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Hydrogen production by thermocatalytic decomposition of butane over a carbon black catalyst

Suk Hoon Yoon[a], No-Kuk Park[a], Tae Jin Lee[a,*], Ki June Yoon[b], Gui Young Han[b]

[a] National Research Laboratory, School of Chemical Engineering & Technology, Yeungnam University, 214-1, Dae-dong, Gyeongsan, Gyeongbuk 712-749, Republic of Korea
[b] Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea

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ABSTRACT

Catalytic activity of carbon black for decomposition of butane was investigated for CO_2-free hydrogen production. The carbon black employed was a rubber black and the range of reaction temperature was from 500 to 1100 °C. Although the primary decomposition of butane occurred mostly by non-catalytic thermal decomposition, the butane conversion and the hydrogen yield obtained in the presence of the carbon black were higher than those obtained by non-catalytic thermal decomposition. This is mainly due to the catalytic effect of carbon black which accelerates decomposition of butane as well as subsequent decomposition of propylene, ethylene and methane that have been produced by the primary decomposition. The catalytic decomposition of ethylene was pronounced from 750 °C and that of methane from 950 °C. A variety of products such as methane, ethylene, ethane, propylene and propane were formed, but in the presence of carbon black ethane, propylene and propane were negligible above 900 °C and ethylene was so at and above 1000 °C. Deactivation of the catalyst was not observed at least for 200 min in spite of carbon deposition.

1. Introduction

Hydrogen is attracting a great interest as an alternative energy source for the future. Fossil fuels such as oil, coal and natural gas, which are used as the main energy resources in modern society, expose many problems such as environmental pollution, inability to be recycled and limited supply. Especially, the global warming is aggravated due to the emission of greenhouse gases such as carbon dioxide (CO_2) from the fossil fuels. In this respect, hydrogen is considered promising as one of the clean energy resources of the next generation. Hydrogen can be produced from water. However, the clean production of hydrogen by water splitting using a renewable energy source, such as solar energy and electricity from hydraulic and wind power, is not competitive with current energy costs or practicable in efficiency. A current method widely used for hydrogen production is steam reforming of hydrocarbons. However, this conventional process accompanies simultaneous production of massive CO_2 [1,2]. Recently there appeared several studies on CO_2-free hydrogen production from hydrocarbons. One of them is decomposition of methane (Reaction (1)) such as follows.

$$CH_4 \rightarrow C(s) + 2H_2, \qquad \Delta G^\circ = 50.75\,\mathrm{kJ/mol} \tag{1}$$

In decomposition of methane, high purity hydrogen can be produced without any CO/CO_2 and the produced clean carbon may have a reasonable commercial value [3–8]. Therefore, the methane decomposition process is considered environmentally benign. Even though the decomposition of methane has several advantages, development of such processes has been delayed due to the reasons as described below. The non-catalytic thermal decomposition of methane requires quite a high temperature (1200–1700 °C) in order to obtain a reasonable hydrogen yield and the reactor tube is frequently blocked if not properly designed. Catalytic decomposition is a suitable method to lower the required temperature for decomposition of methane. However, although transition metals (Ni, Fe, Co, Pb, etc.) showed superior catalytic activity in decomposition of methane, deactivation of the catalysts was observed due to the carbon build-up [9–15]. In addition, CO_2 is produced in the regeneration process of the catalyst. In order to circumvent these problems, Muradov [3–7] proposed various carbon-based materials as the catalyst, such as activated carbon, carbon black, acetylene black, glassy carbon, graphite, diamond, fullerene and carbon nanotube. He reported that activated carbons and carbon blacks showed reasonably high activity. While activated carbons deactivated rapidly during the reaction, carbon blacks showed quite stable behavior in spite of carbon deposition. Other investigators have also confirmed this [2,8,16–21]. The produced carbon adheres on the original carbon black catalyst and this carbon product forms another type of carbon black which may

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[*] Corresponding author. Tel.: +82 53 810 2519; fax: +82 53 810 4631.
E-mail address: tjlee@ynu.ac.kr (T.J. Lee).

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be utilized in a similar application, such as rubber reinforcement, to that of the original carbon black. Therefore, removal of the produced carbon from the original catalyst is not required in this case and the process becomes much simpler.

Likewise to methane, other light hydrocarbons may also be used as the raw material. Studies on decomposition of propane over activated carbon and carbon black have been reported recently [4,5,22]. This work focused on the production of CO_2-free hydrogen by decomposition of butane. The merits of butane are its low cost and its weak C–C and C–H bonds. Thermal decomposition of butane is much easier than that of methane or propane due to the relatively low C–H bond energy (381 kJ/mol) in butane when compared with that in methane (439 kJ/mol) or propane (406 kJ/mol). Non-catalytic (homogeneous, thermal) decomposition of butane was investigated first and then the decomposition of butane by employing a carbon black catalyst was studied. By comparing the two sets of results, the catalytic effects of the carbon black were discussed. In addition, deactivation of the carbon black catalyst was also examined.

