Hydrogasification of an Activated Carbon and Carbonaceous Deposits on Ni/SiO₂ Catalyst by Atomic Hydrogen

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Reaction of an activated carbon with hydrogen atoms was carried out using a microwave discharge flow apparatus to elucidate the conditions under which carbonaceous material such as carbon deposit on the catalyst was efficiently gasified by the interaction with atomic hydrogen. Hydrocarbons mainly consisted of methane were produced steadily. DRIFTS spectra and pyridine extraction of the activated carbon after the reaction with hydrogen atoms showed that functional groups due to partially hydrogenated moieties were not formed on the surface of the activated carbon during the irradiation of atomic hydrogen.

Regeneration of coked Ni/SiO₂ catalyst induced by atomic hydrogen was investigated through the catalytic reaction of CO/H₂ mixture. The catalytic activity and selectivity of the coked catalyst were substantially regenerated by the treatment of hydrogen atoms at 573 K, under 279 Pa for less than 1 h. In contrast, regeneration could not be achieved by the treatment of H₂ at the same temperature. A plausible scheme for the reaction of carbonaceous materials deposited on the catalyst with atomic hydrogen was qualitatively discussed.

Key Words : Atomic hydrogen, Regeneration of catalyst, Microwave discharge, Nickel catalyst, CO/H₂ reaction, Carbonaceous deposit

1. Introduction

It has been pointed out that an extensive deposition of carbonaceous materials on the surface of the catalysts is one of the major problem in hydrocarbon processing[1-4] as well as CO hydrogenation[5]. It can lead to coke formation, which deactivates the catalyst. The deactivation is due to blockage of metal and acid sites, or encapsulation of these active sites, and fouling of pores in the catalyst support. In the case of conventional catalysts such as SiO₂-Al₂O₃, zeolites, Pt/Al₂O₃, and Pt/zeolite, regeneration can be achieved by a controlled burning of the coke with oxygen at high temperatures, *e.g.* 723-923 K[6, 7]. At these temperatures, however, metal sintering, solid state transformation and other thermal deactivation of the support may sometimes occur, resulting in an irreversible deactivation[2, 8].

It has been known that spillover hydrogen may play an important role in hydrogenation/hydrogenolysis of carbonaceous deposits on metal sites and the support, suppressing the formation of the deposits on the catalysts[9-11]. In addition, it has been reported that discharge generated hydrogen atoms induced coal liquefaction and gasification as well as methanation of graphite-like carbon at temperature range of 423-873 K under reduced pressures without an aid of catalysts[12-17]. With an analogy to the spillover hydrogen, authors assumed it may be possible that carbonaceous materials deposited on the catalyst can be removed through the reactions

with hydrogen atoms without deteriorating the properties of the catalyst, if hydrogen atoms can be supplied sufficiently from gas phase to the catalyst under the appropriate conditions.

In the present study, (1) reaction of an activated carbon with hydrogen atoms was carried out in order to elucidate the conditions under which the carbonaceous materials were efficiently removed through the reactions with atomic hydrogen, and (2) hydrogen atoms induced regeneration of coked Ni/SiO₂ catalyst deactivated during the CO/H₂ reaction was investigated. A mechanism for the reaction of carbonaceous materials deposited on the catalyst with atomic hydrogen was also discussed.

2. Experimental

2.1 Materials

Activated carbon used in the present study was purchased from Nacalai Tesque and was prepared from carbonized coconuts shell by stream activation at 1073 K. Oxisorb® filter (Messer Griesheim) was employed to purify H₂ gas, since impurities in H₂ such as H₂O and O₂ are critical contaminants when atomic hydrogens are generated by the microwave discharge of molecular hydrogen. Helium was also treated by a helium purifier (UOP mat/sen) to remove impurities such as hydrocarbons, H₂O, O₂ and CO before using as a carrier gas of atomic hydrogen. Carbon monoxide (99.99%) utilized for the CO/H₂ reaction was purchased from Sumitomo Seiki Chemicals and used as received

without further purification.

