

Articles

Partial Oxidation of Methane over CeO₂ Catalyst

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Partial oxidation of methane has been conducted over CeO₂ and it has been found that CeO₂ has an extraordinary catalytic activity in the reaction. Its activity was strongly dependent on the CH₄/O₂ ratio. Total combustion was dominant with stoichiometric feed ratio (CH₄/O₂ = 2.0) but partial oxidation was favorable with oxygen deficient feed condition. Meanwhile, oscillatory partial oxidation was achieved between the CH₄/O₂ ratio of 3.8 and 4.3 and the period depended upon the feed composition. The proposed reaction mechanism is that oxygen vacancies in reduced ceria are supplied with oxygen molecules from the reactant, and then activate adsorbed oxygen, followed by releasing activated oxygen species reacting with methane to produce H₂ and CO.

Keywords : CeO₂, Methane, Partial oxidation.

Introduction

Catalytic partial oxidation of methane (POM) is of great practical importance in producing hydrogen or synthesis gas by using natural gas.¹⁻³ POM offers the alternatively greatest potential for fast, efficient and economical conversion of methane to hydrogen or synthesis gas, due to the mild exothermicity, high conversion, high selectivity, suitable H₂/CO ratio for the Fischer-Tropsch and methanol synthesis, and the very short residence time. Therefore, POM has been studied over numerous supported metal catalysts such as Ni-based catalysts and supported noble metal catalysts.¹

Rare earth oxides have been widely investigated in catalysis as structural and electronic promoters to improve the activity, selectivity and thermal stability of catalysts.⁴ CeO₂ has been considered as the most important rare earth element in catalysis. It plays an important role in three-way catalysis (TWC) and fluid catalytic cracking (FCC).⁴ Specifically, CeO₂ has potential uses for the removal of soot from diesel engine exhaust,⁵ organics from waste waters (catalytic wet oxidation),⁶ as an additive for combustion catalysts,⁷ in fuel cell systems.⁸ Therefore, much effort has been dedicated to studying the role of ceria. As a result, it is known that the high oxygen storage capacity (OSC) of CeO₂ improves catalytic performance by storing oxygen during oxidation and releasing it during reduction.^{9,10} Otsuka *et al.*¹¹ found that CeO₂ is an unusual oxidant for oxidation of CH₄ into synthesis gas with a H₂/CO ratio of 2 without producing H₂O and CO₂ at 873-1073 K. However, the POM reaction was executed by passing a mixture of CH₄ and Ar (1 : 1) after

CeO₂ was pretreated in a 1 : 1 mixture of O₂ and Ar for 1 h at 973 K. Strictly speaking, CeO₂ was not employed as a catalyst for POM but an oxidant for CH₄ oxidation.

Recently, we have reported that Ni/Ce-ZrO₂ exhibited high activity as well as high stability in POM,^{12,13} steam reforming of methane (SRM),^{14,15} and oxy-SRM (OSRM: simultaneous POM and SRM).¹⁵ In the case of Ni/CeO₂, it showed a very low activity in SRM,^{11,12} however, it exhibited fairly good activity in POM¹² and remarkably high activity as well as stability in OSRM.¹⁵ Thus, we have aimed to investigate the role of CeO₂ in POM and OSRM, resulting in finding out very interesting results. We have reported as a communication¹⁶ that CeO₂ shows extraordinary catalytic behavior strongly depending on the feed composition of CH₄ and O₂ and could catalyze POM giving a H₂/CO ratio of 2 with oxygen deficient feed. We report here the detailed POM results and explain the strange catalytic behavior.

Experimental Section

The CeO₂ sample employed was a reagent-grade (purity > 99.9%) having a BET surface area of 19 m²/g. Activity tests were carried out at 1023 K under atmospheric pressure in a fixed-bed quartz reactor.¹²⁻¹⁶ Each catalyst (50 mg) was loaded into the quartz reactor with an inner diameter of 4 mm. The reaction temperature was measured and controlled by a thermocouple directly inserted into the top layer of the catalyst bed. Prior to each reaction test, the catalyst was reduced in 5% H₂/N₂ at 973 K for 3 h. Effluent gases from the reactor were analyzed by an on-line gas chromatograph (Chrompack CP9001) equipped with a capillary column (CarboPLOT P7) and a thermal conductivity detector.

