ELSEVIER Catalysis Today 29 (1996) 397–402

CATALYSIS TODAY

Direct partial oxidation of methane into synthesis gas over Rh|YSZ|Ag

K. Takehira [a,*], T. Hayakawa [a], S. Hamakawa [a], T. Tsunoda [a], K. Sato [b], J. Nakamura [b], T. Uchijima [b]

[a] *National Institute of Materials and Chemical Research, Tsukuba Research Center, AIST, 1-1, Higashi, Tsukuba, Ibaraki 305, Japan*
[b] *Institute of Materials Science, University of Tsukuba, Tennoudai, Tsukuba, Ibaraki 305, Japan*

Abstract

An electrochemical membrane reactor, Rh|YSZ|Ag, has been tested for the partial oxidation of CH_4 to CO/H_2 under 'oxygen pumping' through YSZ. An ionically transported oxygen species over the Rh anode was highly active for the partial oxidation. The reaction mode of the CH_4 oxidation strongly depends on the surface state of Rh particles; a highly oxidized Rh surface accelerates complete oxidation of CH_4 to CO_2/H_2O, while a reduced Rh surface catalyzes the partial oxidation to CO/H_2. Oxygen concentration over the Rh predominantly determines the selectivity; a high oxygen concentration leads to the complete oxidation, while an adsorbed oxygen species gives the partial oxidation.

Keywords: Rh|YSZ|Ag; CH_4 oxidation

1. Introduction

The conversion of CH_4 into valuable compounds is practically important from the view point of utilization of natural gas. Recently, partial oxidation of CH_4 into synthesis gas has been studied as a promising method for CH_4 conversion [1], where metals in group VIII such as Rh, Ni, Ru, Pt, Ir and Pd are active catalysts for the reaction (1).

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

This reaction is basically composed of several reactions, including complete oxidation of CH_4 to CO_2/H_2O and reforming of CH_4 by H_2O and CO_2, and is normally performed at high temperatures, since the reforming reactions are thermodynamically highly endothermic.

Hickman and Schmidt, using a Rh- or Pt-coated monolith catalyst at a short residence time, recently proposed that CO and H_2 were not the final products but the primary products in this process [2]. They explained the superior behavior of Rh compared to Pt because of the higher activation energy for OH formation from adsorbed hydrogen and oxygen on Rh (20 kcal/mol) than on Pt (2.5 kcal/mol). We [3] have found that adsorbed oxygen species on Rh/SiO_2, from gaseous oxygen, can oxidize CH_4 directly into synthesis gas. Furthermore, an incorporation of oxygen from SiO_2 via the Rh surface into the reaction products was observed in the reaction of adsorbed ^{18}O on Rh/SiO_2 with CH_4 at 300–600°C, suggesting a spillover

---

[*] Corresponding author.

SSDI 0920-5861(95)00310-X

mechanism. Matsumoto and Tanabe [4] have also reported an important role of surface oxygen species on Pd in the Pd-Y zeolite catalyzed partial oxidation of CH_4 to CO/H_2 under oxygen deficient conditions. Another group of the authors (NIMC) have studied solid electrolyte-aided oxidation of hydrocarbons using 8 mol-% yttria-doped zirconia (YSZ) where $M_1|YSZ|M_2$ serves as an 'oxygen pump' [5–9]; O_2 is reduced to form oxide ions at the cathode (M_2), incorporated into the YSZ and are migrated to the anode (M_1), where the oxide ions are reoxidized to O_2. When Au was used as the anode, propene and ethane were partially oxidized into acrylaldehyde [5] and acetaldehyde [8], respectively, over an inert Au anode film under the oxygen pumping; this suggests that oxygen species transported through YSZ onto Au surface were active for the selective oxidation. Moreover, the oxygen species transported through YSZ onto the Au surface also enhanced the activity of molybdate catalysts for alkene oxidation when the molybdate was coupled with the Au|YSZ|Ag system [6,7]. Therefore, it is reasonably expected that CH_4 can be continuously converted into synthesis gas by supplying surface oxygen species onto a Rh anode when Rh is coupled with the oxygen pump. We found that CH_4 was directly oxidized into CO and H_2 over the Rh|YSZ|Ag system [9], which showed a remarkable and stable formation of synthesis gas under oxygen pumping through the YSZ at a low temperature of 500°C. In this paper, we report the behavior of oxygen species generated electrochemically on the Rh anode surface for the partial oxidation of CH_4.

