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Author(s)	Ogawa, Ayumu; Mochizuki, Yuuki; Tsubouchi, Naoto
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# Catalytic Decomposition of Pyridine with Goethite-Rich Limonite in the Coexistence of Fuel Gas or Coke Oven Gas Components

Ayumu OGAWA, Yuuki MOCHIZUKI and Naoto TSUBOUCHI\*

Center for Advanced Research of Energy and Materials, Faculty of Engineering, Hokkaido University, Kita 13 Nishi 5, Kita-ku, Sapporo, 060-8628 Japan.

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Catalytic performance of limonite in the decomposition of 100 ppmv pyridine ( $C_5H_5N$ ) in the coexistence of fuel gas or coke oven gas (COG) components has been studied mainly with a cylindrical quartz reactor at 750–850°C under a high space velocity of  $51\,000\text{ h}^{-1}$  to develop a novel hot gas cleanup method of removing the nitrogen in tar as  $N_2$ . The limonite catalyst achieves the almost complete decomposition of  $C_5H_5N$  in He at 500–850°C and gives a high  $N_2$  yield of more than 85 N% at 500°C. When the decomposition run is performed in the presence of fuel gas or COG components, the coexistence of 20% CO/10%  $H_2$  at 750°C or 50%  $H_2$ /30%  $CH_4$ /5% CO at 850°C deactivates the limonite with remarkable formation of deposited carbon. On the other hand, the addition of a small amount of  $H_2O$  or  $CO_2$  to these atmospheres can improve the catalytic activity without carbon deposition. When 3%  $H_2O$  or 10%  $CO_2$  is added to 20% CO/10%  $H_2$ ,  $C_5H_5N$  conversion and  $N_2$  yield at 750°C become 80–95% and 65–80 N%, respectively, and the extent of the improvement is larger with the  $CO_2$  than with the  $H_2O$ . The addition of 5%  $CO_2$  to 50%  $H_2$ /30%  $CH_4$ /5% CO also restores the conversion or the yield at 850°C to the high level of about 90% or 60–70 N%, respectively, and both values at 950°C are comparable to those at 500°C in inert gas.

KEY WORDS: hot gas cleanup; pyridine decomposition;  $N_2$  formation; limonite; fuel gas; coke oven gas.

## 1. Introduction

Advanced integrated gasification combined cycle (A-IGCC) and fuel cell (A-IGFC) systems are expected to be among the most environmentally acceptable power-generating technologies from coal. A-IGCC and A-IGFC are estimated to achieve high generation efficiencies of more than 57 and 65%, respectively, which corresponds to a reduction of greater than 30% of  $CO_2$  emissions compared to current pulverized coal-fired plants.<sup>1)</sup> Coal-derived fuel gas is composed mainly of syngas ( $CO/H_2 = 2$ ), with low concentrations of  $CO_2$ ,  $CH_4$  and  $H_2O$ .<sup>2–5)</sup> Undesirable impurities, such as hydrogen halide,  $H_2S$ , COS,  $NH_3$ , HCN, alkali metals and trace elements, are also included in raw fuel gas.<sup>2–5)</sup> Cold gas cleaning methods using Venturi water scrubbers and selective amine-based absorbents are conventional technologies to efficiently remove these solid and gaseous impurities from fuel gas before a gas combustion process with gas turbine or fuel cell.<sup>6–8)</sup> However, a hot gas cleanup method that purifies fuel gas at temperatures of  $\geq 300^\circ\text{C}$  can reduce the loss of heat energy of the hot raw gas ( $> 700^\circ\text{C}$ ) and high capital cost for large waste water treatment facilities used in wet processes.<sup>1,3,4,9,10)</sup>

Coke oven gas (COG) produced during coal carbonization is generally used as a fuel source for coke ovens and other combustion units in ironworks, and it has recently

attracted much attention as a low cost source of hydrogen.<sup>11)</sup> In conventional processes, the hot raw COG ( $> 800^\circ\text{C}$ ) must be quenched to near room temperature using aqueous ammonia solution to remove tarry materials contained in COG.<sup>11)</sup> On the other hand, the catalytic or noncatalytic reforming of COG is a promising technology effectively utilizing heat energy of the hot COG.<sup>12–15)</sup> Upon coal carbonization, part of the nitrogen present in coal is retained in the solid phase, and the rest is released as volatile-N ( $N_2$ ,  $NH_3$ , HCN and tar-N).<sup>16)</sup> It is well-known that  $NH_3$ , HCN and tar-N not only serve as a source of  $NO_x$  but also poison catalyst materials used for COG reforming.