2.2 Catalyst preparation

Ni/SiO₂ catalyst was prepared following a impregnation-precipitation method described in the literature[18]. Silica gel (10 g, 16-24 mesh) was impregnated with aqueous Ni(NO₃)₂ solution (65 g of Ni(NO₃)₂ 6H₂O in 250 ml of distilled water). Then aqueous Na₂CO₃ solution (42 g of Na₂CO₃ in 250 ml of distilled water) was added drop-wise to the mixture at 353 K with continuous stirring. After aging at room temperature for 24 h, the particles obtained were filtered and washed with a large amount of distilled water until the pH of the filtrate became below 8.5. Finally, the catalyst was dried at 378 K for 16 h, and calcined at 603 K for 5 h in air. An XRF analysis showed that the content of NiO for the calcined sample was 61%, which corresponded to 55% Ni/SiO₂ catalyst.

2.3 Apparatus and procedures

Activated carbon-hydrogen atom system : Reaction of activated carbon with hydrogen atoms was carried out in an all-glass discharge flow apparatus[12] operated under reduced pressure between 239 and 558 Pa. The activated carbon sample (ca. 0.05 g) was dried in air at 378 K for 1 h and was then placed in a 12.6 mm i.d. tubular reactor in which a mixture of helium and hydrogen flowed. In order to explore stable discharge conditions, partial pressure of hydrogen and total pressure of the reaction system were controlled by adjusting the flow rates of these gases. A desired temperature of the reaction between 298 and 573 K was maintained using an electric furnace. Before the reaction with hydrogen atoms, the activated carbon was heated at 573 K in helium for 3 h. The thermally stabilized sample was then reacted with hydrogen atoms generated by 2.45 GHz microwave discharge with 120 W output. To avoid influence of ions and electrons, the discharge cavity was set at ca. 90 mm upstream from the solid sample. The reaction products were collected in a trap cooled by liquid nitrogen and analyzed by gas chromatography. The analytical conditions were : (a) a VZ-10/Chromosorb W packed column (3 m) at 323 K for the C₁-C₄ fraction, and (b) a silicone OV-1/Uniport HP packed column (1 m) at 323 K to 573 K (temperature programmed) for C₃ and heavier fraction. Methane was not trapped by the above procedure, so that in some cases total reaction products were collected in a gas sampling bag and subjected to the GC analysis.

After the reaction with hydrogen atoms, the irradiated sample was placed in a 50 mL round bottomed flask fitted with a magnetic stirrer bar, and an organic solvent (10 mL of toluene or pyridine) was added. The mixture was stirred at room temperature for 48 h. After the solid was isolated by filtration, excess solvent was evaporated and condensed extract was subjected to GC (OV-1, 1 m) analysis. DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) spectra of activated carbon before and after the irradiation of hydrogen atoms were measured using a Perkin Elmer, Spectrum 2000 FT-IR spectrometer. The sample powder (30 mg) diluted with KBr powder (100 mg) was subjected to the analysis by integrating 256 scans at a resolution of 4 cm⁻¹ in the range of 400-4000 cm⁻¹.

CO/H₂ reaction system : The reactions of CO/H₂ were performed in a continuous flow fixed bed mode using the same reactor used for the reaction of activated carbon-hydrogen atom system described above. The catalyst were reduced in situ in hydrogen flow (50 mL(STP) min⁻¹) at 653 K under atmospheric