2. Experimental

2.1. Catalyst

The carbon black employed was a commercial product from DC Chemical Co., Korea (DCC N330 in fluffy (non-pelletized) type) and its surface area was 81 m^2/g. The main use of this carbon black is for rubber reinforcement and N330 is designated in accordance with ASTM. This carbon black has been found to be a good catalyst for the decomposition of methane [8,17,19].

2.2. Decomposition of butane

The butane used in this study was n-butane of 99.5% purity from RIGAS (Research Institute of Gas Analytical Science, Korea). The temperature of the butane feeding pipe was maintained at 35 °C by winding a heating tape around in order to prevent possible condensation of butane under high pressure. The reactor was a quartz tube and its outer diameter was 1/2 in. The length of heating zone (the constant-temperature zone of the tube furnace) of the reactor was 10 cm for the non-catalytic as well as for the catalytic reaction. The carbon black was placed in the middle of the heating zone for the catalytic experiments.

After the desired reaction temperature was reached under argon flow, the argon flow was stopped and the reactant gas was fed into the reactor. The reaction temperature ranged from 500 to 1100 °C and it was controlled by using a K-type thermocouple inserted in the center of catalytic bed. The catalyst loading was usually 0.15 g and the butane flow rate 25 cm^3(STP)/min, which corresponds to the gas hourly space velocity (GHSV) of 10,000 cm^3(STP)/h g-cat. The catalyst loading and the butane flow rate were changed when necessary in order to adjust GHSV in the range of 2140–38,400 cm^3(STP)/h g-cat. Here '/g-cat' denotes per mass (in gram) of the carbon black loaded initially; this should be distinguished from the total mass of carbon black which is the sum of the initial carbon black and deposited carbon that increases with time. The GHSV was changed by adjusting the butane flow rate from 12.5 to 96 cm^3(STP)/min with a fixed catalyst loading of 0.15 g (which corresponds to the GHSV of 5000–38,400 cm^3(STP)/h g-cat) or by varying the catalyst loading from 0.70 to 0.15 g with a fixed butane flow rate of 25 cm^3(STP)/min (which corresponds to the GHSV of 2140–10,000 cm^3(STP)/h g-cat). The gaseous decomposition products were analyzed by using a gas chromatograph (GC: Simadzu 14-B) with a TCD (thermal conductivity detector) and a mass spectrometer connected in series. Argon was used for the GC carrier gas and its flow rate was 25 cm^3(STP)/min. A packed 3-m Hayesep Q (Alltech Associates, Inc.) column was used to separate hydrogen, methane, ethylene, ethane, propylene, propane and butane. The GC oven temperature was programmed from 80 to 180 °C: after 10 min at constant temperature of 80 °C, the temperature ramp rate was set to 10 °C/min. The detector temperature was 190 °C. The concentrations of the gaseous products were determined by using calibrated data. Unless specified otherwise, the conversion and product distribution data in this work are those obtained after around 60 min time on-stream at which the reaction reaches a steady state.

The amount of carbon deposited on the catalyst was calculated based on the mass balance, i.e., the difference between the carbons in the butane fed and the total carbons in the gas phase at the exit of the reactor. Some of the amounts of the produced carbon were also confirmed directly by a Cahn balance. The structural and surface studies of the carbon products were performed by SEM (scanning electron microscopy) and TEM (transmission electron microscopy).

3. Results and discussion

3.1. Thermal decomposition of butane

Gas mixtures after the decomposition of butane contained hydrogen, methane, ethylene, ethane, propylene, propane and butane. Butane was decomposed almost completely above 800 °C, but the product distribution was changed diversely depending on the temperature.

Since the C–C bond (297 kJ/mol) is much weaker than the C–H bond, the primary products will be the lower hydrocarbons resulted from the C–C bond rupture. The butane conversion and the mole fractions of the gaseous products in thermal (non-catalytic) and catalytic decomposition are summarized in Tables 1 and 2. Butane was not decomposed almost below 550 °C. The butane conversion at 600 °C was only 10.1% and the observed products were hydrogen, methane, ethylene, ethane and propylene; hydrogen, ethylene and

Table 1
Product distributions (mol%) in thermal decomposition of n-butane.

