

Partial oxidation of methane over Pd/Ni/LaAlO₃ catalyst at low temperature

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Introduction

Recently, catalytic partial oxidation of methane (POx) for synthesis gas production has been studied extensively for its high energy efficiency [1]. Ni catalysts have been widely used for this reaction, and investigated mainly at high temperature [2]. However, because POx is exothermic reaction, the development of catalysts which show high activity at low temperature is necessary. So far, we have discovered that Ni/LaAlO₃, Pd/LaAlO₃ and Pd/Ni/LaAlO₃ show high catalytic activities for POx at low temperature as 673 K. Ni/LaAlO₃ showed catalytic activity at 673 K with pre-reduction, and the activity coincided with the indirect POx (combustion + steam reforming + water gas shift) equilibrium composition at 823 K. This was due to the reduction of NiO to Ni⁰ by the pre-reduction. Pd/LaAlO₃ showed high catalytic activity at 673 K without any pre-reduction, but H₂ selectivity was lower than that of Ni/LaAlO₃. We found that selective H₂ combustion proceeded on Pd species. Pd/Ni/LaAlO₃ showed almost the same catalytic activity as Ni/LaAlO₃ without any pre-reduction. So, it was indicated that NiO on Pd/Ni/LaAlO₃ was reduced to Ni⁰ *in-situ* without any pre reduction. In this research, the objective is to clarify the mechanism of NiO reduction on Pd/Ni/LaAlO₃ by catalytic activity tests of Ni/LaAlO₃, Pd/LaAlO₃ and Pd/Ni/LaAlO₃ in low conversion region and CH₄ pulse tests on Ni/LaAlO₃.

Experimental

The LaAlO₃ support was prepared by citric acid method. Ni catalyst supported on LaAlO₃ was prepared by an impregnation method, and Ni loading was 6.6 wt%. Moreover, Pd was impregnated to Ni/LaAlO₃, and Pd loading was 0.25 wt%. Partial oxidation of methane was carried out at atmospheric pressure in a fixed bed reactor. Catalytic activity tests were generally performed at 673 K, Ar/CH₄/O₂ = 210/140/70 SCCM, total flow rate = 420 mL min⁻¹, and W/F = 0.233 g h mol⁻¹. Catalytic activity tests in low conversion region were performed at 823 K, Ar/CH₄/O₂ = 210/70/35 SCCM, total flow rate = 315 mL min⁻¹, and W/F = 0.015-0.233 g h mol⁻¹. CH₄ pulse tests on Ni/LaAlO₃ were performed at 673 K and 823 K, respectively.

Results/Discussion

In order to clarify the role of Pd over Pd/Ni/LaAlO₃, catalytic activity tests of Ni/LaAlO₃, Pd/LaAlO₃ and Pd/Ni/LaAlO₃ in low conversion region were performed, and selectivities to H₂ over three catalysts were compared. This result is shown in figure 1. From figure 1, Pd/Ni/LaAlO₃ showed lower H₂ selectivity than that of Ni/LaAlO₃ at W/F = 0.015 and 0.029 g h mol⁻¹. Therefore, it was suggested that Pd species, which had an ability for H₂ combustion, participated in the reaction over Pd/Ni/LaAlO₃ at low W/F.

From figure 1, the formation of H₂ was not observed over Pd/LaAlO₃ at W/F = 0.015 g h mol⁻¹. This was due to the proceeding of H₂ combustion and the low steam reforming activity over Pd species. So, in order to find out whether the NiO is reduced by H₂ or CH₄, we performed CH₄ pulse tests on Ni/LaAlO₃ at 673 K and 823 K, respectively. After CH₄ pulse tests on Ni/LaAlO₃, XRD of Ni/LaAlO₃ was measured. XRD patterns of Ni/LaAlO₃ as made and after CH₄ pulses are shown in figure 2. From figure 2, surface Ni state was NiO as made and after CH₄ pulses at 673 K, and this NiO was reduced to Ni⁰ after CH₄ pulses at 823 K. From these results together with catalytic activity test of Pd/Ni/LaAlO₃ in low conversion region, it was inferred that the exothermic reaction over Pd species raised catalyst bed temperature up to 823 K from 673 K on Pd/Ni/LaAlO₃, and then, CH₄ reduced NiO at the 823 K condition.

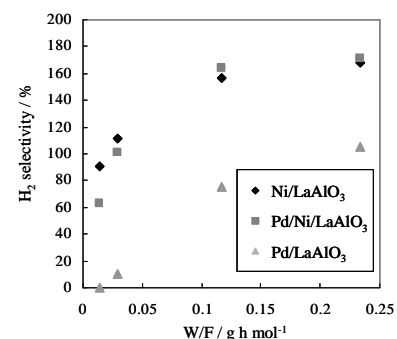


Figure 1 H₂ selectivity over three catalysts at 823 K, Ar/CH₄/O₂ = 210/70/35, total flow rate = 315 mL min⁻¹.

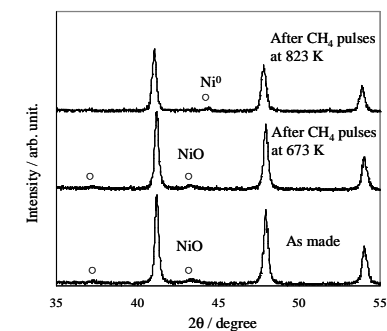


Figure 2 XRD patterns of Ni/LaAlO₃ as made and after CH₄ pulses.

References.

1. A.P.E. York, T. Xiao, and M.L.H. Green, *Top. Catal.*, **22** 345-358 (2003).
2. B.C. Enger, R. Lødeng, A. Holmen, *Appl. Catal. A*, **346** 1-27 (2008).