pressure for 12 h, followed by cooling down to the reaction temperature. Then the reactions were started with a feed of CO-H₂ (1 : 3) at space velocity (SV) of 9600 mL (g-catalyst)⁻¹ h⁻¹. The effluent from the reactor was analyzed by gas chromatography described before. CO and CH₄ were determined using a thermal conductivity detector (TCD), while light hydrocarbons (C₁ and higher fraction) were analyzed using a flame ionization detector (FID). After the CO/H₂ reactions, an accelerated deactivation of the catalyst was carried out in situ at 523 K for 12 h in a flow of CO at a rate of 20 mL(STP) min⁻¹. Then, the resultant catalyst was again subjected to the CO/H₂ reactions to evaluate the effect of the carbonaceous deposit on the activity of the catalyst. Reactions of the carbonaceous materials deposited on the catalyst with hydrogen atoms were also carried out in situ using the same apparatus under conditions similar to those of activated carbon-hydrogen atom system as mentioned above. The irradiated catalyst was subjected to the CO/H₂ reaction to evaluate the activity of the treated catalyst. The surfaces of the reduced (fresh), deactivated, and regenerated (or H-atom irradiated) catalysts were examined using a Hitachi S-4500 field emission scanning electron microscope. This allowed an assessment of the morphology of the catalyst surface and the carbonaceous deposit. The temperature programmed oxidation of the carbons deposited on the catalyst was performed using a Rigaku TG8120 TG-DTA analyzer. The carrier gas was air and the samples were heated from 303 to 973 K at a rate of 20 Kmin⁻¹.

3. Results and Discussion

3.1 Activated carbon - hydrogen atom system

Formation rate of reaction products : Effect of pressure of H₂ on the formation rate of the total reaction products is shown in Figure 1. Upon irradiation of hydrogen atoms onto the surface of activated carbon at 573 K, gaseous hydrocarbons were steadily produced at a rate shown in Figure 1. The formation rate increased rapidly with increasing pressure of H₂ up to about 66 Pa, and then slightly decreased at higher H₂ pressures. This may reflect the change in rate of hydrogen atoms supplied to the sample. Since the pressure of H₂ was proportional to the flow rate of H₂ in the
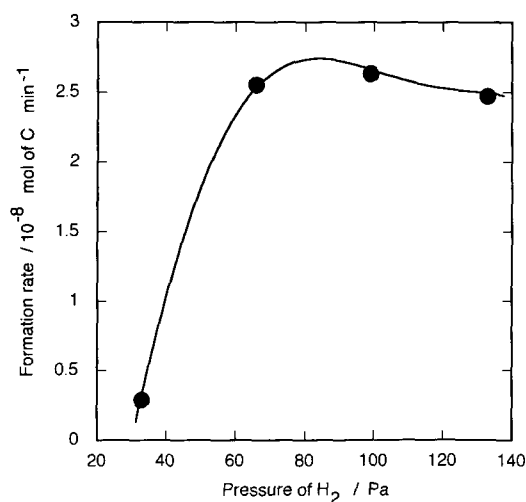

Figure 1   Effect of hydrogen pressure on the formation rate of total reaction products
Reaction temperature and pressure of helium were 573 K and 213 Pa, respectively

present study, the rate of production of atomic hydrogen in the vicinity of discharge zone would be in proportion to the flow rate of H_2, if the efficiency of microwave discharge to generate hydrogen atoms is substantially independent to the pressure of H_2. On the other hand, loss of atomic hydrogen is caused by heterogeneous and homogeneous recombinations of them at the surface of the reactor and in gas phase, respectively. In this case, it is reasonable to consider that the rates of disappearance of hydrogen atom on the reactor wall and in gas phase are proportional to the first power and the square of the pressure of hydrogen atom, respectively. Therefore, it is expected that the rate of hydrogen atoms supplied to the sample, which is determined by the difference between the rates of production and disappearance of hydrogen atoms, will show a maximum value, with the increase in the pressure of H_2.

Effect of reaction temperature on the formation rate is shown in Figure 2. Products were steadily produced when hydrogen atoms were supplied to the sample at 523 and 573 K. However, the formation rate of the total reaction products at 473 K was smaller and decreased gradually with irradiation time. These results indicate that the activated carbon comprises at least two components in terms of the reactivity, i.e. highly reactive parts which interact with atomic hydrogen even at lower temperatures, and less reactive portions which essentially require relatively large thermal energy, or high temperature, in order to react with hydrogen atoms. The former may be ascribed to the structure which contains electron-rich sites or radical sites on the activated carbon, since it was recognized that atomic hydrogen can react with alkene and alkyl radicals at ambient temperatures and activation energies of these reactions have been reported to be less than several kJ mol⁻¹ [13,19,20]. The latter may correspond to the stable or less reactive structures in activated carbons, e.g. graphitic carbon sheets of hexagonal networks.

