

Hydrogen Production by Catalytic Decomposition of Methane over Activated Carbons: Deactivation Study

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Abstract—The amount of deposited carbon on activated carbons was adjusted by varying the space time and the time on stream. Carbon nuclei formation appeared to occur initially but was terminated soon and then the carbon crystallite growth became dominant. The methane decomposition rate over activated carbons had a nearly linear relationship with the amount of carbon deposited. This suggests that the carbon deposition occurs uniformly and the activity decreases due to pore blocking, resulting in loss of accessibility to the active sites. The rate was also nearly proportional to the surface area for the same kind of activated carbon, which is contrasted with the previous finding that no discernible trend was observed between the initial activity and the surface area among different kinds of the activated carbons.

Key words: Activated Carbon, Deactivation, Hydrogen, Methane Decomposition, Surface Area

INTRODUCTION

Hydrogen is regarded as the ultimate clean power source of the future. Its application to fuel cells is a typical example. However, conventional processes of hydrogen production, such as the steam reforming and partial oxidation of fossil fuels, accompany simultaneous production of CO₂, which is to be reduced due to the greenhouse effect. Clean production of hydrogen, e.g., by water electrolysis, is not competitive with current energy costs. The decomposition of methane, on the other hand, produces no CO₂ [Fulcheri and Schwob, 1995; Gaudernack and Lynum, 1998; Jun et al., 2003; Liu et al., 2002; Muradov, 1993; Steinberg and Cheng, 1989].

Noncatalytic thermal decomposition of methane requires quite a high temperature (1,500-2,000 K) in order to obtain a reasonable hydrogen yield, so that overall CO₂ emission may not be reduced significantly. Transition metals such as Ni and Fe showed remarkable activity at much lower temperatures, but rapid catalyst deactivation associated with coking induces other problems such as bothersome catalyst regeneration and reactor blocking [Baker, 1979; Aiello et al., 2000]. Catalyst regeneration by burning the coke produces CO₂ again. Another approach is a plasma process without CO₂ emission. Even though the cost of electricity occupies quite a high portion, this process could be economical depending on the revenues from the carbon black product [Fulcheri and Schwob, 1995; Gaudernack and Lynum, 1998].

Recently, CO₂-free production of hydrogen via catalytic decomposition of methane and other hydrocarbons over carbon catalysts has been proposed as a viable alternative to the conventional steam reforming and partial oxidation [Muradov, 2001a, b]. When carbon is used as the catalyst, the clean carbon produced can be used

as a valuable byproduct and it eliminates the need for catalyst regeneration and CO₂ removal, which significantly simplifies the process. The heat required for the decomposition of methane can be supplied by burning 10-15% of the produced hydrogen, and thus no CO₂ emission occurs. Muradov [2001a, b] investigated various kinds of carbon, such as activated carbons, carbon blacks, acetylene black, glassy carbon, graphite, diamond, fullerenes and carbon nanotubes. Among these, activated carbons and carbon blacks showed reasonably high activity and moderate stability at around 1,123 K.

In a very recent work of the authors [Kim et al., 2003], several domestic activated carbons were investigated. The important findings of this kinetic study were that all the activated carbons showed similar catalytic characteristics and deactivation pattern; for different kinds of activated carbons no discernible relationship was observed between the surface area and the initial activity (this indicates that only a portion of the entire surface is active and the active portion may be different between different samples); H₂ was the only gaseous product detected; due to the intraparticle mass transport effect, smaller particles exhibited higher activity than larger particles, and below about 200 µm the mass transport effect was small; the reaction order was 0.5; the activation energy was ca. 200 kJ/mol; and the effect of the ash on the activity was small (these findings indicate that the reaction mechanism is the same on any activated carbon).

In this work, as a continuation of the previous work, a few samples of the domestic activated carbons were selected and the effects of carbon build-up on the deactivation behavior, that is, relationships between the amount of deposited carbon, the surface area and the activity, were investigated. To adjust the amount of deposited carbon, the space velocity and the reaction time were varied.