Our research group has been working on the decomposition of  $NH_3$  or model tar-N compounds (pyridine or pyrrole) using inexpensive iron catalysts.<sup>17–26)</sup> We have found that fine particles of metallic iron ( $\alpha\text{-Fe}$ ) formed from low-valued iron ore (limonite) show higher activity in the decomposition of  $NH_3$  compared to Ni-, Cu-, Mo- and Ru-based catalysts reported previously.<sup>2,19–23,26)</sup> The limonite can achieve almost complete decomposition of 2 000 ppmv  $NH_3$  diluted with inert gas at  $500^\circ\text{C}$ <sup>19)</sup> and exhibit stable activity in the presence of fuel gas components at  $850^\circ\text{C}$ .<sup>20–23,26)</sup> We have recently shown that limonite-derived  $\alpha\text{-Fe}$  can give a  $N_2$  yield of more than 80% in the decomposition of 100 ppmv pyridine ( $C_5H_5N$ ) in inert He at  $500^\circ\text{C}$  under a high space velocity of  $51\,000\text{ h}^{-1}$ .<sup>25)</sup> In this paper, therefore, we focus on investigating the catalytic performance of an Australian limonite in the decomposition of  $C_5H_5N$  in the coexistence of fuel gas or COG components to develop a novel gas

\* Corresponding author: E-mail: tsubon@eng.hokudai.ac.jp  
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cleaning method for removing tar-N as N<sub>2</sub>.

## 2. Experimental

### 2.1. Catalyst Material and Preparation

An Australian natural limonite ore comprising about 70% of goethite ( $\alpha$ -FeOOH) was employed as a catalyst precursor in the present study. The metal composition of the limonite was: Fe, 44; Si, 9.4; Al, 7.2; Mg, 0.15; Ca, 0.07 mass%-dry.<sup>25)</sup> The as-received limonite was sieved to select the 250–500  $\mu$ m size fraction, and the Brunauer-Emmett-Teller (BET) specific surface area was measured at 40 m<sup>2</sup>/g.<sup>25)</sup>

### 2.2. Pyridine Decomposition

Catalytic decomposition of C<sub>5</sub>H<sub>5</sub>N was carried out with a cylindrical fixed-bed quartz reactor (8 mm i.d.) under ambient pressure. The details of the experimental apparatus have been described elsewhere.<sup>17)</sup> The temperature was controlled by a K-type thermocouple attached to the exterior surface of the reactor. Approximately 0.25 g of the limonite was first charged into the reactor with quartz wool, and a flow of high-purity He (>99.99995%) was then passed through the reactor until the concentration of N<sub>2</sub> in the experimental system was decreased to less than 20 ppmv. The height of catalyst bed in the reactor was about 7.0 mm. After taking precautions against leakage, the reactor was heated electrically up to 500°C. At this temperature, the He was replaced with high-purity H<sub>2</sub> (>99.9999%), and the catalyst material was reduced with the H<sub>2</sub> for 2 h. The reduced limonite catalyst is present as  $\alpha$ -Fe with the average crystalline size of 25 nm as mentioned later (Section 3.4). After the reduction pretreatment, the atmosphere was restored to the He, and the reactor was held at a temperature between 300–950°C. The C<sub>5</sub>H<sub>5</sub>N decomposition experiment began by passing 100 ppmv C<sub>5</sub>H<sub>5</sub>N diluted with the He, simulated fuel gas (20% CO/10% H<sub>2</sub>, 20% CO/10% H<sub>2</sub>/3% H<sub>2</sub>O and 20% CO/10% H<sub>2</sub>/10% CO<sub>2</sub>) or simulated COG (50% H<sub>2</sub>/30% CH<sub>4</sub>/5% CO and 50% H<sub>2</sub>/30% CH<sub>4</sub>/5% CO/5% CO<sub>2</sub>) over the catalyst bed. The space velocity was maintained at 51 000 h<sup>-1</sup> throughout the run.

### 2.3. Gas Analysis

The amount of N<sub>2</sub> produced in the decomposition of C<sub>5</sub>H<sub>5</sub>N was measured at 3 min intervals with a high-speed micro gas chromatograph (Agilent) equipped with a thermal conductivity detector. Concentrations of C<sub>5</sub>H<sub>5</sub>N, NH<sub>3</sub> and HCN were determined at 2 min intervals with a photoacoustic multigas monitor (Innova). In the C<sub>5</sub>H<sub>5</sub>N decomposition runs in the coexistence of CO, CO<sub>2</sub>, CH<sub>4</sub> and/or H<sub>2</sub>O, the C<sub>5</sub>H<sub>5</sub>N, NH<sub>3</sub> and HCN were analyzed independently by the Gastec standard detector tube (Gastec) because the analytical accuracy of the multigas monitor may be deteriorated by CO, CO<sub>2</sub>, CH<sub>4</sub> and/or H<sub>2</sub>O. The amount of C<sub>5</sub>H<sub>5</sub>N fed was calculated using the concentrations of C<sub>5</sub>H<sub>5</sub>N before and after reaction. The yield of N<sub>2</sub>, HCN or NH<sub>3</sub> was estimated using the amounts of both C<sub>5</sub>H<sub>5</sub>N fed and N<sub>2</sub>, HCN or NH<sub>3</sub> formed, respectively, and it was expressed in percent on a nitrogen basis.

