

Reaction scheme of partial oxidation of methane to synthesis gas over yttrium-stabilized zirconia

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Abstract

The partial oxidation of methane to synthesis gas over yttrium-stabilized zirconia (YSZ) was studied with in situ FTIR and both steady-state and transient experiments. The four major products, CO, H₂, CO₂, and H₂O, are primary products of CPOM over YSZ. Besides these major products and traces of hydrocarbons, traces of formaldehyde and formic acid were observed in the product mixture for the first time, especially at high reaction temperatures. In situ IR showed that formate was formed by activation of methane on the surface of YSZ catalysts under reaction conditions at temperatures between 400 and 475 °C. Adsorbed formaldehyde was never observed, due to rapid conversion to formate. Temperature-programmed desorption/decomposition (TPD/TPDE) of formate resulted in an essentially identical mixture of CO, CO₂, H₂, and H₂O to normal CPOM. Addition of formaldehyde to the CPOM reaction mixture caused the yields of CO, CO₂, and H₂ to increase without influencing the product distribution. This is a strong indication that CH₂O is indeed an intermediate product, in agreement with the fact that traces of formaldehyde were observed in the product mixture. A reaction scheme is proposed that contains exclusively reaction pathways that contribute significantly; the ratios between the competing pathways is strongly influenced by temperature but does not vary at all when formaldehyde is added. CO and H₂ are formed via decomposition of both adsorbed formaldehyde and formate, while CO₂ is produced via decomposition of formate mainly. Activation of methane is the rate-determining step at 600 °C and higher temperatures. © 2004 Elsevier Inc. All rights reserved.

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1. Introduction

The large amounts of natural gas found worldwide has recently led to extensive research in the area of methane conversion. None of the catalytic processes proposed as direct methods for methane utilization, such as oxidative coupling and partial oxidation to methanol or formaldehyde, is yet mature for industrial exploitation [1] due to the limited yields, despite the efforts and resources devoted to increase those yields. Therefore, indirect utilization of natural gas has attracted more and more attention. Catalytic partial oxidation of methane to synthesis gas (CPOM) is one of the most attractive options among these indirect transformation routes, because of its mild exothermic heat of reaction and its suitable H₂/CO ratio for downstream processes, such as

methanol synthesis and Fischer–Tropsch synthesis. Green and co-workers [2] discussed three main types of catalysts for CPOM in detail: the first group of catalysts are supported nickel, cobalt, and iron, the second group is based on noble metals, and transition metal carbide catalysts are the third group. A considerable amount of work concerning the reaction mechanism of CPOM over the metallic catalyst has been done. Two general mechanisms for the partial oxidation of methane to synthesis gas have been proposed. The so-called “indirect mechanism” claims that methane is combusted to CO₂ and H₂O, followed by both steam and carbon dioxide reforming [3,4] as consecutive reactions. The “direct mechanism” proposed by Schmidt and co-workers [5–7] assumes that methane is directly converted to CO and H₂, without initial deep oxidation. This issue is important because the indirect mechanism will cause huge temperature gradients in the reactor.

However, metallic catalysts are suffering from deactivation by sintering of metal and/or support and from evapora-

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tion of the metal in the form of volatile metal oxide formed at very high temperatures, especially in the presence of oxygen [8,9]. Metal loss in the form of volatile oxide, which contributes to deactivation of the catalyst, is also a serious problem in the ammonia oxidation process over Pt–Rh gauzes operated under similar conditions as CPOM [10].

Mixed oxides have been extensively studied for the oxidative conversion of methane to methanol [11–13], formaldehyde [12–14,20], methyl formate [15], hydrocarbons [16,17], and oxidative coupling of methane [18,19]. CPOM has often been reported as a major side reaction in these processes. Steghuis [20] and Stobbe [21] investigated the oxidation of methane over some oxide catalysts, such as ZrO₂, Y₂O₃, La₂O₃/ZrO₂, yttrium-stabilized zirconia (YSZ), and TiO₂. Among these irreducible oxides, YSZ was the most active catalyst for CPOM. These catalysts show lower activity and selectivity compared to metal catalysts. However, catalyst stability is superior and the issue of lower selectivity can be dealt with by introducing a second metal-based reforming catalyst that can be kept stable because contact with oxygen at high temperatures is avoided as described in our previous work [22].

Stobbe [21] concluded, based on the relation between methane conversion and selectivities over ZrO₂, that CO and H₂ are primary products of CPOM over ZrO₂, whereas CO₂ is formed by water-gas shift and oxidation of CO. Steghuis [20] proposed a reaction mechanism of CPOM over YSZ, including homolytic dissociation of methane over O_(S)⁻ sites followed by conversion to CO, H₂, and H₂O via the formation and decomposition of formaldehyde as an intermediate. CO₂ is produced by further oxidation of the reaction intermediate. However, a H₂/CO ratio in the product mixture significantly larger than one is observed [20], implying that formaldehyde cannot be the only source of CO and H₂.

The objective of the present work is to solve these issues and to complete the reaction scheme of CPOM over a YSZ catalyst, including all essential reaction pathways. This information is essential to define a research strategy to achieve higher selectivity with YSZ-based catalysts. In this work, CPOM over YSZ catalyst was studied with in situ FTIR and catalytic experiments with methane and/or formaldehyde in both steady-state experiments and transient experiments. Based on the obtained results, a modified reaction scheme will be proposed, including an estimation of the relative rate of each path.

2. Experimental

2.1. Catalysts

Yttrium-stabilized zirconia (Gimex, The Netherlands), which consists of 12 wt% yttria in zirconia, was calcined at 600 and 900 °C, respectively, for 15 h. The BET surface areas of two resulting samples were 56 and 22 m²/g after calcination. We refer to these catalysts as YSZ12 and

YSZ12A, respectively. YSZ12 powder was used mainly for in situ infrared experiments because of its higher surface area. YSZ12A was crushed and sieved to 0.3–0.6-mm particles for catalytic testing.

