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Partial oxidation of methane to synthesis gas: Elimination of gas phase oxygen

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Abstract

The reaction between methane and cerium oxide to produce syngas has been studied at 700°C in a pulse apparatus. The cerium oxide was supported on γ-Al_2O_3 and promoted by re-impregnation with Pt or Rh. The promoters drastically enhanced the conversion of methane. TPR with hydrogen shows that Pt and Rh also lowered the temperature necessary to reduce the cerium oxide. Studies of the reaction between methane and promoted cerium oxide showed that the selectivity to syngas depends on the degree of reduction of the cerium oxide. The promoters also led to some carbon formation. Regeneration of the reduced oxide was studied both with oxygen and carbon dioxide. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Partial oxidation; Methane; Synthesis gas; Cerium oxide; Platinum; Rhodium

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1. Introduction

Partial oxidation of methane is an attractive way to produce synthesis gas [1]. The partial oxidation of methane to synthesis gas can proceed through two routes: (1) indirectly through combustion (reactions (1)+(2)+(3)) followed by subsequent reforming (reactions (4) and (5)) of methane and (2) through the direct reaction between methane and oxygen (reaction (1)). It has been shown that under certain conditions over certain catalysts, the direct formation of synthesis gas from methane and oxygen is possible [2–5]. This strongly depends on the availability of oxygen on the catalyst surface and on the oxygen–surface bond-strength [2]. The problem with industrial implementation of synthesis gas production through this route is the reactivity between oxygen and the primary products carbon monoxide and hydrogen to form carbon dioxide and water [5]. This limits the possible yields of synthesis gas from the direct reaction between methane and oxygen at lower temperatures:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad (1)$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \qquad (2)$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad (3)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (4)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (5)$$

Recent research has been directed towards reaction between methane and solid oxygen carriers. A recent study has shown that oxygen in solid oxidized platinum has high activity for methane oxidation to syngas and at the same time a low activity for oxidation of hydrogen and carbon monoxide [4]. Oxygen bound or dissolved in a solid platinum matrix was found to be less reactive than oxygen supplied from a gas phase

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and thereby largely increasing the syngas selectivity. This was proposed relative to the diffusion rate of oxygen in platinum and the surface residence times of the reacting species. However, platinum is a rather expensive material and large volumes would be necessary if it was used only as an oxygen reservoir. Cerium oxide has been shown to have capacity to store and release oxygen in many applications [6–9]. Otsuka et al. [8,9] have studied the reaction between methane and cerium oxide and found that synthesis gas indeed can be formed. Physical mixing with platinum black had a large effect on the conversion of methane.

This study deals with the reaction between methane and cerium oxide promoted directly with platinum and rhodium. Reoxidation of the same materials with oxygen and carbon dioxide has also been studied. The carbon deposition during reaction with methane and the carbon removal with oxygen or carbon dioxide has been measured.

2. Experimental

2.1. Catalyst preparation and characterization

The materials were prepared by incipient wetness impregnation of about 20% CeO_2 on γ-Al_2O_3. The γ-Al_2O_3 material was supplied by Alfa Aesar in pellets and crushed down to particles in the size 300–710 μm. The γ-Al_2O_3 was impregnated with $Ce(NO_3)_3 \cdot 6H_2O$ dissolved in distilled water, dried at 150°C and calcined in air at 600°C for 10 h. The materials were re-impregnated with either 0.5 wt.% Pt [$Pt(NH_3)_4(NO_3)_2$] or Rh [$Rh(NO_3)_3$] and calcined again in air at 600°C for 10 h. Table 1 shows the BET surface areas of the samples before and after impregnation. Temperature programmed reduction (TPR) with H_2 (7% H_2 in Ar) was performed with a heating rate of 10°C/min. Pt/γ-Al_2O_3 and Rh/γ-Al_2O_3 were also studied to have reference peaks for Pt and Rh. X-ray diffraction was performed on the CeO_2/γ-Al_2O_3, the Pt/CeO_2/γ-Al_2O_3 and a sample of Pt/CeO_2/γ-Al_2O_3 that had been studied in the reaction with methane and reoxidized in oxygen.

