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TAP Investigations of the CO_2 Reforming of CH_4 over Pt/ZrO_2

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The adsorption and reaction characteristics of methane, carbon dioxide, carbon monoxide, and hydrogen have been investigated over a ZrO_2 support and a Pt/ZrO_2 catalyst by using a temporal analysis of products reactor system. It was observed that on Pt/ZrO_2 both methane and carbon dioxide dissociate independently of one another. The dissociation of carbon dioxide acts as an oxygen supplier, while the decomposition products of methane scavenge the oxygen from the catalyst. When an abundance of oxygen is present, pulsing of methane leads to the production of carbon dioxide. It is concluded that both the selectivity with which methane produces carbon monoxide or carbon dioxide and the carbon dioxide conversion is determined by the same reaction: $CO_{ads} + O_{ads} \Leftrightarrow CO_{2,ads}$.

INTRODUCTION

Over the past few years, the carbon dioxide reforming of CH_4 (dry reforming) has attracted interest from both an environmental and an industrial perspective. The environmental viewpoint stems from the fact that both CO_2 and CH_4 are viewed as "harmful" greenhouse gases (1–4) and hence the reaction provides a method of disposing of these gases. However, the use of the carbon dioxide reforming reaction as a CO_2 scavenger is debatable. This is due to the endothermic nature of the reaction, which requires a heat input and hence fuel combustion and CO_2 generation. From the industrial view the reaction is attractive as it produces synthesis gas with a higher purity (5) and a lower H_2 to CO ratio than does either partial oxidation or steam reforming. However, compared with the latter two processes, the dry reforming has a higher risk of catalyst deactivation due to carbon deposition; this is thermodynamically more favoured when the carbon content in the feed mixture increases.

Several patents (6–8) and our own research (9–11) have shown that ZrO_2-based catalysts are very effective for the CO_2 reforming of CH_4; not only are they more active but they are also more stable in comparison to Pt/Al_2O_3 and Pt/TiO_2 catalysts (11). The aim of the present study was to investigate the mechanism of the CO_2 reforming of CH_4 using a temporal analysis of products (TAP) reactor system (12).

EXPERIMENTAL

Catalyst Preparation

The ZrO_2 support, used for the catalyst investigated here (1 wt% Pt/ZrO_2), was prepared by heating $Zr(OH)_4$ extrudates (MEL Chemicals, XZ0706/3) at a rate of 5°C min^{-1} to 800°C and maintaining that temperature for 15 h in flowing air. The sample was then crushed and sieved to obtain the fraction with particle sizes in the range 0.21–0.50 mm. The 1 wt% Pt/ZrO_2 catalyst was prepared by wet impregnation of the zirconia support with a 0.5 wt% H_2PtCl_6 solution (PGP Industries). After allowing overnight equilibration, the resultant slurry was dried and subsequently heated at a rate of 5°C min^{-1} to 600°C in flowing air, maintaining that temperature for 6 h. A more detailed description is given elsewhere (11). The BET surface areas of the fresh samples were 41 m^2/g for the Pt/ZrO_2 and 42 m^2/g for the ZrO_2 support.

The TAP experiments with the ZrO_2 were conducted with 0.90 g of sample. For the experiments with Pt/ZrO_2 a total of 0.30 g was used, corresponding to a total amount of 9×10^{18} atoms of Pt and 1.3×10^{21} atoms of Zr. To minimise the void space in the microreactor, nonporous α-Al_2O_3 (particle size 0.25–0.30 mm) was used as packing material.

TAP Reactor System

A detailed description of the TAP system has been given by Gleaves *et al.* (12). In essence, it consists of a microreactor, two high-speed pulse valves which can inject between 10^{14} and 10^{18} molecules per pulse and a mass spectrometer which can continuously monitor selected *m*/*e* values. Three different types of transient experiments were performed: single pulse, pump-probe, and multipulse. The single pulse experiments were conducted by pulsing a single gas through one of the pulse valves and observing the interaction of that

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gas with the sample. The pump-probe experiments were performed by operating the two pulse valves, each pulsing a different gas, independently of each other, at various time intervals. Both the single pulse and the pump-probe experiments consisted of repeated pulse cycles, with signal averaging to improve the signal to noise ratio. This procedure can be applied if the responses obtained do not vary during the measurement. This can be satisfied when (i) enough time is allowed between each pulse for the gases to exit the reactor and (ii) the pulse intensity is sufficiently small as not to create a significant change on the sample surface. In general, a pulse intensity smaller than 1% of the number of atoms exposed at the sample surface is considered acceptable. The multipulse experiments were a series of single experiments for which no signal averaging was applied and all the individual responses were recorded as a function of time.

Experimental Conditions

The gases used were methane (purity: 99.9995%), hydrogen (99.999%), carbon monoxide (99.997%), carbon dioxide (99.999%), and argon (99.99995%), all supplied by Air Products. The $^{13}CH_4$ had a purity of 99% and was supplied by Messer Griesheim (Lot F-5007). As the responses were measured with mass spectrometry, the following m/e values were selected as being characteristic of each of the individual gases: H_2, 2; CH_4, 15 (pump-probe experiments) and 16 (single pulse experiments); $^{13}CH_4$, 17; H_2O, 18; CO, 28; ^{13}CO, 29; Ar, 40; CO_2, 44; and $^{13}CO_2$, 45. Since CO_2 also gave a response at $m/e = 28$ and $^{13}CO_2$ one at 29, the fragmentation patterns of CO_2 and $^{13}CO_2$ were obtained and the appropriate corrections were made to give the CO or ^{13}CO responses, whenever either of these gases was present in the reactor effluent. It should be noted that H_2 is difficult to detect in a quadrupole mass spectrometer and so quantification of the H_2 signal was not attempted.

