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Origin of transient species present on the surface of a $PdO/\gamma\text{-}Al_2O_3$ catalyst during the methane combustion reaction

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Abstract

Operando DRIFTS was applied to the study of the evolution of surface species formed on a Pd (2 wt.%)/γ-Al_2O_3 catalyst in various conditions. No differences were observed as a function of the initial oxidation state of palladium. Formates/carbonates species were identified at low temperature (<400 °C) and disappeared when CO_2 production started. These species come from the Pd-catalyzed interaction of CO with the alumina support, while CO_2 induces hydrogenocarbonates formation at low temperature (<300 °C). Their presence does not explain the inhibiting effect of CO_2 observed in CCM on Pd/γ-Al_2O_3 catalysts.

Keywords: Palladium; Catalytic combustion; Methane oxidation; Operando spectroscopy; In situ DRIFTS

1. Introduction

Pd-based catalysts are very efficient for low temperature catalytic combustion of methane (CCM) [1,2]. However many fundamental aspects concerning the behaviour of such catalysts remain unclear so far. In this paper, we try to elucidate the origin and the formation conditions of transient species which can be formed on the surface of the catalyst under reaction conditions, as discussed in another paper reporting in situ DRIFT spectroscopy results [3]. In particular, a peak assigned to formates and/or carbonates species progressively vanished when CO_2 production began to develop. Formates/carbonates species are not involved in the overall reaction pathway of methane oxidation and were suggested to be spectator species. Their production needs a continuous source of CO to occur and would come from the interaction of CO with OH-groups of the γ-alumina support [3]. However, the detailed formation conditions of the various surface species observed were not completely elucidated. This is important in order to better understand the very unclear reaction pathway of CCM on Pd-based catalysts. In this paper, we dwell on this aspect by investigating the origin, the formation process and the stability of these surface species under various conditions.

2. Experimental and methods

2.1. Catalyst preparation

The Pd (2 wt.%)/γ-Al_2O_3 catalyst (65 $m^2\,g^{-1}$) was prepared by the wet impregnation technique, using $Pd(NH_3)_4Cl_2$. H_2O as palladium precursor, as detailed elsewhere [3].

2.2. In situ DRIFTS

In situ diffuse reflectance infrared Fourier transform spectroscopy spectra were collected on a Bruker Equinox 55 infrared spectrometer equipped with an air cooled MIR source with KBr optics and a MCT detector. Spectra were obtained by collecting 200 scans with a resolution of 4 cm^{-1} and are presented in absorbance mode without any manipulation. Figures are indicated by numbers while spectra are referred to by letters. Samples were placed without packing or dilution inside a commercial in situ cell (Spectra-Tech 0030-102) with ZnSe windows. Simultaneous analysis of the products was achieved using a quadrupole mass spectrometer (Balzers QMS 200) coupled to the DRIFTS apparatus.

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A flow of He was first introduced in the DRIFTS cell for 1 h and the spectrum of the original sample collected. Various experiments, summarized below, were then performed:

1. *CCM reaction conditions*: A pre-reduced (H_2 40 vol.%/He at 350 °C for 2 h) sample was heated up to 500 °C under CCM reaction conditions ($CH_4/O_2/He = 5/20/75$ (v/v/v), 10 ml min^{-1}) in a 50 °C stepwise way.
2. *Adding CO_2 to the reactants feed*: An untreated sample was heated up to 500 °C under CO_2-containing CCM reaction conditions ($CH_4/O_2/CO_2/He = 5/20/10/65$ (v/v/v/v), 10 ml min^{-1}) in a 50 °C stepwise way.
3. *Experiments with γ-alumina*: Pure γ-alumina was heated up to 500 °C under (i) CO 1 vol.%/He, (ii) $CO/O_2/He = 1/20/79$ (v/v/v), (iii) CO_2 25 vol.%/He and (iv) $CO_2/O_2/He = 13/18/69$ (v/v/v). The gaseous flow rate was 10 ml min^{-1} in every case.
4. *CO_2 feed*: CO_2 10 vol.%/He (10 ml min^{-1}) was fed to a pre-oxidized (O_2 at 400 °C for 2.5 h) sample at 400 °C. After 1.5 h under CO_2/He mixture, helium was replaced for 5 min by a H_2 40 vol.%/He mixture. Then, H_2 40 vol.%/He was removed and the system was, thus, fed with pure CO_2, still at 400 °C.