Distribution of reaction products : It was reported that C_3-C_5 fractions clearly reflect the combined action of atomic hydrogen with an appropriate amount of thermal energy in homogeneous gas phase reactions of hydrocarbons[20]. Therefore, product
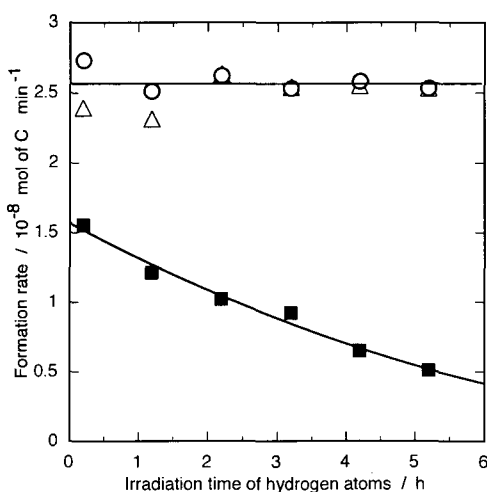
Table 1 Product distributions in C_3-C_5 fraction formed in the reactions of activated carbon with hydrogen atoms[a]

Reaction temperature / K	Distribution in C_3 - C_5 fraction / mol%				
	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	C_5H_{10}+C_5H_{12}
473	17.2	34.8	9.4	28.3	10.3
523	21.5	31.9	10.9	25.3	10.4
573	27.5	31.8	10.7	20.1	9.9

a) Pressures of hydrogen and helium were 66 and 213 Pa, respectively.

distributions of these fractions produced from the activated carbon-atomic hydrogen system were examined to elucidate cooperative effect between hydrogen atoms and thermal energy. As listed in Table 1, the product distributions with the reaction temperature revealed general features of the reactions, i.e. as the temperature increased, (1) the formation of olefins increased, (2) the proportions of C_4 decreased, those of C_3 increased, while those of C_5 were substantially unchanged. This tendency, that the formation of C_3 olefin became significant at higher temperatures as a result of hydrogenolysis of higher hydrocarbons, was also observed in the reactions of butenes with hydrogen atoms above 500 K[20]. In that system, it was believed that the reaction took place mainly through H-atom attack onto electron-rich atoms in the substrate molecule. Due to the heat evolved, the H-atom added complex so formed were vibrationally activated and were susceptible to the unimolecular decomposition of the bond adjacent to the electron-rich atom when heated at higher temperatures, resulting in the formation of radical species and corresponding olefins of lower molecular weight[19,20]. Formation of methane and benzene in the reactions of toluene with atomic hydrogen above 550 K was also interpreted in terms of the similar radical exchange mechanism which became predominant at higher temperatures[21-23]. Therefore, it is likely that the mechanism proposed for the homogeneous reactions of hydrocarbons with hydrogen atoms is also operative and predominant for the heterogeneous reactions of the activated carbon with hydrogen atoms.

Distribution of the reaction products formed at 573 K was as follows : CH_4, 74.8 ; C_2H_6+C_2H_4, 20.2 ; C_3H_8+C_3H_6, 3.01 ; C_4H_{10}+C_4H_8, 1.52 ; C_5H_{10} and higher hydrocarbons, 0.47 mol%, suggesting that severely hydrocracked products such as methane, ethane and ethylene were selectively produced from the reaction of activated carbon with atomic hydrogen. In the studies similar to this work it was reported that the reaction of atomic hydrogen with solid carbons such as electro-graphitized carbon or soot prepared from benzene delivered only methane[14,15]. In addition, coals generated light hydrocarbons containing more than 72 mol% of methane and lesser amounts of hydrocarbons up to C_5 in the reaction with hydrogen atoms[14,15]. It was also reported that light hydrocarbons except methane were mainly produced through reactions of hydrogen atoms with non-aromatic precursor structures in coals[15]. On the other hand, on the formation of methane, it was proposed that $\equiv CH$ on the edge of a small graphitic sheet, lamellar, was progressively hydrogenated to -CH_3, and then detached and stabilized itself as CH_4 [14]. As the structural units in the activated carbon, which are small graphitic crystallites containing a few layer planes or randomly curved carbon sheets, are oriented randomly and cross-linked strongly to impede movement of the layers into a more parallel arrangement[24-26], activated carbon is supposed to possess structural features between