2. Experimental

An electrochemical reactor (Fig. 1) was constructed from an YSZ disk (diameter of 32 mm and in thickness of 1 mm) as described elsewhere [9]. Thin compact films of Ag (2.0 μm thick) and Rh (0.5 μm thick) were prepared as the cathode and the anode, respectively, on each face of the disk by vacuum evaporation [5,9]. SEM observation of the Rh anode clearly showed cracks in the texture of the Rh film, suggesting the presence of triple phase boundary, i.e., Rh-YSZ-atmosphere. The two electrodes of the disk were connected with gold wires to an electrical circuit, and the oxygen transfer flux, across the YSZ from the Ag cathode to the Rh anode, was controlled by changing the applied voltage. The cell system was placed in a furnace to control the temperature [5], and the oxidation of CH_4 was carried out at 500°C under the following conditions: an oxygen pressure of 101.3 kPa was maintained on the cathode of the cell and a gaseous mixture of CH_4 (0.4%) and nitrogen was passed (1 l/h) over the anode side for testing the activity of oxygen species generated on the Rh anode film. The products in the effluent gas were analyzed by gas chromatography using a thermal conductivity detector.

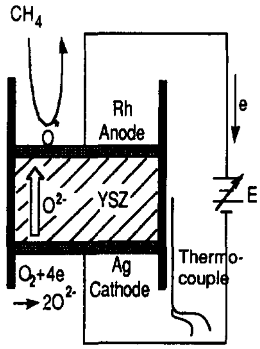

Fig. 1. Schematic diagram of the reactor.

3. Results and discussion

When CH_4 was oxidized over the Rh|YSZ|Ag at 500°C under oxygen pumping, the partial oxidation to CO/H_2, as well as the complete oxidation, proceeds on the Rh anode surface [9]. Changes in the product distributions and the electric current during cyclic voltametries, under various atmospheres in the anode room, strongly suggest that oxygen evolves at the triple phase boundary through YSZ and then migrates to the Rh surface by a reverse spillover mechanism. We previously reported the propene oxidation over a Au|YSZ|Ag system [5], and showed that the best oxygen pumping through the YSZ disk as well as the highest rate and the highest selectivity for acrylaldehyde production from propene was obtained over 1.0 μm thick Au film. When increasing the thickness above 1.0 μm, not only the oxygen pumping but also the acrylaldehyde production decreased. These observations strongly suggest that the partial oxidation of propene to acrylaldehyde takes place at the Au-YSZ-atmosphere triple phase boundary. Also in the present Rh|YSZ|Ag system, a good oxygen pumping with the Rh film of 0.5 μm thick supports the existence of triple phase boundary of Rh-YSZ-atmosphere as previously mentioned in the experimental section. We observed both the partial oxidation of CH_4 to CO/H_2 and the complete oxidation to CO_2/H_2O over the Rh anode and the reaction pathways were independent each other, as shown by the dependence of the reaction behavior on the applied potential and the reaction time course [9]. It is likely that the complete oxidation was accelerated by the oxygen species evolved at the triple phase boundary, while the direct partial oxidation was carried out by the adsorbed oxygen species migrating from the triple phase boundary onto the Rh surface [9]. An experiment using 5 g of YSZ (Tosoh Zirconia TZ-8Y; specific surface area, 16 m^2/g) as a fixed bed catalyst showed formations of CO (11 μmol/h) and CO_2 (4 μmol/h) at 500°C under a mixed gas flow (1 l/h) of CH_4 (0.5%) and O_2 (0.5%) in N_2. When a geometric surface area of 8.0 cm^2 of the YSZ disk is taken into account, the activity of the YSZ surface itself must be negligible in the present study. Here, we have studied the effect of oxygen pumping during the CH_4 oxidation over the Rh|YSZ|Ag system as well as the CH_4 oxidation by the pre-adsorbed oxygen species at the Rh anode surface in order to establish a more precise view of the reaction mechanism.