3. Results

3.1. CCM conditions on a pre-reduced catalyst

After the reducing pre-treatment and the He flushing (Fig. 1), two peaks located at 1590 and 1460 cm^{-1} are observed on the surface of the catalyst at 200 °C under both He (A) and reaction conditions (B). They are still present at 350 °C (C). At 400 °C, the peak at 1590 cm^{-1} is severely decreased whereas that at 1460 cm^{-1} does not vary (D); this is correlated to a massive production of CO_2. Further increasing the temperature up to 450 °C induces a higher CO_2 production and causes the disappearance of the peak at 1590 cm^{-1}, whereas the 1460 cm^{-1} peak is still present on the surface of the catalyst (E). These trends are confirmed at 500 °C (F). After the temperature reached 500 °C, the sample was cooled down to 350 °C, still under reaction conditions, and the 1590 cm^{-1} peak progressively reappeared after the severe decrease in CO_2(g) production (result not shown).

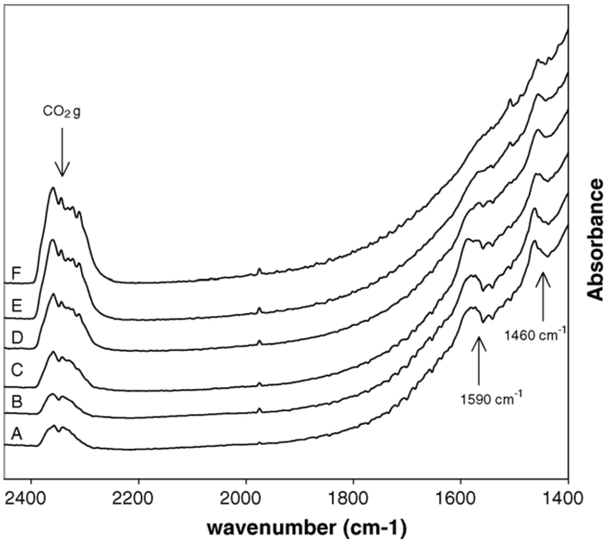

Fig. 1. Under CCM reaction conditions ($CH_4/O_2/He = 5/20/75$ (v/v/v)) on a pre-reduced (2 h at 350 °C under H_2 40 vol.%/He) Pd (2 wt.%)/γ-Al_2O_3 catalyst between 200 and 500 °C. After He flushing (A), under reaction conditions at 200 °C (B), 350 °C (C), 400 °C (D), 450 °C (E) and 500 °C (F).

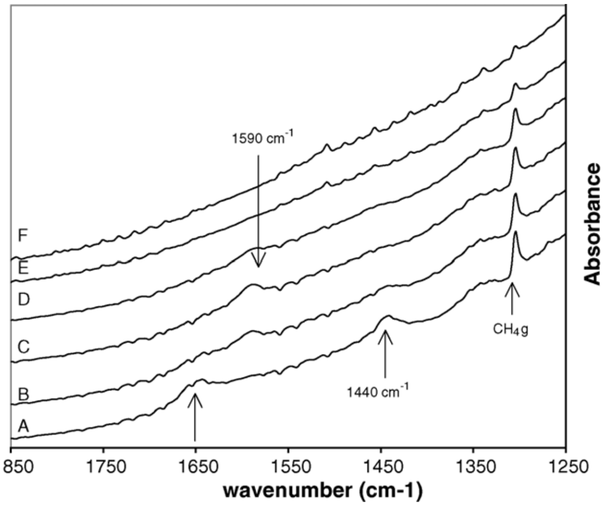

Fig. 2. Under CO_2-containing CCM reaction conditions ($CH_4/O_2/CO_2/He = 5/20/10/65$ (v/v/v/v)) on a Pd (2 wt.%)/γ-Al_2O_3 catalyst at 200 °C (A), 300 °C (B), 350 °C (C), 400 °C (D), 450 °C (E) and 500 °C (F).

3.2. Experiments adding CO_2 in the feed

When the reactants mixture is fed to the catalyst at 200 °C (Fig. 2), two peaks can be observed at 1650 and 1440 cm^{-1} (A). Their intensities decrease when the temperature is raised and are completely removed at 350 °C (C). In the same time, the peak at 1590 cm^{-1} appears at 300 °C (B), and is well resolved at 350 °C (C). It vanishes when T is raised up to 400 °C (D), while some CO_2 production is detected by MS, and is totally removed at 450 °C (E). Heating up to 500 °C did not induce any spectral difference, except the diminution of the CH_4(g) signal, at 1304 cm^{-1} (F).

