

Partial Oxidation of Methane to Synthesis Gas over Rhodium Vanadate, RhVO₄: Redispersion of Rh Metal during the Reaction

Kimio KUNIMORI,* Shinichi UMEDA, Junji NAKAMURA, and Toshio UCHIJIMA

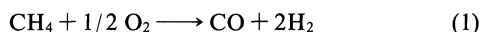
Institute of Materials Science, University of Tsukuba,

Tsukuba, Ibaraki 305

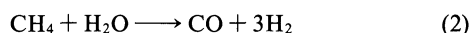
(Received March 18, 1992)

Synopsis. Partial oxidation of methane to synthesis gas (CO + H₂) has been carried out over both RhVO₄/SiO₂ and unpromoted Rh/SiO₂ catalysts at temperatures between 300°C and 720°C and 1 atmosphere pressure, with a CH₄:O₂ of 2:1 under nitrogen dilution. It is found that the RhVO₄ compound supported on SiO₂ was reduced to Rh metal and V₂O₃ during the reaction, and the catalyst showed onset of activity to CO and H₂ around 500°C reaching a maximum conversion in excess of 90% at 650°C, while the unpromoted Rh/SiO₂ catalyst showed the onset of activity at the higher temperature (above 600°C) reaching almost 100% conversion at around 700°C. The different catalytic activity may be ascribed to both the morphology change (Rh dispersion) and the Rh-vanadia interaction after the reduction of the RhVO₄ compound.

Recently, the partial selective oxidation of methane to synthesis gas over the ruthenium-containing rare-earth pyrochlores, LnRu₂O₇ (where Ln is a lanthanide) has been reported by Ashcroft et al.⁽¹⁾



Synthesis gas production is usually achieved by the steam reforming of methane according to:



However, the steam reforming reaction is highly endothermic, and side reactions, including the water gas shift reaction, result in a product containing substantial amount of CO₂. By contrast, the partial oxidation of CH₄ (1) is a mildly exothermic and more selective reaction, and produces a more desirable H₂/CO ratio (2:1) for the methanol synthesis process etc.

Further studies of this reaction revealed that high yields of synthesis gas (above 90% at 1050 K) can also be obtained over the transition metals such as Ru and Ir, either supported on alumina or present in mixed-metal oxide precursors such as Pr₂Ru₃O₇ and Eu₂Ir₂O₇.^(2,3) At the very same time when Ashcroft et al. reported their results, we have also found the reaction (1) occurred over rhodium double oxides such as RhVO₄ and related metal catalysts.^(4,5) We wish to report here our results of the partial oxidation of CH₄ to synthesis gas over both RhVO₄/SiO₂ and unpromoted Rh/SiO₂ catalysts.

Experimental

The unpromoted 5 wt% Rh/SiO₂ catalyst was prepared by impregnation of SiO₂ (JRC-SIO-3) with an aqueous RhCl₃ solution,⁽⁶⁾ followed by H₂ reduction at 500°C. The rhodium vanadate, RhVO₄, supported on the SiO₂ was prepared by the calcination of a vanadia-promoted 4 wt% Rh/SiO₂ catalyst in air at 700°C.⁽⁶⁾

The oxidation of CH₄ was performed with a conventional

fixed-bed flow reactor system.⁽⁵⁾ The reactant gases, CH₄ and O₂, were diluted with N₂ to 5 and 2.5%, respectively, and the total flow rate was 39 ml min⁻¹ at atmospheric pressure. The catalyst sample of 200 mg was used in this experiment. The reactant and product gases, CH₄, O₂, CO₂, CO, H₂O, and H₂, were analyzed by a gas chromatograph using Porapak Q and Molecular Sieve 5A columns. The XRD measurements were performed with an X-ray diffractometer (Rigaku Co. Ltd.) with a graphite monochromator for Cu Kα (40 kV, 30 mA) radiation.⁽⁶⁾

Results and Discussion

Figure 1 shows the result of the reaction of CH₄ oxidation over the RhVO₄/SiO₂ catalyst. The product yields were expressed as the percent (%) CH₄ converted to CO, H₂, H₂O, and CO₂, and the % concentration of the unreacted CH₄ was also plotted as a function of reaction temperature. The products CO₂ and H₂O were obtained at around 500°C. In this case, the reaction is ascribed to the complete oxidation of CH₄. At the higher temperatures, however, the amounts of CO₂ and H₂O diminished, and the amounts of CO and H₂ were increased drastically as the reaction temperature was increased. The conversions of CO and H₂ were about 90% at 650°C. It has already been suggested that the reaction pathway in the partial oxidation process involves an initial conversion of some methane to CO₂ and H₂O, followed by a series of steps involving the reaction (2) and the CO₂ reforming reaction (3) as follows:⁽²⁻⁵⁾