EXPERIMENTAL

Methane (99.99%) was used without further purification. An acti-

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vated carbon made from coal (in this article the sample name was designated as CL-SCR; supplied from Samchulli Carbotech with the commercial product name of SPW210, 12-30 mesh (average diameter=1,140 μm), surface area=910 m^2/g) and its powdered sample (average diameters of 137 μm) were used. Another sample made from coconut shell (designated here as CCN-SCR; its commercial name of SPW110 of Samchulli Carbotech, surface area=970 m^2/g), which was powdered to an average diameter of 214 μm , was also used. The powdered samples had the size sufficient for the intraparticle mass transport effect to be negligible [Kim et al., 2003].

The decomposition reaction was carried out under atmospheric pressure at 1,123 K (850 $^{\circ}\text{C}$) in a fixed-bed, quartz-tube flow reactor heated by an electric tube furnace. The catalyst charge ranged from 0.2 to 0.8 g and the volume hourly space velocity (VHSV) ranged from 1 to 15 $\text{L/g}\cdot\text{h}$ (the space time: roughly from 0.6 to 9 s). The product gas was analyzed by gas chromatography, using a Carboxen 1004 column (Supelco), Ar carrier gas and a TCD. The concentration of hydrogen or the methane conversion was determined by using calibrated data. The first sampling and analysis was usually done at 5 min after the methane was flowed, since it took some time for the reaction system to reach steady state in order to flush the argon initially present. Because the stainless steel sheath of the thermocouple is a good catalyst for hydrocarbon decomposition, the thermocouple was removed before CH_4 flowing after the desired temperature was adjusted in flowing Ar. The N_2 BET surface area and the pore size distribution (Micromeritics ASAP 2000) were measured before and after the reaction.

RESULTS AND DISCUSSION

The reaction experiments were performed with different space velocity by changing the methane flow rate or the amount of catalyst. The results for CCN-SCR (214 μm) are presented in Fig. 1.

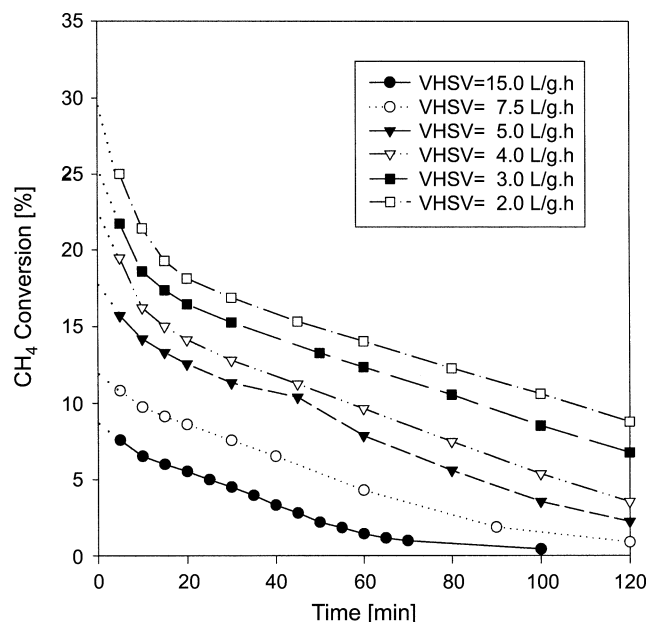


Fig. 1. Methane conversion vs. time over CCN-SCR (214 μm) with different space velocity at 1,123 K.