3.3. Experiments with γ-alumina

If the γ-alumina support is heated up to 500 °C under CO 1 vol.%/He (Fig. 3), the peak at 1590 cm^{-1} weakly appears at 400 °C (B) but immediately disappears at 450 °C (C). Nothing is observed at 500 °C. Identical features were observed when performing a temperature rise under the same conditions but adding 20 vol.% O_2 to the feed. When CO_2 25 vol.%/He is fed to the alumina support at 200 °C, two broad peaks appear at 1650 and 1440 cm^{-1} (D). They decrease when the temperature is raised and are completely removed at 350 °C (E). No other change is observed up to 500 °C. The same spectral features were recorded when the experiment was carried out with a mixture of CO_2 (13 vol.%) and O_2 (18 vol.%), balanced with He. The peak located at 1590 cm^{-1} never appeared under such conditions.

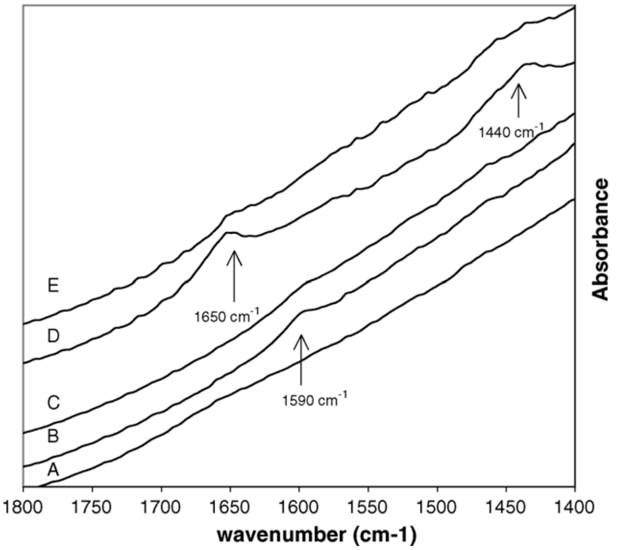

Fig. 3. Heating under CO 1 vol.%/He at 200 °C (A), 400 °C (B) and 450 °C (C). Heating under CO_2 25 vol.%/He at 200 °C (D) and 350 °C (E).

3.4. CO_2 feed

CO_2 10 vol.%/He was fed to a pre-oxidized sample at 400 °C (Fig. 4). After 1.5 h under CO_2/He mixture, no IR spectral feature is observed, except the CO_2(g) fingerprint around 2300 cm^{-1} (B); in particular, no band is observed at 1590 cm^{-1}. When helium is replaced for 5 min by H_2 40 vol.%/He, a broad band around 1900 cm^{-1} immediately appears and the peak at 1590 cm^{-1} begins to grow (C and D). Some CH_4(g) formation is also detected in IR at 3017 cm^{-1} (not visible on the IR window of Fig. 4). When H_2 is removed from the feed (pure CO_2 remaining in the cell), peaks at 3017, 1900 and 1590 cm^{-1} almost instantaneously decrease and are completely removed after 2 min (E).

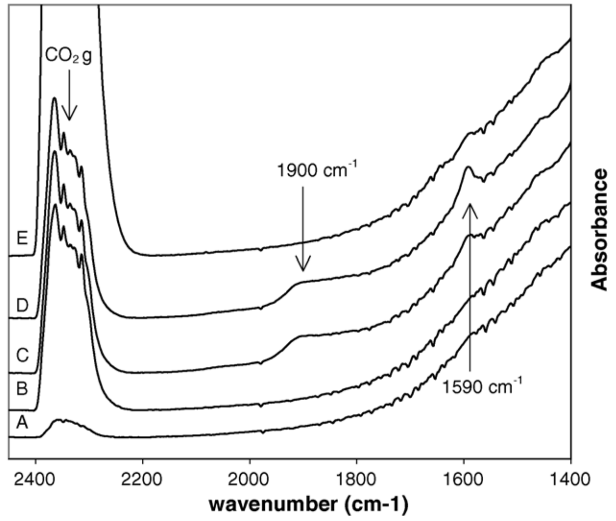

Fig. 4. CO_2 10 vol.%/He on a pre-oxidized (2.5 h at 400 °C under pure O_2) Pd (2 wt.%)/γ-Al_2O_3 catalyst at 400 °C. After O_2 pre-treatment (A), under CO_2 10 vol.%/He after 1.5 h (B), under CO_2/H_2/He = 10/35/55 (v/v/v) after 1 min (C) and 5 min (D), and under pure CO_2 after 2 min (E).