Pulse experiments using CH₄, O₂ and CH₄/O₂ mixed gas

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($\text{CH}_4/\text{O}_2 = 2$) were performed in the quartz micro-reactor with an inner diameter of 4 mm. Before the reaction, 15 mg of each catalyst was loaded in the reactor and reduced *in situ* in 5% H_2/N_2 at 700 °C for 3 h. Detailed procedures for pulse experiments were described previously.^{17,18} The conversion and selectivity were calculated on the basis of 100% carbon and oxygen balances. The CO and CO_2 selectivities were defined in elsewhere.¹⁷

Results and Discussion

Continuous reaction. Figure 1 shows catalytic performance of CeO_2 at the stoichiometric feed ratio ($\text{CH}_4/\text{O}_2 = 2.0$). CH_4 and O_2 conversions were 26% and 87%, respectively. However, both H_2 and CO selectivities were less than 5%, indicating that the resultant products were H_2O and CO_2 resulting from total combustion. Figure 2 illustrates catalytic performance of CeO_2 at the condition of $\text{CH}_4/\text{O}_2 = 3.0$. Initially CH_4 conversion was 7% and O_2 conversion was almost zero with a H_2/CO ratio of 2.0. This is mainly due to the fact that mobile oxygen species on CeO_2 were consumed to react with CH_4 . With increasing time on stream, both CH_4

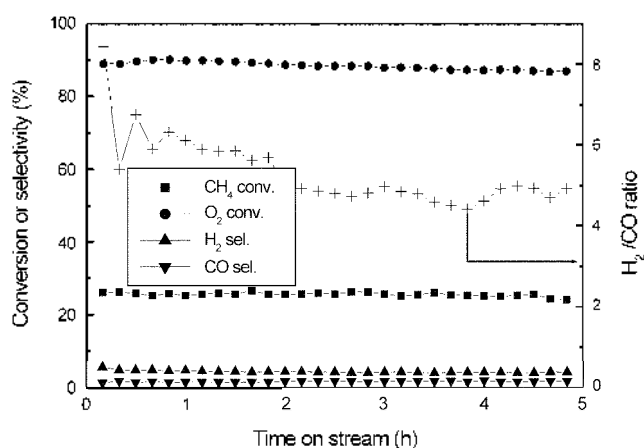


Figure 1. CH_4 oxidation over CeO_2 with a CH_4/O_2 ratio of 2.0 ($\text{CH}_4 = 30$ mL/min, 50 mg catalyst, $T = 1023$ K, $P = 1$ atm).

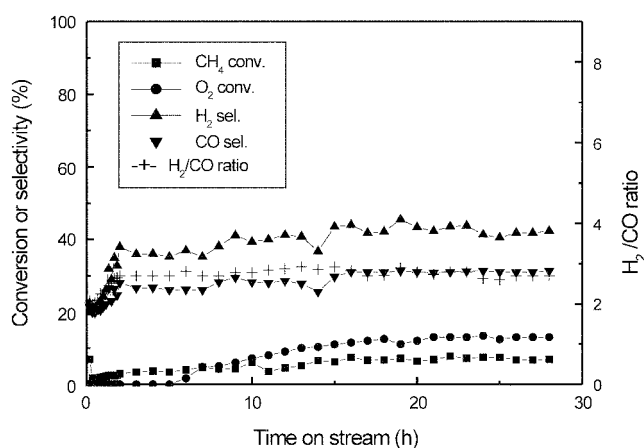


Figure 2. CH_4 oxidation over CeO_2 with a CH_4/O_2 ratio of 3.0 ($\text{CH}_4 = 30$ mL/min, 50 mg catalyst, $T = 1023$ K, $P = 1$ atm).

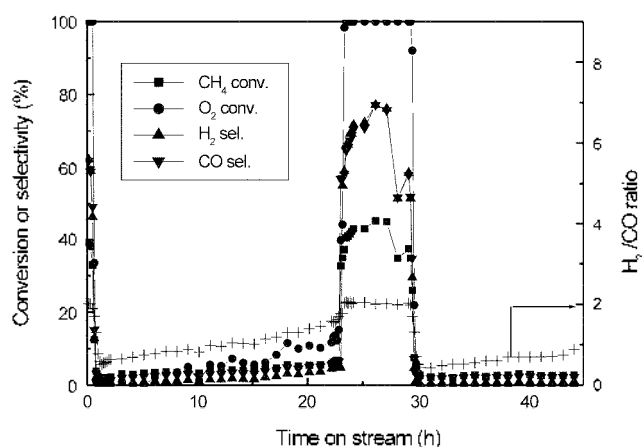


Figure 3. CH_4 oxidation over CeO_2 with a CH_4/O_2 ratio of 3.8 ($\text{CH}_4 = 30$ mL/min, 50 mg catalyst, $T = 1023$ K, $P = 1$ atm).