Table 1
Composition and surface areas of the materials

Sample	CeO_2 (wt.%)	Pt	Rh	BET surface area (m^2/g)
γ-Al_2O_3	–	–	–	198
CeO_2/γ-Al_2O_3	20	–	–	158
Pt/CeO_2/γ-Al_2O_3	20	0.5	–	159
Rh/CeO_2/γ-Al_2O_3	20	–	0.5	157

2.2. Reactor set-up and experimental procedure

Reactions with methane, oxygen and carbon dioxide over the various materials were carried out by injecting 0.25 Nml (10 μmol) of reactant pulses into a steady flow of He (50 Nml/min) that passed over the material samples (0.5 g) which were placed inside an electrically heated quartz reactor. Downstream of the reactor, the He flowed through a packed Porapak Q column (2.1 m, $\frac{1}{4}$ in.) that was isothermal at 70°C. At the exit of the column, there were both a TCD detector and in certain cases a Gaslab 300 mass spectrometer. The total pressure in the reactor was always 1.8 bars. All lines downstream of the reactor were heated to avoid condensation upstream of the analytic tools. The reactor was a quartz tube with an inner diameter of 3 mm. This gave a linear gas velocity of 0.22 m/s at 700°C (1.8 bars) and a contact time between the reactant gases and the material samples (void fraction 0.4) of about 0.26 s. Complete separation and analysis (12–15 min) of the products from a reactant pulse was allowed before a new pulse was introduced. The materials were studied in cycles of multiple pulses of oxygen and subsequently multiple pulses of methane. The materials were then reoxidized in a pulse series of oxygen or carbon dioxide before again starting new series of methane pulses. Carbon deposition was studied in the above-described procedure by measuring the formation of carbon oxides while pulsing oxygen over the used samples.

3. Results and discussion

3.1. Characterization

The TPR analysis is shown in Fig. 1A–C. First the calcination temperature of the $Ce(NO_3)_3$ impregnated γ-Al_2O_3 was studied. Three samples calcined at 400, 500 and 600°C for 10 h were analyzed and the resulting TPR patterns of the calcined samples are shown in