Figure 2 Effect of time and temperature of H-atom irradiation on the formation rate of total reaction products

| ■ 473 K | △ 523 K | ○ 573 K |

Pressures of hydrogen and heilum were 66 and 213 Pa, respectively

coals and graphitized carbons. Thus, it is highly probable that the mechanism of the reaction of hydrogen atoms with activated carbon is similar to those proposed for the reactions with coals and graphitic carbons.

DRIFTS spectra of irradiated samples : DRIFTS spectra of activated carbon samples before and after irradiation of hydrogen atoms at 573 K were examined. As shown in Figure 3, absorption band newly appeared in the difference spectra of irradiated sample, however, was hardly detected with reference to the sample before H-atom irradiation. This means that any functional groups due to hydrogenation of aromatic nuclei or carbon sheets of hexagonal network were not formed on the surface of the sample when hydrogen atoms were irradiated. Thus, it is suggested that the
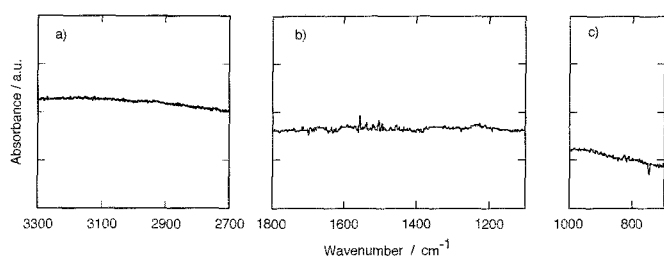

Figure 3   DRIFTS spectra of activated carbon irradiated by hydrogen atoms at 573 K for 1 h

Reference spectrum is that for activated carbon heated at 573 K for 3 h

a) C-H stretches in aromatic CH group $(3075\text{-}3030\,cm^{-1})$ and in methyl and methylene groups $(3000\text{-}2800\,cm^{-1})$

b) symmetric and asymmetric bending (in-plane) in methyl and methylene groups $(1460\text{-}1375\,cm^{-1})$

c) bending (out-of-plane) in aromatic CH groups $(897\text{-}754\,cm^{-1})$
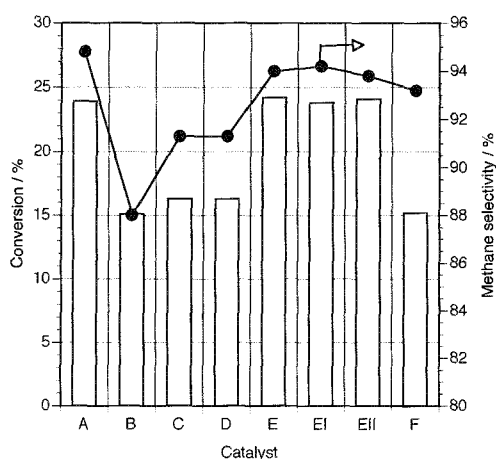

Figure 4   Conversion of CO and selectivity to methane formation in CO/H₂ reactions catalyzed by fresh, coked, and regenerated Ni/SiO₂ catalysts

Catalysts A to F are the same as Table 2.

