Extraordinary Catalytic Behavior of CeO_2 in Partial Oxidation of Methane

Hyun-Seog Roh, Ki-Won Jun, Seung-Chan Baek, and Sang-Eon Park*
Catalysis Center for Molecular Engineering, Korea Research Institute of Chemical Technology,
P.O. Box 107, Yuseong, Daejeon 305-600, Korea

(Received July 9, 2001; CL-010641)

CeO_2 exhibits extraordinary catalytic activity in partial oxidation of methane to synthesis gas. Total combustion was observed at stoichiometric feed ratio, while oscillatory partial oxidation was achieved at O_2 deficient feed ratio.

CeO_2 has an important role in three-way catalysis (TWC) and fluid catalytic cracking (FCC).[1] 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 CeO_2 improves catalytic performance by storing oxygen during oxidation and releasing it during reduction.[2] Otsuka et al.[3] have shown that CeO_2 shows POM activity with a H_2/CO ratio of 2 at 873–1073 K. However, the POM reaction was executed by passing a mixture of CH_4 and Ar (1:1) after CeO_2 was pretreated in a 1:1 mixture of O_2 and Ar for 1 h at 973 K.

Recently, we reported that Ni/Ce–ZrO_2 exhibited high activity as well as high stability in partial oxidation of methane (POM),[4] steam reforming of methane (SRM),[5] and oxy-steam reforming of methane (OSRM: simultaneous POM and SRM).[5] In the case of Ni/CeO_2, it showed very low activity in SRM,[5] however, it exhibited fairly good activity in POM[4] and remarkably high activity as well as stability in OSRM.[5] Thus, we have aimed to investigate CeO_2 as a catalyst for POM, resulting in finding out very interesting results such as follows. Catalytic behavior of CeO_2 is extraordinary during the reaction and strongly depends on the feed composition of CH_4 and O_2. Therefore, we report here that reduced CeO_2 could catalyze POM giving a H_2/CO ratio of 2 with oxygen deficient feed and explain the strange catalytic behavior.

The CeO_2 employed was a reagent-grade (purity > 99.9%) having a BET surface area of 19 m^2/g. Activity tests were carried out at 1023 K under atmospheric pressure in a fixed-bed microreactor.[6] Each catalyst (50 mg) was loaded into a quartz reactor with inner diameter of 4 mm. The reaction temperature was measured and controlled by a thermocouple inserted directly into the top layer of the catalyst bed. Prior to reaction tests, the catalysts were reduced in 5% H_2/N_2 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.

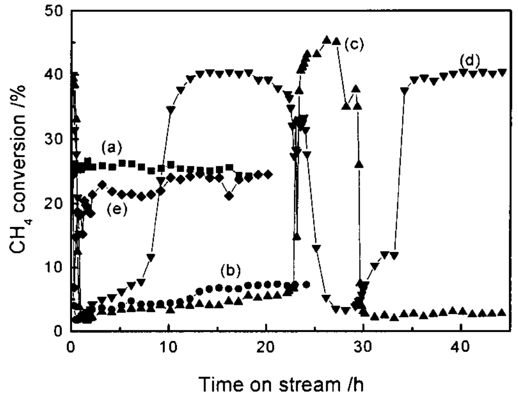

Figure 1. The effect of CH_4/O_2 ratio on CH_4 conversion: (a) ■, CH_4/O_2 = 2.0; (b) ●, CH_4/O_2 = 3.0; (c) ▲, CH_4/O_2 = 3.8; (d) ▼, CH_4/O_2 = 4.3; (e) ◆, CH_4/O_2 = 6.0; (CH_4 = 30 mL/min, 50 mg catalysts, T = 1023 K, p = 1 atm).

Table 1. CH_4 conversion, O_2 conversion, H_2 selectivity, CO selectivity and H_2/CO ratio over CeO_2 with various CH_4/O_2 ratios

CH_4/O_2 ratio	X_{CH_4} /%	X_{O_2} /%	S_{H_2} /%	S_{CO} /%	H_2/CO ratio
2.0	26	87	4	1.5	5.0
3.0	7	13	46	31	2.7
3.8[a]	45	100	77	77	2.0
4.3[a]	40	100	75	75	2.0
6.0	25	100	68	66	2.1

[a]Data at maximum CH_4 conversion. (Reaction conditions: CH_4 = 30 mL/min, 50 mg catalysts, T = 1023 K, p = 1 atm).