Since lower space velocity means longer contact time, the conversion became higher as the space velocity decreased. The initial conversions were estimated by extrapolation as shown by the dotted lines. Nevertheless, the initial conversion was not exactly inversely proportional to the VHSV, that is, the initial activity decreased with the space velocity. One reason for this is that as the space velocity is lowered the methane partial pressure gets lower, which results from the higher conversion of methane together with dilution by the produced H_2 . For instance, when the conversion is 25%, the methane partial pressure becomes 0.6 atm. Another reason may be that carbon nuclei formation occurs predominantly during the initial stage. In general, the carbon nuclei formation whose activation energy is 316.8 kJ/mol tends to be slower than carbon crystallite growth whose activation energy is 227.1 kJ/mol [Muradov, 2001a, b]. Since activated carbons have very large surface area, the carbon nuclei formation can occur predominantly on the fresh surface [Muradov, 2001b]. But this will be terminated in a short period of time owing to the exhaustion of the sites, and then the crystallite growth will become predominant [Kim et al., 2003]. This argument is supported by the fact that initial sharp decrease of the activity was observed especially at low space velocity. That is, when methane is fed more slowly, it takes some more time for the nucleation to terminate. The sharp initial decrease was more pronounced for another sample, CL-SCR (137 μm), as shown in Fig. 2.

If one assumes, as an approximation, that the activity decreases linearly with the amount of deposited carbon, the following equation may be used:

$$r_A = r_{A0} [1 - (W_C / W_{CM})] \quad (1)$$

where r_{A0} and r_A are the initial activity and the activity at a given time (in $\text{mmol/min}\cdot\text{g-cat}$), W_C the amount of deposited carbon per g-cat at a given time, and W_{CM} the maximum amount of deposited carbon per g-cat. Eq. (1) can alternatively be derived from the ex-

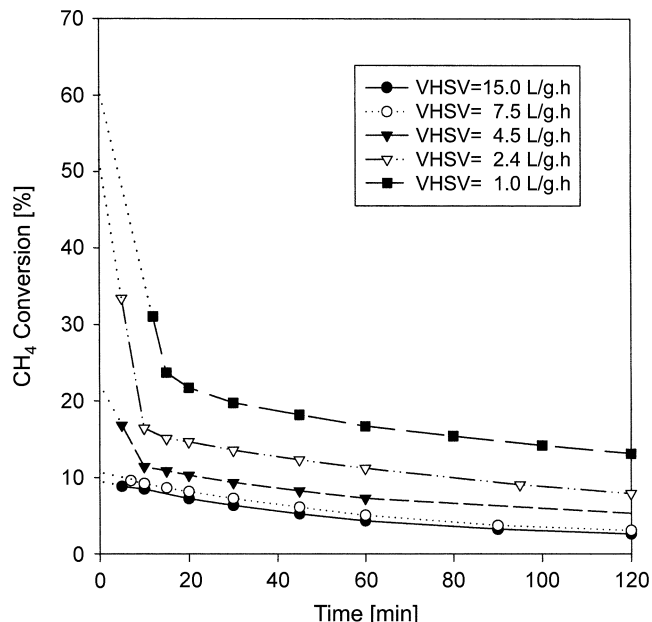


Fig. 2. Methane conversion vs. time over CL-SCR (137 μm) with different space velocity at 1,123 K.

ponential activity decay with time [Naccache, 1985] and by assuming that the activity is proportional to the active surface area and that the active surface area decreases linearly with the amount of deposited carbon [Kim, 2003]. This assumption implies that the carbon deposition occurs uniformly on the surface.

The extent of deactivation is not necessarily proportional to the amount of deposited carbon or poison. A typical example is a structure-sensitive reaction [Boudart and Djéga-Mariadassou, 1984; Franck and Martino, 1985]. Another example is pore-mouth poisoning (or blocking) associated with diffusional resistance, by which initial deactivation is rapid but gradually-slowng deactivation follows with respect to the fraction of catalyst poisoned (that is, exponential decrease against the amount of poison or deposited coke) [Hegedus and McCabe, 1984]. Therefore, Eq. (1) cannot be applicable in these cases.

The amounts of carbon deposited in the samples were calculated from the conversion-time data in Figs. 1 and 2. The decomposition rate at a given time was plotted against W_c as shown in Figs. 3 and 4. Most of the lines look roughly linear. Although initial rapid decrease followed by much slower linear decrease was observed in some cases especially with low space velocities, as seen in Fig. 4, this may be due to change of the dominant reaction, from the carbon nuclei formation to the crystallite growth as discussed above, and partly due to significant lowering of the methane partial pressure. Hence, this should be considered as an exception to the general trend.

