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Partial Oxidation of Methane Using the Redox of Cerium Oxide

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Direct conversion of methane into synthesis gas of H_2/CO ratio of 2 has been demonstrated using CeO_2 as an oxidant at 873-1073 K. The reaction was accelerated in the presence of Pt black (1 wt%). The reduced cerium oxide after the oxidation of methane can be used to convert carbon dioxide into carbon monoxide.

Ultimate remaining recoverable reserves of natural gas surpasses those of crude oil.[1,2] Therefore, natural gas will play a growing role as carbon-sources for the world's supply of fuel and base chemicals. Proven technologies for chemical utilization of methane, the major component of natural gas, as a chemical feedstock consist of the formation of synthesis gas (H_2/CO) through steam reforming and, then, their further transformation to desired chemicals.[3] By contrast, many researchers have suggested that the partial oxidation of methane ($CH_4 + 1/2O_2 \dashrightarrow 2H_2 + CO$) could be an attractive alternative to steam reforming as a process for synthesis gas production.[4-8] In general, the mechanism of the partial oxidation of CH_4 into synthesis gas involves the conversion of CH_4 to CO_2 and H_2O followed by the reforming of the remaining CH_4 with steam and CO_2.[4-6,8,9] The direct conversion of CH_4 into synthesis gas of a H_2/CO ratio of 2 has never been observed.

One of the authors has shown that a simple redox process of metal oxide can be applied for the conversion of CO_2 to CO or of H_2O to H_2.[10-12] CeO_2 has been suggested to be one of the potential metal oxides that can be used in this redox process.[12]

Very recently we have found that CeO_2 is an unusual oxidant for oxidation of CH_4 into H_2 and CO of the ratio of 2 with producing neither H_2O nor CO_2. We now demonstrate the conversion of CH_4 directly to the synthesis gas in Eq. 1 and subsequent conversion of CO_2 to CO by the reduced cerium oxide in Eq. 2:

$$CeO_2 + nCH_4 \longrightarrow CeO_{2-n} + nCO + 2nH_2 \qquad (1)$$

$$CeO_{2-n} + nCO_2 \longrightarrow CeO_2 + nCO \qquad (2)$$

The CeO_2 used was a reagent-grade powder (purity > 99.9%) having a BET surface area of 19 m^2/g. The Pt black used as a catalyst was thoroughly mixed with the CeO_2. Oxidation of CH_4 (Eq. 1) and reduction of CO_2 (Eq. 2) were carried out using a fixed bed qualtz tubular reactor. CeO_2 was pretreated in a 1:1 mixture of O_2 and Ar for 1 h at 973 K. The reaction of Eq. 1 was started by passing a mixture of CH_4 and Ar (1:1) through the CeO_2 bed (3.0 g) at a pressure of 101 kPa and a total flow rate of 120 ml/min. After the experiment of Eq. 1, all the gases in the reactor were flashed out by an Ar flow. Subsequent reaction of CO_2 with the reduced cerium oxide (Eq. 2) was carried out with a 1 : 7 mixture of CO_2 and Ar under atmospheric pressure at a flow rate of 40 ml/min.

The oxidation of methane by CeO_2 occurred at the temperatures higher than 873 K. A typical example for the reaction sequence is shown in Fig. 1. The kinetic curves in Fig. 1 show that H_2O and CO_2 are produced at the early stage of the reaction. However, the formations of these products ceased after 40 min. The main products after 20 min were H_2 and CO. This was true at all the temperatures examined in this work (873-

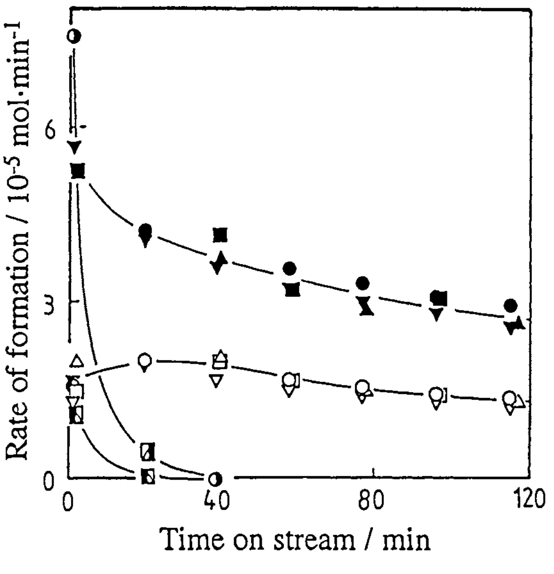

Fig. 1. Partial oxidation of CH_4 with CeO_2 at 973 K as functions of time-on-stream. Data for four fresh samples are plotted. Run 1, circles; run 2, triangles; run 3, reverse triangles; run 4; squares. (●, ▲, ▼, ■), H_2; (○, △, ▽, □), CO; (◑, ▲, ▼, ◨), H_2O; (◐, ▲, ▼, ◧), CO_2.

