Specific Reactivity of the Carbon Filaments Formed by Decomposition of Methane over Ni/SiO_2 Catalyst: Gasification with CO_2

Sakae Takenaka and Kiyoshi Otsuka*
Department of Applied Chemistry, Graduate School of Science and Engineering,
Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552

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Carbon filaments formed by the decomposition of methane over Ni/SiO_2 catalyst are converted efficiently with conversions > 91% into CO by gasification with CO_2.

Hydrogen is a clean fuel in the sense that no CO_2 is emitted when it is used in H_2-O_2 fuel cells. At present, hydrogen is produced mainly through steam reforming or partial oxidation of petroleum and natural gas. In these processes, CO is inevitably formed and it remains as an impurity even after purification process in the hydrogen fuel produced by these routes. The CO poisons strongly the anode-electrocatalysts in the H_2-O_2 fuel cells. Thus, decomposition of methane into hydrogen and carbon is of a current interest from a viewpoint of an alternative route of hydrogen production from natural gas.[1–3] Hydrogen produced by the decomposition of methane can be utilized directly as a fuel of the H_2-O_2 cell without any purification treatment because no CO is contained in the hydrogen. However, the most serious problem for this hydrogen-production process is to develop an appropriate utilization of a large amount of carbon coproduced with hydrogen. The gasification with steam into synthesis gas may be one of the potential utilization of the carbon in the chemical industry.[4] If the gasification with CO_2 into CO can be operated efficiently and repeatedly, the total process, i.e., the decomposition of methane and the subsequent gasification with CO_2, may realize a zero CO_2-emission process for the production of pure hydrogen to the H_2-O_2 fuel cell and that of CO to chemical industry. CO is an indispensable chemical used in the carbonylations of methanol and acetylene, hydroformylation of alkenes, synthesis of phosgene or in the formation of metal carbonyls.

It is well known that silica-supported Ni (Ni/SiO_2) is one of the catalysts effective for the decomposition of methane.[5–7] The decomposition of methane proceeds over the Ni/SiO_2 catalyst at temperatures > 673 K to form hydrogen and filamentous carbon selectively. In the present paper, we will report the specific reactivity of the filamentous carbons on the Ni/SiO_2 catalyst in the gasification with CO_2 forming CO.

Ni (5 wt%)/SiO_2 was prepared by impregnating a fumed SiO_2 (Cab-O-Sil from CABOT Co.) with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$, followed by calcinating the impregnated sample at 873 K under an air stream. We have reported that the fumed SiO_2 is the most favorable carrier of Ni for the methane decomposition.[8] Methane decomposition over the Ni/SiO_2 catalyst was carried out at an atmospheric pressure in a conventional gas-flow system. The Ni/SiO_2 catalyst (0.040 g) was treated under a stream of hydrogen at 873 K prior to the methane decomposition. The methane decomposition was initiated by contact of methane with the catalyst and the reaction was continued until the complete deactivation of the catalyst was observed. Then, CO_2 was introduced into the same reactor without any treatment of the catalyst which had been deactivated completely in the methane decomposition. During the reaction, a part of gas in stream out of the catalyst-bed was sampled out and analyzed by GC.

Figure 1 shows the changes in the formation rate of hydrogen in the decomposition of methane at 803 K and those of CO in the reaction of deposited carbons with CO_2 at 903 K over the Ni/SiO_2 catalyst as the functions of the time on stream. In the decomposition of methane over the Ni/SiO_2 catalyst, only hydrogen was formed as a gaseous product and filamentous carbons were deposited on the catalyst.[9–11] The formation rate of hydrogen decreased with time on stream and finally the catalyst was deactivated completely after 200 min from the introduction of methane into the reactor. In the methane decomposition, the amount of hydrogen formed was calculated to be 1.63 mol·g-cat^{-1} and the amount of carbon atoms deposited per one nickel atom in the Ni/SiO_2 catalyst (C/Ni) was 918.