2.2. Catalytic measurements

The CPOM was performed with a fixed-bed reactor made of an alumina tube (inner diameter, 4 mm; length, 450 mm) at atmospheric pressure. A mixture of 0.3 g YSZ12A with 0.3 g α -Al₂O₃ particles with the same particle size was fixed in the isothermal zone of the reactor by quartz wool. In order to minimize the contribution of the gas-phase reaction, two thin alumina sleeves (outer diameter, 3 mm) were put above and below the catalyst bed in the reactor, which were used as thermocouple wells as well. The reaction temperature was varied and the system was allowed to reach steady state within 2 h. Reactants, CH₄ and O₂, were diluted with helium (CH₄:O₂:He = 2:1:14), and total flow rate was about 170 ml/min (STP). On-line gas chromatography with Carboxan 1000 and Haysep N columns was used to analyze the effluent gas from the reactor. N₂ was used as an internal standard. Conversions (*X*) and yields (*Y*) were calculated according to

$$X_{\text{CH}_4} = \frac{\text{CH}_4^{\text{in}} - \text{CH}_4^{\text{out}}}{\text{CH}_4^{\text{in}}}; \quad X_{\text{O}_2} = \frac{\text{O}_2^{\text{in}} - \text{O}_2^{\text{out}}}{\text{O}_2^{\text{in}}};$$

$$Y_{\text{CO}} = \frac{\text{CO}^{\text{out}}}{\text{CH}_4^{\text{in}}}; \quad Y_{\text{CO}_2} = \frac{\text{CO}_2^{\text{out}}}{\text{CH}_4^{\text{in}}};$$

$$Y_{\text{H}_2} = \frac{\text{H}_2^{\text{out}}}{2\text{CH}_4^{\text{in}}}; \quad Y_{\text{H}_2\text{O}} = \frac{\text{H}_2\text{O}^{\text{out}}}{2\text{CH}_4^{\text{in}}}.$$

Mass spectrometry was used to detect trace products, such as HCHO, CHOOH and C₂ products (C₂H₆, C₂H₄, and C₂H₂) by measuring mass-to-charge ratio (*m/z*) values [23]: 30 (HCHO), 46 (CHOOH), and 25 (C₂ hydrocarbons).

To study conversion of formaldehyde over YSZ under typical conditions for CPOM, a second tubular reactor was mounted to the catalytic setup, which was connected to the catalytic reactor. para-Formaldehyde with particle sizes of 0.3–0.6 mm was loaded in this second reactor to generate formaldehyde gas flow by passing 100 ml/min He through the reactor. The partial pressure of formaldehyde in the feed was controlled by the temperature of the second reactor. The formaldehyde stream was co-fed to the catalytic reactor with O₂ (10 ml/min), CH₄ (20 ml/min) and balanced with helium. The conversions (*X*) and yields (*Y*) were calculated according to

$$X_{\text{CH}_4} = \frac{\text{CH}_4^{\text{in}} - \text{CH}_4^{\text{out}}}{\text{CH}_4^{\text{in}}}; \quad X_{\text{O}_2} = \frac{\text{O}_2^{\text{in}} - \text{O}_2^{\text{out}}}{\text{O}_2^{\text{in}}};$$

$$Y_{\text{CO}} = \frac{\text{CO}^{\text{out}}}{\text{CH}_4^{\text{in}} + \text{CH}_2\text{O}^{\text{in}}}; \quad Y_{\text{CO}_2} = \frac{\text{CO}_2^{\text{out}}}{\text{CH}_4^{\text{in}} + \text{CH}_2\text{O}^{\text{in}}};$$

$$Y_{\text{H}_2} = \frac{\text{H}_2^{\text{out}}}{2\text{CH}_4^{\text{in}} - \text{CH}_2\text{O}^{\text{in}}}; \quad Y_{\text{H}_2\text{O}} = \frac{\text{H}_2\text{O}^{\text{out}}}{2\text{CH}_4^{\text{in}} + \text{CH}_2\text{O}^{\text{in}}}.$$

Temperature-programmed oxidation of formaldehyde was also carried out in the same setup. The composition of the product mixture was analyzed with mass spectrometry by following mass-to-charge ratio (m/z) values: 32 (O_2), 30 (HCHO), 16 (CH_4), 31 (CH_3OH), 28 (CO), 2 (H_2), 44 (CO_2), 18 (H_2O), 46 (CHOOH), and 25 (C_2 hydrocarbons).

2.3. In situ infrared spectroscopy

Fig. 1 shows a scheme of the in situ IR system, which consists of a Nicolet 20SXB FTIR spectrometer and a mass spectrometer. The stainless-steel IR cell was constructed as a continuously stirred tank reactor (1.5 cm^3) equipped with two CaF_2 windows. Mass-flow controllers were used to control all gas flow rates. The catalyst powder (about 10 mg) was pressed into a self-supporting wafer. By switching the four-port valve, the composition of the gas can be changed between inert (helium) and reactive gas. The IR spectra were collected with a resolution of 4 cm^{-1} and treated by the Nicolet OMNIC software. IR results are presented as difference spectra by subtracting the spectrum of the catalyst sample in helium. Before measurement, the catalyst sample was activated in situ at $600\text{ }^\circ\text{C}$ for 30 min with 20% O_2 in helium and subsequently cooled down to the reaction temperature in helium. The effluent composition was monitored with a quadrupole mass spectrometer (Balzers QMG 420). A blank experiment was carried out with an empty cell under identical conditions; no conversion of CH_4 and O_2 was observed.

2.4. Temperature-programmed desorption/decomposition (TPD/TPDE)

2.4.1. TPD/TPDE in the IR cell

After formation of formate species via reaction of CH_4 and O_2 on YSZ12 at $400\text{ }^\circ\text{C}$ in the in situ IR experiment (see results), the sample was cooled down to $50\text{ }^\circ\text{C}$ in He and kept at $50\text{ }^\circ\text{C}$ for 30 min in helium flow, subsequently heated up with a ramp of $10\text{ }^\circ\text{C}/\text{min}$ to $600\text{ }^\circ\text{C}$, and kept at $600\text{ }^\circ\text{C}$

for 10 min. The effluent composition was monitored with a quadrupole mass spectrometer (Balzers QMG 420).

2.4.2. TPD/TPDE in TPD setup

A homemade TPD setup equipped with a mass spectrometer (BALZERS QMS 200F) was used for temperature-programmed desorption or temperature-programmed decomposition experiments. About 0.15 g of catalyst YSZ12A was placed in a quartz tube (reactor). After the catalyst was activated at $500\text{ }^\circ\text{C}$ and 10^{-3} mbar for 7 h and subsequently cooled down to $50\text{ }^\circ\text{C}$, the mixture of reactants ($CH_4/O_2 = 2/1$) was introduced to the system till 7 mbar. Subsequently, the reactor was heated up to $400\text{ }^\circ\text{C}$. After reaction at $400\text{ }^\circ\text{C}$ for 2 h, the system was evacuated at $400\text{ }^\circ\text{C}$ for 2 h to remove unconverted reactants and weakly adsorbed molecules. Then, the reactor was cooled down to $50\text{ }^\circ\text{C}$, and TPD/TPDE was carried out with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ to $800\text{ }^\circ\text{C}$ and dwelled at $800\text{ }^\circ\text{C}$ for 1 h.