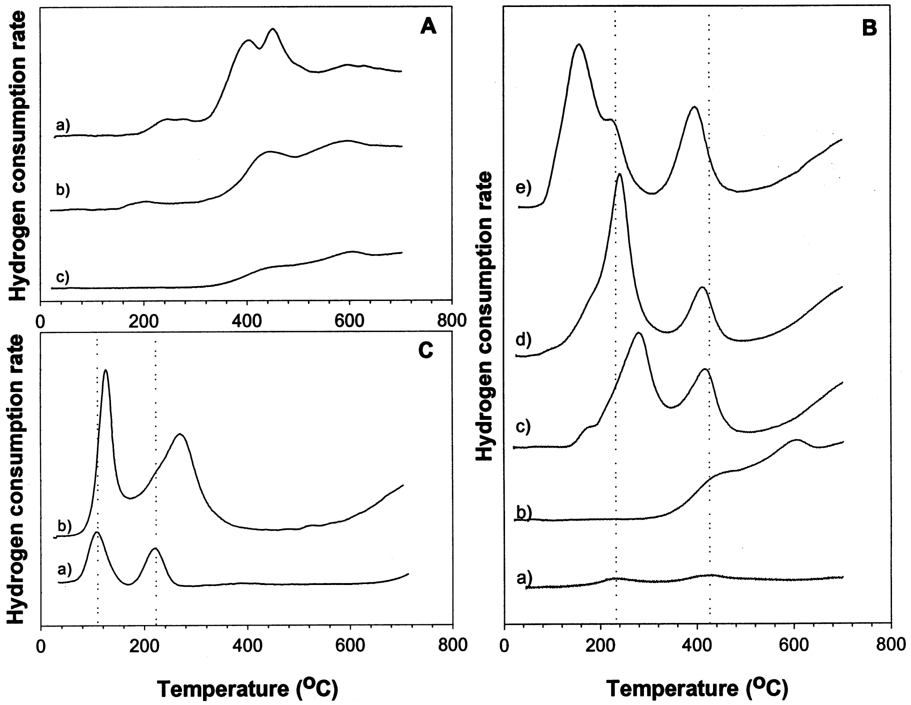

Fig. 1. TPR analysis. (A) $Ce(NO_3)_2 + \gamma\text{-}Al_2O_3$ calcined in air at: a, 400°C; b, 500°C; c, 600°C. (B): a, 0.5 wt.% $Pt/\gamma\text{-}Al_2O_3$; b, 20 wt.% $CeO_2/\gamma\text{-}Al_2O_3$; c, 0.25 wt.% $Pt/CeO_2/\gamma\text{-}Al_2O_3$; d, 0.5 wt.% $Pt/CeO_2/\gamma\text{-}Al_2O_3$; e, 1.0 wt.% $Pt/CeO_2/\gamma\text{-}Al_2O_3$. (C): a, 0.5 wt.% $Rh/\gamma\text{-}Al_2O_3$; b, 0.5 wt.% $Rh/CeO_2/\gamma\text{-}Al_2O_3$.

Fig. 1A. The sample calcined at 400°C had some broad peaks below 500°C. These peaks were smaller on the sample calcined at 500°C, and were not present on the sample calcined at 600°C. The TPR shown in curve c of Fig. 1A is also identical to TPR curves obtained from pure CeO_2 in the literature [6,9]. This showed that a calcination temperature of 600°C was necessary to obtain complete decomposition of the cerium nitrate. The calcination temperature was therefore set to be 600°C. Fig. 1B shows the effect of adding platinum. The unpromoted 20 wt.% $CeO_2/\gamma\text{-}Al_2O_3$ showed no hydrogen consumption before the temperature reached 350°C. The pure 0.5 wt.% $Pt/\gamma\text{-}Al_2O_3$ had two peaks of hydrogen consumption at approximately 230 and 430°C. The peaks were relatively small indicating that the amounts of hydrogen consumed were relatively low. In the cases where cerium oxide was present, as in the rest of the samples in Fig. 1B, the hydrogen consumption was several orders of magnitude greater. For the 0.5 wt.% $Pt/CeO_2/\gamma\text{-}Al_2O_3$, the peaks were approximately at the same temperatures as for the 0.5 wt.% $Pt/\gamma\text{-}Al_2O_3$, but the areas underneath them were much larger. This indicates that the Pt largely affected the reduction of cerium oxide. There was also an effect of the Pt weight loading. The temperature necessary for reduction decreased with increasing weight loading of Pt. The low temperature peak of Pt was most affected and displaced from 280 to about 160°C with an increasing weight loading from 0.25 to 1.0%. The shoulder of the low temperature peak switched from being below to above the main peak with increasing Pt loading. Peak shoulders and peak displacements with variations in the Pt loading on CeO_2 have also been reported in the literature [6]. Fig. 1C shows the reduction of the calcined rhodium catalyst with and without cerium oxide. The areas underneath the Rh-peaks were also here greatly affected by the cerium oxide. The peak of $Rh/\gamma\text{-}Al_2O_3$ at 210°C was much broader was displaced about 50°C higher in the presence of CeO_2.

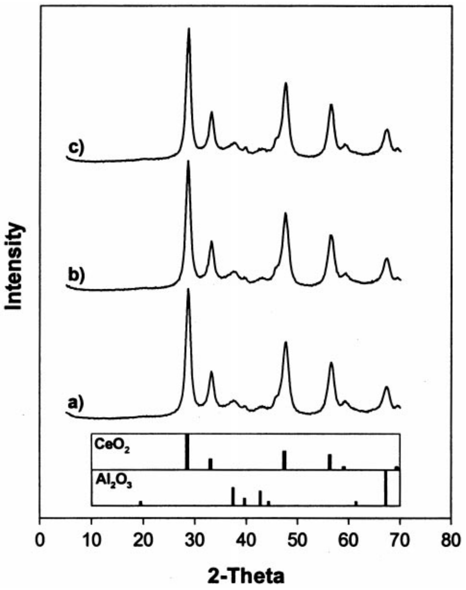

Fig. 2. X-ray diffractograms of (a) 20 wt.% CeO_2/γ-Al_2O_3 calcined in air at 600°C; (b) 0.5 wt.% $Pt/CeO_2/\gamma$-Al_2O_3; (c) 0.5 wt.% $Pt/CeO_2/\gamma$-Al_2O_3 reduced with methane and reoxidized in oxygen at 700°C.