3.1. Effect of the oxygen pre-pumping on the CH_4 oxidation over the Rh anode

We investigated the effect of oxygen pre-pumping through the YSZ on the CH_4 oxidation since adsorbed oxygen on the Rh anode can affect synthesis gas formation [3]. The CH_4 oxidation was carried out over the Rh (0.5 μm)|YSZ|Ag system under oxygen pumping at 5 mA and 500°C for 60 min (Fig. 2). Before the reaction, the Rh anode surface was treated for 30 min at 500°C in air and then reduced with H_2 (20% in N_2, 1 l/h) for 30 min. Each run of the CH_4 oxidation was done just after pre-pumping of oxygen at the electric current of 0 (open circuit), 0.01, 0.1, 1 and 5 mA, respectively, for 20 min at 500°C. For the CH_4 oxidation, 0.4% CH_4 in N_2 (1 l/h) was passed over the Rh anode under oxygen pumping at 5 mA, which corresponds to a CH_4/O_2 molar ratio of 4/1. Under open circuit conditions, in the first step in Fig. 2, a part of CH_4 was decomposed into H_2 and CH_x ($x = 0$–3) species. Upon pumping of oxygen at 5 mA, CH_4 was converted mainly into synthesis gas, where the H_2/CO molar ratio was 2/1, and a small amount of CO_2 was formed. The amount of synthesis gas increased while that of CO_2 was

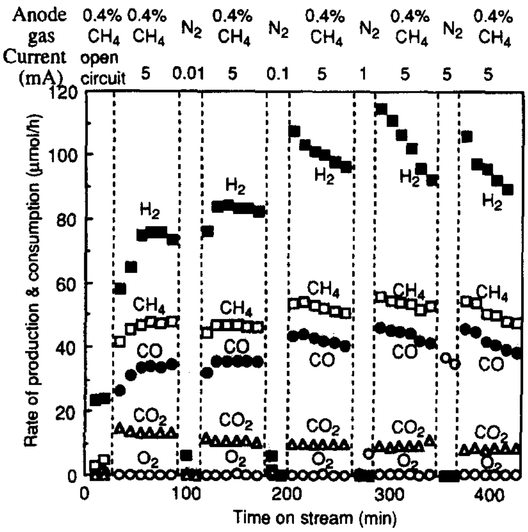

Fig. 2. Effect of pre-pumping of oxygen on the CH_4 oxidation.

almost constant during the reaction for 60 min. After the oxygen pumping at 0.01 mA for 20 min, the rate of synthesis gas formation increased compared with that after no oxygen pumping under open circuit conditions. When the current of oxygen pre-pumping increased up to 1 mA, the rate of synthesis gas formation increased while CO_2 formation slightly decreased. The highest rate of synthesis gas formation was observed at 1 mA. Further increasing the current (5 mA) resulted in a slight decrease in the formation rate of synthesis gas as well as in the evolution of oxygen gas in the anode space during the pre-pumping. No evolution of oxygen gas in the anode space during pre-pumping at 1 mA suggests that all oxygen species pumped through the YSZ were adsorbed on the Rh anode surface. A moderate pre-adsorption of oxygen strongly enhanced the synthesis gas formation in the present study, suggesting the direct partial oxidation of CH_4 to CO/H_2. It is thus likely that, in the present system, adsorbed oxygen species over the Rh anode are important in the synthesis gas formation from CH_4.