All gas volumes dosed contained 10 vol% of Ar, which was added as a tracer to allow for the determination of the pulse sizes and the conversions of (some of) the reactants. Only with $^{13}CH_4$ was no Ar added due to experimental limitations. The pulse intensity used in the single pulse experiments varied between 4×10^{15} and 7×10^{16} molecules per pulse, whereas the pulse intensities with the pump-probe experiments were of the order of 5×10^{15} to 10×10^{15} molecules. With the Pt/ZrO_2 sample, these pulse sizes corresponded to coverages of 0.1–1.4% of the total available number of Pt atoms (1 wt% Pt/ZrO_2, 0.30 g, and 45% dispersion). For the multipulse experiments with $^{13}CH_4$ the pulse intensity was estimated to be 5×10^{15} molecules. Note that most of these pulse intensities were too large for the gas transport mechanism to be determined by Knudsen diffusion only. For mechanistic investigations (as opposed to kinetic studies) the gas transport mechanism is less relevant. These pulse intensities were chosen as they resulted in better signal to noise ratios.

In experiments with the ZrO_2 support, a total of 0.90 g was used. The pretreatment consisted of evacuation at a pressure of 10^{-8} bar and a temperature of 250°C. Single pulse experiments were then conducted. The interaction of each gas was first measured at 50°C and subsequently at higher temperatures, up to 700°C. After completing the experiments with one gas, the sample was maintained under vacuum at 700°C to allow for the desorption of the gas used before it was cooled down under vacuum to 50°C for the experiments with the next gas.

A total of 0.30 g of the 1 wt% Pt/ZrO_2 sample was used; this was pretreated by heating at a rate of $2°C \cdot min^{-1}$ to 700°C in a hydrogen stream with continuous evacuation, maintaining that temperature for 1 h. The sample was then cooled down overnight to 100°C under high vaccum. The single pulse experiments were performed in the same manner as with the ZrO_2 support. However, before starting the experiments with $^{13}CH_4$, the catalyst was treated extensively with CO_2 pulses.

When possible, the conversions were calculated based on the quantity of reactant and product measured. If that was not possible, the conversions were calculated using the reactant and Ar peak areas. The CO and CO_2 selectivities (during CH_4 pulsing) were based on the quantity of products detected, assuming a carbon balance of 100%. The maximum absolute error in the conversions and selectivities was determined to be 5%.

RESULTS

Before the results are presented, there are some points which need to be discussed. First, the residence time of the gases in the reactor is determined by the degree of interaction (adsorption/desorption) with the sample and by gas phase diffusion. Gleaves *et al.* (12) has discussed that when the pulse intensity is less than 10^{16} molecules, the gas phase diffusion is governed by Knudsen diffusion. This has the consequence that the residence time of each molecule is directly proportional to the square root of the molecular weight. If no interaction takes place between the gases and the sample in the reactor, the molecules will exit the reactor at different times, with the lightest first and the heaviest last. For the pump-probe experiments and the experiments with the $^{13}CH_4$, the pulse intensities were 10^{16} or smaller, and so gas phase diffusion was mainly Knudsen diffusion in those experiments. This indicates that the order in which the various molecules exited the reactor was H_2 followed by CH_4, H_2O, CO, Ar, and finally CO_2.

A second important point is that no carbonaceous species remained on the catalyst during any of the experiments. This was observed in preliminary experiments and the evidence for this conclusion is presented towards the end of this section, in relation to the results of the long term $^{13}CH_4$ experiment.

Single Pulses over the ZrO_2 Support

When the individual gases were pulsed over the sample of 0.90 g of the zirconia support at temperatures of 50, 550, and 700°C, the following results were obtained. When H_2 was pulsed, it appeared rapidly at all temperatures examined (50, 550, and 700°C). At 550 and 700°C the ratio of the H_2 to Ar peak areas was an order of magnitude smaller than at 50°C, suggesting that most of the hydrogen was converted at the higher temperatures. As small quantities of H_2O were detected it seems probable that the H_2 reduced the support.

When CO_2 was pulsed, a strong interaction was observed at all temperatures. For example, at 50°C no CO_2 was detected in the gas phase. Subsequent heating at $20°C \cdot min^{-1}$ revealed that the CO_2 which had been adsorbed at 50°C desorbed from the zirconia above 200°C. At 550°C the CO_2 pulses took more than 10 s to exit the reactor, while at 700°C the delay was more than 2 s.

Both CH_4 and CO eluted rapidly, each appearing before Ar at each of the temperatures examined. If only Knudsen diffusion occurs, these gases would appear before Ar, so it is concluded that they did not have a significant interaction with the zirconia support. Note that the ratio of the CH_4 to the Ar peak areas at 50 and 700°C were within 2%, showing that no CH_4 had reacted over the support.