3. Results

3.1. Partial oxidation of methane over YSZ

Blank experiments in the empty alumina tubular reactor and with diluent $\alpha\text{-Al}_2O_3$ particles exclusively were carried out to check the activity of both reactor wall and $\alpha\text{-Al}_2O_3$ particles. In the empty reactor only about 1% methane conversion was observed at $900\text{ }^\circ\text{C}$. Compared with YSZ, $\alpha\text{-Al}_2O_3$ was much less active for CPOM. The methane conversion over $\alpha\text{-Al}_2O_3$ was less than 0.5% at $700\text{ }^\circ\text{C}$, while at this temperature YSZ12A converted oxygen completely and about 40% of the methane already as shown in Fig. 2. Besides the four major products CO, H_2 , CO_2 , and H_2O , small amount of hydrocarbons (C_2H_6 , C_2H_4 , and C_2H_2), formed via methane coupling, were observed as well over YSZ12A.

Traces of formaldehyde and formic acid were detected by mass spectrometry in the product mixture of CPOM. As shown in Fig. 3, mass signals of HCHO (m/z , 30) and

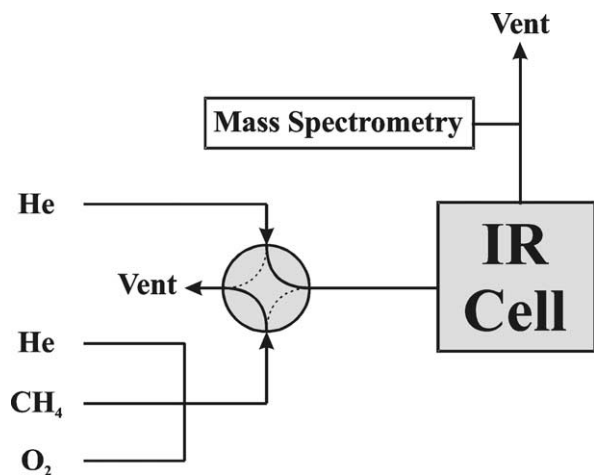


Fig. 1. Scheme of a flow system for in situ IR measurement.

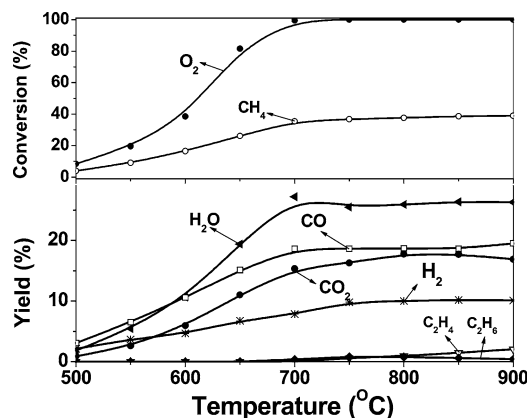


Fig. 2. Conversion/yield as a function of reaction temperature. Conditions: catalyst 0.3 g YSZ12A diluted with 0.3 g $\alpha\text{-Al}_2O_3$, $CH_4/O_2/He = 2/1/14$, $F_{total} = 170\text{ ml}/\text{min}$.

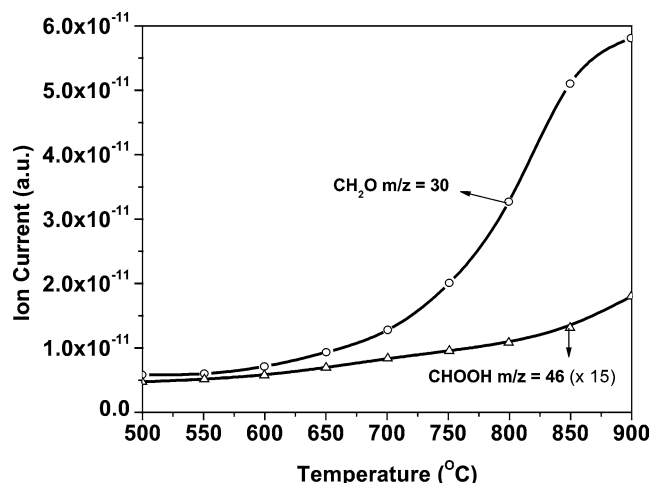


Fig. 3. Trace products in CPOM detected by mass spectrometer during CPOM over YSZ12A. Conditions: as shown in Fig. 2.

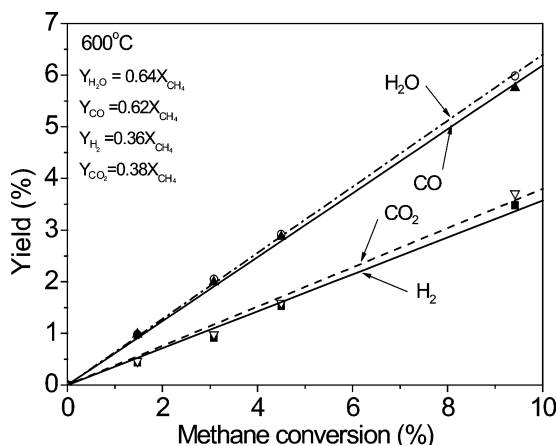


Fig. 4. Yield as a function of methane conversion. Catalyst, YSZ12A; temperature, 600 °C.

CHOOH (m/z , 46) increase with increasing reaction temperature.

Fig. 4 shows that the yields of CO, CO₂, H₂ and H₂O increase linearly with the methane conversion at 600 °C up to 10% conversion, which was varied via the contact time by varying the amount of catalyst. In other words, the selectivities of the products are independent of the methane conversion, which indicates that CO, CO₂, H₂, and H₂O are primary products of CPOM. At 600 °C, the selectivities to CO and CO₂ were 62 and 38%, and the H₂/CO and H₂/CO₂ ratios were 1.16 and 1.89, respectively.

3.2. In situ IR study

In situ IR measurements were conducted on both YSZ12A and YSZ12 catalysts in the same gas mixture (11.8% CH₄, 5.9% O₂, and balance He) as used in the catalytic experiments. Very weak bands were observed on the surface of YSZ12A due to its low surface area. Therefore, an in situ IR study was carried out on YSZ12 in the present work, which

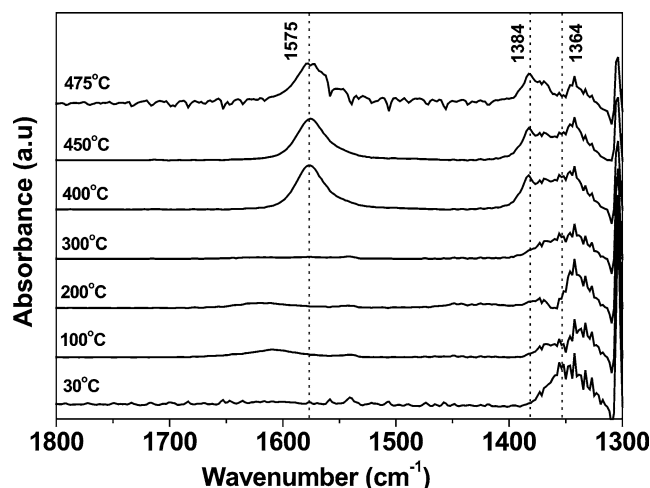


Fig. 5. In situ IR spectra obtained during CPOM. Catalyst, YSZ12; reactive gas, CH₄/O₂/He = 2/1/14; Total flow rate, 100 ml/min.

