Production of Hydrogen through Decomposition of Methane with Ni-supported Catalysts

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(Received July 21, 1999; CL-990642)

Active and selective Ni-based catalysts for the production of hydrogen through the decomposition of methane were looked for. The most active catalyst having the longest life time was a nickel catalyst supported on Cab-O-Sil. Approximately 1200 carbon atoms per a nickel atom deposited on the Ni(5 wt%)/Cab-O-Sil catalyst at 793 K before a complete deactivation was observed.

The increase in CO_2 concentration in the atmosphere due to increasing burning of fossil fuels (petroleum, coal, and natural gas) may lead to irreversible disastrous changes in the climate of our planet. Hydrogen is a clean burning, non-polluting fuel that can contribute directly to eliminating many of our insufferable environmental, economic, and health problems. However, current processes of hydrogen production use fossil fuels and water, emitting huge quantities of CO_2 into the atmosphere. All of these processes are highly endothermic and require additional fossil fuels as energy sources. The production of hydrogen from water by using sun or other renewable energy sources (wind power, tides, geothermal, atomic and others) is expected to be realized in the next two decades. At the moment, we believe that a realistic way to produce hydrogen without CO_2 emission is to utilize methane, the main component of natural gas, as the source of hydrogen. Hydrogen can be produced through thermal decomposition of methane,[1-3]

$$nCH_4 \longrightarrow nC + 2\,nH_2 \qquad (1)$$

The hydrogen is used as energy and the carbon should be buried back into the natural gas fields or can be used as functional materials, such as fibers, plastics, composites, etc. A huge amount of methane resources on the earth (natural gas, petroleum-associated gas, and methane hydrate) guarantees the reserve to production ratio for more than 1000 years.

The thermodynamic data for the reaction (1) assuming the formation of graphite show that methane decomposition can be realized at > 1000 K. For example, the conversion of methane at 1073 K is ca. 94% at atmospheric pressure. If a hydrogen absorbing alloy coexists in the system during the decomposition of methane, the complete conversion of methane can be realized at much lower temperatures $\leq$ 773 K due to the removal of the thermodynamic limitation for reaction (1).[4] Thus, for the operation of reaction (1) at relatively low temperatures, the development of active catalysts with a long-life time is needed.

It is well known that the cracking of methane takes place over Ni/SiO_2 at > 673 K.[5-7] We have demonstrated that Ni/SiO_2 is one of the most active catalysts for the forward and backward reactions of equation (1).[8] The purpose in this work is to look for a better catalyst in activity as well as in catalytic life time for the decomposition of methane.

The catalysts were prepared by impregnation of metal cations into supports from aqueous solutions of metal nitrates. The supports used in this work were SiO_2 (JRC-SIO8, supplied from Catalysis Society of Japan), Cab-O-Sil and graphite. The weight percent of Ni was adjusted to be 5%. The metal promoters (M) (M/Ni = 1/2 molar ratio) were added to the supported-Ni catalysts. The catalysts were calcined at 873 K for 5 h under a flow of air. The apparatus used for the decomposition of methane was a glass-made closed gas-circulation system with a dead volume of ca. 200 ml. The catalysts in a quartz-made reactor were pre-reduced at 823 K under a hydrogen pressure of 26 kPa. The decomposition of methane was performed with a catalyst of 20 mg at 673 or 723 K by introducing and circulating methane (initial pressure 60 kPa, amount 4.6 mmol). Continuous decomposition of methane to examine the life-time of catalysts was performed by introducing methane after the residual gases in the previous experiment had been evacuated. For all the catalysts tested under the experimental conditions in this work, H_2 was the only product in the gas phase. In other words, no hydrocarbon other than CH_4 was detected in the gas phase.

The effect of various metal additives to Ni/SiO_2 (Mg, Al, K, Ca, V, Mn, Fe, Ga, Co, Cu, Zn, Sr, Zr, Mo, W, Ru, Rh, Pd, Ag and Pt) on the initial rate of decomposition of methane was observed at 673 K. The average initial rate was evaluated from the conversion of methane in 15 min (conversion was less than 1.5% for every catalysts). The catalytic activity of the Mg^{2+}-added Ni/SiO_2 increased by ca. 1.5 times compared to that for the host Ni/SiO_2 catalyst. However, the other additives did not enhance or rather reduced the catalytic activity of the Ni/SiO_2.