## 2.4. Catalyst Characterization

The powder X-ray diffraction (XRD) (Shimadzu) measurements of catalyst samples as received, after H<sub>2</sub> reduction and after C<sub>5</sub>H<sub>5</sub>N decomposition were performed with Mn-filtered Fe-K $\alpha$  radiation. The average crystallite size of  $\alpha$ -Fe was determined by the Debye-Scherrer method. To avoid rapid oxidation of  $\alpha$ -Fe particles upon exposure to laboratory air, the limonite after H<sub>2</sub> reduction or C<sub>5</sub>H<sub>5</sub>N decomposition was passivated using 2% O<sub>2</sub>/He at room temperature and then recovered from the reactor.<sup>19)</sup>

## 3. Results and Discussion

### 3.1. Decomposition of Pyridine in Inert Gas

The results for the decomposition of 100 ppmv C<sub>5</sub>H<sub>5</sub>N in inert He with the limonite catalyst have mostly been shown elsewhere<sup>25)</sup> and are thus summarized simply in **Table 1**. In a blank experiment with quartz wool alone at 850°C, C<sub>5</sub>H<sub>5</sub>N conversion was less than 1%. At 300–500°C, the conversion and N<sub>2</sub> yield after 4 h increased with increasing temperature in many cases (Table 1). The reason for it may be that the extent of the transformation of C<sub>5</sub>H<sub>5</sub>N into N<sub>2</sub> is larger at a higher temperature. The limonite also provided a high N<sub>2</sub> yield of more than 80 N% for at least 10 h at 500°C.<sup>25)</sup> At a temperature of more than 600°C, although the conversion was greater than 99% during 4 h reaction, the yield decreased gradually after 3 h (Table 1). The catalysts after reaction at 300–500°C were apparently homogeneous, however, the samples after the reaction at  $\geq$  600°C were divided into two layers. According to XRD analyses, the upper layer was rich in crystallized carbon and cementite (Fe<sub>3</sub>C) derived from C<sub>5</sub>H<sub>5</sub>N decomposition, whereas the lower layer was rich in  $\alpha$ -Fe formed upon the H<sub>2</sub> reduction. Thus, the decrease in N<sub>2</sub> yield observed at  $\geq$  600°C may be ascribed to the adsorption of C<sub>5</sub>H<sub>5</sub>N onto the carbon deposited at the upper layer and/or the transformation of catalytically active  $\alpha$ -Fe into the carbide species. We have recently shown that the limonite-catalyzed N<sub>2</sub> formation from C<sub>5</sub>H<sub>5</sub>N in inert gas takes place via a cycle mechanism involving  $\alpha$ -Fe and the nitride species (for example, Fe<sub>2</sub>N, Fe<sub>3</sub>N and Fe<sub>4</sub>N).<sup>25)</sup> When N<sub>2</sub> yields at 600–850°C were compared, as provided in Table 1, the yield was larger at a higher temperature. The reason may be that the extent of the transformation of nitrogen element incorporated in C<sub>5</sub>H<sub>5</sub>N-driven carbona-

**Table 1.** C<sub>5</sub>H<sub>5</sub>N conversion and yield of N<sub>2</sub>, HCN or NH<sub>3</sub> in the limonite-catalyzed decomposition of C<sub>5</sub>H<sub>5</sub>N in inert He at different temperatures.

Temperature (°C)	C <sub>5</sub> H <sub>5</sub> N conversion (%) <sup>a</sup>	N <sub>2</sub> yield (N%) <sup>a</sup>	HCN yield (N%) <sup>a</sup>	NH <sub>3</sub> (N%) <sup>a</sup>	Ref. no
300	5	<1	5	<1	(25)
350	7	1	3	<1	(25)
400	7	7	3	<1	(25)
450	88	76	2	<1	(25)
500	>99	85	2	<1	(25)
600	>99	72	2	<1	This work
750	>99	74	3	<1	This work
850	>99	78	2	<1	This work

<sup>a</sup>After 4 h reaction.

aceous materials into N<sub>2</sub> is larger at a higher temperature.<sup>25)</sup> The yield of HCN or NH<sub>3</sub> was less than 5 N% and 1 N%, respectively, under all conditions. It has been reported that most of the nitrogen in pyridine is decomposed into cyanide species at above 800°C.<sup>27)</sup> It might thus be possible that the limonite catalyzed the decomposition of C<sub>5</sub>H<sub>5</sub>N into HCN, which might subsequently be transformed into N<sub>2</sub>.<sup>24)</sup>