The BET surface area measurements in Table 1 showed that the pure γ-Al_2O_3 support lost some surface area when impregnated with 20% cerium oxide. Re-impregnating the CeO_2/γ-Al_2O_3 with the promoters Pt or Rh did not affect the surface area of the material significantly.

The X-ray diffractograms of the material samples are shown in Fig. 2. The CeO_2 and the γ-Al_2O_3 phases were easily identified [10,11]. No unassigned peaks were discovered. In addition, the diffractogram shows that the peaks were relatively broad. This means that the crystal planes corresponding with the peaks were relatively small. This was not unexpected, considering the porous nature of the γ-Al_2O_3. As expected, the X-ray diffractogram of $Pt/CeO_2/\gamma$-Al_2O_3 was identical to that of pure CeO_2/γ-Al_2O_3. As little as 0.5 wt.% Pt is invisible by XRD, but this shows that the CeO_2 phase was not affected to a detectable degree by the presence of Pt. The diffractogram of the used and reoxidized sample of $Pt/CeO_2/\gamma$-Al_2O_3 was identical to that of fresh sample indicating no permanent structural change of the oxide after being treated in cycles with methane and oxygen.

3.2. Partial oxidation of methane

The reduction of the oxidized materials with methane was studied at 700°C. Bar charts were chosen to represent the results from these experiments for two major reasons: firstly, the material balance is very well visualized. The amount of methane injected was 10 μmol. On basis of the carbon and hydrogen balance, the sum of the different product yields therefore easily show if there was any accumulation in the reactor. This was the case in all the experiments. Secondly, the bar charts illustrate well the discontinuous nature of the experiments. Methane was injected as separate pulses and not as a continuous flow.

Figs. 3 and 4 show the products from 28 pulses of methane injected over CeO_2/γ-Al_2O_3, $Rh/CeO_2/\gamma$-Al_2O_3 and $Pt/CeO_2/\gamma$-Al_2O_3. The hydrogen and water in Fig. 4 were detected by the mass spectrometer. These materials were fresh after the calcination. They had in addition been pretreated in situ with pulses of oxygen at 700°C to ensure complete oxidation. There was no reoxidation in between the pulses of methane. The absolute first pulse of methane yielded mostly carbon dioxide with all the materials. For the unpromoted cerium oxide, the conversion of methane became low after a few pulses. However, there were drastic promoter effects from both Rh and Pt. The first pulses gave full conversion of methane

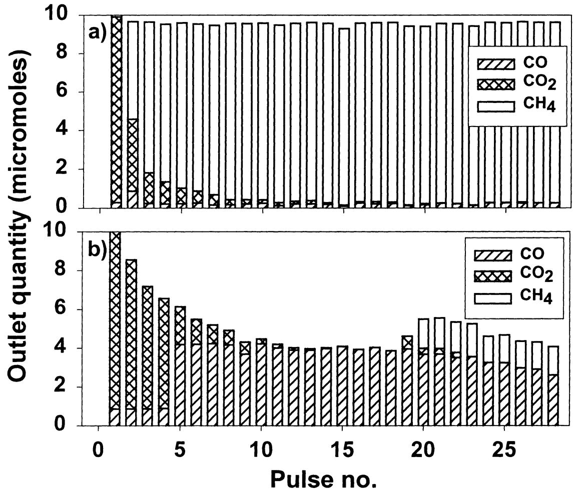

Fig. 3. Methane pulsing (10 μmol/pulse) over fresh samples (0.50 g) of (a) CeO_2/γ-Al_2O_3 and (b) 0.5 wt.% $Rh/CeO_2/\gamma$-Al_2O_3 at 700°C.

