Supported Ni–Pd Catalysts Active for Methane Decomposition into Hydrogen and Carbon Nanofibers

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(Received August 29, 2002; CL-020737)

The supported (Ni–Pd) catalysts showed high activity and long life for methane decomposition to form hydrogen and carbon nanofibers of a unique structure.

Methane decomposition is of current interest from a viewpoint of hydrogen synthesis for H_2–O_2 fuel cells,[1,2] because the reaction does not produce CO which deactivates Pt electrocatalysts at the anode. In addition, methane decomposition can be performed at relatively low temperatures (<873 K) and emits no CO_2 in the atmosphere. Thus, the reaction is environmentally benign compared to the current process, i.e., steam reforming of methane, followed by CO shift reaction. Concerning the catalysts for methane decomposition, it is well known that Ni/SiO_2 is one of the effective ones.[3,4] We have reported that Ni supported on fumed silica (Cab-O-Sil, supplied from Cabot Co.) shows high catalytic activity for methane decomposition.[5] However, better catalysts should be explored because the catalytic activity of Ni/Cab-O-Sil decreased with time on stream and finally the catalysts were deactivated completely. Therefore, it is required to develop catalysts with a long life and high activity.

Methane decomposition over supported Ni catalysts produces hydrogen and carbon nanofibers. The research in the field of carbon nanofibers has undergone an explosive growth since discovery of carbon nanotubes.[6] Ni metal particle is present at the tip of carbon nanofibers produced by methane decomposition. The Ni metal particle adsorbs methane and decomposes it into carbon and hydrogen atoms. The process is followed by the diffusion of carbon atoms on the metal surface and/or through the metal particle to the precipitation site to form carbon nanofibers. Thus, the modification of Ni metal with another metal species may bring about the formation of carbon nanofibers different from those formed by Ni metal only. This may bring about an increase in the yield of hydrogen.

In the present study, we investigated the catalytic performance of supported Ni catalysts modified with other metal species for methane decomposition. We would report superior performance of supported Ni–Pd catalyst and formation of carbon nanofibers with a unique structure.

Catalysts used in this study were prepared by impregnation of catalytic supports with mixed aqueous solutions containing $Ni(NO_3)_2$ and another metal salt ($Cu(NO_3)_2$, $RhCl_3$, $PdCl_2$, $IrCl_3$ or H_2PtCl_6), followed by drying in air at 353 K. Prior to methane decomposition, the catalysts were reduced with hydrogen at 873 K. When carbon materials were used as catalytic supports, the catalysts were reduced with hydrogen at 573 K in order to avoid the hydrogenation of the support into methane. Methane decomposition was performed with a conventional gas-flow system. The reaction was initiated by the contact of methane ($P(CH_4) = 101$ kPa) with the reduced catalyst. During the reaction, a part of gases in a stream out of the catalyst-bed was sampled out and analyzed by GC.

Figure 1 shows the change of methane conversion as a function of time on stream in methane decomposition over Ni/SiO_2 catalysts without and with different metal species (M; Cu, Rh, Pd, Ir and Pt) at 823 K. Cab-O-Sil was used as the catalytic support. For all the catalysts, Ni metal was supported with 5 wt% and the mole ratio of additives (M) to Ni was 0.1. Hereafter, Ni/SiO_2 modified with M was denoted as M–Ni/SiO_2. For all the catalysts, methane decomposition proceeded selectively to form hydrogen only as a gaseous product. Initial conversion of methane for Ni/SiO_2 was the highest among all the catalysts, i.e., addition of metal species into Ni/SiO_2 brought about a slight decrease in initial conversion, irrespective of the kind of additives. Similar kinetic curves of methane conversion were observed for Ni/SiO_2 and those modified with Rh, Ir and Pt. Significant deactivation of these catalysts was observed after 3, 2 and 1 h for Ni/SiO_2 and Rh–Ni/SiO_2, Pt–Ni/SiO_2, and Ir–Ni/SiO_2, respectively. On the other hand, the addition of Pd moderated the deactivation markedly. The methane conversion after 6 h of time on stream was kept almost constant. The result for Pd/SiO_2 is also shown in Figure 1. The loading amount of Pd in Pd/SiO_2 was adjusted to be the same as that in Pd–Ni/SiO_2. Hydrogen formation was observed for Pd/SiO_2, but its catalytic activity was very low. We estimated the carbon yield (C/(Ni+M): the mole of methane decomposed per mole of metal on the catalyst (mol/mol)) until the complete