### 3.2. Decomposition of Pyridine in the Coexistence of Fuel Gas Components

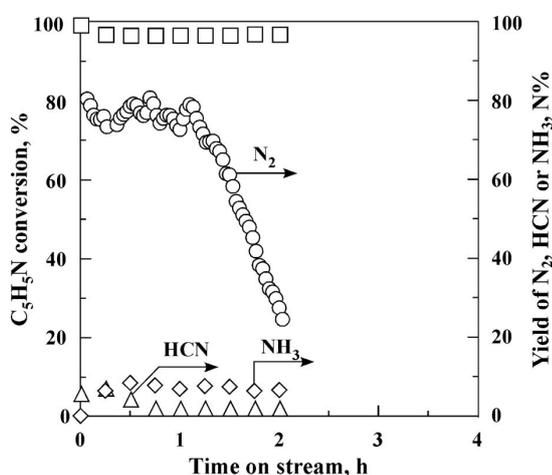
**Figure 1** presents the effect of the limonite catalyst on C<sub>5</sub>H<sub>5</sub>N decomposition in the presence of syngas (20% CO/10% H<sub>2</sub>) at 750°C. C<sub>5</sub>H<sub>5</sub>N conversion after 2 h reaction was as high as >95%, which was comparable to the value in inert He (Table 1). On the other hand, N<sub>2</sub> yield decreased to less than 30 N% after 2 h. The yields of NH<sub>3</sub> and HCN were always less than 10 N%. Since the formation of CO<sub>2</sub> and carbonaceous materials occurred under the present conditions, the catalyst deactivation observed in Fig. 1 may be ascribed to the carbon deposition by the disproportionation of CO in the syngas (Eq. (1)).



On the other hand, the high C<sub>5</sub>H<sub>5</sub>N conversion in Fig. 1 may originate from the adsorption of C<sub>5</sub>H<sub>5</sub>N onto the deposited carbon formed during the reaction.

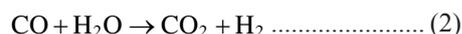
As well-known, fuel gas from air-blown coal gasifiers contains small amounts of H<sub>2</sub>O and CO<sub>2</sub>.<sup>2,3,23)</sup> Thus, the effect of H<sub>2</sub>O or CO<sub>2</sub> addition to syngas on C<sub>5</sub>H<sub>5</sub>N decomposition was investigated.

**Figure 2** shows the influence of 3% H<sub>2</sub>O addition on C<sub>5</sub>H<sub>5</sub>N decomposition under flowing 20% CO/10% H<sub>2</sub> at 750°C. The comparison with Fig. 1 revealed that the co-feeding of the H<sub>2</sub>O could maintain the C<sub>5</sub>H<sub>5</sub>N conversion or N<sub>2</sub> yield at the level of more than 80% or about 65 N%, respectively. NH<sub>3</sub> yield was approximately 20 N% during 4 h reaction, and HCN was always negligibly small. Although the C<sub>5</sub>H<sub>5</sub>N conversion was about 95% in He, the value lowered to 80–90% with the co-feeding of the H<sub>2</sub>O. In addition, N<sub>2</sub> yield after 1 h reaction also decreased from 75% in He (Fig. 1) to 65% in the case of H<sub>2</sub>O co-feeding (Fig. 2). The reason for it may be that part of nitrogen in C<sub>5</sub>H<sub>5</sub>N is transformed into unmeasured N-species other than



**Fig. 1.** Influence of the coexistence of syngas (20% CO/10% H<sub>2</sub>) on C<sub>5</sub>H<sub>5</sub>N decomposition with limonite at 750°C.

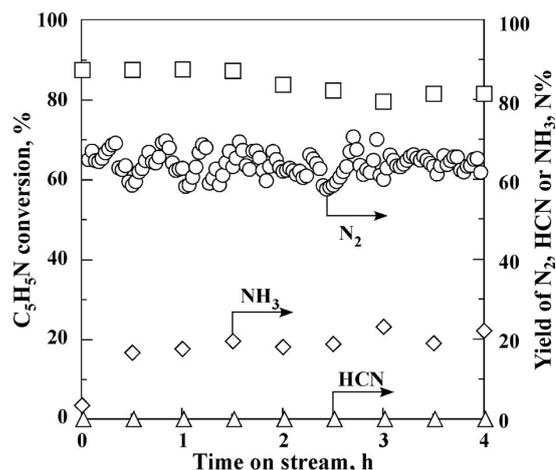
the N-forms mentioned above. **Figure 3** presents the concentration of CO<sub>2</sub> evolved in the runs shown in Figs. 1 and 2. Approximately 1 000–2 000 ppmv of CO<sub>2</sub> was produced during C<sub>5</sub>H<sub>5</sub>N decomposition under flowing syngas alone. This result points out that Eq. (1) occurs significantly. In the coexistence of the H<sub>2</sub>O, as seen in Fig. 3, the concentration at a steady state was about 7 000 ppmv, which was much higher than that without the H<sub>2</sub>O added. It is thus likely that the following CO-H<sub>2</sub>O reaction (Eq. (2)), that is, the water gas shift reaction, takes place in the process of C<sub>5</sub>H<sub>5</sub>N decomposition.