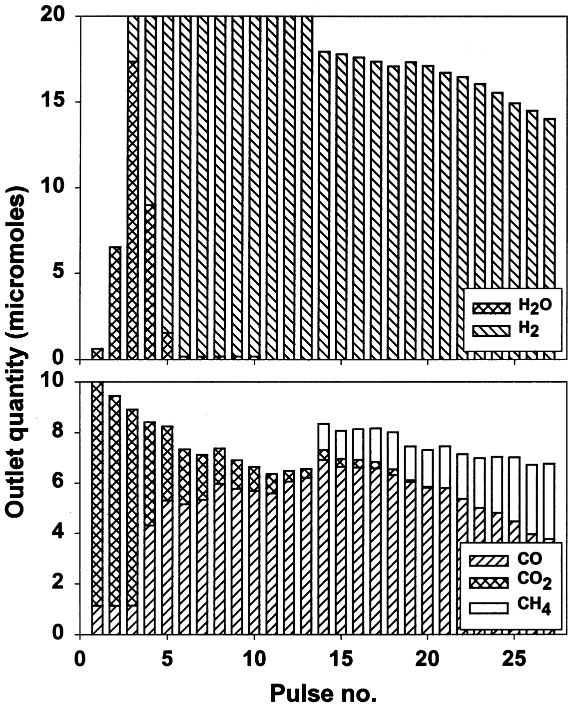

Fig. 4. Methane pulsing (10 μmol/pulse) over fresh a sample (0.50 g) of 0.5 wt.% Pt/CeO_2/γ-Al_2O_3 at 700°C.

and the yield shifted from carbon dioxide towards carbon monoxide. The yield of carbon monoxide was higher with Pt than with Rh. Significant methane slip occurred after 20 pulses with Rh and 14 with Pt as promoter, whereas methane slip occurred after only one methane pulse over the unpromoted CeO_2/γ-Al_2O_3. For the promoted materials it is important to note that after a few pulses the sum of methane, carbon monoxide and carbon dioxide did not add up to the 10 μmol that was the amount of methane injected. The carbon balance therefore strongly indicates that the rest was accumulated in the reactor as some form of carbon. Reactions (6)–(9) describe the formation of carbon and hydrogen and the oxidation to gaseous products by the cerium oxide:

$$CH_4 \rightarrow CH_{4-x} + \tfrac{1}{2}xH_2 \rightarrow C + 2H_2 \qquad (6)$$

$$C + 2CeO_2 \rightarrow CO + Ce_2O_3 \qquad (7)$$

$$CO + 2CeO_2 \rightarrow CO_2 + Ce_2O_3 \qquad (8)$$

$$H_2 + 2CeO_2 \rightarrow H_2O + Ce_2O_3 \qquad (9)$$

The carbon balance shows that more carbon was formed with Rh as promoter than with Pt. It is also very interesting to observe the very low carbon deposition on the unpromoted cerium oxide. This indicates that reaction (6) is catalyzed by the noble metal promoters. The MS analysis of hydrogen and water in Fig. 4 shows that from the absolute first pulse of methane, very little water and no hydrogen came out of the reactor. Cold spots downstream of the reactor were avoided by thorough heating of all lines. The high selectivity towards carbon dioxide in the same first pulse made it reasonable to expect high selectivity towards water at the same time. Since almost no hydrogen containing molecules came out, this must in some way have accumulated on the material in the reactor. This accumulation occurred at a point when the material was relatively fresh and near fully oxidized. Hydrogen accumulation as hydroxyl groups on the ceria surface could explain this accumulation. Hydroxyls could be formed through hydrogen spillover from Pt. Heterolytic splitting of methane on ceria seems less probable as indicated by the higher activity of the material in the presence of a noble metal. Hydroxylation of the ceria surface by water formed in the oxidation reaction is also a possibility.

After the 28 pulses of methane (Fig. 4), the oxygen quantity removed from the material corresponded to a stoichiometric oxide formula of $CeO_{1.6}$. This indicates a one-step reduction mechanism of Ce^{4+} to Ce^{3+}, which would give $CeO_{1.5}$. Otsuka et al. [8] observed a similar degree of reduction. The above experiment also showed that in the reaction between methane and promoted ceria, the selectivity towards carbon monoxide and hydrogen strongly depended on the degree of oxidation of the material. High selectivity was obtained when the most reactive oxygen had been removed as was the case after approximately 50 μmol of methane.