T (°C)	H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	C4 Conv. (%)	H_2 yield (%)	C yield (%)
600	1.2	5.2	3.0	2.1	5.6	0	82.9	10.1	0.3	0.1
650	4.3	13.9	9.5	5.1	13.4	0	53.8	37.0	1.1	0.6
700	8.9	23.8	18.9	7.2	17.0	0.1	24.1	70.9	3.1	2.8
750	14.0	32.5	27.5	6.9	11.9	1.1	6.0	92.8	6.2	8.6
800	19.4	39.9	30.6	5.2	3.8	0.3	0.9	99.0	10.0	17.6
850	30.1	44.2	21.9	2.9	0.6	0	0.5	99.4	17.2	30.5
900	41.8	44.3	11.7	1.3	0.7	0	0.1	99.8	26.0	43.2
950	47.3	50.7	1.8	0.3	0	0	0	100	30.9	55.2
1000	55.5	42.6	1.7	0.2	0	0	0	100	38.4	60.0
1050	69.0	30.1	0.9	0	0	0	0	100	52.7	69.6
1100	74.2	24.9	0.9	0	0	0	0	100	59.0	73.5

Butane flow rate = 25 cm^3(STP)/min; carbon black loading = 0.15 g; GHSV = 5000 cm^3(STP)/h g-cat.

Table 2
Product distributions (mol%) in catalytic decomposition of n-butane.

T (°C)	H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	C4 Conv. (%)	H_2 yield (%)	C yield (%)
600	1.92	5.32	2.96	2.17	5.32	0.12	82.2	10.95	0.42	0.34
650	5.24	13.48	8.8	4.99	12.79	0.13	54.57	38.44	1.39	1.03
700	11.11	24.41	18.05	7.46	16.91	0.16	21.9	73.86	3.98	4.11
750	21.5	34.89	23.13	7.6	8.64	1.06	3.18	95.99	10.42	16.32
800	32.94	43.6	17.24	5.23	0.75	0.12	0.13	99.84	18.97	34.03
850	44.62	44.58	8.19	1.92	0.7	0	0	100	28.24	47.08
900	51.63	44.1	3.12	0.55	0.6	0	0	100	34.53	55.49
950	57.64	41.42	0.83	0.11	0	0	0	100	40.46	62.01
1000	65.42	34.28	0.3	0	0	0	0	100	48.61	67.60
1050	75.08	24.82	0.1	0	0	0	0	100	60.10	74.96
1100	88.04	11.88	0.08	0	0	0	0	100	78.63	86.55

Butane flow rate = 25 cm^3(STP)/min; carbon black loading = 0.15 g; GHSV = 5000 cm^3(STP)/h g-cat.

ethane were below the detection limits. Methane and propylene were produced to similar mole fraction and its moles were higher than that of other products. This indicates that the terminal C–C bond is most easily broken as shown by Reaction (2), primary butane decomposition: this is an already known fact from long-studied thermal cracking of linear hydrocarbons [23].

$$C_4H_{10} \rightarrow CH_4 + C_3H_6, \qquad \Delta G^\circ = 28.02\,\text{kJ/mol} \tag{2}$$

The production of ethylene and ethane can be explained to Reaction (3) by the multiple reaction of butane. In the temperature range of 600–650 °C, hydrogen, methane, ethylene, ethane and propylene were observed. Still methane and propylene were the most abundant hydrocarbon products with quantities comparable to each other. Ethane and ethylene were also produced in considerable amounts although they were somewhat less than methane and propylene. This shows that the breaking of the middle C–C bond is also relatively easy as shown by Reaction (3), another primary butane decomposition of second importance.

$$C_4H_{10} \rightarrow C_2H_4 + C_2H_6, \qquad \Delta G^\circ = 53.07\,\text{kJ/mol} \tag{3}$$

Reaction (4) can also be supposed from both the difference mole fraction of ethylene and ethane and mole fraction of hydrogen. At higher temperatures, ethane appeared to be dehydrogenated to form ethylene and hydrogen and dehydrogenation of ethane became more pronounced as the temperature increased, which is seen by the higher amount of ethylene than ethane accompanied by increase of the hydrogen production [24].

$$C_2H_6 \rightarrow C_2H_4 + H_2, \qquad \Delta G^\circ = 101.0\,\text{kJ/mol} \tag{4}$$

In addition, propylene can also be decomposed to form methane and ethylene, possibly by the following reaction with the assistance of hydrogen.

$$C_3H_6 + H_2 \rightarrow CH_4 + C_2H_4, \qquad \Delta G^\circ = -54.3\,\text{kJ/mol} \tag{5}$$

Hence, methane and ethylene increased rapidly with the temperature at the expense of ethane and propylene. Ethylene in turn could easily be decomposed to elemental carbon and hydrogen by reaction (6).

$$C_2H_4 \rightarrow 2C + 2H_2, \qquad \Delta G^\circ = 24.767\,\text{kJ/mol} \tag{6}$$