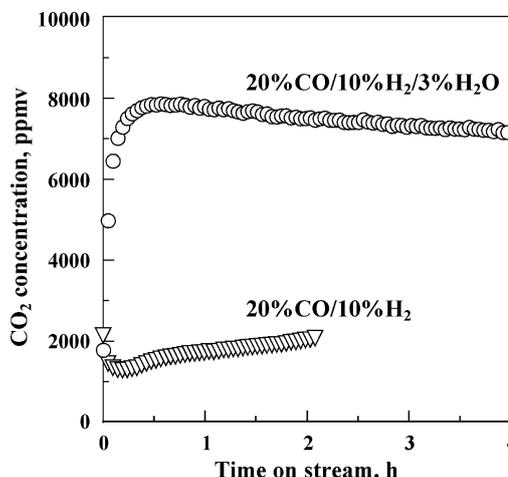
No significant carbon formation was also observed after the decomposition reaction in the H<sub>2</sub>O-containing syngas. This may be ascribed to the suppression of carbon deposition (Eq. (1)) by the CO<sub>2</sub> produced through Eq. (2) and/or the occurrence of the reaction (Eq. (3)) of deposited carbon with the H<sub>2</sub>O added.



It has recently been shown that limonite-catalyzed steam gasification of coal chars can proceed remarkably around 800°C.<sup>28)</sup>



**Fig. 2.** Effect of 3% H<sub>2</sub>O addition on C<sub>5</sub>H<sub>5</sub>N decomposition under flowing 20% CO/10% H<sub>2</sub> at 750°C.



**Fig. 3.** Concentration of CO<sub>2</sub> evolved during C<sub>5</sub>H<sub>5</sub>N decomposition at 750°C in the coexistence of syngas alone or 3% H<sub>2</sub>O-containing syngas.

Figure 4 shows the results under flowing 10% CO<sub>2</sub>-containing syngas. When the CO<sub>2</sub> was added to 20% CO/10% H<sub>2</sub>, C<sub>5</sub>H<sub>5</sub>N conversion or N<sub>2</sub> yield after 4 h was almost the same level as the corresponding value (Table 1) observed at 500°C in inert He. NH<sub>3</sub> and HCN were ≤ 5 N% and almost zero, respectively. The co-feeding of a higher concentration of CO<sub>2</sub> may lower the driving force for Eq. (1) to a larger extent so that the CO<sub>2</sub> added may improve the activity of the limonite catalyst more effectively compared with 3% H<sub>2</sub>O addition (Fig. 2). When the decomposition run given in Fig. 4 was carried out at 650°C, the catalytic performance of the limonite was decreased by carbon deposition, which may come from a higher driving force ( $\Delta G = -2.1$  kcal/mol) for Eq. (1) at 650°C compared with that ( $\Delta G = 2.1$  kcal/mol) at 750°C. The catalytic activity in the CO<sub>2</sub>-containing syngas at 850°C was almost the same level as that (Fig. 4) at 750°C. It is thus probable that the addition of 10% CO<sub>2</sub> to syngas can restore the catalytic performance of the limonite to the high level at  $\geq 750^\circ\text{C}$ .

### 3.3. Decomposition of Pyridine in the Coexistence of Coke Oven Gas Components

It is well-known that a typical COG is composed of 54–59% H<sub>2</sub>, 24–28% CH<sub>4</sub>, 4–7% CO, 3–5% N<sub>2</sub> and 1–3% CO<sub>2</sub> with impurities.<sup>15)</sup> The present section therefore focuses on investigating the effect of the coexistence of H<sub>2</sub>, CH<sub>4</sub>, CO and/or CO<sub>2</sub> on the limonite-catalyzed C<sub>5</sub>H<sub>5</sub>N decomposition.

Figure 5 presents the effect of the limonite catalyst on C<sub>5</sub>H<sub>5</sub>N decomposition in the presence of 50% H<sub>2</sub>/30% CH<sub>4</sub>/5% CO at 850°C. C<sub>5</sub>H<sub>5</sub>N conversion was about 90% during 1 h reaction, whereas N<sub>2</sub> yield decreased with increasing time on stream beyond 30 min to be less than 30 N% after 1 h. On the other hand, HCN and NH<sub>3</sub> yields were almost constant for 1 h. The difference in the behavior of N<sub>2</sub>, HCN and NH<sub>3</sub> formation may occur due to the transformation of C<sub>5</sub>H<sub>5</sub>N into unmeasured N-species, because the catalyst used in this atmosphere was covered with a large amount of deposited carbon, which is likely to be derived from CH<sub>4</sub> (Eq. (4)) and/or CO (Eq. (1)) in the atmosphere. It is probable that the remarkable occurrence of carbon formation is the main reason for the catalyst deactivation observed in Fig. 5.