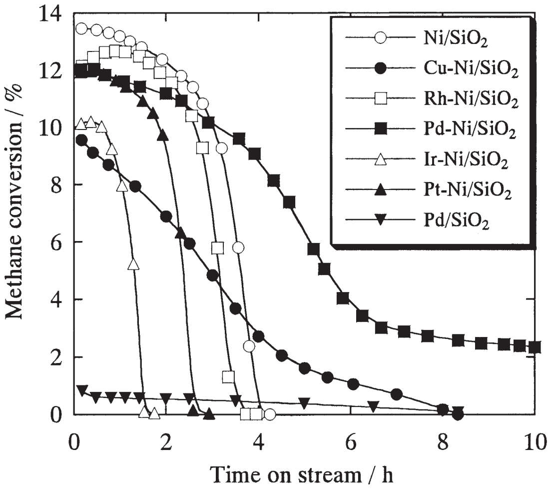

Figure 1. Kinetic curves of methane conversion as a function of time on stream. Decomposition of methane over Ni/SiO_2 with and without metal additives and over Pd/SiO_2 at 823 K. Flow rate $= 40\,ml\cdot min^{-1}$, $P(CH_4) = 101$ kPa, catalyst = 0.04 g.

deactivation of each catalyst. The yields were 1092, 2266, 259, 850, 716 and 629 for Ni/SiO_2, Pd–Ni/SiO_2, Ir–Ni/SiO_2, Rh–Ni/SiO_2, Cu–Ni/SiO_2 and Pt–Ni/SiO_2, respectively. These results indicate that the addition of Pd species into Ni/SiO_2 remarkably improves the catalytic life for methane decomposition. XRD pattern of the reduced Pd–Ni/SiO_2 showed the formation of bimetallic species composed of Pd and Ni metals. Therefore, it is likely that elongation of catalytic life by the addition of Pd into Ni/SiO_2 is caused by the formation of bimetallic species.

In order to enhance the catalytic activity and to extend catalytic life, we have examined the effect of supports for Ni–Pd bimetallic catalyst on the yields of hydrogen and carbon. In addition to silica support, TiO_2, MgO, graphitized carbon fiber and the carbon nanofiber formed by methane decomposition over Ni/SiO_2 (denoted as CF(CH_4)) were utilized as supports for Ni–Pd catalysts. The results showed that CF(CH_4) was the most effective support for methane decomposition. Figure 2 shows the change in methane conversion with time on stream in methane decomposition at 873 K over Pd–Ni/CF(CH_4) catalysts with different mole ratios of Pd to Ni. For all the catalysts, the total mole amounts of Pd and Ni loaded on CF(CH_4) support were adjusted to be 7.8 mol%. Under the reaction conditions noted in the caption of Figure 2, the initial conversion of methane for Ni/CF(CH_4) was more than 17%. However, the catalytic activity was lost completely after 30 min. Thus, the carbon yield for Ni/CF(CH_4) was very low (C/Ni = 75). The catalytic activity of Pd/CF(CH_4) was low and became negligible at 7 h of time on stream. Addition of Pd to Ni/CF(CH_4) with the mole ratio Pd/(Pd+Ni) from 0.05 to 0.25 increased initial catalytic activity. It should be noted that the coexistence of Pd and Ni on the support extended the catalytic life remarkably irrespective of the Pd/Ni ratio. Especially, the catalysts with the Pd/(Pd+Ni) ratio of 0.25 and 0.5 showed a high and continuous catalytic activity. The decrease in activity of these catalysts was remarkably moderated compared to Ni/CF(CH_4) and Pd/CF(CH_4). The carbon yields (C/(Pd+Ni)) evaluated from the kinetic curves of methane conversion from 0 to 50 h were 79, 886, 6540, 6828, 3855 and 79 for the catalysts of the mole ratio Pd/(Pd+Ni) of 0, 0.05, 0.25, 0.50, 0.75, and 1.0, respectively. The Pd–Ni catalysts with Pd/(Pd+Ni) ratio of 0.25, 0.5 and 0.75 were still active after 50 h. If the reactions were observed for longer time, the carbon yields must become greater than 8000 before the complete deactivation of Pd–Ni/CF(CH_4). Recently, the Ni-based catalysts with high activity for the methane decomposition have been designed by some research groups. Avdeeva et al. reported that introduction of Cu into Ni/Al_2O_3 increased the carbon yield (C/(Cu+Ni) = 1250) in methane decomposition.[7] Ermakova et al. investigated methane decomposition over Ni/SiO_2 catalyst.[8] The highest yield of carbon (C/Ni) was 1900, when SiO_2 was added to Ni metal by 10 wt%. Taking these previous reports into consideration, Pd–Ni/CF(CH_4) in this work was by far effective catalysts for the methane decomposition among the catalysts reported so far.