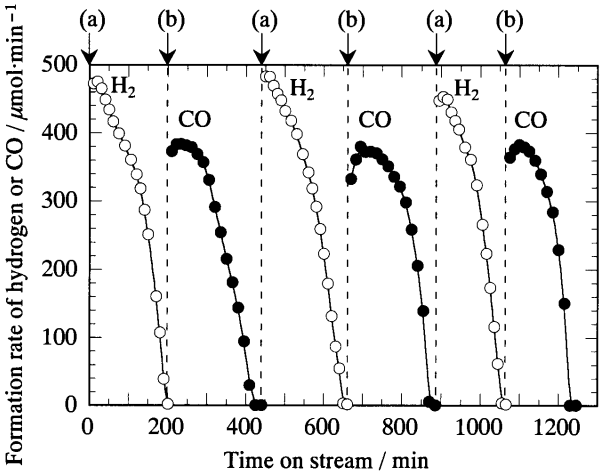

Figure 1. The formation rate of hydrogen in the decomposition of methane at 803 K and that of CO in the reaction of deposited carbons with CO_2 at 903 K over Ni/SiO_2 catalyst as functions of the time on stream. Decomposition of methane, $P(CH_4)$ = 101 kPa, flow rate = 60 mL·min^{-1}. Reaction of deposited carbons with CO_2, $P(CO_2)$ = 37 kPa and $P(Ar)$ = 64 kPa, flow rate = 60 mL·min^{-1}. (a): introduction of CH_4, (b) introduction of CO_2.

After the complete deactivation of the Ni/SiO_2 catalyst by the methane decomposition, CO_2 was introduced into the reactor at 903 K. The contact of CO_2 with carbons deposited on the deactivated catalyst resulted in the selective formation of CO. In the reaction of the carbons with CO_2, the amount of CO formed was twice of the amount of CO_2 consumed, i.e., the reaction, CO_2 +

C(deposited) → 2CO, took place selectively. The formation rate of CO decreased with time on stream and its formation could not be detected after 240 min from the introduction of CO_2. The amount of CO formed by the reaction of deposited carbons with CO_2 was evaluated to be 1.50 mol·g-cat^{-1}. The values of C/Ni were changed by the reaction with CO_2 from 918 to 78, i.e., the deposited carbons more than 91% were converted into CO.

After the reaction of deposited carbon with CO_2, methane was introduced again at 803 K into the reactor at the time-on-stream 440 min in Figure 1 without any treatment of the catalyst. The very similar kinetic curves of the formation of hydrogen for the first (0–200 min) and second (440–650 min) experiments in Figure 1 indicate that the removal of the carbons deposited on the Ni/SiO_2 by the reaction with CO_2 brings about the complete recovery of the catalytic activity of the Ni/SiO_2 for the methane decomposition. In the second methane decomposition, 1.70 mol of hydrogen per 1 g of the Ni/SiO_2 catalyst was formed and the carbon corresponding to C/Ni = 958 were newly deposited on the catalyst. The amount of hydrogen formed in the methane decomposition was almost the same as that formed in the first methane decomposition. Therefore, we consider that the reaction of the deposited carbons with CO_2 was effective not only for the selective formation of CO but for the regeneration of the catalyst.

The switch of the feed gas from methane to CO_2 at a time-on-stream 650 min in Figure 1 produced CO again indicating a similar kinetic curve to the previous one (210–440 min). The amount of CO formed in the second gasification with CO_2 was 1.60 mol·g-cat^{-1}, half of which came from the carbon on the Ni/SiO_2. If we assume that the origin of these reacted carbon are the ones formed in the second methane decomposition during the time on stream 440–650 min, the conversion of the carbons is estimated to be greater than 93%. Therefore, the production of hydrogen from methane and that of CO from the deposited carbon and CO_2 can be carried out reproducibly at least for 2 cycles. However, the results in the third cycle indicated a slight decrease in the catalytic activity of Ni/SiO_2 as can be seen in Figure 1. The deactivation of the catalyst progressed gradually with the repeated cycles after this.