Another notable feature is that all the lines appear to converge as is obviously seen in Fig. 3. By extrapolation, the W_{CM} 's were estimated to be ca. 0.5 and 1.0 g C deposited/g-cat for CCN-SCR (214 μm) and CL-SCR (137 μm), respectively. The pore volumes of CCN-SCR and CL-SCR were measured to be 0.48 and 0.84 cm^3/g , respectively. If the entire pore in CL-SCR were filled completely with carbon, the W_{CM} would be 1.9 g C deposited/g-cat. The actual W_{CM} is

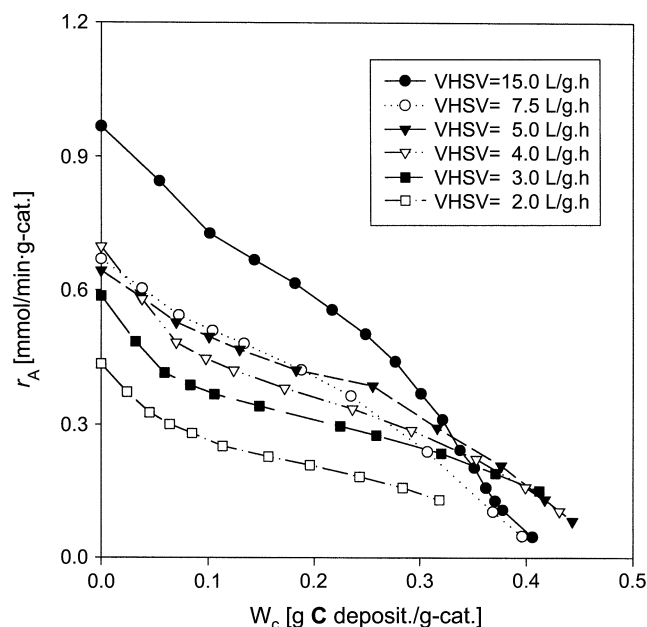


Fig. 3. Methane decomposition rate against the amount of carbon deposited on CCN-SCR (214 μm) at 1,123 K.

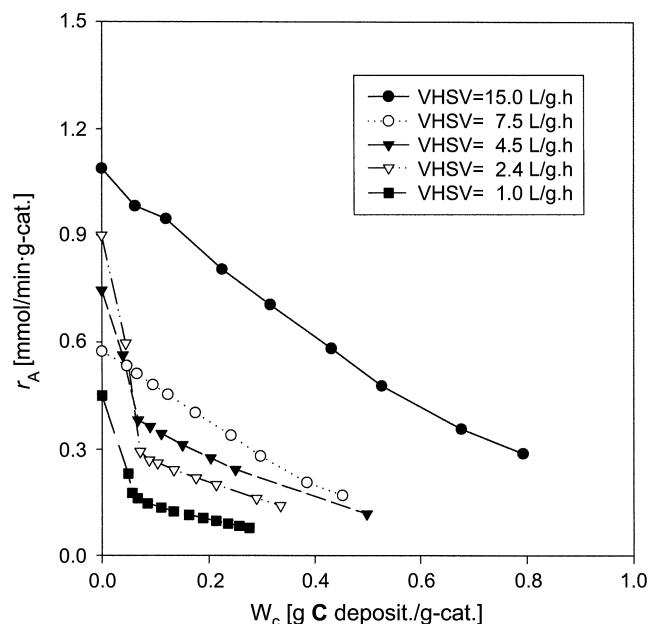


Fig. 4. Methane decomposition rate against the amount of carbon deposited on CL-SCR (137 μm) at 1,123 K.