Single Pulses over the Pt/ZrO_2 Catalyst

The individual gases were pulsed over 0.30 g of a 1 wt% Pt/ZrO_2 sample at temperatures of 50, 550, and 700°C. H_2 exhibited a strong interaction with the Pt/ZrO_2. Multipulse experiments at 50°C revealed that the H_2 was completely adsorbed in the first 55 pulses. Assuming that one H atom is adsorbed per one Pt atom, this corresponds to a Pt dispersion of 55%. This figure compares well with a value of 45% obtained using H_2–O_2 titrations (13). At the other temperatures, more pulses of H_2 also needed to be admitted before a H_2 response became visible. This indicates that the Pt/ZrO_2 adsorbs H_2 well.

CO_2 again exhibited a strong interaction. No CO_2 was detected in the gas phase, even after 300 pulses had been admitted to the sample at 50°C. This corresponds to adsorption of more than 1.5×10^{19} molecules of CO_2, significantly more than the total number of Pt atoms present (9×10^{18} atoms). It is therefore probable that the CO_2 adsorbs strongly on zirconia support, disguising any interaction of CO_2 with the Pt.

CO also exhibited a strong interaction with Pt/ZrO_2. Multipulse experiments with the sample at 50°C revealed that all the CO present in the first 90 pulses was adsorbed; this amount corresponds to 3.6×10^{18} CO molecules. If one assumes a CO to Pt ratio of 1 : 1, then this number indicates a dispersion of 40%, agreeing well with the Pt dispersion of 45% measured using H_2–O_2 titrations (13). At a sample temperature of 550°C, the CO appeared after Ar, with an average residence time of 0.79 s, while the corresponding Ar average residence time was 0.10 s. Since no interaction was observed between CO and the zirconia, the CO most likely interacts with the Pt.

CH_4 was the only molecule which appeared before Ar at all temperatures, suggesting that it has little or no interaction with the Pt/ZrO_2. However, the peak area obtained at 550°C was only between 20 and 25% of the total peak area obtained at 50°C, indicating that 75 to 80% of the CH_4 was consumed. It appeared that the majority of the CH_4 had (irreversibly) reacted over the catalyst.

Combined Pulses

Two sets of experiments were conducted in which gases were pulsed simultaneously over the Pt/ZrO_2 catalyst: (i) H_2 and CO_2 and (ii) CH_4 and CO_2.

As Pt/ZrO_2 is an effective (reverse) water-gas shift catalyst (13, 14), the influence of simultaneous pulsing of H_2 and CO_2 was investigated. The pulse experiments were conducted by pulsing H_2, CO_2, and Ar in the ratio 1 : 1 : 1. At no temperature examined were H_2O and H_2 peaks recorded; only a continuous low partial pressure of each of these molecules was observed, indicating that slow desorption of both took place. Evidence that the reverse water-gas shift reaction had occurred was obtained by comparison of the peak areas of CO and CO_2. At a catalyst bed temperature of 550°C, the CO area was 46% of the CO_2 area; after correction for the fragmentation pattern of CO_2 this corresponds to a CO_2 conversion of about 20%. At a temperature of 700°C, the CO peak area was 63% of that of the CO_2 peak area, corresponding to a CO_2 conversion about 30%.

In the second set of experiments, the influence of simultaneous pulsing of CH_4 and CO_2 was investigated at catalyst bed temperatures of 550 and 700°C. Each pulse consisted of an equimolar mixture of CH_4, CO_2, and Ar (added as reference) with a total pulse intensity of 9×10^{15} molecules. The results obtained at 700°C are presented in Fig. 1, in which the normalised responses of CO_2, CO, H_2, CH_4, and Ar are plotted as a function of time. The response of H_2O is not presented as it had a significant level of noise. The CH_4 peak appeared first, with a peak area corresponding to a conversion of around 95%. Both CO and CO_2 appeared after Ar, while H_2 appeared last. (It should be noted that the apparent increase of the H_2 signal at around 0.01 s is a contribution from the fragmentation of CH_4.) Using the CO_2 and Ar peak areas, a CO_2 conversion of 86% was calculated, which is lower than the CH_4 conversion. The CO produced corresponded (within 10%) to the value expected from the CH_4 and CO_2 conversions, indicating a reasonable carbon balance.

Pump-Probe Experiments

To gain more insight as to how the CO is produced, from the CH_4 or the CO_2, pump-probe experiments were

