Low-temperature oxidation of methane to syngas by zeolite-supported rhodium sub-nano cluster catalyst

Hirokazu Kobayashi,[a,*] **Yuhui Hou**,[a] **Atsushi Fukuoka**[a]
[a]*Institute for Catalysis, Hokkaido University, Sapporo, 001-0021, Japan*
**Corresponding author: +81-11-706-9137, kobayashi.hi@cat.hokudai.ac.jp*

Abstract: Syngas is an essential intermediate in the chemical utilization of methane. We prepared Rh sub-nano clusters with 0.6 nm diameter by an ion-exchange method. In the oxidation of methane, the catalyst gave 84% conversion of methane with 91% selectivity for CO and a H_2/CO ratio of 2.0 even at a low temperature of 600 °C and a very high space velocity (1,200,000 mL h^{-1} g^{-1}). No deactivation was observed in the durability test for 50 h, and turnover number of bulk Rh for the formation of CO reached 2,600,000.

Keywords: Methane, Oxidation, Zeolite.

1. Introduction

The emergence of economical technology for extracting shale-gas and other unconventional natural gas has promoted methane to be a chemical resource.[1] In the current industries, methane is first converted to syngas, and syngas is used for the Fischer-Tropsch synthesis and methanol production. Methanol is further converted to olefins. Thus, syngas is a crucial intermediate in the utilization of methane.

However, conversion of methane to syngas has needed severe reaction conditions above 800 °C. To reduce the temperature, we focused on the fundamental of the partial oxidation of methane (POM) to syngas. POM to syngas (eq. 1) usually occurs *via* complete oxidation of methane (eq. 2) and subsequent slower steps consisting of steam reforming reaction (eq. 3) and reverse water-gas shift (RWGS) reaction (eq. 4).[2] Accordingly, metal active sites for eqs. 3 and 4 are important to determine the overall performance. Kinetic analysis of steam-reforming of methane (eq. 3) has indicated that dissociation of a C–H bond of methane is the rate-determining step in the reaction.[3] Rh is one of the most active metal species for this purpose, and very importantly density functional theory (DFT) calculations have predicted that the C–H activation ability of Rh metal increases with decreasing the coordination number.[4] Therefore, we can expect that a very small Rh particle has high activity for the conversion of methane to syngas due to not only larger dispersion but also low coordination number to accelerate the bottle-neck step, dissociation of C–H bonds of methane. Herein, we report zeolite-supported Rh sub-nano clusters with 0.6 nm diameter for the selective oxidation of methane to syngas at 450–600 °C.[5]

$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$ (1, overall reaction)
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (2)
$CH_4 + H_2O \rightarrow CO + 3H_2$ (3)
$CO_2 + H_2 \rightarrow CO + H_2O$ (4)

2. Experimental

Catalyst was prepared by an ion-exchange method with a mordenite zeolite (JRC-Z-HM90, Si/Al = 45) and $RhCl_3$. The POM was conducted in a fixed-bed flow reactor made of quartz (inner diameter ø7). The catalyst, Rh/MOR-IE, was initially heated to a designated temperature under He flow (9.2 mL min^{-1}). Afterward, a reaction gas mixture of CH_4, O_2, and an inert gas (He or N_2) was fed into the reactor. Products were analyzed by gas-chromatograph.

3. Results and discussion

Rh catalysts prepared by an ion exchange method (Rh/MOR-IE) and an impregnation method

(Rh/MOR-IM) both had 0.25 wt% of Rh, determined by ICP. HAADF-STEM depicted uniform 0.6 nm particles of Rh species as bright dots for Rh/MOR-IE (Figure 1, left side). However, Rh/MOR-IM possessed non-uniform particles of Rh species with an average diameter of 2.9 nm (right side).

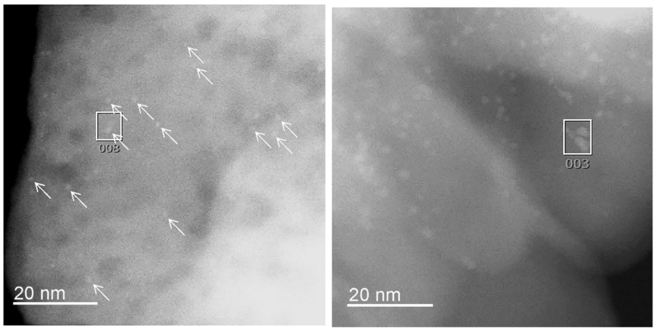

Figure 1. HAADF-STEM images of Rh/MOR-IE (left) and Rh/MOR-IM (right). EDX analysis at the square boxes showed the presence of Rh.

Catalytic activity of Rh/MOR-IE and Rh/MOR-IM was compared in POM with CH_4/O_2 ratio of 2 at 450 °C and at SV of 6000 mL h^{-1} g^{-1}. Rh/MOR-IE gave 38% conversion of methane and 24% yield of CO with 64% selectivity. These values are close to those calculated with Gibbs energies of respective compounds, indicating that the reaction approached thermodynamic equilibrium due to high catalytic activity of Rh/MOR-IE. Rh/MOR-IM gave a similar conversion value of methane (36%), but yield of CO was only 9.5%, corresponding to 27% selectivity. Rh/MOR-IE catalyst is significantly more active than Rh/MOR-IM. In both reactions, O_2 conversion was >99%. Accordingly, combustion of methane (eq. 2) is fast, and CO selectivity is determined by the catalytic activity for steam reforming of methane and RWGS reactions (eqs. 3, 4). We have confirmed that Rh/MOR-IE catalyzes the two reactions in additional controlled experiments.

Selective production of CO and H_2 was demonstrated at 600 °C with a very high SV (1.2×10^{6} mL h^{-1} g^{-1}) (Figure 2). Rh/MOR-IE steadily afforded 83–84% methane conversion and 90–91% CO selectivity, the highest ever reported at the temperature. The turnover number for the formation of CO based on number of bulk Rh atom reached 2,600,000 at 50 h.

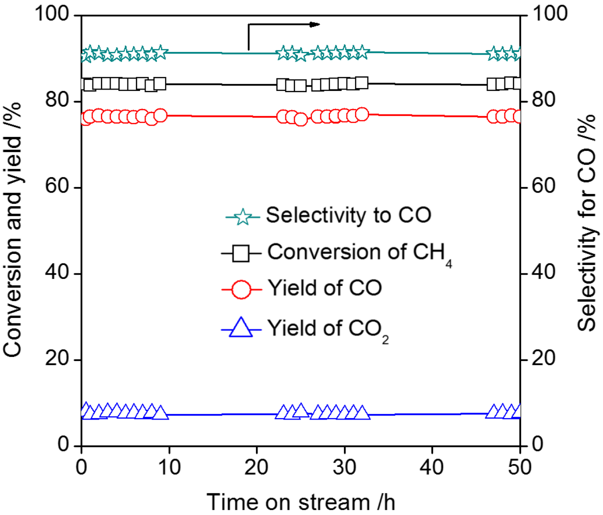

Figure 2. Time course of oxidation of methane over Rh/MOR-IE at 600 °C.

4. Conclusions

Rh sub-nano clusters with 0.6 nm diameter was prepared on mordenite zeolite by an ion-exchange method. The catalyst gave 84% conversion of methane with 91% selectivity for CO and a H_2/CO ratio of 2.0 even at a low temperature of 600 °C and a very high space velocity (1,200,000 mL h^{-1} g^{-1}). We propose that very small size of Rh clusters achieved by using zeolite provides the high catalytic performance.

References

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