has a higher surface area. Fig. 5 shows FTIR absorbance spectra collected during reaction of CH₄ with O₂ on YSZ12 at different temperatures (30–475 °C). Formate is the only surface intermediate observed exclusively above 400 °C, characterized by the bands at 1575 ($\nu_{\text{as}}\text{OCO}$), 1384 (δ_{CH}), and 1364 cm^{-1} ($\nu_{\text{s}}\text{OCO}$). The ν_{CH} mode was observed at 2885 cm^{-1} , which is in agreement with the assignment to formate [24]. The wave numbers measured are similar to those reported by Busca et al. [25] for the formate species formed via the adsorption of formaldehyde on ZrO₂ at room temperature. The intensity of the formate bands hardly varied between 400 °C and 475 °C (the highest temperature that the IR cell can reach), although noise increased at higher temperatures. No reaction products were detected in the effluent stream by mass spectrometry at any temperature from 30 to 475 °C.

3.3. TPD/TPDE of the formate on YSZ surface

After the formate was formed on YSZ12 in the in situ IR experiment, TPD/TPDE was carried out in the infrared cell (Fig. 6). The major decomposition products of the formate species on the surface of YSZ12 are CO, CO₂, H₂, and H₂O.

TPD/TPDE experiments were also carried out on catalyst YSZ12A in a dedicated MS-TPD setup, which could reach a maximum temperature of 800 °C (Fig. 7). Again, the same decomposition products (CO, CO₂, H₂, and H₂O) are observed and in addition also CH₄ desorbed from the surface of YSZ12A. Desorption commenced between 400 and 500 °C and desorption was still not complete at 800 °C. Two desorption peaks were observed for CO, H₂, and especially CO₂ at 580 °C and around 800 °C, respectively. The latter peak is obviously an artifact as the maximum temperature is 800 °C so the actual second maximum temperature would be higher. Both water and methane do not show a convincing second desorption peak. The major amount of water was

desorbed from the catalyst in a relatively low temperature region with the maximum at 580 °C.

3.4. Oxidative conversion of CH₂O

3.4.1. YSZ12A

Temperature-programmed oxidative conversion of CH₂O was carried out over 0.3 g YSZ12A catalyst with CH₂O and O₂ partial pressures of 0.033 and 0.029 bar (balanced with helium). Fig. 8 presents the product distribution at different temperatures. CO, CH₃OH, and CH₄ were major products at temperatures below 350 °C. Maximal yields of CO and H₂O were observed at about 350 °C, coinciding with the temperature at which formaldehyde is just converted completely. At 500 °C the yield of H₂ is maximal whereas the yield of H₂O exhibits a local minimum. At even higher temperatures,

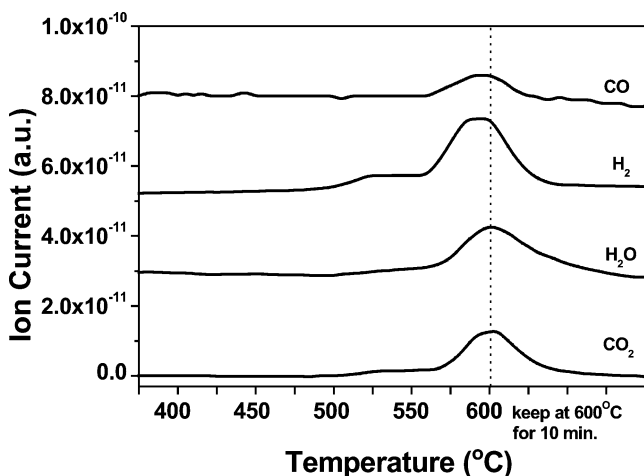


Fig. 6. TPD/TPDE profiles of formate species on YSZ12 surface (in IR cells).

the yields of CO₂ and H₂O increase at the expense of CO and H₂.

3.4.2. Empty reactor

The empty reactor gives completely different results compared to YSZ12A. Fig. 9 shows that CH₂O is not converted at all below 350 °C, and the conversion is not complete even at 900 °C. About 10% formaldehyde remained unconverted in gas phase at 900 °C. CH₃OH and CH₄ were not detected at any temperature between 200 and 900 °C. Production of CO and H₂O increased with reaction temperature, and the maximal yields of CO₂ and H₂ were obtained at 750 °C.

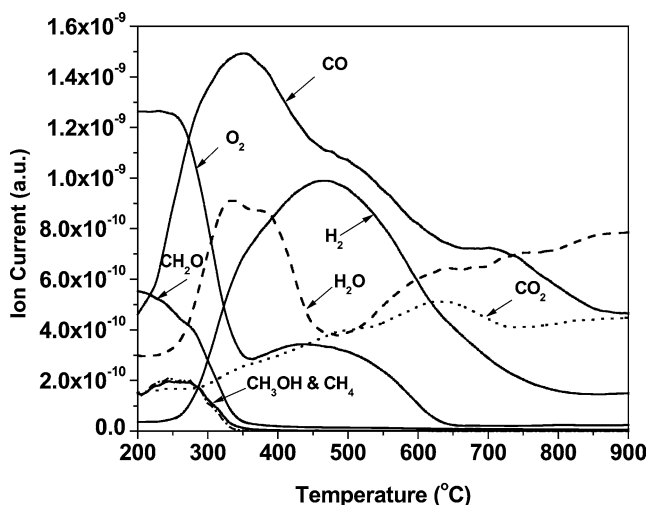


Fig. 8. Temperature-programmed oxidative conversion of CH₂O over YSZ12A with a heat rate of 10 °C/min. $P_{\text{CH}_2\text{O}} = 0.033$ bar; $P_{\text{O}_2} = 0.029$ bar; catalyst: 0.3 g YSZ12A diluted with 0.3 g $\alpha\text{-Al}_2\text{O}_3$.