Another possible reaction is the combination of Reactions (5) and (6), or direct decomposition of propylene. Propylene can be easily decomposed as Reaction (7) due to Gibbs free energy of high negative. However, we cannot determine propylene decomposition with Reaction (7) because that propylene was detected as the product for butane decomposition at 600 °C as shown in Tables 1 and 2. Therefore, it can be concluded that the suitable reaction for propylene decomposition is the series reaction which consists of Reactions (5) and (6).

$$C_3H_6 \rightarrow CH_4 + 2C + H_2, \qquad \Delta G^\circ = -112.5\,\text{kJ/mol} \tag{7}$$

As a consequence, ethane and propylene became quite small above 850 °C and ethylene became so above 950 °C. Since methane is the most stable hydrocarbon, its decrease due to the decomposition to carbon and hydrogen (Reaction (1)) was noticeable above 1000 °C.

The yields of hydrogen, $H_2(g)$, and deposited carbon, C(s), are presented in Table 1. These yields were estimated from the product distribution by calculating the hydrogen and carbon balances. These were defined as follows:

$$H_2\,\text{yield}(\%) = \frac{100(\text{moles of } H_2 \text{ product})}{5(\text{moles of } C_4H_{10} \text{ input})}$$

$$\text{C(s) yield}\,(\%) = \frac{100(C_{\text{input}} - C_{\text{out in gaseous components}})}{C_{\text{input}}}$$

$$C_4H_{10}\,\text{conversion}\,(\%) = \left[\frac{C_4H_{10}\,\text{mole}_{\text{input}} - C_4H_{10}\text{mole}_{\text{output}}}{C_4H_{10}\text{mole}_{\text{input}}}\right] \times 100$$

3.2. *Catalytic effects of carbon black in butane decomposition*

The butane conversions by the thermal decomposition and by the decomposition in the presence of the carbon black are

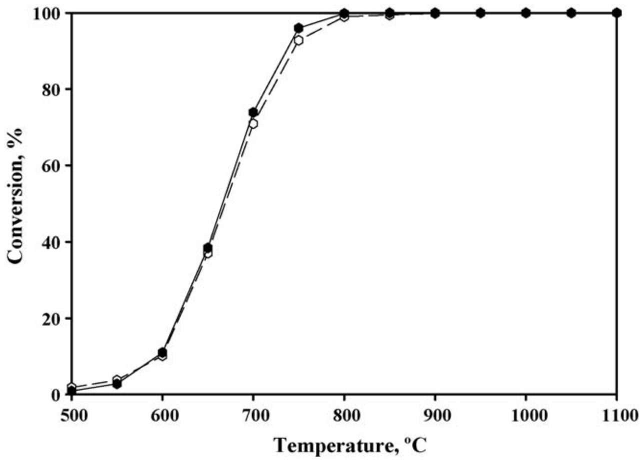


Fig. 1. Butane conversions by thermal decomposition and by thermocatalytic decomposition in the presence of carbon black (butane flow rate = 25 cm^3(STP)/min; GHSV = 10,000 cm^3(STP)/h g-cat, carbon black loading = 0.15 g; thermal decomposition (○); catalytic decomposition (●)).

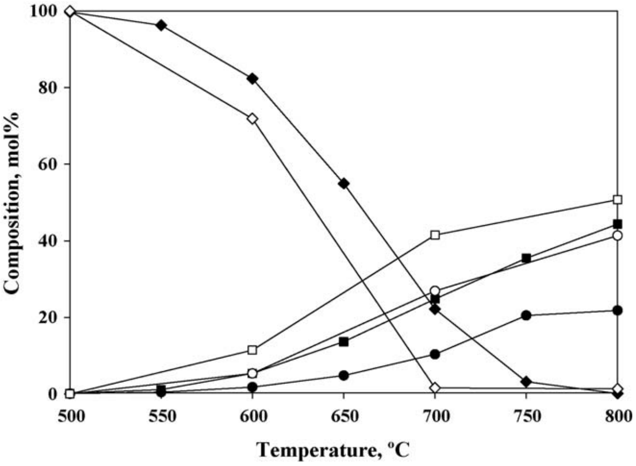


Fig. 2. Effect of the catalyst loading in the thermocatalytic decomposition of butane (butane flow rate = 25 cm^3(STP)/min; GHSV = 10,000 cm^3(STP)/h g-cat: (●) H_2, (■) CH_4, (◆) C_4H_{10}; GHSV 2140 cm^3(STP)/h g-cat: (○) H_2, (□) CH_4, (◇) C_4H_{10}).