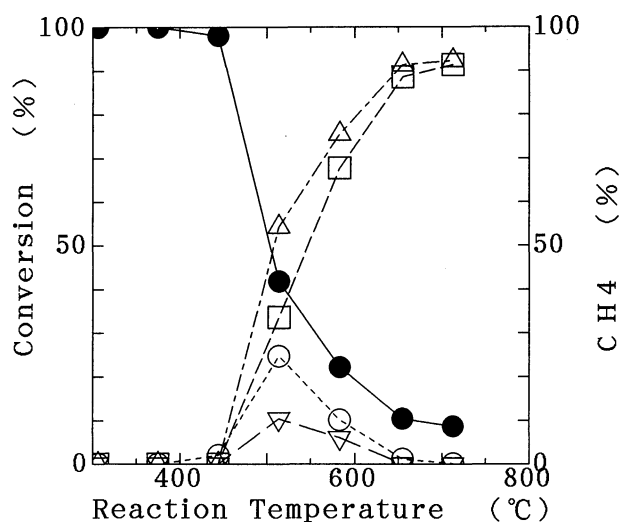
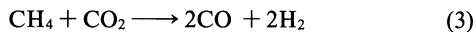


Fig. 1. Product distribution in the CH₄+1/2O₂ reaction over the RhVO₄/SiO₂ catalyst. ● CH₄, ○ CO₂, □ CO, △ H₂, ▽ H₂O.



The present results are consistent with this view. At higher temperature the production of CO and H₂ is thermodynamically favored because these two reactions (2) and (3) are highly endothermic.

As shown in Fig. 2 (1), the X-ray diffraction pattern of the catalyst sample before the reaction exhibited characteristic of the RhVO₄ compound with a small amount of Rh₂O₃. After the catalytic test run, however, the RhVO₄ compound was reduced to Rh metal, as shown in Fig. 2 (2). We have already shown that the RhVO₄ compound was decomposed to Rh metal and V₂O₃ (highly dispersed) on the SiO₂ support above 200°C in a reducing condition.⁶⁾ Therefore, it is probable that the hydrogen produced during the reaction and/or the unreacted CH₄ may trigger the reduction of the ternary oxide. Similar results have been obtained for the Eu₂Ir₂O₇ catalyst,³⁾ which is partially reduced during catalysis, leading to Ir metal particles on Eu₂O₃, and active catalysts comprise those metals (Ru, Ir etc.) that are reduced during the reaction.^{2,3)}

For a comparison, the result of the unpromoted Rh/SiO₂ catalyst at the same reaction condition is shown in Fig. 3. The complete oxidation activity to the products CO₂ and H₂O appears to be lower than that of the RhVO₄ catalyst, and the products of CO and H₂ were not observed at the lower reaction temperature (around 500°C). The onset of activity to CO and H₂ shifted to the higher temperature (above 600°C) reaching almost 100% conversion at around 700°C. The Rh particle size of the Rh/SiO₂ catalyst after the catalytic test run was calculated to be about 17 nm from the X-ray line broadening measurement in Fig. 2 (3). On the other hand, the particle sizes of RhVO₄ and Rh metal were calculated to be 30 nm and 10 nm, respectively, from the XRD peaks in Fig. 2 (1) and (2). Apparently, the large RhVO₄ particles were decomposed into smaller Rh particles (redispersion of Rh metal).⁶⁾ The reduction of RhVO₄ (the decomposition into Rh metal and V₂O₃) on the SiO₂ support resulted in a strong Rh-vanadia interaction, as proved by both hydrogen chemisorption and ethane hydrogenolysis measurements.⁶⁾ Both the morphology change (Rh dispersion) and the vanadia promoter may affect the catalytic performance for the partial oxidation of CH₄, which resulted in the different catalytic behavior in these two catalysts. The RhVO₄/SiO₂ catalyst (which is decomposed to Rh metal and V₂O₃ during the reaction) has a higher activity than the Rh/SiO₂ catalyst at the lower reaction temperature (e.g., 600°C), but at the higher reaction temperature (e.g., 700°C) the unpromoted Rh catalyst appears to be more active than the RhVO₄/SiO₂ catalyst (see Figs. 1 and 3). It may also be noted that a highly dispersed Rh/Al₂O₃ catalyst has a much higher activity for the partial oxidation of CH₄ to synthesis gas.⁷⁾