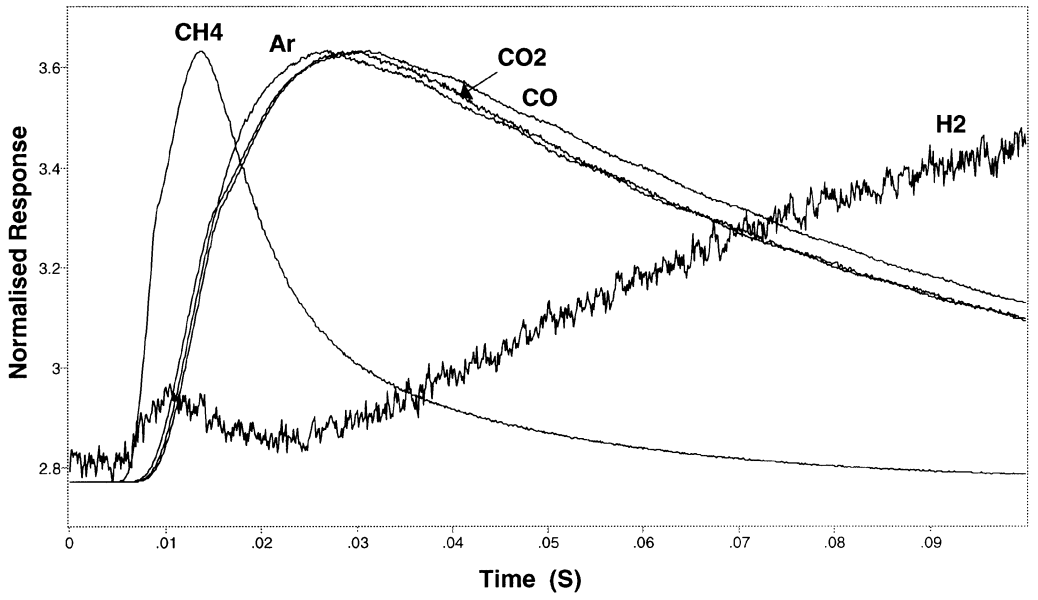

FIG. 1. The normalised responses of CH_4, Ar, CO_2, CO, and H_2 as a function of time when pulsing CH_4, CO_2, and Ar at $t = 0$ s and 700°C. Note that all signals have been normalised to the largest response, which was that of CO_2.

conducted at 700°C. The first series of experiments was carried out by first pulsing (at $t = 0$ s) a CO_2/Ar mixture, and this was followed by pulsing a CH_4/Ar mixture after various time intervals. The total time span of each pump-probe cycle was 3 s. The CO_2 mixture consisted of 90.0% CO_2 and 10.0% Ar, with a pulse intensity of 10×10^{15} molecules, while the CH_4/Ar mixture contained 90.0% CH_4 and 10.0% Ar, with a pulse intensity of 8×10^{15} molecules. The results obtained for the pump-probe with CH_4/Ar pulsed at $t = 2$ s are presented in Fig. 2a and 2b, in which the normalised responses of CO_2, CO, CH_4, and Ar are plotted as a function of time. Note that time scale ranged from 0 to 0.25 s in Fig. 2a and from 2.0 to 2.25 s in Fig. 2b, while the signal normalisation is the same in both figures.

Figure 2a, which presents the situation after a CO_2/Ar pulse, shows that the CO and CO_2 peak maximums appeared after the Ar signal. The (nonnormalised) CO peak area was 106% of the (nonnormalised) CO_2 peak area, this corresponding to a CO_2 conversion of 45%. (The observation that the CO appeared before CO_2, even though it is a product from CO_2, may be explained (as seen earlier) by the fact that the CO_2 has a stronger interaction with the Pt/ZrO_2.)

In Fig. 2b, where the situation after the CH_4/Ar pulse is presented, CH_4 appeared first. The (nonnormalised) peak area corresponded to a conversion of 95%, twice the CO_2 conversion obtained from the results of Fig. 2a. The Ar, CO, and CO_2 signals appeared together. That CO_2 was observed suggests that it is a product of the CH_4. The H_2 response, which for clarity is not presented in the figure, was similar to that shown in Fig. 1.

Variation of the time interval between the CO_2 and the CH_4 pulses in the other pump-probe experiments gave no changes in the peak shapes, all being identical in form to those presented in Figs. 2a and 2b. Only when the time interval between both pulses was short (<0.5 s) were the signal responses apparently different. This, however, was the result of an overlap of the signal responses of the two pulses. Though the peak shapes were identical, it was observed that the peak areas were significantly different. For example, it was found that when CO_2 was pulsed before CH_4, the CO_2 conversion increased when the time interval between the CO_2 and CH_4 pulses was increased. Since the total time of each pulse sequence was 3 s, a larger time interval between the first CO_2 and following CH_4 will also result a shorter time interval between the CH_4 and the next CO_2 pulse.

A second series of pump-probe experiments was therefore conducted, in which either CO_2 or CH_4 was pulsed first and the second gas was pulsed after a time interval of 1 s. Since the peak shapes were identical to those shown in Figs. 2a and 2b, these are not presented. Instead, Table 1 lists the CO_2 and CH_4 conversions based on the peak areas as well as with the selectivities in which the CH_4 is converted into CO and CO_2. The results from the first series are also presented in Table 1. Note that between the two series several experiments were conducted; these resulted in the catalyst being more reduced in the second series. As will be shown in the long-term $^{13}CH_4$ addition section the degree of reduction of the catalyst affects the conversions and selectivities. Therefore the values should be compared within the series, not between the series.