In order to be able to discuss the phenomena that take place in this rector it is necessary to have a good idea of the morphology of the material and the dynamic processes involved. The XRD peaks of the ceria were not affected by the presence of Pt or Rh. The XRD also clearly identified the phase CeO_2. Since the platinum and rhodium were impregnated on the CeO_2/γ-Al_2O_3 after the first calcination, it is reasonable to believe that these metals exist as separate crystallites on top of the cerium oxide phase. The interpretation of the results must therefore take into account that the surface is heterogeneous and consists of two distinctly different phases; one as cerium oxide and other as platinum or rhodium in some oxidized or reduced state. Both TPR and the pulse experiments with methane show large promoter effects. The H_2-TPR results show that the promoters affect the reduction temperature of the cerium oxide. Platinum and rhodium also drastically enhanced the conversion of methane in the pulse experiments. Hence, there is no doubt that these metals must take an active part in the conversion. If the metals are relatively small particles on a large quantity of cerium oxide, the metals are in contact with only a very small fraction of the cerium oxide. The possibility that the metals affect the oxygen dynamics of the whole ceria phase itself is therefore not very likely. On the other hand, it is much more possible that the metals enhance the activation of the reactants. Unpromoted cerium oxide showed very low activity for methane conversion. Methane must therefore be activated on the Pt or Rh surface. Activated methane (carbon or CH_x fragments) is not very likely to be mobile and spill over to the ceria surface. For the reduction of ceria to take place, there must be an exchange (transport) of oxygen to the metal surface where methane appears to react. Oxygen must migrate from the bulk of the cerium oxide to the surface of the promoter metal. Oxygen can be transported not only through bulk diffusion exchange between the two solids, but also through surface spillover [2]. It is probable that both these processes occur at the same time. Surface spillover would be most likely to occur when the surface is rich in oxygen. During multiple pulsing of methane over the material, the surface will be more and more depleted for oxygen and oxygen will be supplied by bulk diffusion from the crystal lattice of cerium oxide.

The unpromoted cerium oxide gave very low carbon formation. This indicates that reaction (6) is the rate-determining step when promoters are not present. However, in the presence of promoters Pt and Rh, carbon formation is significant and the oxidation of carbon appears to be the rate-determining step. More carbon was deposited with Rh than with Pt as promoter. This indicates that coke gasification by oxygen transported from the cerium oxide to the noble metal surface is better with Pt than with Rh. The rate of methane activation with Rh could also be faster than with Pt. The latter would be in good accordance with the lower temperature of reduction with Rh than with Pt during H_2-TPR as shown in Fig. 1.

3.3. Regeneration with oxygen or carbon dioxide

Large amounts of oxygen were taken out of the material during the reduction of cerium oxide by methane. It is also clear from Figs. 3 and 4 that carbon deposition is significant during the methane pulsing. Carbon oxides were also formed when treating the used material with oxygen. Fig. 5 shows what happened during multiple pulsing of oxygen or carbon dioxide over used materials from a treatment as shown in Fig. 4. The regeneration process consisted both in removal of carbon from the surface of the material and recharging the bulk of the cerium oxide with oxygen. Both these processes require oxygen and they are therefore competitive what oxygen is concerned. It was sug-

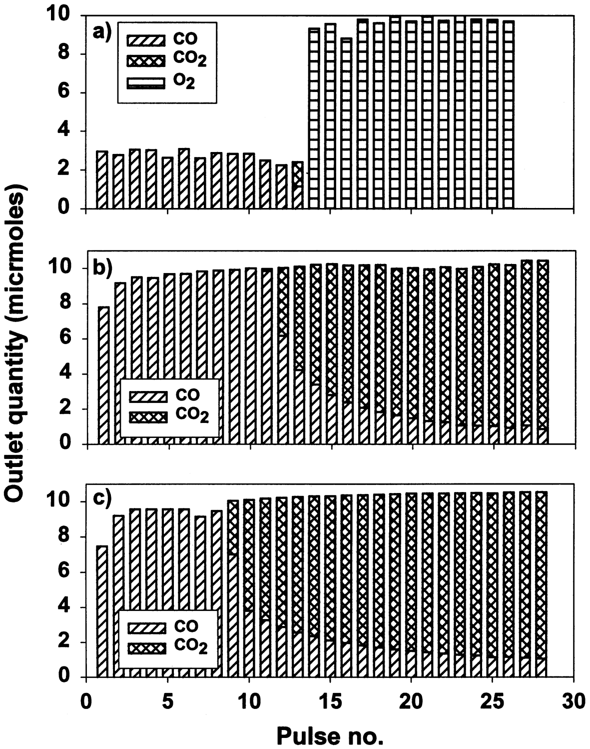

Fig. 5. Regeneration of 0.5 wt.% $Pt/CeO_2/\gamma\text{-}Al_2O_3$ after treatments in methane as shown in Fig. 4 with (a) oxygen at 700°C; (b) carbon dioxide at 700°C; (c) carbon dioxide at 600°C. All pulses of oxygen and carbon dioxide were 10 μmol/pulse.