4. Discussion

4.1. Influence of the initial oxidation state of palladium on the IR features

When a pre-reduced sample is heated up to 500 °C under CCM conditions (Fig. 1), the same features as those observed on a pre-oxidized catalyst (see [3]) are noticed. This in line with previous Raman data which showed that the palladium phase is always in an oxidized form under reaction conditions, even after an in situ reducing pre-treatment [4]. This is also in agreement with results reported by Burch and Urbano who suggest an oxidized form of the palladium under reaction conditions due to the strongly oxidative reaction atmosphere [5]. As in the case of a pre-oxidized sample, the disappearance of the peak located at 1590 cm^{-1} seems to be correlated to the development of some catalytic activity, as evidenced by the increase of CO_2 production. On the contrary, the peak observed at 1460 cm^{-1} does not seem to be influenced by the development of the catalytic activity. The unambiguous assignment of both of these peaks is not an easy task and is largely commented elsewhere [3]. For the convenience of this discussion, the species associated to the 1590 and the 1460 cm^{-1} peaks will be referred to as formates/carbonates and carbonates species, respectively.

4.2. CO_2-induced surface species

The addition of 10 vol.% CO_2 in the feed did not induce dramatic changes on the IR features (Fig. 2), if compared with the situation observed under conventional CCM reaction conditions (Fig. 1). However, two additional peaks can be observed on the catalyst at 1650 and 1440 cm^{-1} below 300 °C. They account for species adsorbed on the alumina support, since they also appear when CO_2 is fed to pure alumina. It is well known that strong CO_2 adsorption on surface oxide and hydroxide ions results in the formation of surface carbonates and bicarbonates species [6]. However, their definitive assignment is not obvious either, even if they probably account for hydrogenocarbonates species [3]. Hydrogenocarbonates formation can be achieved by reaction of CO_2 with hydroxyl groups of the alumina support [7]. These adspecies do not seem to play a key role in the reaction scheme. They were only observed at low temperature and were completely removed at 300 °C. Thus, the hydrogenocarbonates formation does not explain the inhibitory effect of CO_2 observed on Pd/alumina catalysts [8], since they were removed at temperatures lower than the light-off temperature. When CO_2 production started, the formates/carbonates decreased and disappeared, as observed under CCM reaction conditions.

4.3. Origin of formates/carbonates (1590 cm^{-1}) species

The peak at 1590 cm^{-1} appears (weakly) when CO is fed to the γ-alumina support, whereas it does not under CO_2 (+O_2) feed. This clearly evidences that formates/carbonates species arise from the interaction of CO with the alumina support. This reaction is probably catalyzed by the presence of palladium, since the peak is much more intense on the Pd/γ-Al_2O_3 catalyst than on γ-alumina. The presence of palladium is indeed reported to strongly decrease the activation energy of formates formation on alumina [9].

The conditions and process of formates/carbonates production are well depicted in Fig. 4. After 1.5 h under CO_2 10 vol.%/He at 400 °C on a pre-oxidized Pd/γ-Al_2O_3 catalyst, no particular features were observed, but as soon as He was replaced by H_2, a broad band around 1900 cm^{-1} almost instantaneously appeared. This broad band around 1900 cm^{-1} reveals the presence of carbonyl bridging species adsorbed on metallic palladium (Pd_x^0–CO) species [3,10,11]. Their appearance is probably due to the reverse water gas shift (RWGS) reaction between H_2 and CO_2 (Eq. (1)):

$$H_2 + CO_2 \leftrightarrow CO + H_2O \qquad (1)$$

The CO molecules produced adsorb on the palladium reduced by the presence of H_2 and are soon transformed into formates/carbonates species (1590 cm^{-1}). CH_4 produced could be due to the methanation reaction between CO and H_2 (Eq. (2)):

$$3H_2 + CO \leftrightarrow CH_4 + H_2O \qquad (2)$$

As soon as H_2 is removed from the feed (pure CO_2 remaining), all features (CH_4(g), Pd_x^0–CO and formates/carbonates) quickly disappear, due to the removal of the CO source.

5. Conclusions

The results presented here complement and confirm DRIFTS data reported elsewhere [3]:

(1) The initial oxidation state of palladium does not influence the spectral features under reaction conditions.
(2) Formates/carbonates production comes from the interaction of CO with the alumina support, which is probably catalyzed by the presence of palladium.
(3) The disappearance of the formates/carbonates species seems to be correlated to the increase of CO_2 production.
(4) The adsorption of CO_2 on the catalyst surface, probably as hydrogenocarbonates species, does not explain the inhibitory effect of CO_2 observed on Pd/alumina catalysts.

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