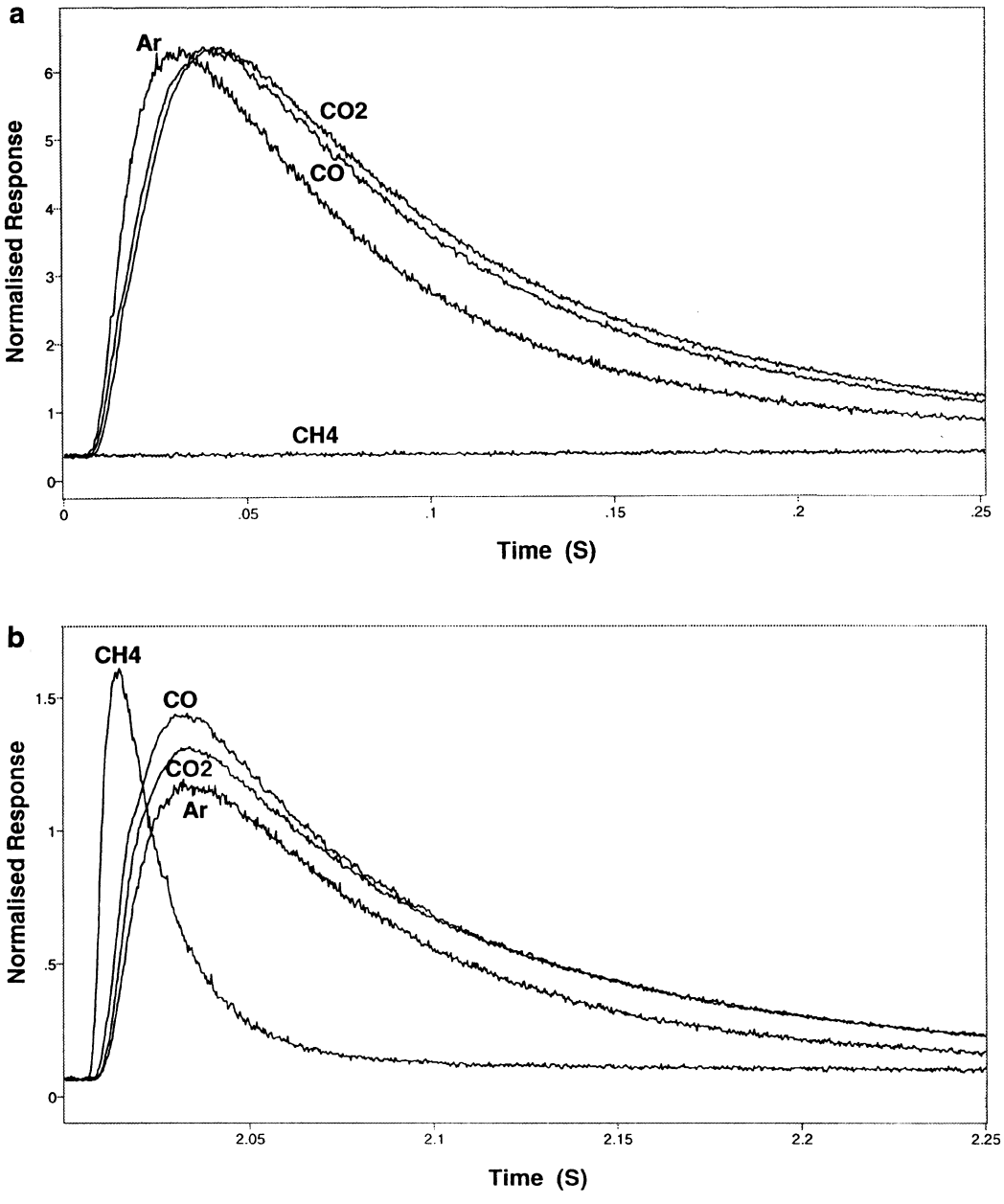

FIG. 2. (a) The normalised responses of CH_4, Ar, CO, and CO_2 as a function of time when pulsing CO_2 and Ar at $t = 0$ s and 700°C. Note that all signals have been normalised to the largest response, which was that of CO_2. (b) The normalised responses of CH_4, Ar, CO, and CO_2 as a function of time when pulsing CH_4 and Ar at $t = 2.0$ s and 700°C. Note that all signals have been normalised to the largest response, which was that of CO_2 in (a).

For both series of experiments there are two trends: (i) the sooner the CO_2 is pulsed after the CH_4, the higher is the CO_2 conversions; and (ii) the sooner the CH_4 is pulsed after the CO_2, the lower is the selectivity for the conversion of the CH_4 to CO. In addition to these trends, it is important to note that the CH_4 conversion remained constant at almost 100% for all experiments, but that the CO_2 conversion varied. The CO_2 conversion was lower than that of CH_4 for each experiment and this resulted in the oxygen balance being more that 100%. It must therefore be concluded that oxygen was removed from the Pt/ZrO_2 material.

Pump-Probe with $^{13}CH_4$

The CO_2 which evolved upon pulsing of CH_4 could have been produced by oxidation of the CH_4 or by desorption of previously adsorbed CO_2 species. Therefore, a series of experiments with methane containing labelled carbon ($^{13}CH_4$) was carried out. Furthermore, in order to gain more information on the incomplete oxygen balance

TABLE 1

The CO_2 and CH_4 Conversions and the Selectivities by Which CH_4 is Converted into CO and CO_2 for Several CO_2/CH_4 Pump-Probe Experiments

Time of pulsing (s)					
CO_2	CH_4	X_{CO_2} (%)	X_{CH_4} (%)	$S_{CO_2}{}^a$ (%)	$S_{CO}{}^a$ (%)
First series					
0	0.5	33	98	63	37
0	1	38	97	59	41
0	2	46	97	51	49
Second series					
0	1	46	97	49	51
1	0	53	96	45	55

[a] These are products of CH_4.

Note. The time between each pulse time was 3 s and therefore pulsing CH_4 1 s after CO_2 can also be viewed as pulsing CH_4 2 s before CO_2.

reported above, the Pt/ZrO_2 sample was pretreated by an extended series of CO_2 pulses. Pump-probe experiments with sequences of CO_2/Ar and $^{13}CH_4$ were then carried out (without Ar present in the $^{13}CH_4$); the CO_2 mixture was the same as that used with the previous pump-probe experiments, while the $^{13}CH_4$ contained 99% $^{13}CH_4$ and 1% $^{12}CH_4$, with a pulse intensity of 5×10^{15} molecules. The experiments were carried out by first pulsing the CO_2/Ar mixture (at $t = 0$ s), followed by pulsing the $^{13}CH_4$ at $t = 1$ s.