gested above that the promoters affected the activation of methane and that oxygen had to be transported to the metal surface by diffusion or spillover. The regeneration process in oxygen or carbon dioxide is not necessarily through the reverse oxygen transport as observed with methane, but can probably also occur directly with the ceria surface. Fig. 5a shows the regeneration in oxygen at 700°C. There was a simultaneous reoxidation of both the cerium oxide and carbon as in reactions (10)–(12):

$$\tfrac{1}{2}xO_2 + CeO_{2-x} \rightarrow CeO_2 \qquad (10)$$

$$O_2 + 2C \rightarrow 2CO \qquad (11)$$

$$O_2 + C \rightarrow CO_2 \qquad (12)$$

The yield of carbon monoxide per pulse of oxygen (Fig. 5a) was fairly constant at only about 3 μmol per 10 μmol of oxygen injected. This shows that the oxidation of cerium oxide and carbon deposits occurred simultaneously. Only small amounts of carbon dioxide formed in the last pulse before the sample was completely oxidized and all the oxygen slipped through the reactor. Since the promoters enhance the activation of methane, carbon is most likely to be present on or near to the metal surface rather than the ceria surface. This was also strongly confirmed by the low formation of carbon on the unpromoted $CeO_2/\gamma\text{-}Al_2O_3$ as shown in Fig. 3a. The surface of the ceria phase must be much greater than the surface of the platinum or rhodium. It is therefore likely that the oxygen that adsorbed on ceria would go through reaction (10) and the oxygen that adsorbed on the metals would oxidize carbon in reactions (11) and (12).

The amount of the carbon oxides formed was used to estimate the total amount of carbon deposits after the treatment in methane. This will be quantitatively discussed below. The XRD pattern of a used and reoxidized sample at 700°C was identical to the pattern of a fresh sample (Fig. 2). Subsequent pulsing of methane after the regeneration in oxygen gave identical behavior as in Fig. 4. The oxygen balance deduced from the oxygenated products in Fig. 4 and the oxygen uptake in Fig. 5 are in fairly good agreement (within 8%). It can therefore be concluded that after the reduction with methane, the regeneration with oxygen gave full recovery of the material. It is, however, interesting to note that the regeneration of the material yielded almost 100% carbon monoxide at the same time as the ceria was recovered. Carbon monoxide is much more applicable as a product from carbon removal than carbon dioxide.

The regeneration in carbon dioxide was studied both at 600 and 700°C. The results are shown in Fig. 5b and c. At both temperatures, the material balance of the first pulse showed that some kind of accumulation must have taken place. Carbonate formation is likely to occur on the cerium oxide surface [7,8,12]. Fig. 5a and b indicate that reactions (13) and (14) occurred simultaneously. Thereafter, the carbon monoxide material balance indicated that carbon was also oxidized by carbon dioxide as in (15):

$$3CO_2 + Ce_2O_3 \rightarrow Ce_2(CO_3)_3 \qquad (13)$$

$$xCO_2 + CeO_{2-x} \rightarrow xCO + CeO_2 \qquad (14)$$

$$CO_2 + C \rightarrow 2CO \qquad (15)$$

The carbon dioxide breakthrough occurred earlier during regeneration at 600°C than at 700°C indicating that high temperatures gave deeper oxidation of the material. The oxygen balance showed that at both temperatures, the reduced ceria had not been completely oxidized to CeO_2. This was also confirmed by pulsing methane over the regenerated samples as shown in Fig. 6. Treatment in oxygen after the reoxidation in carbon dioxide revealed that although some