El : H-atom regenerated catalyst (Catalyst B was irradiated by hydrogen atoms at 573 K for 0.5 h)

El : H-atom regenerated catalyst (Catalyst B was irradiated by hydrogen atoms at 573 K for 10 min)

Reaction conditions : $CO/H_2 = 1/3$

$SV = 9600\,mL\,(g\text{-catalyst})^{-1}\,h^{-1}$, $Temp = 473\,K$

Table 2   Product distribution in CO/H₂ reactions catalyzed by fresh, coked, and regenerated Ni/SiO₂ catalysts

Catalyst	Product distribution / mol%		
	CH_4	$C_2H_6 + C_2H_4$	$C_3H_8 + C_3H_6$
A	94.8	3.8	1.4
B	88.0	8.5	3.5
C	91.7	7.7	0.6
D	91.3	6.4	2.3
E	94.0	4.7	1.3
F	93.2	5.6	1.2

A: Fresh catalyst (Reduced in H₂ at 673 K for 12 h)

B: Coked catalyst (Catalyst A was coked in CO at 523 K for 12 h)

C: H-atom regenerated catalyst (Catalyst B was irradiated by hydrogen atoms at 473 K for 1 h)

D: H-atom regenerated catalyst (Catalyst B was irradiated by hydrogen atoms at 523 K for 1 h)

E: H-atom regenerated catalyst (Catalyst B was irradiated by hydrogen atoms at 573 K for 1 h)

F: H₂ regenarated catalyst (Catalyst B was heated in H₂ at 573 K for 1 h)

Reaction conditions : $CO/H_2 = 1/3$, $SV = 9600\,mL\,(g\text{-catalyst})^{-1}\,h^{-1}$, $Temp. = 473\,K$.

hexagonal networks of carbon in the sample are not hydrogenated to produce partially hydrogenated olefinic and/or naphthenic moieties on the surface of the irradiated sample, but are hydrocracked at the edges of the sheets to evolve methane predominantly. This is consistent with the reaction scheme discussed in the above section and is also supported by the fact that any components heavier than the solvent were not detected in the extract from the irradiated samples.

3.2   CO/H₂ reactions

Performance of Ni/SiO₂ catalysts were evaluated through CO/H₂ reaction at 473 K under atmospheric pressure. Products distribution and conversion of CO in the reactions catalyzed by fresh, deactivated, and regenerated catalysts are shown in Table 2 and Figure 4, respectively. As expected, methane was mainly produced with small amounts of C₂ and C₃ hydrocarbons, when the fresh catalyst was used. Both conversion of CO and selectivity to methane formation in the reaction using the coked catalyst were lower than those in fresh one. This result indicates that change in population as well as chemical nature of active sites is affected by the carbonaceous deposits on the surface of the catalyst. The amount of carbon on the catalyst was determined to be ca. 4.8 wt% by TG-DTA analysis. It is well known that flakes and filamentous carbons were formed at high temperatures of 773-1030 K when CO or methane molecules were in contact with nickel or iron
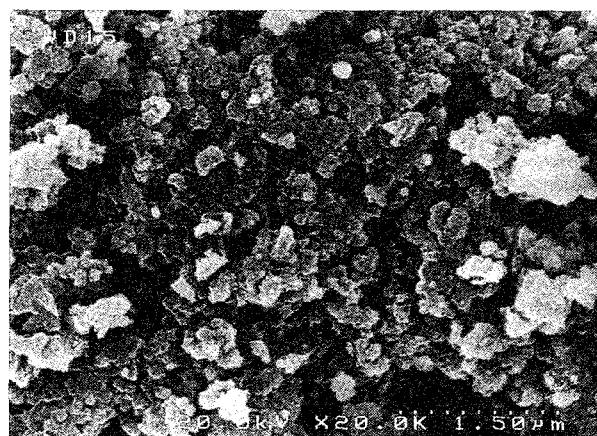