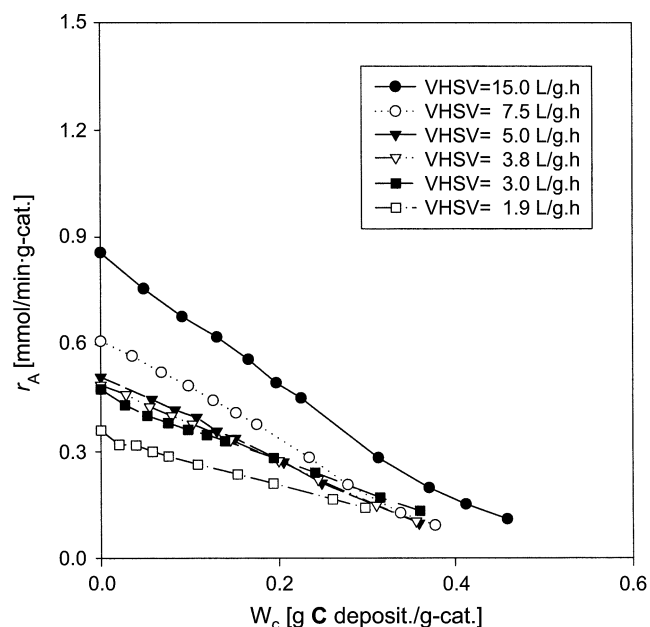


Fig. 5. Methane decomposition rate against the amount of carbon deposited on CL-SCR (1,140 μm) at 1,123 K.

significantly smaller than this, which indicates that the pores are blocked somewhere in the middle. The same experiments were performed on a larger size sample, CL-SCR (1,140 μm). As shown in Fig. 5, the same trend was also observed, but the W_{CM} was estimated to be about 0.5 g C deposited/g-cat, considerably smaller than that for CL-SCR (137 μm). This indicates that the pore blocking occurs to a greater extent in larger particles.

If pore-mouth blocking is dominant, a linear relationship like Eq. (1) would not be applicable but a different trend would have been observed. On the contrary, as mentioned above, the pore blocking

seems to occur somewhere in the middle. That is, a pore would not have a uniform diameter but have a complicated structure with narrow passages, wide passages, large cavities and interconnections. During the nucleation, uniform deposition (which means negligible mass transfer effect) may occur since the nuclei are not yet large enough to block a pore. But the nucleation will be terminated soon and the crystallite growth becomes dominant. The growing crystallite means that it is still small enough and there exist a considerable number of active sites on its surface, although the number might be significantly smaller than the initial number. As the crystallites

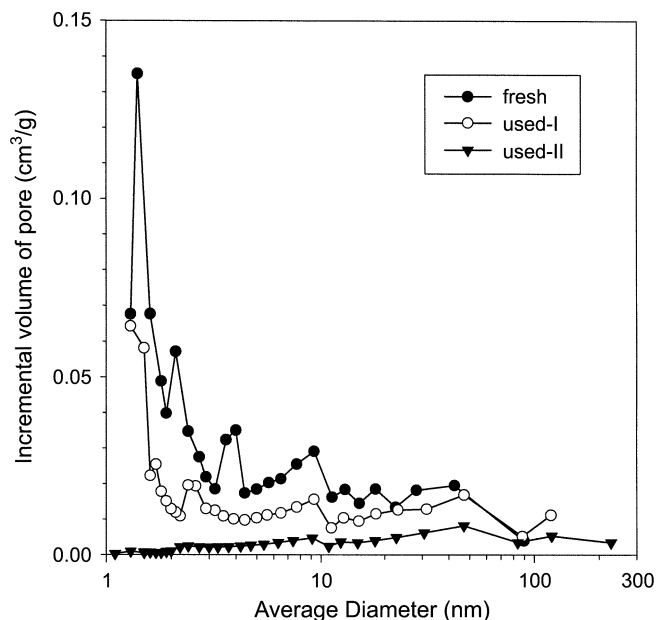


Fig. 6. Pore size distribution of CL-SCR (137 μm). Used-I: VHSV=7.5 L/g-h, at 1,123 K for 0.5 h, pore volume=0.408 cm^3/g , $W_c=0.16$ g/g-cat. Used-II: VHSV=1.0 L/g-h, at 1,123 K for 8.5 h, pore volume=0.070 cm^3/g , $W_c=0.46$ g/g-cat.