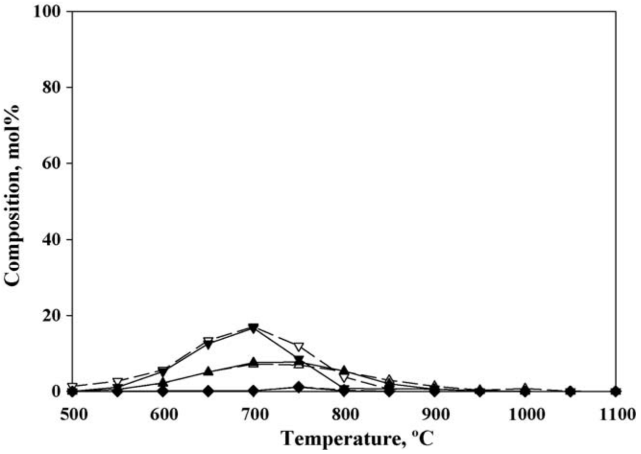


Fig. 4. Effect of temperature on the product (ethane, propylene and propane) distribution in the thermal and thermocatalytic decomposition (butane flow rate = 25 cm^3(STP)/min; carbon black loading = 0.15 g; thermal decomposition: (△) C_2H_6, (▽) C_3H_6, (◇) C_3H_8; catalytic decomposition: (▲) C_2H_6, (▼) C_3H_6, (◆) C_3H_8).

compared in Figs. 1 and 2 with respect to the temperature. As shown in Fig. 1 with the GHSV of 10,000 cm^3(STP)/h g-cat, the conversion by the latter was only just slightly higher than that by the former. However, when the catalyst loading was increased by several times, the butane conversion, the production of methane and the hydrogen yield were significantly increased (Fig. 2). This clearly shows that the carbon black is effective for primary decomposition of butane or the C–C bond rupture of the butane skeleton. The increase of methane production indicates that Reaction (2) is accelerated and, in turn, the increase of hydrogen yield is due to acceleration of the subsequent reactions such as Reactions (4), (5), (6) and/or (7). More detailed product distributions depending on the space velocity will be presented below and later in Section 3.3. Nonetheless, since the portion of non-catalytic, primary thermal decomposition of butane is much greater than the catalytic decomposition, the reaction in the presence of the carbon black may be called 'thermocatalytic decomposition', which means that the overall decomposition is the combination of the thermal and catalytic reactions.

Although the trend in the product distribution with respect to temperature appeared largely similar to each other, a closer look revealed that there were significant differences in the product distribution between the thermal and thermocatalytic decomposition (Figs. 3 and 4). Below 700 °C, there was little difference in the product distribution between the two methods with the GHSV of 10,000 cm^3(STP)/h g-cat. However, ethylene and methane produced by the thermocatalytic decomposition became significantly smaller from 750 and 950 °C, respectively, than those by the thermal decomposition. This is certainly due to the catalytic action of the carbon black on Reactions (6) and (1). As a consequence, the hydrogen yield became considerably higher from 750 °C for the former method. In addition, in the temperature range between 750 and 850 °C, the propylene obtained by the thermocatalytic decomposition was somewhat smaller than that by the thermal decomposition (Fig. 4) while the methane obtained by the former was larger than that by the latter (Fig. 3). This indicates that Reaction (5) or (7) is also accelerated by the presence of the carbon black. Therefore, it can be concluded that the carbon black is effective as the catalyst for Reactions (1), (5), (6) and (7).

When compared with the thermal decomposition, the temperatures at which the maximum quantities of products were obtained by the thermocatalytic decomposition (or called hereafter as the temperature(s) of the maximum) shifted from 800 to 750 °C for ethylene, from 950 to 850 °C for methane. The

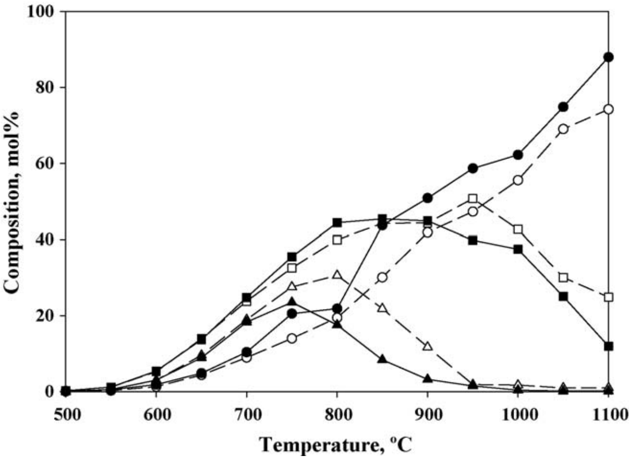


Fig. 3. Effect of temperature on the product (hydrogen, methane and ethylene) distribution in the thermal and thermocatalytic decomposition (butane flow rate = 25 cm^3(STP)/min; carbon black loading = 0.15 g; thermal decomposition: (○) H_2, (□) CH_4, (△) C_2H_4; catalytic decomposition: (●) H_2, (■) CH_4, (▲) C_2H_4).