and O_2 conversions reached steady state with their values of 7% and 13%, respectively. These conversions were lower than those at $\text{CH}_4/\text{O}_2 = 2.0$, however, the selectivities to H_2 and CO were 46% and 31%, suggesting that POM was considerable. These results reveal that POM is favorable over CeO_2 at oxygen deficient environment. Meanwhile, the H_2/CO ratio reached about 2.7 at steady state. This is possibly due to the water gas shift (WGS) reaction or CO combustion reaction. Actually, CeO_2 has been reported to enhance the removal of CO and to promote WGS.^{19,20} The results at a CH_4/O_2 ratio of 3.8 are presented in Figure 3. Surprisingly, maximum CH_4 and O_2 conversions in this condition were 45% and 100%, respectively. Both H_2 and CO selectivities were 77% giving a H_2/CO ratio of 2.0, indicating that POM was dominant in this condition. Besides, catalytic behavior with time on stream was extraordinary. At the beginning, CeO_2 exhibited high CH_4 conversion (39%), H_2 selectivity (62%) and CO selectivity (62%) giving a H_2/CO ratio of 2.0. The activities decreased sharply and became almost zero after 1 h. After that, however, CH_4 conversion increased gradually with time on stream, and it dramatically reached about 40% after 23 h and maintained between 23 and 30 h. After 30 h, the phenomena were repeated. The trends of both H_2 and CO selectivities were similar to that of CH_4 conversion. Interestingly, the H_2/CO ratio was closely 2.0 initially, decreased to 0.5 after 1 h, and steadily increased to 2.0 after 23 h. The increasing rate of the H_2/CO ratio was rather faster than that of CH_4 conversion. These results can be explained as follows. At the beginning, reduced ceria ($\text{Ce}_{1-2y}^{4+}\text{Ce}_{2y}^{3+}\text{O}_{2-y}$) store oxygen molecules from the reactant and release them as active oxygen species reacting with methane to produce synthesis gas at oxygen deficient condition. During the reaction, reduced ceria are fast oxidized by O_2 feed ($\text{Ce}_{1-2y}^{4+}\text{Ce}_{2y}^{3+}\text{O}_{2-y} + 0.5y\text{O}_2 \rightarrow \text{CeO}_2$), showing almost negligible activity in POM. And then, oxidized ceria are gradually reduced by hydrogen produced from POM or methane decomposition ($\text{CeO}_2 + y\text{H}_2 \rightarrow \text{Ce}_{1-2y}^{4+}\text{Ce}_{2y}^{3+}\text{O}_{2-y} + y\text{H}_2\text{O}$). The trend of the H_2/CO ratio supports this mechanism because the ratio was initially 2.0 and sharply

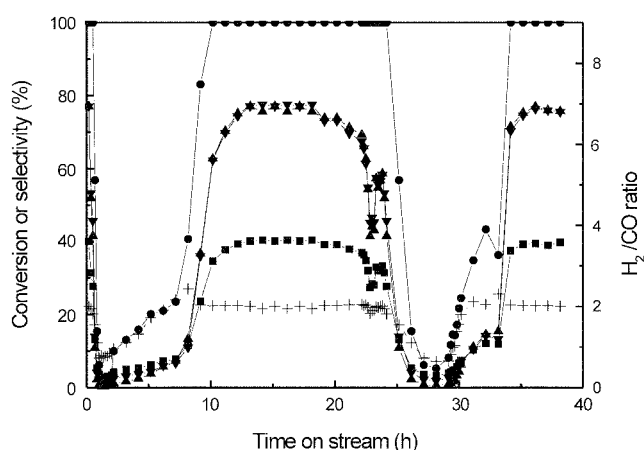


Figure 4. CH₄ oxidation over CeO₂ with a CH₄/O₂ ratio of 4.3 (CH₄ = 30 mL/min, 50 mg catalyst, T = 1023 K, P = 1 atm).