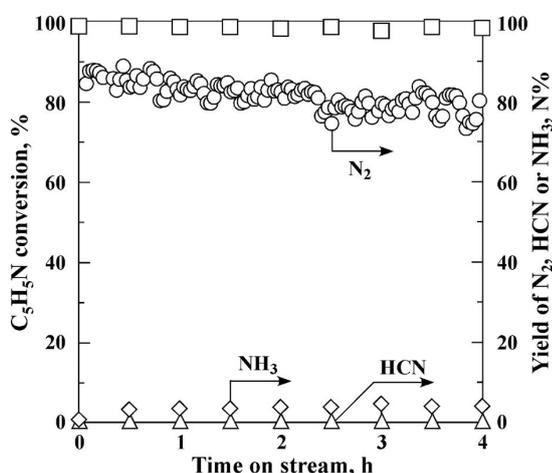


Fig. 4. Effect of 10% CO<sub>2</sub> addition on C<sub>5</sub>H<sub>5</sub>N decomposition under flowing 20% CO/10% H<sub>2</sub> at 750°C.



Figure 6 shows the influence of 5% CO<sub>2</sub> addition on C<sub>5</sub>H<sub>5</sub>N decomposition under flowing 50% H<sub>2</sub>/30% CH<sub>4</sub>/5% CO at 850°C. The added CO<sub>2</sub> could improve the catalytic activity of the limonite remarkably compared with the observation (Fig. 5) without CO<sub>2</sub> added. The conversion was stable at about 90%, and N<sub>2</sub> yield was 60–70 N% during 4 h reaction. NH<sub>3</sub> and HCN were also about 20 N% and almost zero, respectively. No significant carbon deposition was observed under the conditions applied. It is probable that the decrease in carbonaceous materials by CO<sub>2</sub> addition is responsible for the activity improvement observed in Fig. 6. When the temperature was decreased to 750°C, the conversion decreased steeply at the initial step of the reaction to be about 60% after 1 h. At 950°C, on the other hand, the conversion was as high as >95% for 4 h, and N<sub>2</sub> was stable at about 80 N%. Thermodynamic calculations indicate that the driving force for the methane decomposition reaction (Eq. (4)) described above is greater at a higher temperature ( $\Delta G = -5.2$  kcal/mol at 750°C,  $-7.8$  kcal/mol at 850°C and  $-10$  kcal/mol at 950°C). However, the catalytic activity of the limonite was higher at  $\geq 850^\circ\text{C}$  than at 750°C. The reason for this difference is not clear at present, but the occurrence of the Boudouard reaction (the reverse reaction

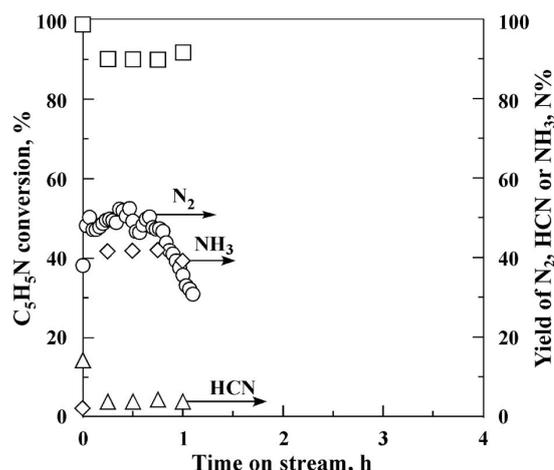


Fig. 5. Influence of the coexistence of 50% H<sub>2</sub>/30% CH<sub>4</sub>/5% CO on C<sub>5</sub>H<sub>5</sub>N decomposition with limonite at 850°C.

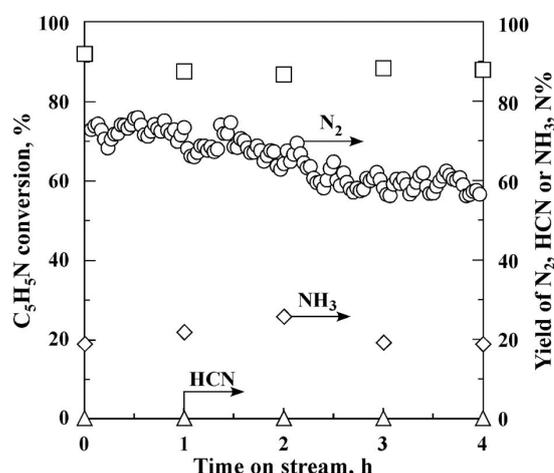


Fig. 6. Effect of 5% CO<sub>2</sub> addition on C<sub>5</sub>H<sub>5</sub>N decomposition under flowing 50% H<sub>2</sub>/30% CH<sub>4</sub>/5% CO at 850°C.

of Eq. (1)) may lead to the increased activity at high temperatures of  $\geq 850^\circ\text{C}$ . The  $\Delta G$  values for the Boudouard reaction at 750–950°C are estimated to be  $-2.1$  to  $-10$  kcal/mol, and the driving force is thus larger at a higher temperature.