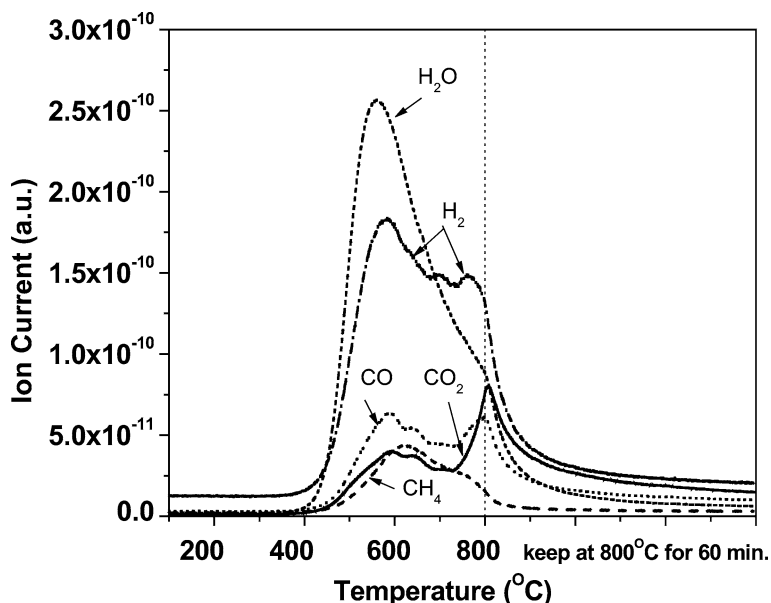


Fig. 7. TPD/TPDE after reaction of CH₄ and O₂ (2:1) at 400 °C for 2 h on YSZ12A pretreated at 500 °C for 7 h under 10⁻³ mbar. Evacuated at 400 °C for 2 h.

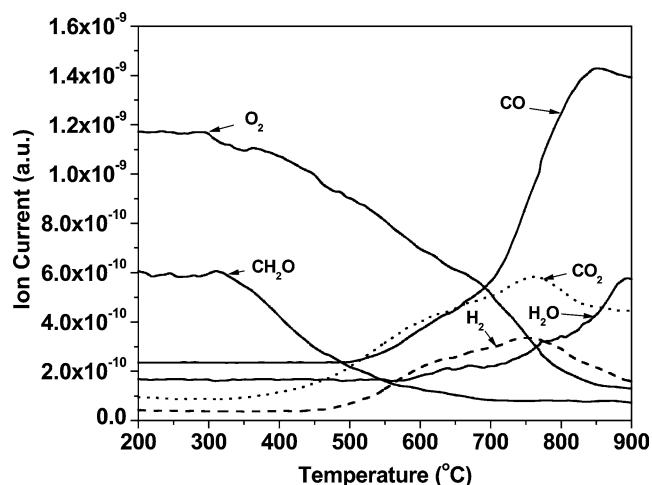


Fig. 9. Temperature programmed oxidative conversion of CH_2O in an empty reactor with a heat rate of $10\text{ }^\circ\text{C}/\text{min}$. $P_{\text{CH}_2\text{O}} = 0.033\text{ bar}$; $P_{\text{O}_2} = 0.026\text{ bar}$.

3.4.3. Cofeeding CH_2O with CH_4 and O_2

In order to study the conversion of formaldehyde over YSZ12A under typical conditions for normal CPOM, a small amount of CH_2O was added continuously to the mixture of feed gases with the same partial pressures of CH_4 and O_2 (balanced with helium) as used in the normal CPOM experiments. Conversions and yields were plotted as a function of CH_2O partial pressure in the feed gas in Fig. 10. Oxygen was completely converted at $800\text{ }^\circ\text{C}$ (Fig. 10a) and the yields of CO , CO_2 , and H_2 increased significantly with the increase of CH_2O partial pressure. In contrast, methane conversion and the yield of H_2O decreased with CH_2O introduced to the feed. At lower temperatures, e.g., $600\text{ }^\circ\text{C}$ (Fig. 10b), where oxygen had not been consumed completely, the methane conversion was constant at 16%, independent of CH_2O partial pressure in the feed. The oxygen conversion, and yields of CO , CO_2 , and H_2 increased significantly with the CH_2O partial pressure. In contrast, the effect on the yield of H_2O was rather modest. In both experiments at 600 and $800\text{ }^\circ\text{C}$, the trace of formaldehyde detected in the effluent mixture from the reactor was about the same as detected in normal CPOM. The H_2/CO ratio and selectivities to CO and CO_2 as a function of CH_2O partial pressure at $600\text{ }^\circ\text{C}$ are shown in Fig. 11. Only minor changes in selectivities and H_2/CO ratio were observed when increasing the CH_2O partial pressure.

4. Discussion

4.1. Activation of methane

The formation of formate on surface of YSZ12, shown in Fig. 5, clearly indicates that methane is activated and reacts with oxygen at relatively low temperatures (around $400\text{ }^\circ\text{C}$). The actual temperature of the sample wafer could be lower

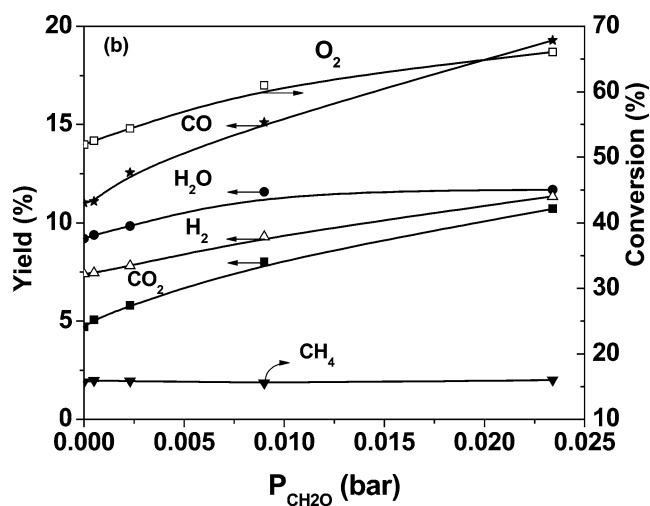
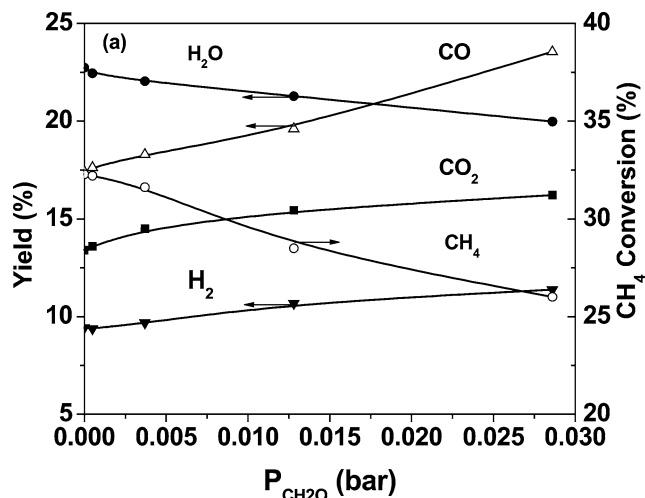


Fig. 10. The effects of CH_2O addition to the feed gas on conversions and yields at different reaction temperatures (a) $800\text{ }^\circ\text{C}$ (O_2 conversion, 100%). (b) $600\text{ }^\circ\text{C}$. Catalyst, 0.3 g YSZ12A; feed gases, $P_{\text{CH}_4} = 0.118\text{ bar}$, $P_{\text{O}_2} = 0.059\text{ bar}$, balance He. Total flow rate: 170 ml/min.