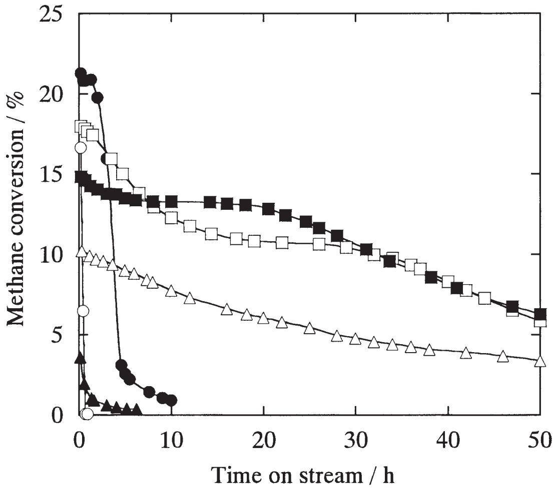

Figure 2. Kinetic curves of methane conversion as a function of time on stream. Decomposition of methane over Pd–Ni/CF(CH_4) catalysts with different mole ratio of Pd to Ni. Reaction temperature = 873 K, flow rate = 50 ml·min^{-1}, catalyst = 0.02 g, P(CH_4) = 101 kPa. Pd/(Pd+Ni) as mole ratio: 0, ○; 0.05, ●, 0.25, □; 0.50, ■; 0.75, △; 1.0, ▲.

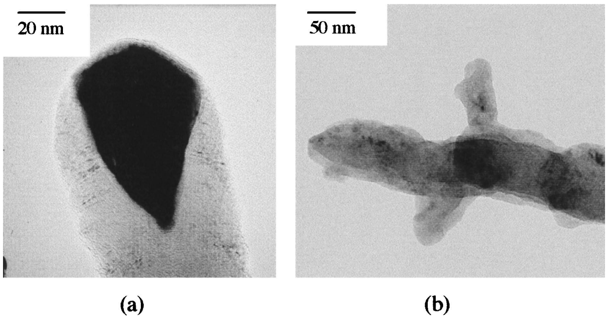

Figure 3. TEM images of carbon nanofibers formed by methane decomposition over Ni/SiO_2 (a) and Pd–Ni/CF(CH_4) (b).

Figure 3 shows TEM images of carbon nanofibers formed by methane decomposition over Ni/SiO_2 and Pd–Ni/CF(CH_4). A Ni metal particle was present at the tip of carbon nanofiber formed on Ni/SiO_2, as reported by many researchers.[6] On the other hand, many branched carbon fibers were observed in addition to the same type of carbon nanofibers as that in Figure 3(a) after methane decomposition over Pd–Ni/CF(CH_4). In addition, the branched carbon fibers were observed for supported Pd–Ni catalysts after methane decomposition, irrespective of the types of catalytic supports (MgO, SiO_2 and TiO_2). Formation of the branched carbon fiber is a rare case in catalytic methane decomposition. The results suggest that mechanism for formation of carbon nanofiber over Pd–Ni catalyst is quite different from that over Ni catalyst.

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