The results obtained are presented in Figs. 3a and 3b, in which the normalised responses of $^{12}CO_2$, $^{13}CO_2$, ^{12}CO, ^{13}CO, $^{13}CH_4$, and Ar are plotted as a function of time. The time-scale ranges from 0 to 0.25 s in Fig. 3a and from 1.0 to 1.25 s in Fig. 3b, while the signal normalisation is the same in both figures. In Fig. 3a, where the effect of pulsing $^{12}CO_2$/Ar is examined, only $^{12}CO_2$, ^{12}CO, and Ar are detected. A slight change in the signals of $^{13}CO_2$ and ^{13}CO was also detected, but this could be ascribed to the natural occurrence of $^{13}CO_2$ in $^{12}CO_2$ (due to this the fragmentation pattern of $^{12}CO_2$ will contain a trace of the $^{13}CO_2$). In all other ways the figure is identical to Fig. 2a. Figure 3b shows that mainly $^{13}CO_2$ and ^{13}CO are produced after pulsing of $^{13}CH_4$. Small quantities of $^{12}CO_2$ and ^{12}CO were also formed, but these could be accounted for by an impurity level of $^{12}CH_4$, present in the $^{13}CH_4$. It can be concluded that the CO_2 detected after pulsing CH_4 is a reaction product of the CH_4. In these experiments the $^{13}CH_4$ conversion was nearly complete at 95%, identical to what had been observed with the nonlabelled species. However, selectivity to $^{13}CO_2$ was 90%, much higher than was found in the previous pump-probe experiments, while the CO_2 conversion was 3% much lower than observed before. Since the CO_2 did not supply much oxygen, these results indicate that $^{13}CH_4$ must have extracted oxygen from the Pt/ZrO_2 sample, producing $^{13}CO_2$ and ^{13}CO.

Long-Term $^{13}CH_4$ Addition

Extensive CO_2 pretreatment before the pump-probe experiments resulted in lower CO_2 conversions and higher $^{13}CO_2$ selectivities than when no CO_2 pretreatment was carried out. Therefore, it was decided to examine the effect of a long-term sequence of $^{13}CH_4$ pulses on the Pt/ZrO_2 catalyst. A total of 2500 $^{13}CH_4$ pulses were admitted to the sample, these corresponding to a total of $1.3\ (\pm 0.2) \times 10^{19}$ molecules, or 1.4 ($\pm$0.2) methane molecules per Pt atom present in the sample. During these pulses $^{13}CH_4$, ^{13}CO, and $^{13}CO_2$ were monitored continuously. The $^{13}CH_4$ conversion remained stable, while the selectivity to $^{13}CO_2$ dropped, from 91% at the start of the sequence to 13% after 1200 pulses and to 2% after 2500 pulses, while the ^{13}CO selectivity increased accordingly. Unfortunately, accurate determination of how much oxygen had been removed from the Pt/ZrO_2 sample was not possible as none of the H_2O produced could be detected. However, if one assumes that complete methane conversion occurs, with only CO_2, CO, and H_2 as products, the amount of oxygen extracted during the sequence corresponded to 1.7 oxygen atoms per Pt atom or 0.01 oxygen atom per Zr atom. However, the true value will be higher, since H_2O will also have been formed.

After 1200 pulses of the labelled methane had been admitted, $^{12}CO_2$ was pulsed and the formation of ^{12}CO and ^{13}CO was monitored to see if any carbonaceous species had been formed on the catalyst surface. The $^{12}CO_2$ conversion was 86% and the products were ^{12}CO together with a small amount of ^{13}CO. However, the ^{13}CO peak area corresponded to what would be expected on the basis of the naturally occurring of $^{13}CO_2$ in $^{12}CO_2$. It was therefore concluded that no carbonaceous species were formed on the sample surface during the pulsing of the $^{13}CH_4$.

After 2500 pulses of labelled methane, a $^{13}CH_4$ and CO_2/Ar pump-probe experiment was again conducted, both gases being pulsed at the same time. A conversion of the $^{13}CH_4$ of 98% was observed, this being identical to what has been found previously. However, the selectivity to $^{13}CO_2$ was now only 1%, while ^{13}CO was the predominant product. Furthermore, the CO_2 conversion was 90%, the highest observed in all the pulse experiments carried out. It can therefore be concluded that removal of oxygen from the catalyst not only enhances the CO_2 conversion but also diminishes the production of CO_2 from CH_4.

DISCUSSION

Table 1 shows that when the time interval between the CH_4 and the CO_2 pulses was varied, the CH_4 conversion remained constant. However, the conversion of CO_2 did vary, increasing when the CO_2 was pulsed sooner after the CH_4 pulse. Also, when the CH_4 was pulsed sooner after the CO_2, the selectivity to CO_2 also increased. Both changes could have been caused by some adsorbed species still being