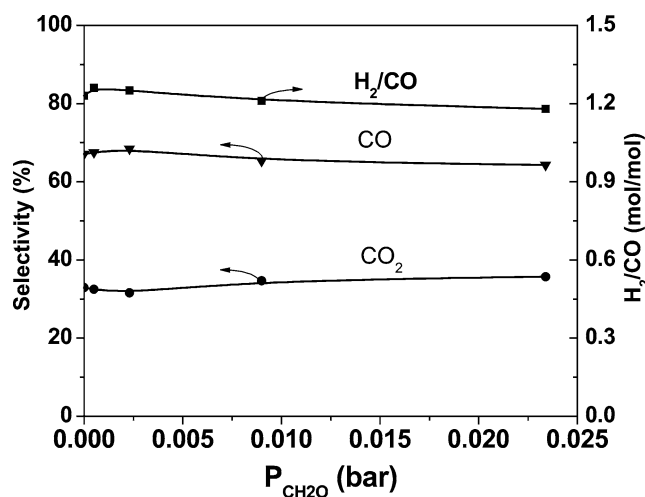


Fig. 11. Product distribution of formaldehyde oxidation over YSZ12A at $600\text{ }^\circ\text{C}$ under CPOM conditions. Conditions: as shown in Fig. 10.

than that indicated in Fig. 5 because the measured temperature was that of the sample holder surrounded by heating wires. The same products (CO, CO₂, H₂, and H₂O) are observed during TPD/TPDE of formate in both the IR cell and the TPD setup (quartz tube). The decomposition temperature on YSZ12 ($S_g = 56 \text{ m}^2/\text{g}$) (Fig. 6) and on YSZ12A ($S_g = 22 \text{ m}^2/\text{g}$) (Fig. 7) varies and the experiment in the dedicated TPD (Fig. 7) gives much more details because the IR cell is not optimized for TPD experiments. The difference in the decomposition temperature might be caused by the different surface areas of these two catalysts. The formate species is so stable that no decomposition products could be detected in the effluent from IR cells at temperatures between 400 and 475 °C, which agrees well with the TPD/TPDE result in Fig. 6. This indicates that in the low temperature region, the rate-determining step of CPOM over YSZ is not activation of methane but decomposition of the formate. Nevertheless, the detection of a small amount of CO₂ during TPO of formaldehyde (Fig. 8) indicates that oxidation of formate at low temperatures is possible. We will discuss the rate-determining step in more detail later.

The mechanism of activation of methane is one of the most important aspects in methane oxidation. However, the mechanism is still far from being understood on no-redox oxides. Most of the proposals for the mechanism of methane activation on irreducible oxides, like ZrO₂, YSZ, and Al₂O₃, are based on the characterization of physical adsorbed methane on oxides at low temperatures (<0 °C) [20,26]. Information on surface intermediates during methane oxidation over irreducible oxides under reaction conditions (e.g., temperatures above 400 °C) is not available due to rapid transformation of the intermediates on oxides. Here, it is the first time, to the best of our knowledge, that formate is observed on the surface of irreducible oxides, formed via oxidation of methane at relatively low temperatures.

Doping ZrO₂ with yttrium results in not only the formation of a stable tetragonal or cubic phase but also the generation of defects (oxygen vacancies) in the bulk of YSZ, strongly influencing the ion conductivity of the material. The extent of the presence of those vacancies on the surface of YSZ is not known, but it seems reasonable to assume that the surface contains oxygen vacancies as well. The role of such oxygen vacancies or different types of surface oxygen species (e.g., O⁻ as reported by Steghuis [20]) in the activation of methane and oxygen on YSZ is also not clear yet. Investigation of the effects of the oxygen vacancies and surface hydroxyl groups is in progress in our lab. In this contribution we will limit ourselves to the reaction pathway, without going into details about the active sites that are involved in the reactions.

4.2. Reaction intermediates

Formaldehyde is often detected in the product mixture of the partial oxidation of methane over many oxide catalysts [15,19,27,28]. The detection of formaldehyde as an inter-

mediate product here (Fig. 3) is not surprising. However, addition of a small amount of formaldehyde to the feed gas of CPOM results in a product mixture with identical H₂/CO ratio and selectivities to CO, CO₂ as observed in normal CPOM (Fig. 11). These identical results confirm that CH₂O is indeed a reaction intermediate. The product distribution in Fig. 11 would have changed significantly, e.g., in the case that all formaldehyde added would have decomposed to CO and H₂.

The observation of formate on the surface of YSZ in the in situ IR experiments and the similarity between the product distribution during TPD/TPDE of the formate intermediate (Figs. 6 and 7) and the product distribution during steady-state CPOM (Fig. 2) indicate strongly that formate is also a reaction intermediate in CPOM. The observation of traces of formic acid in the mixture of CPOM product (Fig. 3), although very small, gives further support for this hypothesis. The surface formate was found on oxides in many processes, such as dry reforming of methane on Ru/ γ -Al₂O₃ [29], hydrogenation of CO₂ over Ru/TiO₂ [30], and adsorption of methanol and formaldehyde on Ce_xZr_{1-x}O₂ [24] and on ZrO₂, TiO₂, and Al₂O₃ [25]. Decomposition of formic acid and formate on oxides has been studied by many researchers [31,32]. Two reaction routes are widely accepted for decomposition of adsorbed formate [32]: dehydrogenation to CO₂ and H₂ versus dehydration to CO and H₂O.

Adsorption of formaldehyde on different oxides has been studied by Busca et. al [25] using FTIR spectroscopy between 170 and 570 K. Adsorbed formaldehyde can be observed only at an extremely low temperature (around 170 K), and transformation of formaldehyde to polyoxymethylene, dioxymethylene, formate, and methoxy already occurs at such low temperatures. After heating up to 270–300 K, only formate and methoxy species are observed on the surface of titania and zirconia. We studied adsorption of formaldehyde on YSZ by IR at room temperature. Only adsorbed formate and methoxy were observed on the surface of YSZ12. More detailed results of formaldehyde adsorption on YSZ will be reported in a future publication. However, the fast transformation of formaldehyde to formate on YSZ explains the fact that no adsorbed formaldehyde was observed on YSZ in the in situ IR experiments.