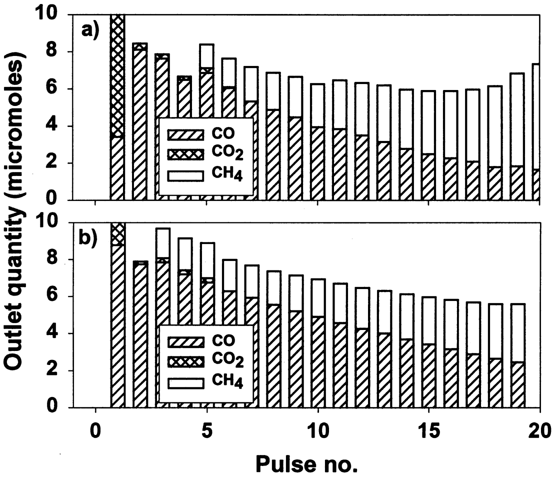

Fig. 6. Methane conversion at 700°C over regenerated 0.5 wt.% $Pt/CeO_2/\gamma\text{-}Al_2O_3$: (a) regenerated with CO_2 at 700°C; (b) regenerated with CO_2 at 600°C.

carbon had been removed according to reaction (15) the total did not correspond to all the amount of carbon deposited during the treatment in methane. After the regeneration with carbon dioxide at 600 and 700°C the carbon removal (measured by subsequent pulsing of oxygen) was estimated to 58 and 74%, respectively.

There were as mentioned some systematic discrepancies in the carbon and oxygen material balances when comparing the accumulation deducted from the sum of products during the pulsing of methane and carbon dioxide, and the actual carbon oxide formation measured from pulsing oxygen. These amounts were in general not equal and there was a clear general trend. The material balances from the pulsing of methane did always give more carbon than was measured afterwards with oxygen. The reactant pulsing over the material proceeded as follows: the gas pulse was injected and transported with helium over the material sample where it immediately reacted with oxygen in the material. The products that desorbed immediately were transported along with the helium further downstream to the packed column where they were separated and finally detected in the detectors. The helium flow through the system had to proceed for 12 min before all the products had come out of the column. It is also possible that there was a slow gasification of carbon deposits during the time in between the reactant pulses and the material was being flushed in helium. The discrepancies in the material balances all indicate that such a slow gasification took place.

Fig. 3a shows that carbon was not formed on the unpromoted cerium oxide during pulsing with methane at 700°C. Figs. 3b and 4 show that carbon was not formed on fully oxidized Rh and Pt promoted material (first pulse). During reduction with successive methane pulses significant amounts of carbon were indeed deposited on the promoted material. This result indicates that carbon is formed on the reduced noble metals.

Ruckenstein and Wang [13] pulsed a mixture of methane and oxygen in the ratio 2:1 over different catalyst samples. Successive pulsing over pure cerium oxide and over Rh promoted cerium oxide gave no carbon deposition at 750°C. Oxygen in the pulse seemed to prevent carbon deposition. During successive pulsing the conversion of methane decreased, while the selectivity to CO increased from zero up to a certain level. This is similar to the trend in our results where carbon was formed.

4. Conclusion

The reaction between methane and cerium oxide to produce synthesis gas is strongly promoted by platinum and rhodium. The selectivity to synthesis gas depends on the degree of reduction of the cerium oxide. The reduction of CeO_2 with methane was carried out until an estimated overall formula of $CeO_{1.6}$. This indicates a one step reduction of Ce^{4+} to Ce^{3+}. During this reduction the conversion of methane decreased. The product ratios $H_2/(H_2O + H_2)$ and $CO/(CO_2 + CO)$ increased with increasing degree of reduction of the cerium oxide. The results indicate that carbon was formed on reduced Pt and Rh.

Regeneration of the used samples with oxygen gave complete removal of carbon as carbon monoxide with high selectivity. Simultaneously, the reoxidation of cerium oxide became complete. Regeneration with carbon dioxide gave incomplete carbon removal and incomplete cerium oxide regeneration. During regeneration with carbon dioxide, the obtainable degree of oxidation increased with increasing temperature.

The present results suggest a highly selective route to synthesis gas from methane and oxygen in cyclic reaction with cerium oxide. In such a route, the cerium oxide acts as an intermediate oxygen carrier. The necessary temperature in such a process (∼700°C) is significantly lower than temperatures usually applied during conventional synthesis gas production (∼900°C).

Acknowledgements

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