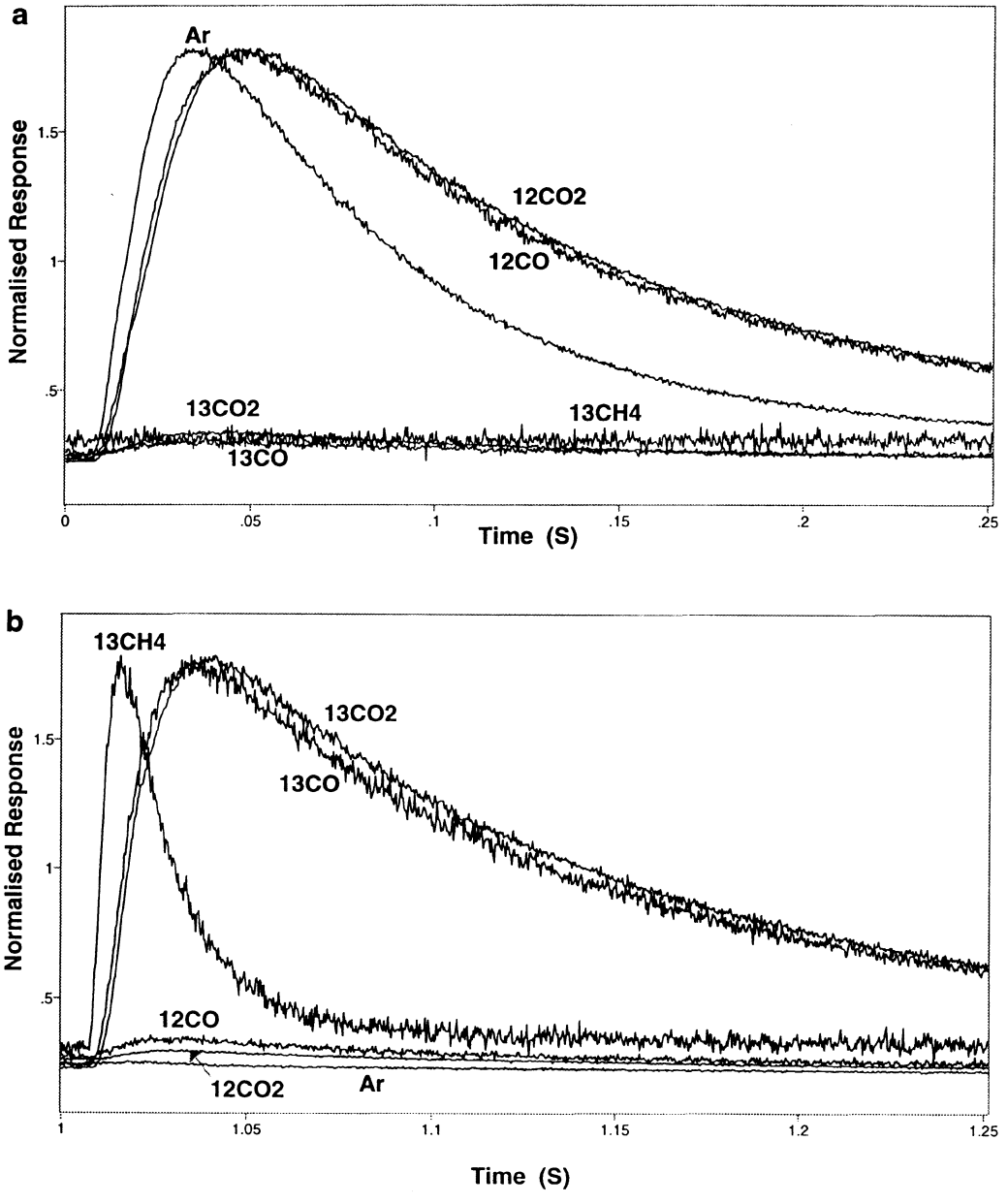

FIG. 3. (a) The normalised responses of $^{13}CH_4$, Ar, ^{12}CO, ^{13}CO, $^{12}CO_2$, and $^{13}CO_2$ as a function of time when pulsing $^{12}CO_2$ and Ar at $t = 0$ s and $T = 700°C$. Note that all signals have been normalised to the largest response, which was that of $^{12}CO_2$. (b) The normalised responses of $^{13}CH_4$, Ar, ^{12}CO, ^{13}CO, $^{12}CO_2$, and $^{13}CO_2$ as a function of time when pulsing $^{13}CH_4$ at $t = 1.0$ s and $T = 700°C$. Note that all signals have been normalised to the largest response, which was that of $^{12}CO_2$ in (a).

present on the surface and/or by the surface gradually being modified by the pulsing of CH_4 or CO_2.

From the single pulse experiments, it can be concluded that the only species which remain sufficiently long on the catalyst to be able to react with subsequent pulses are either adsorbed hydrogen or hydroxyl groups. It is possible that the adsorption of CO_2 is enhanced by the presence of hydroxyl groups or by the formation of HCO_3^- species. On the other hand, adsorbed hydrogen does react with CO_2 as was demonstrated in the experiments with combined H_2 and CO_2 pulses. Solymosi *et al.* (15) have suggested that an enhanced dissociation of CO_2 occurs in the presence of H_2, and Basini *et al.* (16) reported that CO_2 chemisorption on Rh clusters was enhanced by hydrogen due to the formation of a hydridocarbonyl cluster. It could thus be argued that pulsing the CO_2 soon after the CH_4 will result in an enhanced CO_2 reaction due to the presence of more hydrogen on the surface.