decreased to 0.5, and then gradually increased to 2.0. In other words, the hydrogen produced from POM or CH₄ decomposition was gradually consumed to reduce CeO₂ resulting in low H₂/CO ratio. In the case of CH₄/O₂ = 4.3, maximum CH₄ and O₂ conversions were 40% and 100%, respectively (Figure 4). Both H₂ and CO selectivities were 75% giving a H₂/CO ratio of 2.0. The general feature of CH₄ conversion was similar to that with CH₄/O₂ = 3.8, in the point of giving oscillatory catalytic behavior. However, the period was shorter than that with CH₄/O₂ = 3.8, and the increasing rate of CH₄ conversion after 1 h was high. Besides, the period giving high CH₄ conversion was longer than 10 h. These results indicate that the reduction of ceria could be accelerated and maintained for a long time when the degree of oxygen deficiency was heavier. Another interesting point is that O₂ conversion was 100% when CH₄ conversion was maintained to about 40%. Thus, it could be suggested that the vacancies of CeO₂ should be effectively supplied with gas-phase O₂ molecules followed by the release of active oxygen species reacting with CH₄ to produce synthesis gas when the degree of O₂ deficiency was heavier. In addition, the H₂/CO ratio was maintained to 2.0

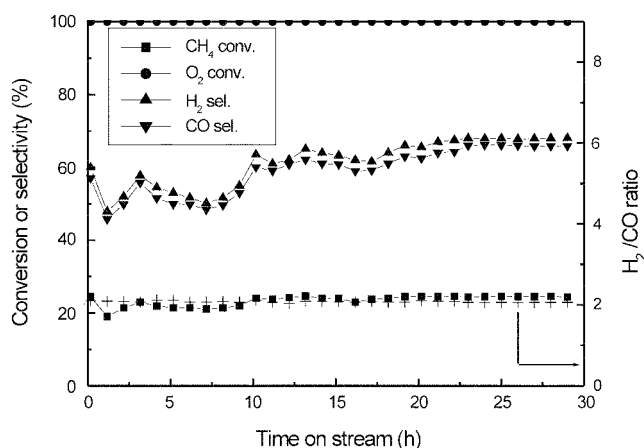


Figure 5. CH₄ oxidation over CeO₂ with a CH₄/O₂ ratio of 6.0 (CH₄ = 30 mL/min, 50 mg catalyst, T = 1023 K, P = 1 atm).

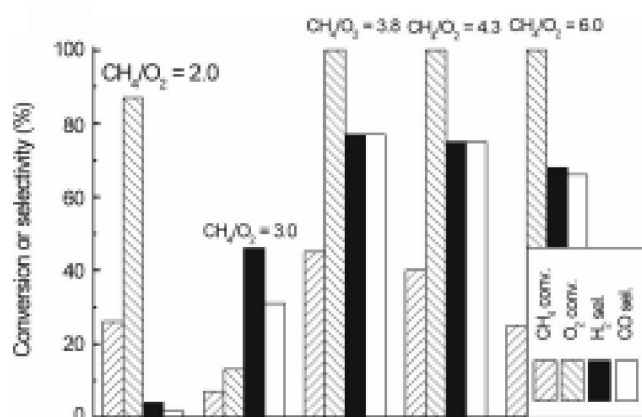


Figure 6. The effect of CH₄/O₂ ratio on CH₄ oxidation over CeO₂ (CH₄ = 30 mL/min, 50 mg catalyst, T = 1023 K, P = 1 atm; Data at maximum CH₄ conversion).

when O₂ conversion was 100%, indicating that POM was dominant at the condition. Figure 5 describes the results at a CH₄/O₂ ratio of 6.0. In this condition, CeO₂ exhibited continuous 100% O₂ conversion, 25% CH₄ conversion, 68% H₂ selectivity, and 66% CO selectivity with a H₂/CO ratio of 2.1 at steady state. This strongly indicates that continuous partial oxidation reaction can be possible over CeO₂ by controlling the CH₄/O₂ ratio, namely, the degree of oxygen deficiency. Figure 6 summarizes the effect of CH₄/O₂ ratio on CH₄ oxidation over CeO₂ with various CH₄/O₂ ratios. The data shown in Figure 6 were taken from the maximum CH₄ conversion during the reaction. As shown in Figure 6, it is clear that catalytic performance of CeO₂ extremely depends on the feed ratio of CH₄ and O₂. It is noteworthy that CeO₂ can be used as a catalyst for POM. Thus, it can be expected that the combination of Ni and CeO₂ should give enhanced catalytic performance in the reaction related with POM. This is possibly why Ni/CeO₂ has been reported to give rather good activity in POM and exhibit high catalytic performance in OSRM.^{12,15}