### 3.4. Iron Forms of the Limonite after Reaction

As described above, the co-feeding of 20% CO/10% H<sub>2</sub> at 750°C or 50% H<sub>2</sub>/30% CH<sub>4</sub>/5% CO at 850°C with 100 ppmv C<sub>5</sub>H<sub>5</sub>N lowered the catalytic performance of the limonite considerably compared with the observation in inert He (Table 1, Figs. 1 and 5). On the other hand, the addition of H<sub>2</sub>O or CO<sub>2</sub> to the syngas and main COG composition restored the catalytic activity (Figs. 2, 4 and 6). The used limonite catalysts were thus subjected to the XRD measurements to identify crystalline forms of Fe species. The  $\alpha$ -FeOOH in as-received limonite was transformed into  $\alpha$ -Fe with the average crystalline size of 25 nm after H<sub>2</sub> reduction.<sup>25</sup> Figure 7 presents the XRD profiles for the limonite used in the presence of fuel gas components. As seen in Fig. 7(a),  $\alpha$ -Fe was transformed predominantly into Fe<sub>3</sub>C after C<sub>5</sub>H<sub>5</sub>N decomposition at 750°C in the coexistence of syngas alone. The formation of Fe<sub>3</sub>C may be expressed as follows:



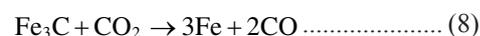
The  $\Delta G$  value for Eq. (5) at 750°C is calculated to be 0.2 kcal/mol. The carbide species may also be produced by the direct reaction (Eq. (6)) of  $\alpha$ -Fe with CO fed.



The  $\Delta G$  for Eq. (6) at 750°C is 2.3 kcal/mol, which means that the driving force for Eq. (6) is smaller than that for Eq. (5). Thus, Eq. (5) may be likely to be the main reaction for the formation of Fe<sub>3</sub>C. It may therefore be reasonable to see that carbon formed by Eq. (1) and/or CO coexisted

react with catalytically active  $\alpha$ -Fe to provide Fe<sub>3</sub>C, which causes the deactivation of the limonite catalyst.

When 3% H<sub>2</sub>O or 10% CO<sub>2</sub> was added to syngas at 750°C, the XRD peaks attributable to Fe<sub>3</sub>C and crystallized carbon disappeared almost completely, and  $\alpha$ -Fe became the main species (Figs. 7(b) and 7(d)). The similar XRD profile was also observed with the used limonite after the reaction at 850°C in the CO<sub>2</sub>-containing syngas (Fig. 7(e)). The disappearance of Fe<sub>3</sub>C may be ascribed to the suppression of carbon deposition (Eq. (1)) by CO<sub>2</sub> coexisted or produced through Eq. (2), the gasification of C<sub>5</sub>H<sub>5</sub>N-derived carbon by the Boudouard reaction or H<sub>2</sub>O coexisted (the reverse reaction of Eqs. (1) or (3), respectively), and/or the transformation of Fe<sub>3</sub>C into  $\alpha$ -Fe by the reaction of Fe<sub>3</sub>C with H<sub>2</sub>O (Eq. (7)) or CO<sub>2</sub> (Eq. (8)).



The  $\Delta G$  values for Eqs. (7) and (8) at 650–850°C are estimated to be 0.1 to  $-5.8$  and 1.4 to  $-6.1$  kcal/mol, respectively. It is thus probable that the two oxidizing gases can protect catalytically active  $\alpha$ -Fe from being carbonized and/or covered with deposited carbon, and the extent of the protection is larger at a higher temperature. After C<sub>5</sub>H<sub>5</sub>N decomposition at 650°C in 10% CO<sub>2</sub>-containing syngas, as seen in Fig. 7(c), the diffraction peaks of Fe<sub>3</sub>C and crystallized carbon were detected, whereas  $\alpha$ -Fe did not appear. The reason may be that the driving force ( $\Delta G = -2.1$  kcal/mol) for Eq. (1) at 650°C is larger than that ( $\Delta G = 1.4$  kcal/mol) for Eq. (8) at this temperature.

Figure 8 illustrates the XRD patterns for the limonite used in the coexistence of COG components. After the decomposition reaction at 850°C in 50% H<sub>2</sub>/30% CH<sub>4</sub>/5%