Generally in the CH_4 conversion over metal catalysts, carbon formation occurs during the dissociation of CH_4 into adsorbed carbon atoms followed by nucleation (CH_4–CH_x–$C_{(ads)}$–$C_{(dep)}$]) [10]. In the presence of surface oxygen, adsorbed CH_x can be oxidized to CO or CO_2. Algahtany et al. [11] reported that ionically transported oxygen through the YSZ promoted CO formation more than gaseous O_2, while these two oxygen species showed no clear difference for H_2 formation, in CH_4 oxidation over Fe|YSZ|Pt at 950°C. These observations suggest that oxygen pumping through the Fe|YSZ|Pt allows oxygen to be utilized more efficiently in promoting CO rather than carbon formation. In the present work over the Rh anode, we already reported that both the partial oxidation of CH_4 to CO/H_2 and the complete oxidation to CO_2/H_2O simultaneously occur and the reaction pathways are independent of each other, by considering dependency of each reaction on the applied potential and the reaction time course [9]. It is likely that oxygen evolves through the triple phase boundary and then migrates to the Rh surface by a reverse spillover mechanism; the oxygen species appearing at the triple phase boundary are active for the complete oxidation to CO_2/H_2O, while the species migrating onto the surface of the Rh anode are active for the selective partial oxidation to CO/H_2 [9]. It will be necessary to study the behavior of the 'adsorbed' oxygen species on the Rh anode for each oxidation to

$$CH_4 + O_{(ads)}/Rh \rightarrow CO + 2H_2 \qquad (2)$$

establish a more precise view of the reaction mechanism.

3.2. CH_4 oxidation with ionically transported and adsorbed oxygen

The activity of 'adsorbed' oxygen species was tested in the CH_4 oxidation. Oxygen was transported through the Rh|YSZ|Ag at various electric currents for 20 min and stored on the Rh anode under N_2 gas flow (1 l/h). Then, the anode gas was replaced by CH_4 gas (0.4% in N_2, 1 l/h) and the products in the effluent gas were analyzed. The results obtained after the oxygen pumping at 5 mA are shown in Fig. 3. CO_2 was detected as the first peak, 6–7 min

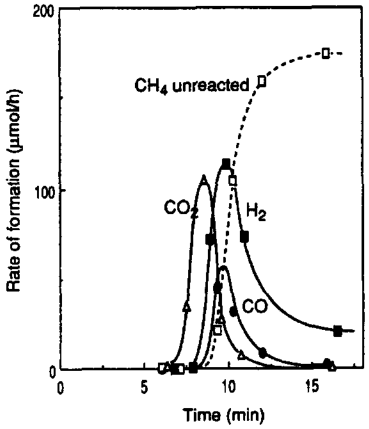

Fig. 3. CH_4 oxidation with adsorbed oxygen. CH_4 oxidation was carried out after the oxygen pumping for 20 min at 5 mA.

after replacing the anode gas, followed by CO/H_2 and then unreacted CH_4. The delay of 6–7 min corresponds to the time for replacing N_2 gas completely with the CH_4 mixed gas in the reactor, and coincides well with the value calculated from the reactor size and the gas velocity. Each product showed its own characteristic formation curve during time on stream, with a peak of the maximum rate. CO_2 showed an almost symmetrical shape, while both CO and H_2 showed asymmetrical shapes with significant tailing, i.e., the rates slowly decreased with time after passing the peak. A peak of CO_2 appeared at 7–8 min and reached the maximum value of 100 μmol/h, while those of H_2 and CO simultaneously appeared at 8–9.5 min. The maximum H_2 formation rate was 100 μmol/h, and the ratio of each peak height (CO/H_2) was nearly 1/2. Peak position of each product did not substantially vary even when the electric current, i.e., the amount of oxygen pumped, was changed.