In order to get information about the specific reactivity of the carbons deposited from methane on the Ni/SiO_2, we compared the reactions of various carbon samples with CO_2 catalyzed by Ni impregnated in the carbon. The Ni-containing carbon samples were prepared by impregnating the carbon samples (active carbon, graphite and carbon black) with aqueous solutions of $Ni(NO_3)_2\cdot 6H_2O$. The amount of Ni in the samples was 5 wt%. The samples were treated under a stream of hydrogen at 773 K prior to the reactions with CO_2. All the carbon samples without Ni species were inactive for the reaction with CO_2 into CO. Figure 2 shows the formation rates of CO in the reaction of carbons with CO_2 at 903 K catalyzed by the Ni added to the carbons. The weight of the Ni-added carbons used in the reaction with CO_2 was 0.35 g. This amount of the carbon samples corresponds to that of the carbons deposited on the Ni (5 wt%)/SiO_2 (0.040 g) after complete deactivation for the methane decomposition at the first cycle in Figure 1. It should be noted that the amount of Ni in the carbons deposited from methane was 0.5 wt% which was far less than those in the other carbon samples (5 wt%). The results in Figure 2 indicate that CO was formed for all the carbon samples. However, the formation rates of CO decreased quickly with time on stream at the early period for the graphite and the active carbon. The amounts of CO in 250 min were roughly estimated to be 11, 8, and 0.5 mmol for the active carbon, the graphite, and the carbon black, respectively, and the amounts were significantly less than that of CO (59.8 mmol) formed from the carbons deposited on Ni/SiO_2. These results suggest that the carbons deposited on Ni/SiO_2 are specifically active in the reaction with CO_2. From XRD studies on the deactivated Ni/SiO_2 catalyst, it was suggested that the carbon deposited on the catalyst was graphite with low crystallinity. This was confirmed by laser Raman spectra of the deposited carbons.[9] On the other hand, the XRD pattern of the active carbon was similar to that of the carbon black and the structure of the two samples was amorphous. Therefore, the differences in the reactivities of the carbons in the reaction with CO_2 in Figure 2 can not be explained by the extent of graphitization of the samples. In the methane decomposition over the Ni/SiO_2 catalyst, the carbons deposited on the catalyst grow with filamentous structure and Ni metal particles are present on the tips of carbon filaments, which have been confirmed by many research groups[10–12] as well as by us.[8] We believe that the carbon filaments deposited on Ni/SiO_2 catalyst is specifically reactive in the formation of CO because of a strong contact of Ni metal particles with the carbon filaments at the tip of each filament.

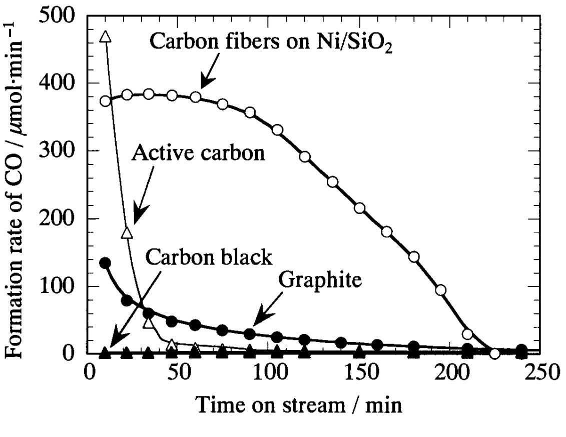

Figure 2. The formation rates of CO in the reactions of Ni-added carbon samples with CO_2 at 903 K as functions of the time on stream. $P(CO_2)$ = 37 kPa and P(Ar) = 64 kPa, flow rate = 60 mL·min^{-1}.

References and Notes

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