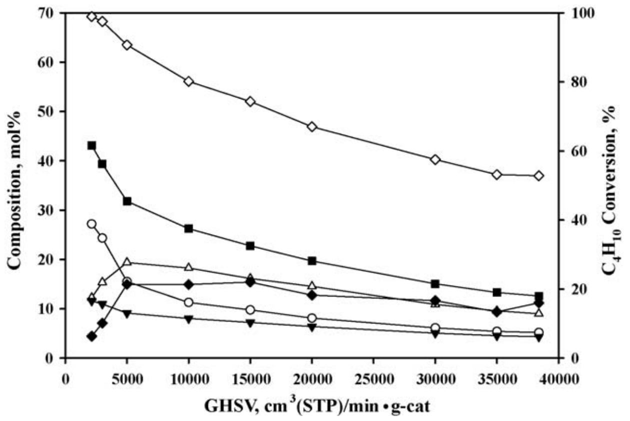
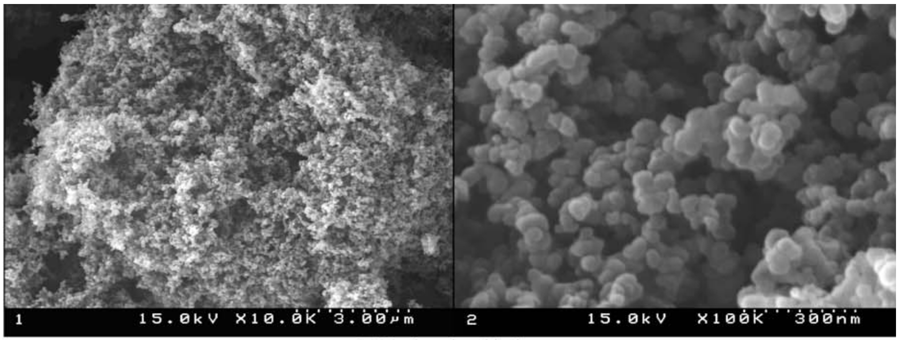
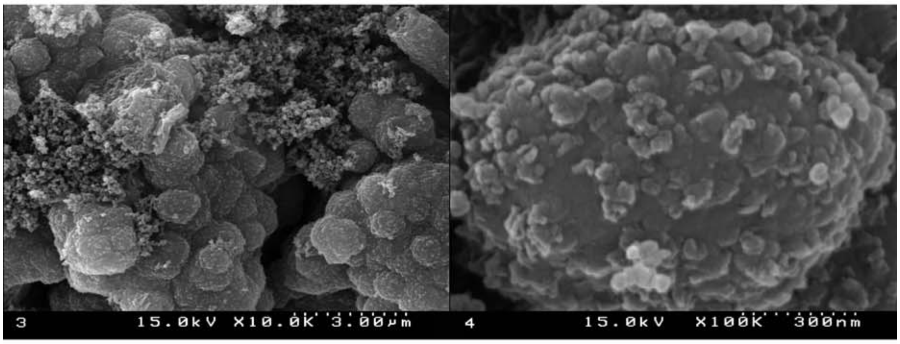


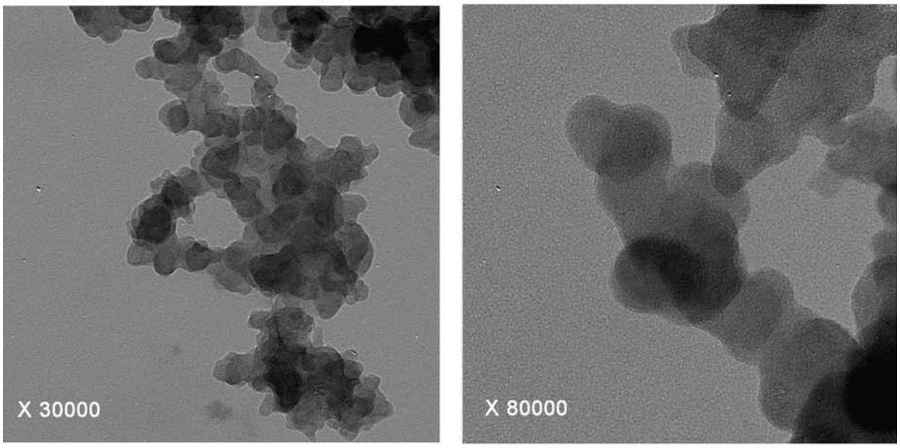
Fig. 5. Effect of space velocity on butane conversion and product distribution in the thermocatalytic decomposition of butane (temperature = 700 °C; (○) H_2, (■) CH_4, (△) C_2H_4, (▼) C_2H_6, (◆) C_3H_6, (◇) conversion; propane not shown due to too low amount).