However, the changes in the selectivity with which CO_2 is produced from CH_4, brought about by pulsing CH_4 at

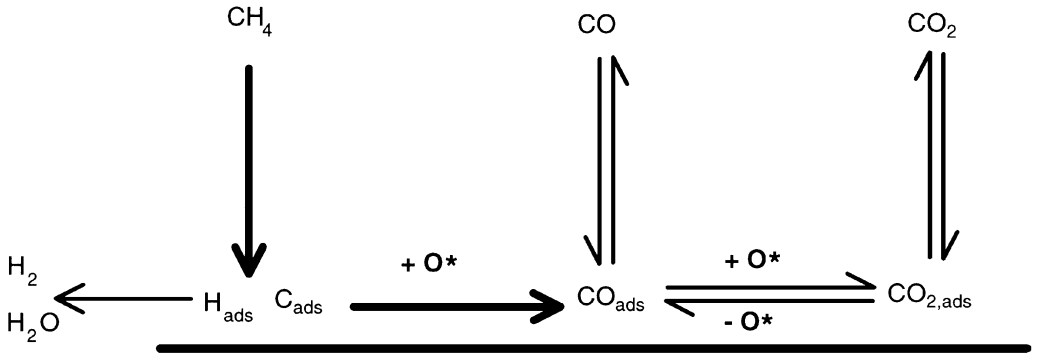

FIG. 4. A scheme of the reaction pathway of the over Pt/ZrO_2.

various intervals after the CO_2, cannot be explained by the presence of hydrogen or hydroxyl groups on the surface. Furthermore, the low CO_2 conversions occurring after pretreatment with CO_2 cannot be explained in this manner either.

The second possibility, a modification of the surface, provides a good explanation for the observations above. As all the pump-probe and labelled experiments exhibited a constant methane conversion while the CO_2 conversion varied considerably, it can be concluded that these two molecules react independently of each other. As CO_2 is converted into CO and the CH_4 into CO, CO_2, H_2, and H_2O, this implies that the intermediate species between CO_2 and CH_4 is an oxygen-containing species. We therefore suggest that there is an oxygen pool on the surface, with CO_2 contributing and CH_4 extracting oxygen. As the long-term pulsing of methane resulted in the removal of at least 1.7 oxygen atoms per Pt atom, this gives an indication of the size of this pool. What exactly is the nature of the pool is not yet known. However, as the Pt/ZrO_2 catalyst is more active and stable than Pt supported on other materials (11, 17), it may be assumed that the zirconia plays a role. There is evidence that ZrO_2 can be reduced partially in the presence of Pt (13, 18); Tournayan *et al.* (18) explained this reduction of the ZrO_2 by the formation of a $Pt_{1-x}Zr_x$ alloy. This suggests that the oxygen pool used for the reactions described here is present in the vicinity of the Pt crystallites.

The existence of an oxygen pool explains the observation that the oxygen balance was never complete. Furthermore, the low CO_2 conversion which occurred after the CO_2 pretreatment can be explained by assuming that the oxygen pool was full so that no oxygen was needed. Moreover, it may also explain that the CO_2 pretreatment resulted in the CH_4 being converted preferentially into CO_2 instead of CO. In other words, the quantity of oxygen (O∗) present in the pool determines whether or not the CO_2 dissociation reaction occurs:

$$CO_{2,ads} \Leftrightarrow CO_{ads} + O*.$$

(Note that the nature of the O∗ has not been identified; the oxygen could be present as adsorbed oxygen species, hydroxyl species, or perhaps even as an carbonate species.)

Figure 4 shows a possible mechanism for the reaction over a Pt/ZrO_2 catalyst. It is probable that the CH_4 decomposes on the Pt, producing C_{ads} and H_{ads}, since no reaction of CH_4 was observed on the ZrO_2. What happens to the H_{ads} cannot be ascertained from the present experiments, but it may be assumed that it will desorb, mainly as H_2 but also partly as H_2O. The CO_2 also dissociates on the catalyst, producing an oxygen species and CO. Though the CO_2 dissociation on supported noble metals has been previously observed (15, 16), the literature is not clear on how it dissociates. Tol *et al.* (19) reported that CO_2 does not dissociate on Pt, even though dissociation did occur on Rh (20). On the other hand, Huinink (21) found that oxygen exchange of CO_2 occurred when it was pulsed over a Pt surface and Bitter *et al.* (22) observed, using infrared spectroscopy, that a Pt–CO bond was formed.

The C_{ads} formed subsequently reacts with the O∗ of the pool to produce CO; as there was no evidence for the existence of C_{ads}, it must be assumed that the reaction of C_{ads} is fast. The CO formed can either be oxidised to CO_2 or remain as CO, depending on the concentration of O∗. If there is an abundance of O∗, the CO will be oxidised preferentially and CO_2 will not dissociate. On the other hand, if there is a shortage of O∗, CO_2 will dissociate to produce CO and CO will not be oxidised. The quantity of O∗ present determines the direction of the CO_2 dissociation reaction: $CO_{2,\,ads}, \Leftrightarrow CO_{ads} + O_a*$.

CONCLUSIONS

It was found that CO_2 and CH_4 react independently of each other on Pt/ZrO_2. An oxygen pool is present on the material; CO_2 acts as an oxygen supplier, while CH_4 extracts the oxygen. When there is an abundance of oxygen on the catalyst surface, the CH_4 can be oxidised to CO_2. The quantity of oxygen present in the pool determines the selectivity with which CH_4 produces CO and CO_2. The direction of the CO_2 dissociation reaction $CO_{2,ads} \Leftrightarrow CO_{ads} + O_{ads}$ (and

its reverse) is affected by the quantity of oxygen in the pool and the presence of adsorbed hydrogen.

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