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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

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Synopsis. Partial oxidation of methane to synthesis gas ($CO+H_2$) has been carried out over both $RhVO_4/SiO_2$ and unpromoted Rh/SiO_2 catalysts at temperatures between 300 °C and 720 °C and 1 atomosphere pressure, with a $CH_4:O_2$ of 2 : 1 under nitrogen dilution. It is found that the $RhVO_4$ compound supported on SiO_2 was reduced to Rh metal and V_2O_3 during the reaction, and the catalyst showed onset of activity to CO and H_2 around 500 °C reaching a maxium conversion in excess of 90% at 650 °C, while the unpromoted Rh/SiO_2 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 $RhVO_4$ compound.

Recently, the partial selective oxidation of methane to synthesis gas over the ruthenium-containing rare-earth pyrochlores, $LnRu_2O_7$ (where Ln is a lanthanide) has been reported by Ashcroft et al.:[1)]

$$CH_4 + 1/2\ O_2 \longrightarrow CO + 2H_2 \qquad (1)$$

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

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad (2)$$

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 CO_2. By contrast, the partial oxidation of CH_4 (1) is a mildly exothermic and more selective reaction, and produces a more desirable H_2/CO ration (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 $Pr_2Ru_2O_7$ and $Eu_2Ir_2O_7$.[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 $RhVO_4$ and related metal catalysts.[4,5)] We wish to report here our results of the partial oxidation of CH_4 to synthesis gas over both $RhVO_4/SiO_2$ and unpromoted Rh/SiO_2 catalysts.

Experimental

The unpromoted 5 wt% Rh/SiO_2 catalyst was prepared by impregnation of SiO_2 (JRC-SIO-3) with an aqueous $RhCl_3$ solution,[6)] followed by H_2 reduction at 500 °C. The rhodium vanadate, $RhVO_4$, supported on the SiO_2 was prepared by the calcination of a vanadia-promoted 4 wt% Rh/SiO_2 catalyst in air at 700 °C.[6)]

The oxidation of CH_4 was performed with a conventional fixed-bed flow reactor system.[5)] The reactant gases, CH_4 and O_2, were diluted with N_2 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 experment. The reactant and product gases, CH_4, O_2, CO_2, CO, H_2O, and H_2, 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 $K\alpha$ (40 kV, 30 mA) radiation.[6)]

Results and Discussion

Figure 1 shows the result of the reation of CH_4 oxidation over the $RhVO_4/SiO_2$ catalyst. The product yields were expressed as the percent (%) CH_4 converted to CO, H_2, H_2O, and CO_2, and the % concentration of the unreacted CH_4 was also plotted as a function of reaction temperature. The products CO_2 and H_2O were obtained at around 500 °C. In this case, the reaction is ascribed to the complete oxidation of CH_4. At the higher temperatures, however, the amounts of CO_2 and H_2O diminished, and the amounts of CO and H_2 were increased drastically as the reaction temperature was increased. The conversions of CO and H_2 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 CO_2 and H_2O, followed by a series of steps involviing the reaction (2) and the CO_2 reforming reaction (3) as follows:[2–5)]

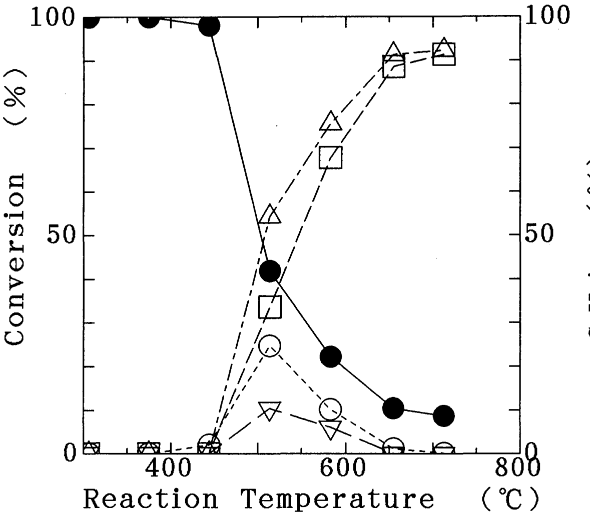

Fig. 1. Product distribution in the $CH_4+1/2O_2$ reaction over the $RhVO_4/SiO_2$ catalyst. ● CH_4, ○ CO_2, □ CO, △ H_2, ▽ H_2O.