The catalytic activities of Ni(5 wt%) supported on various carriers (MgO, TiO_2, Al_2O_3, ZrO_2, $SiO_2{\cdot}Al_2O_3$, yttria stabilized zirconia powder, Cab-O-Sil, and graphite) were also measured. The better supporters than SiO_2 (JRC-SIO8) were Cab-O-Sil and, surprisingly, graphite. The relative catalytic activities of the supported Ni catalysts measured at 723 K were Ni/Cab-O-Sil : Ni/graphite : Ni/SiO_2 = 1.46 : 1.20 : 1.00. The BET surface areas of these catalysts were 150, < 1.7, and 303 m^2g^{-1}, respectively. The trend of catalytic activities cannot be ascribed to the dispersion of Ni on the surface of the supporters.

The apparent activation energies for the decomposition of methane over the Ni/SiO_2, Mg^{2+}-added Ni/SiO_2, Ni/Cab-O-Sil and Ni/graphite were calculated from the slopes of ln (r) vs 1/T plots, where r was the rate of methane conversion evaluated from the conversion at 15 min. The activation energies were 152 (Ni/SiO_2), 134 (Mg^{2+}-added Ni/SiO_2), 131 (Ni/Cab-O-Sil), and 121 $kJmol^{-1}$(Ni/graphite). The activation energies are different considerably between Ni/SiO_2 and Ni/graphite.

The another important factor to be examined in this work is the life-time of the catalysts. This was examined for the four active catalysts described above. The integrated amount of methane converted (= accumulated amount of carbon deposited) and that of hydrogen formed are plotted according to

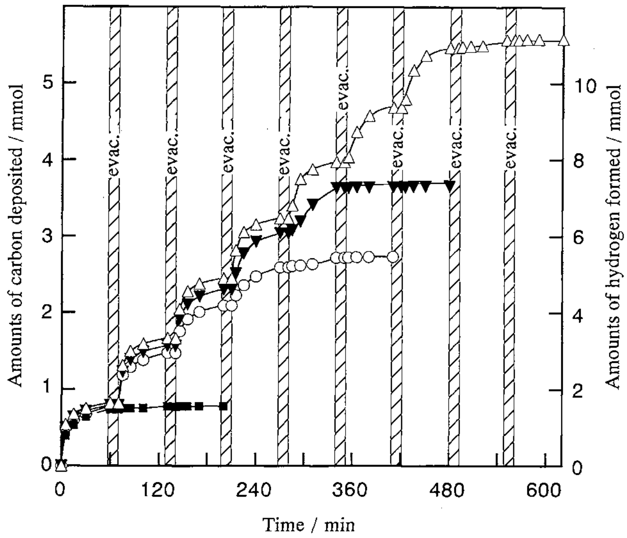

Figure 1. Decomposition of methane over Ni-supported catalysts at 723 K. The reactions were repeated till complete deactivation of the catalysts was observed.
△, Ni/Cab-O-Sil (C/Ni=328); ▼, Mg^{2+}-added Ni/SiO$_2$ (C/Ni =215); ○, Ni/SiO$_2$ (C/Ni=161); ■, Ni/graphite (C/Ni=46).
The values in parentheses were the molar ratio of the carbon finally-deposited to nickel.

the integrated reaction time in Figure 1. The decomposition of methane was performed at 823 K using the catalysts 20 mg. The experiments were continued till complete deactivation of catalysts had been confirmed. The results in Figure 1 indicate that the Ni/graphite was deactivated completely after only one cycle of methane decomposition. On the other hand, a deactivation of Ni/Cab-O-Sil did not occur till 7 repeated cycles. The total amount of hydrogen obtained was the highest (11.2 mmol) for the Ni/Cab-O-Sil. The highest C/Ni ratio of 328 was obtained for the accumulated carbon on this catalyst. The C/Ni ratio was evaluated from the amount of methane decomposed and that of total Ni in the catalyst. The catalytic activity as well as the life-time were the highest at this catalyst.