More detailed studies, including effects of metal-oxide and metal-support interactions and metal dispersion etc., will be needed to find good catalysts for the selective partial oxidation of CH₄ to synthesis gas. The mixed oxide catalyst systems such as RhVO₄ may have some advantages as a precursor material of active catalysts;

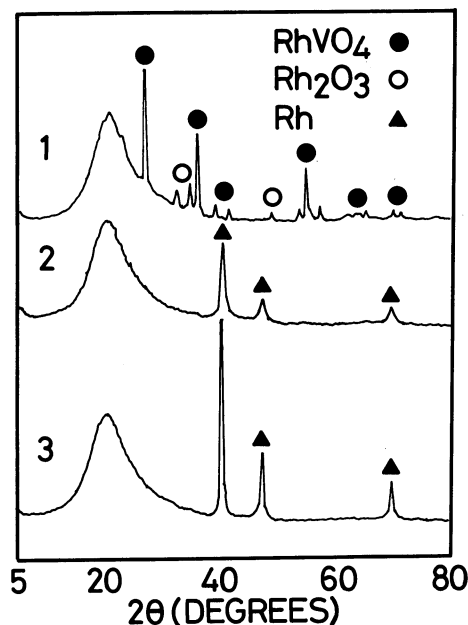


Fig. 2. X-ray diffraction patterns of the Rh catalysts. (1) RhVO₄/SiO₂; before the catalytic reaction, (2) RhVO₄/SiO₂; after the catalytic reaction, (3) Rh/SiO₂; after the catalytic reaction.

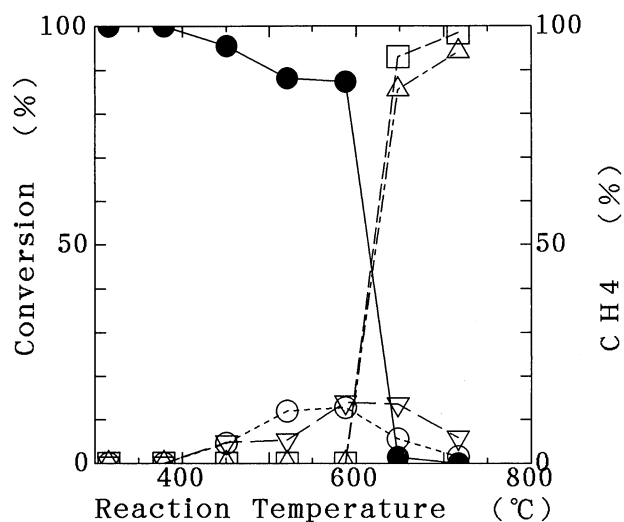


Fig. 3. Product distribution in the CH₄+1/2O₂ reaction over the Rh/SiO₂ catalyst. ● CH₄, ○ CO₂, □ CO, △ H₂, ▽ H₂O.

e.g., the RhVO₄ compound can be reproduced by the high-temperature (700°C) oxidation of a sintered Rh catalyst (i.e., regeneration of the catalyst).⁶⁾

This work was partially supported by a Grant-in-Aid from the Ministry of Education, Science and Culture.

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**, 319 (1990).
- 2) P. D. F. Vernon, M. L. H. Green, A. K. Cheetham, and

A. T. Ashcroft, *Catal. Lett.*, **6**, 181 (1990).

3) R. H. Jones, A. T. Ashcroft, D. Waller, A. K. Cheetham, and J. M. Thomas, *Catal. Lett.*, **8**, 169 (1991).

4) S. Umeda, J. Nakamura, S. Ito, K. Kunimori, and T. Uchijima, Proc. of the 66th Annual Meeting of Catalysis Society of Japan, Hiroshima, 1990, Abstr., p. 314.

5) J. Nakamura, S. Umeda, K. Kubushiro, K. Kunimori,

and T. Uchijima, submitted to J. of Petroleum Society of Japan.

6) Z. Hu, T. Wakasugi, A. Maeda, K. Kunimori, and T. Uchijima, *J. Catal.*, **127**, 276 (1991).

7) K. Sato, S. Umeda, J. Nakamura, K. Kunimori, and T. Uchijima, Proc. of the 63th Annual Meeting of Chemical Society of Japan, Osaka, 1992, Abstr., I, p. 177.