When the electric current for the oxygen pumping increased, the peak height of each product increased, i.e., the maximum rate of each formation increased (Fig. 4). The increase in the CO_2 formation compared with that in synthesis gas formation was more significantly observed at high electric current, i.e., under high oxygen supply. These observations suggest that the selectivity for the formation of CO or CO_2 is predominantly determined by the concentration of oxygen on the surface of Rh or in the bulk of Rh, as observed previously for the product selectivity in the reaction between CH_4 and adsorbed oxygen on the Rh surface of Rh/SiO_2 [3]. CH_4 will be completely oxidized to CO_2 in the presence of a high concentration of oxygen on the Rh surface. On the other hand, CH_4 might be oxidized to CO/H_2 when the Rh surface is moderately oxidized or covered with the adsorbed oxygen. When the oxygen supply increased, by increasing the current, the surface of the Rh anode may be oxidized to form rhodium oxide even at 500°C because of its film character. XRD measurement of the Rh surface, after a sufficient oxygen pumping, showed some weak peaks corresponding to Rh_2O_3. CH_4 first reacts with the rhodium oxide to form CO_2 as the first peak, and the surface rhodium oxide is consequently reduced to form the rhodium surface covered with the adsorbed oxygen, which in turn reacts with CH_4 giving the second peaks of CO and H_2 (Fig. 3). This would explain the time lag of around 1 min which appears between the peaks of CO_2 and CO/H_2 formations.

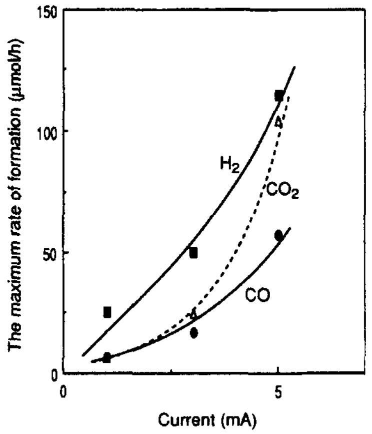

Fig. 4. Effect of the electric current on the maximum rate of formation. CH_4 oxidation was carried out after the oxygen pumping for 20 min at each electric current.

It is considered that, under the oxygen pumping conditions, the oxidation state of Rh is controlled by the kinetic balance between the migration of oxygen evolved from the triple phase boundary leading to oxidation of Rh, and the reaction of CH_4 with the migrated oxygen forming CO and CO_2. Under a sufficient oxygen supply, the surface of Rh is oxidized to become more active for the complete oxidation; the active oxygen for the complete oxidation must be more abundant than the $O_{(ads)}/Rh$ species active for the partial oxidation, as seen from the relative rates of CO_2 and CO production in Fig. 4. It is likely that synthesis gas formation proceeds via dissociation of CH_4 into CH_x $(x = 0–3)$ and hydrogen atoms over Rh followed by a reaction of CH_x with $O_{(ads)}/Rh$ to form CO and a recombination of hydrogen atoms to H_2 [2]. This mechanism also suggests that synthesis gas can not be formed over the highly oxidized Rh surface, which is unfavorable for the dissociation of CH_4. We observed that the complete oxidation proceeds at the triple phase boundary, while the selective partial oxidation occurs with the adsorbed oxygen over the Rh surface [9]. The concentration of oxygen must be high at the triple phase boundary compared to the Rh anode surface during a high oxygen pumping, where the oxygen concentration predominantly determines the selectivity of CH_4 oxidation either to the complete oxidation or to the partial oxidation. Under a stable supply of adsorbed oxygen species over the Rh anode through the YSZ, the $O_{(ads)}/Rh$ can continuously react with CH_4 leading to the formation of CO and H_2.

4. Conclusions

In the Rh|YSZ|Ag electrochemical reactor, ionically transported oxygen through the YSZ showed high activity for the partial oxidation of CH_4 into synthesis gas. Details of the behavior of oxygen species, generated electrochemically and adsorbed on the Rh anode surface for the partial oxidation of CH_4, have been studied. When oxygen accumulated on the Rh anode by high oxygen pre-pumping, the Rh surface was oxidized to become rhodium oxide and was active for the complete oxidation of CH_4 into CO_2. After the accumulated oxygen species was spent by the complete oxidation, the adsorbed oxygen species appeared over the Rh surface and partially oxidized CH_4 to CO/H_2. It is likely that the adsorbed oxygen species can be formed over the Rh surface and continuously oxidizes CH_4 to CO and H_2 under the oxygen pumping conditions.