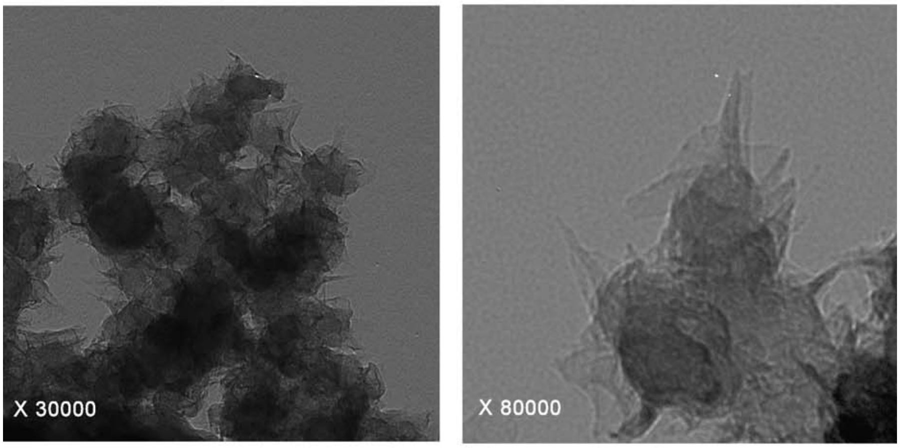
(a) Fresh carbon black



(b) Used carbon black after 3 h at 1000 °C (Wc= 0.89 g dep. C(s)/g-cat)



(c) Fresh carbon black



(d) Used carbon black after 3 h at 1100 °C (Wc= 1.35 g dep. C(s)/g-cat)

Fig. 6. SEM and TEM images of the carbon black catalyst: (a) fresh carbon black; (b) used carbon black after 3 h at 1000 °C (Wc = 0.89 g dep. C(s)/g-cat); (c) fresh carbon black; (d) used carbon black after 3 h at 1100 °C (Wc = 1.35 g dep. C(s)/g-cat).

temperatures of the maximum quantities of ethane, propylene and propane were 700, 700 and 750 °C, respectively, and these were the same in both methods. The temperature of the maximum quantity of a product may be considered a rough measure of the decomposition rate, but it is not sufficient enough because it actually reflects the balance between the rates of generation and disappearance of the product; its generation rate depends on the amount of the precursor reactant while its disappearance rate on the present amount of that product. Therefore, in order to better understand the decomposition rates, a more careful analysis of the data or separate experiments are required. However, combination of the temperature of the maximum quantity of the product and its maximum amount (which reflect the generation rate of that product or the decomposition rate of the precursor reactant with temperature) together with the slope after the maximum point (which reflects the rate of disappearance of that product) may provide a qualitative measure for comparison of the decomposition rate. All in all, either in the thermal decomposition or in the thermocatalytic decomposition, the decomposition rates of hydrocarbons may be assessed to be in the following order: butane > propylene (lower temperature of the maximum and steep slope) > ethylene (medium high temperature of the maximum and steep slope) > ethane (medium high temperature of the maximum and sluggish slope) > methane (highest temperature of the maximum and sluggish slope). It is not easy to assess for propane because of its too low amount, but roughly, its decomposition rate is considered comparable to that of ethylene. This analysis result is considered in agreement with the thermodynamic data and earlier works on the kinetic study [23].

In the presence of carbon black, ethane, propylene and propane were negligible above 900 °C and ethylene was so at and above 1000 °C. If the decomposition is operated at and above 1000 °C, the separation of the product stream would become much easier and more efficient because there remain practically only two components, hydrogen and methane.

3.3. Effect of space velocity

The product distribution at 700 °C with respect to the space velocity (in terms of GHSV) is presented in Fig. 5. As generally expected, the butane conversion and the hydrogen yield decreased with increase of the space velocity due to decrease of the contact time, but the decrease was not proportional to the space velocity. Below 5000 cm^3(STP)/h g-cat of the GHSV, the conversion was near 100%. The saturated hydrocarbon products such as methane and ethane also decreased monotonically with the space velocity. In the regime higher than 10,000 cm^3(STP)/h g-cat, ethylene and propylene also decreased with increase of the space velocity. However, they decreased as the space velocity decreased from 10,000 cm^3(STP)/h g-cat down to 2140 cm^3(STP)/h g-cat and this accompanied very high conversion of butane and rapid increase of methane and hydrogen. This means that, particularly under the long contact time, the carbon black catalyst acts effectively not only on the primary decomposition of butane such as Reaction (2) but also on the decomposition of ethylene and propylene such as Reactions (6) and (7).