Figure 1 clearly shows the effect of CH_4/O_2 ratio on CH_4 conversion with time on stream, and Table 1 summarizes CH_4 conversion, O_2 conversion, H_2 selectivity, CO selectivity and H_2/CO ratio over CeO_2 with various CH_4/O_2 ratios. At the stoichiometric feed ratio (CH_4/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. At the condition of CH_4/O_2 = 3.0, CH_4 and O_2 conversions were 7% and 13%, respectively. These conversions were lower than those at CH_4/O_2 = 2.0, however, the selectivities to H_2 and CO were 46% and 31%, respectively, suggesting that POM was considerable. These results tell us that POM is favorable over CeO_2 at oxygen deficient environment. Surprisingly, in the case of CH_4/O_2 = 3.8, maximum CH_4 and O_2 conversions 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 steam was extraordinary. The detailed reaction data with time on stream are illustrated in Figure 2. 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, and dramatically it reached about 40% after 23 h and

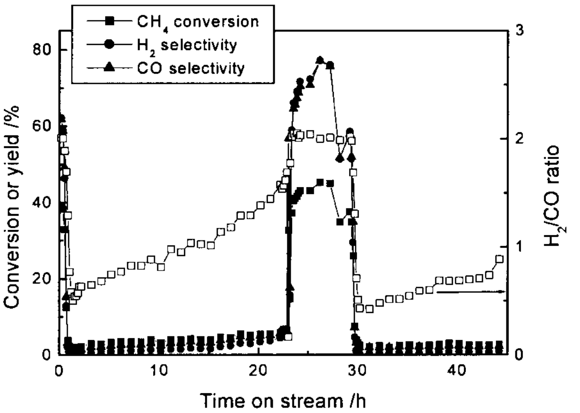

Figure 2. POM over CeO_2 with CH_4/O_2 ratio of 3.8 (CH_4 = 30 mL/min, 50 mg catalysts, T = 1023 K, p = 1 atm).

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, H_2/CO ratio was close to 2.0 initially, decreased to 0.5 after 1 h, and increased steadily to 2.0 after 23 h. The increasing rate of H_2/CO ratio was rather fast than that of CH_4 conversion. These results can be explained as follows. At the beginning, reduced ceria store oxygen molecules from the reactant and release them as active oxygen species reacting with methane to produce synthesis gas at oxygen deficient condition. After that, reduced ceria are oxidized fast by O_2 feed, showing almost negligible activity in POM. And then, oxidized ceria is reduced gradually by hydrogen produced from POM. These schemes are clearly illustrated in Figure 3. By the way, in the case of CH_4/O_2 = 4.3, maximum CH_4 and O_2 conversions were 40% and 100%, respectively. Both H_2 and CO selectivities were 75% giving a H_2/CO ratio of 2.0. The general feature was similar to that with CH_4/O_2 = 3.8, in the point of giving oscillatory catalytic behavior. However, the period was shorter than that with CH_4/O_2 = 3.8, and the increasing rate of CH_4 conversion after 1 h was faster. Besides, the period giving high CH_4 conversion was longer than 10 h. These results indicate that reduction of ceria could be accelerated and maintained for a long time when oxygen deficiency was heavier. When CH_4/O_2 ratio was 6.0, CeO_2 exhibited continuous 100% O_2 conversion, 68% H_2 selectivity, and 66% CO selectivity with a H_2/CO ratio of 2.1. This indicates that continuous partial oxidation reaction could be possible under oxygen deficient condition.

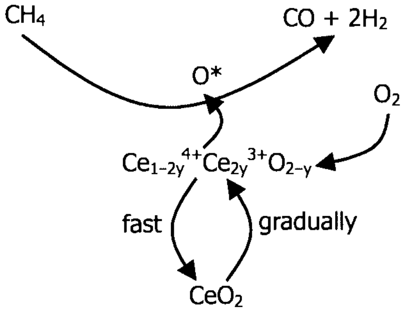

Figure 3. Schematics of producing syngas over CeO_2 catalyst.

In order to investigate the reaction mechanism, pulse experiments using CH_4, O_2 and CH_4/O_2 mixed gas (CH_4/O_2 = 2.0) were performed in a micro-reactor. Prior to reaction, 15 mg catalyst was loaded in the reactor and reduced in situ in 5% H_2/N_2 at 1023 K for 3 h. After that, the sample was heated to 1073 K in He (30 mL/min), held for 90 min to remove any residual gases in the system, and then exposed to pulses of CH_4, O_2 or CH_4/O_2 (1 mL pulse, 10 min interval). According to the pulse reaction results, CeO_2 did not show any activity with only CH_4 pulses. With CH_4/O_2 pulses, CeO_2 gave the same activities for total combustion as continuous flow reaction results. When CH_4 pulses were introduced after CH_4/O_2 pulses or O_2 pulses, CeO_2 did not show any activity, either. Therefore, it was confirmed that methane oxidations including both POM and total combustion occur with coexistence of methane and oxygen.

In summary, the POM activity over CeO_2 is strongly dependent on the CH_4/O_2 ratio. Total oxidation was dominant with stoichiometric feed ratio (CH_4/O_2 = 2.0) and partial oxidation was favorable with oxygen deficient feed. Strangely, between 3.8 and 4.3 of CH_4/O_2 ratio, CeO_2 exhibited oscillatory catalytic behavior, and the period depended upon the feed composition. The reaction mechanism can be explained as follows. Oxygen vacancies in reduced ceria are supplied with oxygen molecules from the reactant, and then activate adsorbed oxygen, followed by releasing active oxygen species reacting with methane to produce H_2 and CO.

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