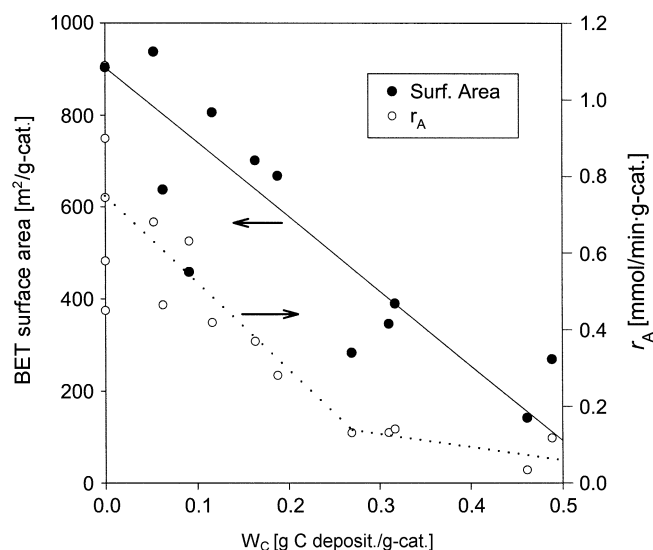


Fig. 7. BET surface area and methane decomposition rate against the amount of carbon deposited on CL-SCR (137 μm) at 1,123 K.

grow, narrower passages will be blocked sooner and the inner active surface may not be accessible by the reactant. As the crystallite growth proceeds further, the larger passages will be blocked gradually but still uniform deposition proceeds on the accessible surface. This may explain the linear relationship of Eq. (1) and the W_{CM} smaller than the theoretical one. The results shown in Fig. 6 support this argument. When the amount of deposited carbon was small (used-I), the shape of the pore size distribution curve remained similar to that of the fresh sample; a considerable portion of the small pores below around 3 nm were not yet blocked while the total pore volume and the surface area decreased. However, when the deposited amount was large (used-II), almost all of the small pores were blocked. Hence, Eq. (1) may be applicable as a good approximation of the deactivation equation in this case.

Fig. 7 shows the BET surface area and the decomposition rate against the amount of carbon deposited on CL-SCR (137 μm). In this figure, some additional data, which were obtained from the experiments with shorter and longer ending times on-stream, were also included. The surface area was nearly proportional to W_{CM} although the data were more and less scattered. This scattering might be due to the blocking of irregular pores at random positions. The rate had a nearly linear relationship with W_c up to 0.3 g C deposited/g-cat where the rate was about 20% of the initial activity. Down to this point, therefore, it may be said that the rate is nearly proportional to the surface area. To recapitulate, for the same kind of activated carbon, the decomposition rate is shown to be nearly proportional to the surface area above a certain value, while no such a trend has been observed between different kinds of fresh activated carbons [Kim et al., 2003].

When W_c became greater than 0.3 g/g-cat or the surface area became smaller than about 300 m^2/g , the deactivation appeared to proceed very slowly and the decomposition rate did not seem to be linear with the surface area or W_c . But now it is not certain whether the activity will become null eventually or some activity will be maintained even though it is quite low. Up to this point, we have assumed that the deposited carbon has negligible catalytic activity. This may be acceptable in a practical sense since very low activity is not practically useful. However, if it were not, it means that some active sites, even though the number of them is quite small, might be generated on the deposited carbon surface. About this, no definite conclusion can be made at present and further study may be needed.

CONCLUSIONS

Carbon nuclei formation appeared to occur during an initial short period of time and then carbon crystallite growth became dominant. The methane decomposition rate over activated carbons had a nearly linear relationship with the amount of deposited carbon up to a certain value. This suggests that uniform deposition, with negligible mass transport effect, occurs in the pore and the pores are blocked as the crystallites grow, resulting in deactivation by gradual loss of accessibility to the active surface. The pore blocking might occur randomly somewhere in the middle positions, and it appeared to occur to a greater extent in larger particles. The decomposition rate was also nearly proportional to the surface area above a certain value for the same kind of activated carbon, which is contrasted

with the previous finding that among different kinds of the activated carbons any discernible trend was not observed between the initial rate and the surface area.

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