3.4. SEM and TEM images of the produced carbon

The fresh carbon black particles and the carbon produced by the catalytic decomposition after reaction at 1000 and 1100 °C were investigated by SEM and TEM as shown in Fig. 6. The fresh carbon black particles were mostly round and their surfaces were smooth. For the carbon after the reaction, the particles became larger, stuck together and formed big particles. The deposited carbon also formed many protrusions on the particle surface.

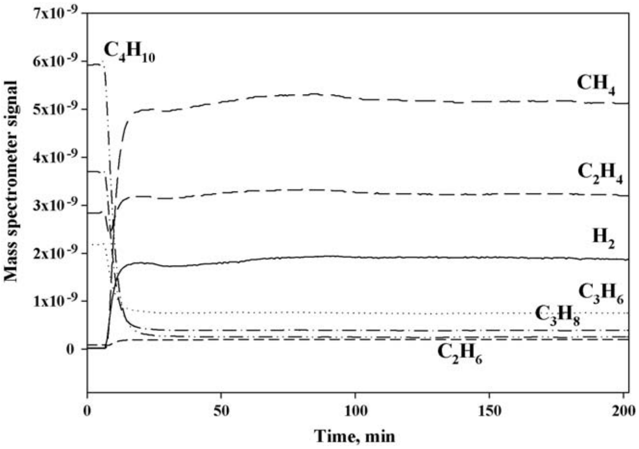


Fig. 7. Product distribution measured by mass spectrometer with respect to time in the thermocatalytic decomposition of butane (GHSV = 5000 cm^3(STP)/h g-cat, temperature = 700 °C).

3.5. Stability of catalyst

The stability of the catalyst was investigated at 700 and 750 °C by measuring the product distribution with respect to time. The mass spectrometer was used for continuous monitoring and the results are shown in Figs. 7 and 8. After a short, initial transition period during which the system approached a steady state, the amounts of all the products maintained almost constant. Fig. 8 shows stable production of the hydrogen either in the thermal or in the thermocatalytic decomposition as well as the enhancing catalytic effect of carbon black on the hydrogen production. These results show that the catalyst does not deactivate in spite of the carbon deposition such as observed in Fig. 6. This kind of stable activity despite the carbon deposition has also been observed in earlier works on methane decomposition over carbon blacks. The reason for this has been suggested that the overall number of the active site remains almost constant during the reaction, which is because some active sites may disappear due to the carbon deposition while

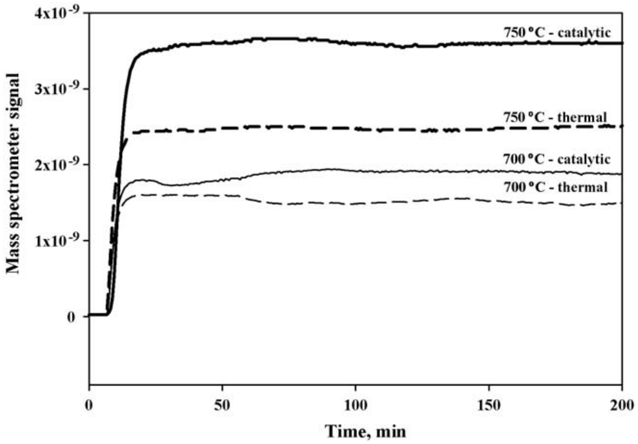


Fig. 8. Hydrogen production measured by mass spectrometer with respect to time in the thermal and thermocatalytic decomposition of butane (GHSV = 5000 cm^3(STP)/h g-cat).

new active sites may be generated on the surface or edges of graphene layers of growing carbon deposits [8,17].

4. Conclusion

A variety of products such as hydrogen, methane, ethylene, ethane, propylene and propane were produced in decomposition of butane. The primary products of homogeneous thermal decomposition of butane were methane plus propylene and ethane plus ethylene. The butane conversion and the hydrogen yield became significantly higher in the presence of carbon black when compared with those obtained from the thermal decomposition. This is mainly due to the catalytic effect of carbon black which accelerates decomposition of propylene, ethylene and methane among the primary thermal decomposition products, for these products diminished more rapidly than those obtained by the thermal decomposition. The primary decomposition of butane was also accelerated by carbon black especially under low space velocity. Since the primary thermal decomposition of butane took place to a much greater extent than the catalytic decomposition, the overall decomposition can be called as thermocatalytic decomposition. Propylene disappeared most rapidly and became negligible from 800 °C by the thermocatalytic decomposition. The catalytic decomposition of ethylene was pronounced from 750 °C and that of methane from 950 °C. In the presence of carbon black, ethane and ethylene became negligible above 900 and 1000 °C, respectively. Deactivation of the catalyst was not observed at least for 200 min in spite of the carbon deposition.

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