of the support (e.g., reactive toward the reduction of CO_2).

In this hypothesis, the slope change observed on Fig. 6 (plot of the percentage of deactivation against the amount

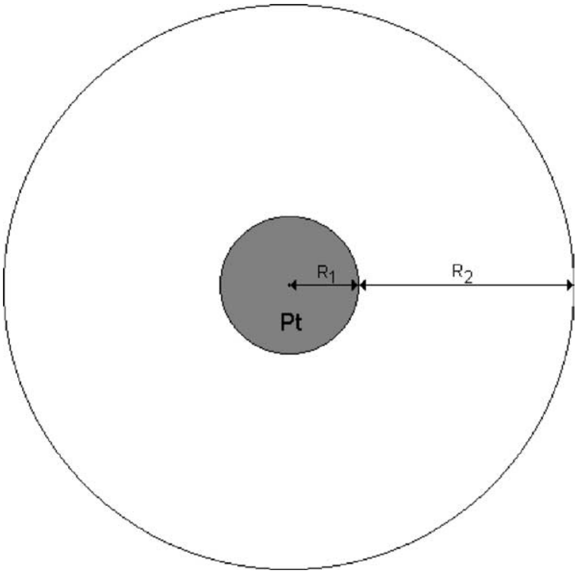

Fig. 10. Schematic representation of the carbon ring surrounding the platinum particles.

of carbon deposited) could find an explanation. This slope change would correspond to the point at which the whole active part of the support is covered by carbon deposits. The remaining activity, beyond the point of slope change, would be the activity of the platinum only. Note that this interpretation was reinforced by the results obtained with the 2% Pt/SiO_2. For this catalyst the support is obviously inactive and the conversion observed (∼2%) was relatively close to the 4% conversion observed after 80% loss of activity of the 2% Pt/CeO_2.

Moreover, on the basis of this hypothesis, it is likely that the carbon was deposited directly on the support and not on the metal first. That would mean that the progressive coverage by the carbon would start from the support followed by the metal when the active part of the support was covered and not the reverse.

Note that this hypothesis is also compatible with the mechanism proposed by Fu and co-workers [23] more recently. These authors proposed that the metal phase is not directly involved in the mechanism of the reaction in the case of the ceria-supported metal catalysts. In this approach, the real role of the metal would be to increase the reducibility of the support rendering the support as the active phase. If such a mechanism is indeed taking place, only a direct coverage of the support by the carbon deposits could be responsible for the deactivation of the catalyst.

Our study clearly demonstrates that carbon deposition is at least one of the main components of the deactivation of Pt/ceria catalysts for the RWGS reaction. It also clearly shows the crucial role of the support in being at least part of the active phase of the reaction. The exact role of the metallic phase could not be totally clarified and will be addressed in more detail in a future publication.

5. Conclusion

Carbon deposition plays a major role in the deactivation of the 2% Pt/CeO_2 catalyst under RWGS reaction conditions. Experiments consisting of measuring catalytic activity before and after exposure of the catalyst to CO followed by subsequent TPO experiments showed that exposing the catalyst to increasing amounts of CO clearly led to increasing deposits of carbon and increasing loss of activity for the RWGS reaction.

A clear correlation was found between the percentage of deactivation and the amount of carbon deposited. Moreover, the results obtained seemed to indicate that the carbon deposition is located primarily on the support (ceria) and not on the platinum. This result indicates that the support was "active" in the reaction and that the deactivation took place through gradual coverage of the support. Further information about the fraction of active support was also revealed. It was found that a very small coverage of the total surface area of the support led to strong deactivation of the catalyst. This result indicated that the fraction of the support involved in the reaction is small, probably located next to the metal and corresponding, at most, to a ring of four times the radius of the metallic particles. It is proposed that, during the reaction, the portion of the support close to the metal particles could be in a highly reduced state (a gradient is created between the vicinity of the metal particles and outer edge of this support ring) and would correspond to the active part of the support. This portion of active support is thought to be involved in the reduction of the CO_2 to CO.

Moreover, these results are consistent with results obtained with the RWGS reaction mixture. TPO experiments following the exposure of the 2% Pt/CeO_2 catalyst to the RWGS reaction mixture led to the occurrence of a peak at 260–290 °C, characteristic of carbon deposits. This peak grew in intensity with the time of exposure of the catalyst to the RWGS reactant mixture. These results confirmed that, during the course of the RWGS reaction on this catalyst, carbon deposit took place and was thus one of the major reasons for the slow deactivation that is observed for 2% Pt/CeO_2.

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