Figure 5   SEM micrograph of a deactivated catalyst sample prepared by the reaction of CO at 523 K for 12 h

particles which catalyzed the Boudouard reaction : $2 CO = C + C$ O_2 [27-29] or cracking of methane : $CH_4 = C + 2H_2$ [30, 31], while bulk nickel carbide was found to form[32-34] and then the graphitic carbon grew on the carbidic surface at temperatures as low as 400-500 K[35-37]. A SEM micrograph of deactivated catalyst is shown in Figure 5. After the catalyst was exposed to the CO environment at 523 K for 12 h, neither flake nor filamentous carbon was observed, which was in good agreement with the observations reported in the literatures[35-37], suggesting the formation of carbidic carbon on the surface of the catalyst in the present study. Irradiation of hydrogen atoms on the surface of the deactivated catalyst at 473 K or 523 K under 279 Pa for 1 h was not enough to recover the activity and the selectivity to the original levels inherent in the fresh catalyst. However, short time (10-30 min) irradiation of H-atom at higher temperature, e.g. 573 K, led to the substantial recovery of both activity and selectivity. In contrast, treatment of the deactivated catalyst by gaseous H_2 flow at 573 K for 1 h under atmospheric pressure did not recover the catalytic activity, although methane selectivity was slightly regenerated. The amount of carbon remaining in the catalyst after H-atom irradiation at 573 K was estimated to be ca. 3.8 wt%, indicating that 21% of deposited carbons were removed by the treatment. Any morphological changes were not observed before and after the treatment with hydrogen atoms. Light hydrocarbons rich in methane (CH_4, 97.9 ; $C_2H_6 + C_2H_4$, 1.3 ; $C_3H_8 + C_3H_6$, 0.8 mol%) were produced when hydrogen atoms were irradiated onto the surface of the coked catalyst at 573 K. Content of methane in the products for the deactivated catalyst-hydrogen atom system is higher than that for activated carbon-hydrogen atom system. This may reflect both (1) participation of the reactions of carbidic carbons with hydrogen atoms, and (2) activity of Ni as a methanation catalyst is enhanced by the presence of hydrogen atoms irradiated to the catalyst. It is suggested that irradiation of H-atom at moderate temperature, e.g. 573 K, can effectively remove carbonaceous materials such as carbidic and graphitic carbons from the surface of the deactivated catalyst, and regenerate active sites that are responsible for the catalytic properties of the Ni/SiO₂.

In the conventional procedures, regeneration of nickel catalysts deactivated by carbon deposition can be successfully achieved by a controlled burning of the deposited coke with oxygen at 683-823 K[31], followed by the reduction of nickel oxide in the stream of H_2 at elevated temperatures. Availability of atomic hydrogen to regenerate the coked Ni/SiO₂ catalyst by a single step treatment may be presented in this study. This technique may allow to provide a rapid and simple way in comparison with the conventional one to remove carbonaceous deposits and to regenerate the catalytic properties, although applicability of this method to other catalysts systems and the quantitative effects of atomic hydrogen should be studied in further

4. Conclusion

Under the conditions that hydrogen atoms were sufficiently supplied, i.e. pressure of H_2, 66-99 Pa, gaseous hydrocarbons containing mainly methane were produced steadily in the reaction of activated carbon with hydrogen atoms at temperatures above 523 K. DRIFTS spectra of H-atom irradiated samples showed that functional groups due to partial hydrogenation of activated carbon were not formed on the surface of the samples. Polynuclear aromatic hydrocarbons and their hydrogenation products were

not extracted from the irradiated samples by pyridine. These results suggest a plausible reaction mechanism that hydrogen atoms adsorbed on the sites of electron-rich or radical sites which may locate at the edges of the hexagonal network of carbon sheets, and then the surface adducts so formed were decomposed, in conjunction with thermal energy, to produce extremely hydrogenated products rich in methane.

Deactivated Ni/SiO₂ catalyst prepared through the reaction of CO at 523 K gave lower activity and methane selectivity for the CO/H_2 reactions. The catalytic activity and selectivity were almost regenerated by the irradiation of hydrogen atoms onto the deactivated catalyst at 573 K, under 279 Pa, for 10-30 min. In contrast, regeneration of the catalyst could not be achieved by the conventional H_2 treatment at the same temperature for 1 h. It is indicated that the irradiation of atomic hydrogen under such conditions can remove carbonaceous deposits from the surface of the catalyst according to the scheme proposed for the activated carbon-hydrogen atom system, providing an alternate way of regeneration for the coked Ni/SiO₂ catalyst.

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