Steghuis [20] proposed that the decomposition of adsorbed formaldehyde is the only source of CO and H₂. If that were the case, the H₂/CO ratio in the product mixture would be 1:1. It was shown before that consecutive reactions, like steam reforming, CO₂ reforming, and water-gas-shift reaction, which would obviously influence the CO/H₂ ratio, can be neglected for temperature below 900 °C [20]. We have also investigated all possible reactions that may occur between CH₄ and CPOM products, such as CO₂ and steam reforming of methane, and among products, like water-gas-shift and reverse water-gas-shift reactions over YSZ catalysts in a wide temperature window (500–1100 °C). The results are consistent with Steghuis' conclusions and will be reported soon. On the other hand, if all formaldehyde would

transfer to surface formate that decomposes to CO, H₂O, CO₂, and H₂ under CPOM conditions, the ratio of H₂/CO₂ in the product mixture would be 0.5:1. However, the higher H₂/CO (> 1.0) and H₂/CO₂ ratios (> 0.5), shown in Fig. 4, imply that CO and H₂ are produced from both formaldehyde and formate.

Therefore, both formaldehyde and formate are reaction intermediates in CPOM over YSZ. A part of the adsorbed formaldehyde decomposes to CO and H₂, while the rest is oxidized to formate, which decomposes to CO and H₂O via dehydration, and to CO₂ and H₂ via dehydrogenation. Obviously, the H₂/CO ratio of the product mixture strongly depends on the relative rate of each reaction pathway, which will be discussed in more detail hereafter.

4.3. Reaction scheme

Based on the discussion so far we propose the reaction scheme shown in Fig. 12. As discussed in Section 4.2, activation of methane on the surface of the YSZ results in formation of surface formaldehyde (reaction 1). A part of the formaldehyde is further oxidized to formate on the surface (reaction 2). The rest of the formaldehyde decomposes on the YSZ surface to CO and H₂ (reaction 5), and also possibly desorbs (step 6) and decomposes to CO and H₂ (reaction 8) in the gas phase. We also include the possibility that desorbed formaldehyde can be oxidized in the gas phase to CO₂ and H₂O via reaction 7. Surface formate decomposes to a mixture of CO, CO₂, H₂, and H₂O (Figs. 6 and 7), which is in agreement with the reactions 3 and 4, as proposed earlier by Bianchi et al. [32]. The surface formate species may be oxidized further to carbonate species, which decomposes to CO₂ at high temperature. Most of the water is produced in the first step (reaction 1), which explains well the fact that methane conversion influences water formation dramatically, as observed in Fig. 10a, whereas a very little contribution of CH₂O oxidation to the water formation was observed in Fig. 10b.

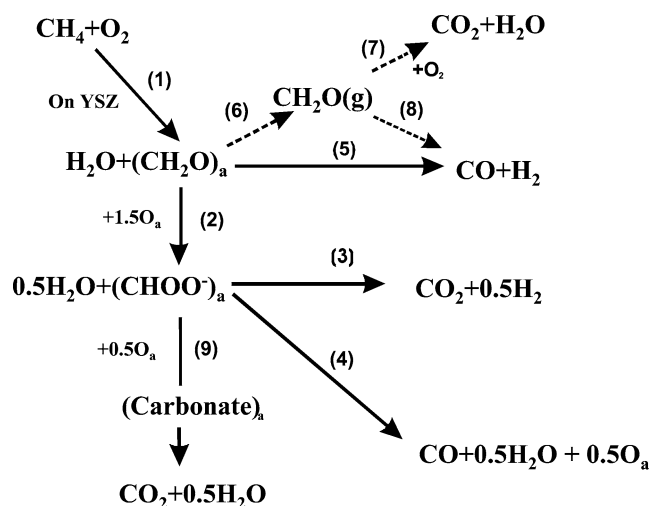


Fig. 12. The proposed reaction mechanism of CPOM on YSZ.

A number of reaction steps can be ruled out based on the experimental results. Oxidative conversion of formaldehyde was studied with temperature-programmed reaction over YSZ12A and in the empty reactor (Figs. 8 and 9). Compared with the reaction in the empty reactor, the oxidation of formaldehyde over YSZ12A is much faster. The conversion of formaldehyde in the gas phase is far from completion and does not exceed 90% even at 900 °C (Fig. 9). In contrast, only a trace of formaldehyde was detected in the normal CPOM experiment under the same conditions. This suggests that the conversion of formaldehyde on the surface of YSZ12A is much faster than its desorption. Moreover, compared with decomposition of formaldehyde over YSZ, the decomposition in the gas phase is minor [20] and this is also evident from the comparison between Figs. 8 and 9. Therefore, the conversion of adsorbed formaldehyde predominately occurs via decomposition and oxidation on the surface of YSZ12A (reactions 2 and 5). The contribution of reactions in the gas phase (reactions 6, 7, and 8) is not significant. Thus, the reaction paths with dotted arrows in Fig. 12 are not essential and can be neglected.

A remarkable decrease of methane conversion was observed when formaldehyde is added at 800 °C, when oxygen is exhausted as shown in Fig. 10a. This indicates competition in oxygen consumption by methane oxidation and oxidative conversion of formaldehyde. Apparently, the latter is much faster than the former, especially when it is taken into account that the formaldehyde concentration is roughly one order of magnitude lower than the methane concentration. On the other hand, at 600 °C and incomplete conversion of oxygen, the addition of formaldehyde causes a significant increase in yield of all major products due to complete conversion of the formaldehyde added to the reaction mixture. Therefore, it can be concluded that methane activation is the rate-determining step of CPOM over YSZ at 600 °C and above.

Earlier we have seen that below 500 °C methane is converted to adsorbed formate, without detectable further reaction to desorbed products. Apparently, methane activation is faster than decomposition of formate. On the other hand, between 600 and 800 °C the activation of methane is the rate-determining step. If this is to be explained in terms of the activation energy of both steps, it would follow that the activation energy of formate decomposition would be larger than for methane activation, which is very unlikely. Therefore, we propose that the activation of methane below 500 °C proceeds via a reaction channel that is not accessible at higher temperatures. This would be the case, e.g., if a relatively labile surface oxygen species is responsible, which is not stable above 600 °C.

4.4. Relative reaction rates

Based on the reaction scheme proposed (Fig. 12), the rates of formation of the four main products and the consumption rate of oxygen can be expressed as $R_{\text{H}_2} = R_5 + 0.5R_3$;

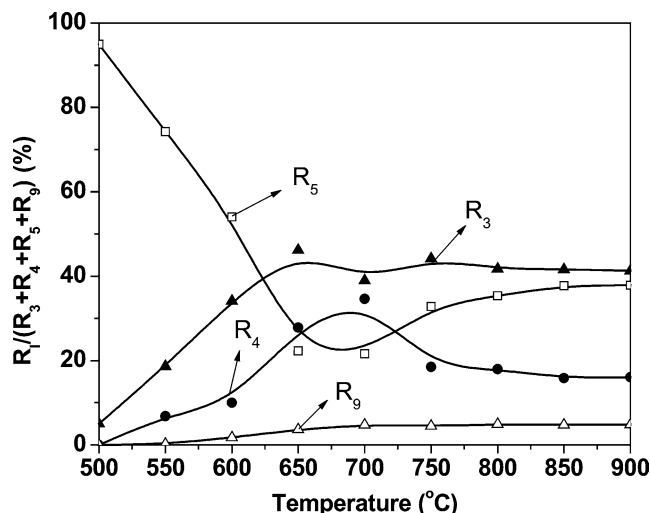


Fig. 13. The estimated relative rates of main reaction pathways as a function of reaction temperature. Based on the catalytic performance of YSZ12A presented in Fig. 1.