References

[1] A.T. Ashcroft, A.K. Cheetham, J.S. Foord, M.L.H. Green, C.P. Grey, A.J. Murrell and P.D.F. Vernon, Nature, 344 (1990) 319; R.H. Jones, A.T. Ashcroft, D. Waller, A.K. Cheetham and J.M. Thomas, Catal. Lett., 8 (1991) 169; D. Dissanayake, M.P. Rosynec, K.C.C. Kharas and J.H. Lunsford, J. Catal., 132 (1991) 117; J. Nakamura, S. Umeda, K. Kubushiro, K. Kunimori and T. Uchijima, Bull. Jpn. Petrol. Inst., 36 (1993) 97; T. Hayakawa, A.G. Anderson, M. Shimizu, K. Suzuki and K. Takehira, Catal. Lett., 22 (1993) 299.

[2] D.A. Hickman and L.D. Schmidt, J. Catal., 138 (1992) 267; D.A. Hickman, E.A. Haufear and L.D. Schmidt, Catal. Lett., 17 (1993) 223; D.A. Hickman and L.D. Schmidt, Science, 259 (1993) 343.

[3] J. Nakamura, K. Kubushiro and T. Uchijima, Stud. Surf. Sci. Catal., 77 (1993) 373; J. Nakamura, K. Aikawa, K. Sato and T. Uchijima, Catal. Lett., 25 (1994) 26.

[4] H. Matsumoto and S. Tanabe, J. Chem. Soc., Faraday Trans., 90 (1994) 3001.

[5] T. Hayakawa, T. Tsunoda, H. Orita, T.Kameyama, H.Takahashi, K. Takehira and K. Fukuda, J. Chem. Soc., Chem. Commun., (1986) 961; T. Tsunoda, T. Hayakawa, K. Sato, T.Kameyama, K. Fukuda and K. Takehira, J. Chem. Soc., Faraday Trans., 91 (1995) 1111.

[6] T. Hayakawa, T. Tsunoda, H. Orita, T. Kameyama, H. Takahashi, K. Fukuda and K. Takehira, J. Chem. Soc., Chem. Commun., (1987) 780; T. Tsunoda, T. Hayakawa, T. Kameyama, K. Fukuda and K. Takehira, J. Chem. Soc., Faraday Trans., 91 (1995) 1117.

[7] T. Hayakawa, T. Tsunoda, H. Orita, T. Kameyama, T. Ueda, K. Fukuda and K. Takehira, J. Chem. Soc., Chem. Commun., (1988) 1593; T. Tsunoda, T. Hayakawa, T. Kameyama, K. Fukuda and K. Takehira, J. Chem. Soc., Faraday Trans., 91 (1995) 1125.

[8] T. Hayakawa, K. Sato, T. Tsunoda, K. Suzuki and K. Takehira, J. Chem. Soc., Chem. Commun., (1994) 1743.

[9] T. Hayakawa, K. Sato, T. Tsunoda, S. Hamakawa, K. Suzuki, J. Nakamura, K. Takehira and T. Uchijima, J. Chem. Soc., Chem. Commun., (1994) 1899; K. Sato, J. Nakamura, T. Uchijima, T. Hayakawa, S. Hamakawa, T. Tsunoda and K. Takehira, J. Chem. Soc., Faraday Trans., in press.

[10] J.R. Rostrup-Nielsen, Catal. Sci. Technol., 5 (1984).

[11] H. Algahtany, D. Eng and M. Stoukides, J. Electrochem. Soc., 140 (1993) 1677.