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \qquad (3)$$

The present results are consistent with this view. At higher temperature the production of CO and H_2 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 $RhVO_4$ compound with a small amount of Rh_2O_3. After the catalytic test run, however, the $RhVO_4$ compound was reduced to Rh metal, as shown in Fig. 2 (2). We have already shown that the $RhVO_4$ compound was decomposed to Rh metal and V_2O_3 (highly dispersed) on the SiO_2 support above 200 °C in a reducing condition.[6] Therefore, it is probable that the hydrogen produced during the reaction and/or the unreacted CH_4 may trigger the reduction of the ternary oxide. Similar results have been obtained for the $Eu_2Ir_2O_7$ catalyst,[3] which is partially reduced during catalysis, leading to Ir metal particles on Eu_2O_3, and active catalysts comprise those metals (Ru, Ir etc.) that are reduced durig the reaction.[2,3].

For a comparison, the result of the unpromoted Rh/SiO_2 catalyst at the same reaction condition is shown in Fig. 3. The complete oxidation activity to the products CO_2 and H_2O appears to be lowere than that of the $RhVO_4$ catalyst, and the products of CO and H_2 were not observed at the lower reaction temperature (around 500 °C). The onset of activity to CO and H_2 shifted to the higher temperature (above 600 °C) reaching almost 100% conversion at aronund 700 °C. The Rh particle size of the Rh/SiO_2 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 $RhVO_4$ 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 $RhVO_4$ particles were decomposed into smaller Rh particles (redispersion of Rh metal).[6] The reduction of $RhVO_4$ (the decompostion into Rh metal and V_2O_3) on the SiO_2 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 CH_4, which resulted in the dfferent catalytic behavior in these two catalysts. The $RhVO_4$/SiO_2 catalyst (which is decomposed to Rh metal and V_2O_3 during the reaction) has a higher activity than the Rh/SiO_2 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 $RhVO_4$/SiO_2 catalyst (see Figs. 1 and 3). It may also be noted that a highly dispersed Rh/Al_2O_3 catalyst has a much higher activity for the partial oxidation of CH_4 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 partical oxidation of CH_4 to synthesis gas. The mixed oxide catalyst systems such as $RhVO_4$ may have some advantages as a precursor material of active catalysts; e.g., the $RhVO_4$ compound can be reproduced by the high-temperautre (700 °C) oxidation of a sintered Rh catalyst (i.e., regeneration of the catalyst).[6]

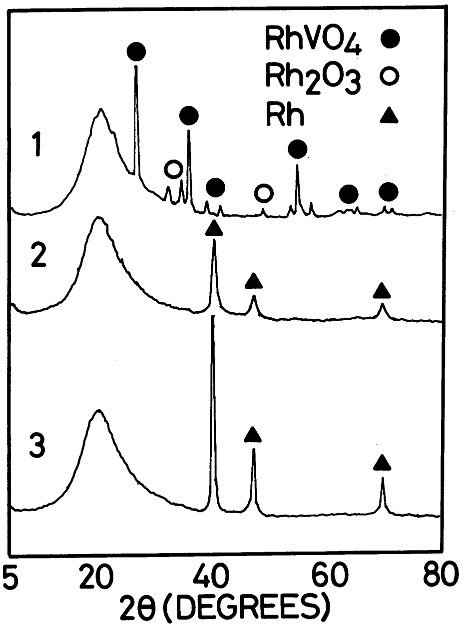

Fig. 2. X-ray diffraction patterns of the Rh catalysts. (1) $RhVO_4$/SiO_2; before the catalytic reaction, (2) $RhVO_4$/SiO_2; after the catalytic reaction, (3) Rh/SiO_2; after the catalytic reaction.

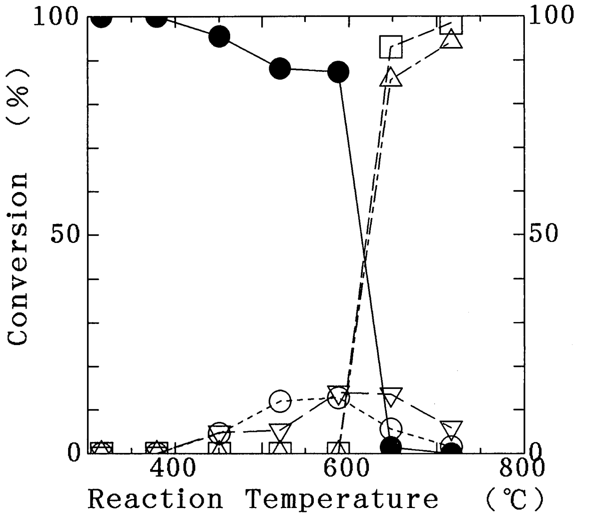

Fig. 3. Product distribution in the CH_4+1/2O_2 reaction over the Rh/SiO_2 catalyst. ● CH_4, ○ CO_2, □ CO, △ H_2, ▽ H_2O.

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