$R_{CO} = R_5 + R_4$; $R_{CO_2} = R_3 + R_9$; $R_{H_2O} = R_1 + 0.5R_2 + 0.5R_4 + 0.5R_9$; $R_{O_2} = R_1 + 0.75R_2 - 0.25R_4 + 0.25R_9$. At steady state, $R_2 = R_3 + R_4 + R_9$ and $R_1 = R_2 + R_5 = R_3 + R_4 + R_5 + R_9$.

Because $R_{H_2} = 2Y_{H_2}F_{CH_4}$; $R_{CO} = Y_{CO}F_{CH_4}$; $R_{CO_2} = Y_{CO_2}F_{CH_4}$; $R_{H_2O} = 2Y_{H_2O}F_{CH_4}$, and $R_{O_2} = X_{O_2}F_{O_2}$, where Y is yield, X is conversion and F is flow rate ($F_{CH_4} = 2F_{O_2}$), the relative rate of each reaction pathway can be expressed as below.

Dehydrogenation of formate (reaction 3),

$$\frac{R_3}{R_3 + R_4 + R_5 + R_9} = \frac{12Y_{H_2} - 14Y_{CO} - 16Y_{CO_2} + 4X_{O_2}}{Y_{CO} + Y_{CO_2}}$$

Dehydration of formate (reaction 4),

$$\frac{R_4}{R_3 + R_4 + R_5 + R_9} = \frac{4Y_{H_2} + 2X_{O_2} - 6Y_{CO} - 8Y_{CO_2}}{Y_{CO} + Y_{CO_2}}$$

Decomposition of formaldehyde (reaction 5),

$$\frac{R_5}{R_3 + R_4 + R_5 + R_9} = \frac{7Y_{CO} + 8Y_{CO_2} - 4Y_{H_2} - 2X_{O_2}}{Y_{CO} + Y_{CO_2}}$$

CO₂ formation via decomposition of carbonate (reaction 9):

$$\frac{R_9}{R_3 + R_4 + R_5 + R_9} = \frac{14Y_{CO} + 17Y_{CO_2} - 12Y_{H_2} - 4X_{O_2}}{Y_{CO} + Y_{CO_2}}$$

So, the relative rate of each reaction pathway can be estimated based on the catalytic results shown in Fig. 2. Fig. 13 shows the estimated relative rates at different reaction temperatures. With increasing temperature, the rate of formaldehyde decomposition (reaction 5) decreases and reaches a constant value at about 750 °C. In contrast, the relative rates of decomposition of formate (reactions 3 and 4) are almost zero at 500 °C. This is in agreement with the fact that stable formate species on the surface of YSZ is observed in

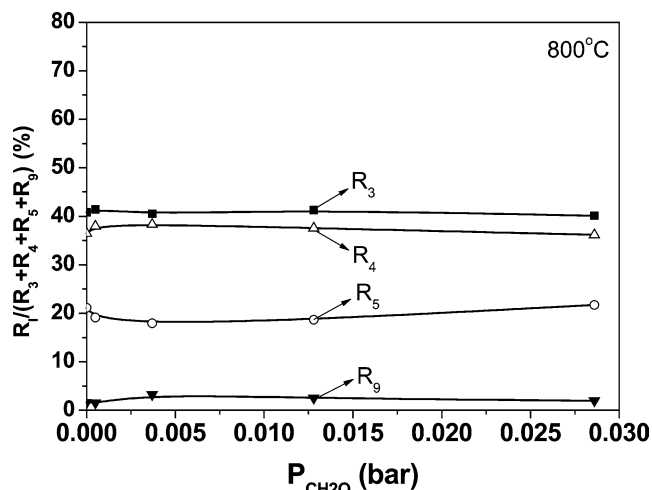


Fig. 14. Influence of formaldehyde added to the feed of normal CPOM on the relative rates, which is estimated based on product distribution as different partial pressures of formaldehyde presented in Fig. 10a.

the TPD/TPDE experiments. Both dehydration and dehydrogenation of formate increase with increasing temperature, and only slight changes are observed at temperatures above 750 °C. CO₂ is formed mainly via the decomposition of formate (reaction 3) and only about 10% of CO₂ is formed via decomposition of carbonate at temperatures above 700 °C. Combining the fact that the carbonate species was not observed on the surface of YSZ12 in the in situ IR experiment, it is concluded that the route via carbonate is minor in the formation of CO₂.

Relative rates are also estimated based on the product distribution (Fig. 10a) when CH₂O was cofed with CH₄ and O₂. The identical relative rates presented in Fig. 14, independent of partial pressure of formaldehyde in the feed, indicate that oxidation of methane on YSZ proceeds indeed via both decomposition and oxidative conversion of formaldehyde.

It is obvious, as shown in Fig. 12, that selectivity to synthesis gas depends strongly on the relative rates of three dominating reactions, reactions 3, 4, and 5. However, because of the fast oxidation of formaldehyde on the surface of oxide catalysts (reaction 2), the challenge in this system is to accelerate formaldehyde decomposition (reaction 5) or to prevent the oxidative conversion of formaldehyde to formate (reaction 2) in order to increase the selectivity to synthesis gas.

5. Conclusions

Partial oxidation of methane to synthesis gas has been investigated over YSZ. CO, H₂O, CO₂, and H₂ are primary products. Methane can be activated at 450 °C to form a relatively stable formate species; however, this reaction channel is probably not available at high temperatures. Formaldehyde and formate are two key reaction intermediates. CO and H₂ are formed via decomposition of both adsorbed formaldehyde and formate on the surface of YSZ, while

CO₂ is produced via decomposition of the surface formate mainly. Most of H₂O is produced in the first step, the oxidation of methane to formaldehyde. Desorption of formaldehyde and subsequent decomposition or oxidation in the gas phase do not contribute significantly. Further oxidation of formate to carbonate, which decomposes to CO₂ at elevated temperatures, is also minor but still significant.

At a low temperature (< 500 °C), the decomposition of the stable formate species is the step that prevents any reaction occurring. However, activation of methane is the rate-determining step at 600 °C and above. A reaction scheme is proposed that contains exclusively reaction pathways that contribute significantly; the ratios between the competing pathways are strongly influenced by temperature but do not vary at all when formaldehyde is added.

Acknowledgments

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