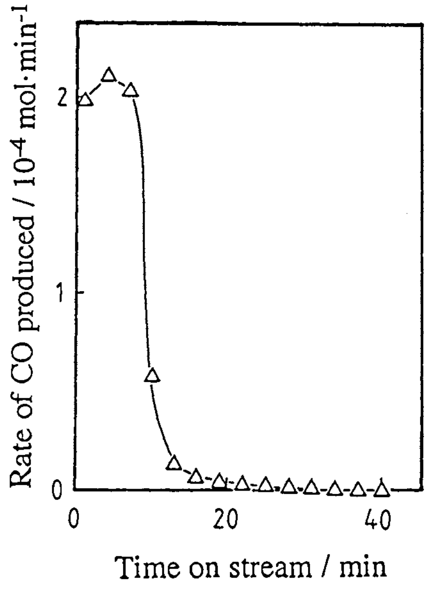

Fig. 2. Conversion of CO_2 to CO with the reduced cerium oxide: Formation rate of CO at 723 K as a function of time-on-stream. Initial degree of reduction was 8%.

1073 K). The most striking feature of this synthesis gas formation after 20 min is that the H_2/CO ratio is always 2.0 ± 0.2 if the degree of reduction of CeO_2 does not exceed 10%. The formation of synthesis gas in Fig. 1 can be ascribed neither to the steam reforming of CH_4 nor to the reforming of CH_4 by CO_2 because the synthesis gas formation occurs in the absence of H_2O and CO_2. This is supported by the fact that the initial formations of H_2O and CO_2 did not enhance the formations of H_2 and CO, respectively. The final degree of reduction of the sample evaluated from Fig. 1 on the basis of the quantities of the oxygen containing products was about 8%.

The cerium oxide sample used in the experiment of Fig. 1 was subjected to the reaction with CO_2. Figure 2 shows the rate of CO formation as a function of time-on-stream of the gas mixture of CO_2 and Ar. The conversion of CO_2 to CO was 100% at the early stage of the reaction (< 7 min). The reaction was completed in 30 min. The degree of oxygen recovery to CeO_2 evaluated from the quantity of CO was about 82%. The oxygen recovery was not improved by raising temperatures to 873 K. Probably the surface oxygen responsible for the formations of H_2O and CO_2 in Fig. 1 may not be recovered through the reaction with CO_2.

The second run of the reactions (Eqs. 1 and 2) using the same sample as that in the first run indicated a decrease about 30% in the rate of reduction of cerium oxide with CH_4 but the rate of reoxidation by CO_2 was not reduced at all. Further repetitions of the cycle did not change the reactivity of the cerium oxide appreciably.

Addition of Pt black (1 wt%) to CeO_2 enhanced the rate of oxidation of CH_4 as demonstrated in Fig. 3. The reactions in the absence and in the presence of Pt black were carried out at 873 K. For both cases, rapid formations of H_2O and CO_2 were observed at the very early stage of the reaction (not shown in Fig. 3), but these products were not observed after 20

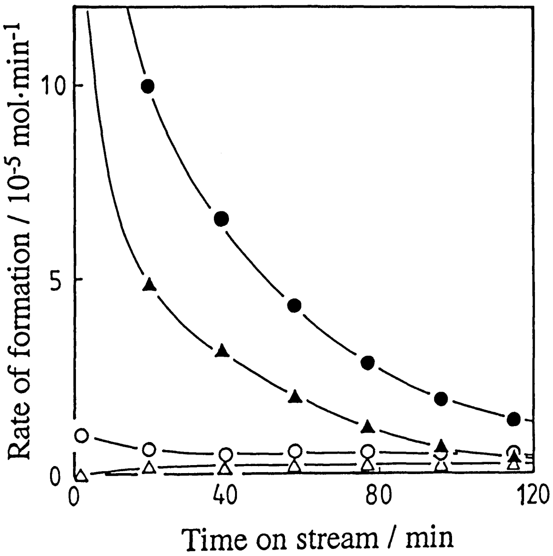

Fig. 3. Effect of Pt black on the rate of synthesis gas formation at 873 K. With Pt black: ●, H_2; ▲, CO. With-out Pt black: ○, H_2; △, CO. The rates of H_2 and CO formations at 1 min for the sample with Pt black were 4.8×10^{-4} and 2.2×10^{-4} mol/min, respectively.

min. Surprisingly, the results in Fig. 3 indicate that the composition of synthesis gas at < 60 min was also 2 to 1 for H_2 and CO even in the presence of Pt black which is a well known catalyst for the combustion of CH_4. However, H_2/CO ratio becomes greater than 2 at > 60 min. This observation suggests the coke formation on the surface of cerium oxide. The discrepancy of the H_2/CO ratio from 2 in the presence of Pt black became more and more notable at higher temperatures > 873 K and at larger degrees of reduction > 10%.

In conclusion, redox cycle of cerium oxide enables the direct conversion of CH_4 into synthesis gas and the conversion of CO_2 into CO. This process in Eq. 1 provides an appropriate composition of synthesis gas (H_2/CO=2) for conventional synthesis of bulk chemicals. CO without H_2, an indispensable feedstock for carbonylation reactions, can be produced in Eq. 2.

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