According to the above results, it was found that total oxidation of methane (TOM) is favorable at the stoichiometric feed ratio (CH₄/O₂ = 2.0), POM is considerable at the condition of CH₄/O₂ = 3.0, POM is dominant at the CH₄/O₂ ratio of 6.0, and there is an oscillation of POM and TOM at the CH₄/O₂ ratio of between 3.8 and 4.3. This is possibly related to the oxidation state of Ce. It is due to the fact that the reduced ceria having oxygen vacancies (Ce³⁺) could perform POM at oxygen deficiency condition. However, it is speculated that the state of oxygen vacancies are not so stable that Ce³⁺ quickly changes into Ce⁴⁺ having negligible activity in POM. The change between Ce³⁺ and Ce⁴⁺ is reversible but the rate from 3+ to 4+ is faster than that from 4+ to 3+. This is possibly why CH₄ conversion decreased sharply at the initial stage and gradually increased to some extent when the oscillation was observed.

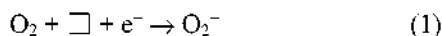
Pulse reaction. In order to investigate the reaction mechanism, pulse experiments using CH₄, O₂ and CH₄/O₂ mixed gas (CH₄/O₂ = 2.0) were performed in a micro-reactor at

Table 1. Pulse reaction results over CeO₂

Pulse type	X _{CH₄} (%)	X _{O₂} (%)	S _{H₂} (%)	S _{CO} (%)	H ₂ /CO ratio
CH ₄ ^a	0	—	0	0	—
O ₂ ^b	—	0	0	0	—
CH ₄ ^c	0	—	0	0	—
CH ₄ /O ₂ ^d	26	87	4	1.5	5.0
CH ₄ ^e	0	—	0	0	—

^aCH₄ pulse was injected after the reduction of the fresh catalyst. ^bO₂ pulse was injected after 5 CH₄ pulses. ^cCH₄ pulse was re-injected after 5 O₂ pulses. ^dCH₄/O₂ (2/1) pulse was injected after the reduction of the fresh catalyst. ^eCH₄ pulse was injected after 5 CH₄/O₂ pulses.

1023 K. The pulse reaction results are summarized in Table 1. According to the pulse reaction results, CeO₂ did not show any activity with only CH₄ pulses. With O₂ pulses after 5 CH₄ pulses, CeO₂ did not show any O₂ conversion, either. When CH₄ pulse was re-introduced after 5 O₂ pulses, CeO₂ did not show any activity, either. This indicates that lattice oxygen present in CeO₂ does not react with CH₄. Therefore, it was confirmed that CeO₂ has no activity to decompose CH₄ without regard to the oxidation state of Ce. On the contrary, in the case of CH₄/O₂ pulses, CeO₂ gave the same activities for total combustion as the continuous flow reaction results. When CH₄ pulse was introduced after CH₄/O₂ pulses, CeO₂ did not show any activity. Therefore, it was confirmed that methane oxidations including both POM and TOM occur with coexistence of methane and oxygen over the CeO₂ catalyst, indicating that lattice oxygen does not participate in the reaction over CeO₂. Namely, active oxygen species reacting with CH₄ should be supplied from the gas-phase oxygen. Consequently, in order to perform POM, the active sites, Ce³⁺, should activate adsorbed oxygen immediately supplied from gas-phase oxygen to release activated oxygen species reacting with CH₄. Generally, the Mars-van Krevelen mechanism is applicable in partial oxidation reactions catalyzed by oxide surfaces.²¹ This mechanism explained a stepwise donation of electrons which proceed through free-radical intermediates, *e.g.*,



where, \square indicates oxygen vacancies. It is obvious that oxygen vacancies, Ce³⁺, are active sites for POM and activated oxygen species should be one of the intermediates or the set of the intermediates. However, further spectroscopic study is necessary to verify it.

Conclusions

The CH₄ conversion and the selectivities to H₂ and CO over CeO₂ are strongly dependent on the CH₄/O₂ ratio as follows. (1) CeO₂ catalyzes total oxidation with a CH₄/O₂ ratio less than 2.0. (2) Continuous partial oxidation reaction is achieved over CeO₂ only under significant oxygen deficient condition (CH₄/O₂ ≥ 6.0). (3) CeO₂ exhibits oscillatory catalytic behavior, and the period depends upon the feed composition under intermediate oxygen deficient condition (4.3 ≥ CH₄/O₂ ≥ 3.8).

In POM over CeO₂, lattice oxygen does not participate in the reaction. The most probable reaction mechanism is that oxygen vacancies in reduced ceria are supplied with oxygen molecules from the reactant, and then activate adsorbed oxygen, followed by releasing activated oxygen species reacting with methane to produce H₂ and CO.

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