Figure 2 compares the SEM images of the carbon deposited on Ni/SiO$_2$ and Ni/Cab-O-Sil. The decomposition of methane was performed at 793 K under a flow of methane of 101 kPa (flow rate = 42.0 ml min^{-1}) by using a conventional flow system. The amounts of carbon deposited before the complete deactivation of catalysts were 19.0 and 60.8 mmol for 60 mg of the Ni/SiO$_2$ and Ni/Cab-O-Sil, respectively. These values correspond to carbon/Ni ratio 370 and 1190. The continuous decomposition of methane using the gas-flow system enhanced the accumulation of carbon or the life time of the catalysts. The carbon/Ni ratio obtained for Ni/Cab-O-Sil is one of the highest values ever reported.[9] The images in Figure 2 indicate that the thickness of the carbon fibers on Ni/Cab-O-Sil is in a diameter range of 80~10 nm, mostly in 40~20 nm. On the other hand, the thickness of the carbon on Ni/SiO$_2$ distributes in a diameter range of 110~30 nm, mostly in 80~40 nm. It is clear that the carbon fibers on Ni/Cab-O-Sil are thinner than those on Ni/SiO$_2$.

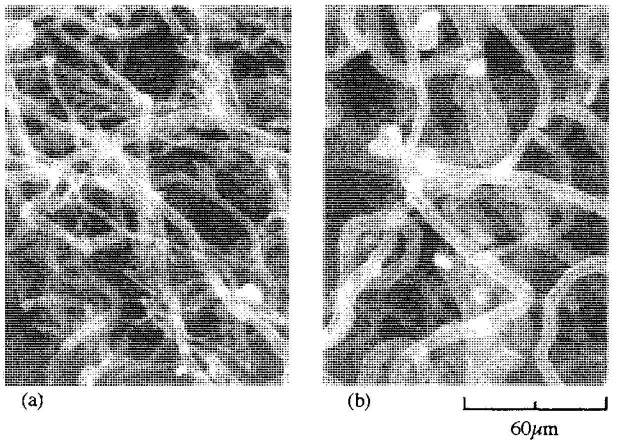

Figure 2. SEM images for the carbon fibers formed on Ni/Cab-O-Sil (a) and Ni/SiO$_2$ (b).

The back-scattering electron images (BEI) obtained at the same time for the measurement of SEM images in Figure 2 indicated the distribution and the size of Ni particles by bright spots. The BEI of the carbons on Ni/SiO$_2$ indicated the presence of many large Ni particles with the size ranged from 100 to 40 nm at the tips of carbon fibers. On the other hand, the BEI for the carbon fibers on Ni/Cab-O-Sil showed no detectable bright spots, suggesting that the size of Ni particles is smaller than 4 nm (detectable limit). The best catalytic performance observed for the Ni/Cab-O-Sil may be ascribed to the dispersion of Ni into small particles which catalyze the decomposition of methane as well as the growth of carbon whiskers. The absence of micropores in Cab-O-Sil might prevent the formation of large Ni particles during the decomposition of methane.

Reference and Notes

1 *Chem. Engng.*, **69**, 90(1962).
2 N. Z. Muradov, *Int. J. Hydrogen Energy*, **18**, 211 (1993).
3 B. Gaudernack and S. Lynum, *Int. J. Hydrogen Energy*, **23**, 1087 (1998).
4 K. Otsuka, N. Nakajima, and I. Yamamaka, *Chem. Lett.*, **1998**, 873.
5 P. K. de Bokx, A. J. H. M. Kock, E. Boellaard, W. Klop, and J. W. Geus, *J. Catal.*, **96**, 454 (1985).
6 T. Ishihara, Y. Miyashita, H. Iseda, and Y. Takita, *Chem. Lett.*, **1995**, 93.
7 T. Zhang and M. D. Amiridis, *Appl. Catal. A*, **167**, 161 (1998).
8 K. Otsuka, S. Kobayashi, and S. Takenaka, *Appl. Catal. A*, in press.
9 L. B. Avdeeva, O. V. Goncharova, D. I. Kochubey, V. I. Zaikovskii, L. M. Plyasova, B. N. Novgorodov, and Sh. K. Shaikhutdinov, *Appl. Catal. A*, **141**, 117 (1996).