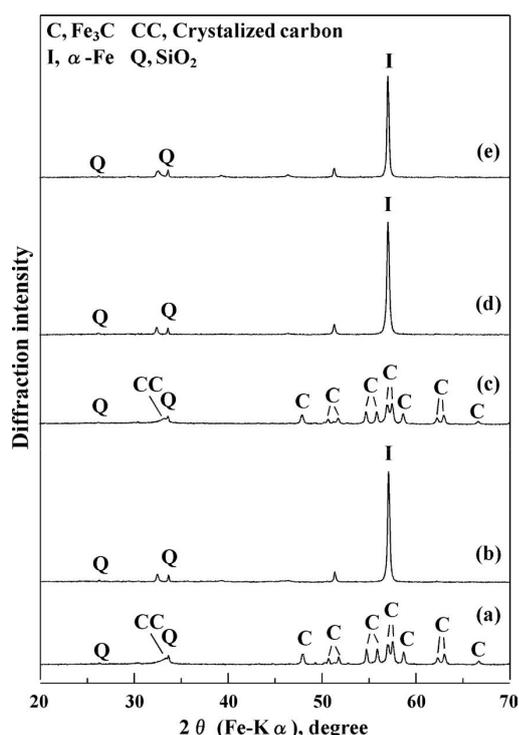


Fig. 7. XRD profiles for limonite samples after C<sub>5</sub>H<sub>5</sub>N decomposition in syngas/He at 750°C (a), H<sub>2</sub>O/syngas/He at 750°C (b) and CO<sub>2</sub>/syngas/He at 650°C (c), 750°C (d) and 850°C (e).

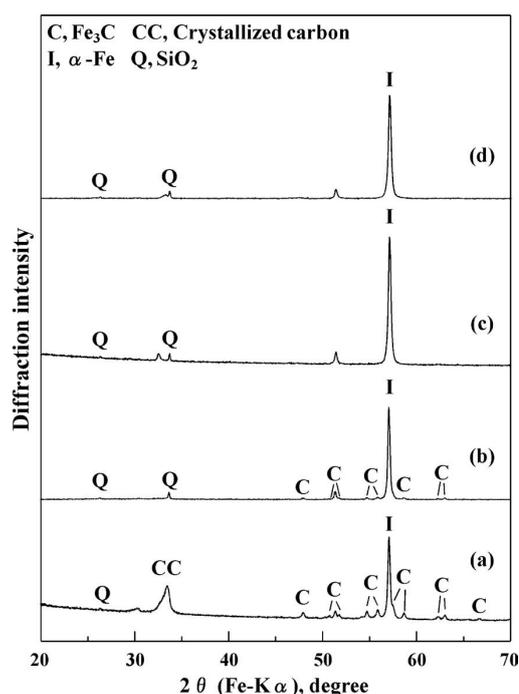
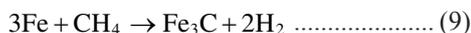


Fig. 8. XRD profiles for limonite samples after C<sub>5</sub>H<sub>5</sub>N decomposition in 50% H<sub>2</sub>/30% CH<sub>4</sub>/5% CO/He at 850°C (a) and 50% H<sub>2</sub>/30% CH<sub>4</sub>/5% CO/5% CO<sub>2</sub>/He at 750°C (b), 850°C (c) and 950°C (d).

CO, the XRD signals attributable to  $\alpha$ -Fe, Fe<sub>3</sub>C and crystallized carbon appeared (Fig. 8(a)). The  $\Delta G$  values for the CO disproportionation (Eq. (1)) and the methane decomposition (Eq. (4)) reactions at 850°C are calculated to be 6.3 and -7.8 kcal/mol, respectively. The crystallized carbon is considered to be predominantly formed via Eq. (4). On the other hand, the formation of Fe<sub>3</sub>C may proceed through the following equation (Eq. (9)) in addition to reactions involving deposited carbon (Eq. (5)) and/or CO (Eq. (6)).



The  $\Delta G$  value for Eq. (9) at 850°C is -8.0 kcal/mol, which is lower than that for Eq. (5) ( $\Delta G = -0.2$  kcal/mol) or 6 ( $\Delta G = 6.1$  kcal/mol) at 850°C. It is thus likely that the catalyst deactivation observed in Fig. 5 comes mainly from the occurrence of Eq. (4) and/or Eq. (9).

When 5% CO<sub>2</sub> was added to 50% H<sub>2</sub>/30% CH<sub>4</sub>/5% CO above 850°C, the diffraction lines of crystallized carbon and Fe<sub>3</sub>C disappeared almost completely, and  $\alpha$ -Fe became the predominant Fe form (Figs. 8(c) and 8(d)). The disappearance of the former two species may be ascribed to the suppression of carbon formation (Eq. (1)) by CO<sub>2</sub> coexisted, the CO<sub>2</sub> gasification of CH<sub>4</sub>- and C<sub>5</sub>H<sub>5</sub>N-derived carbonaceous materials (the reverse reaction of Eq. (1)), and/or the transformation of Fe<sub>3</sub>C into  $\alpha$ -Fe by the reaction between Fe<sub>3</sub>C and CO<sub>2</sub> (Eq. (8)). On the basis of the above-mentioned results, it is evident that the coexistence of CO<sub>2</sub> can suppress the deactivation of the limonite catalyst in 50% H<sub>2</sub>/30% CH<sub>4</sub>/5% CO at  $\geq 850^\circ\text{C}$ . At 750°C, as seen in Fig. 8(b), the weak XRD peaks of Fe<sub>3</sub>C were observed. This may be ascribed to a lower driving force for the Boudouard reaction (the reverse reaction of Eq. (1)) at 750°C compared with those at 850 and 950°C (section 3.3).

To clarify the mechanism of the limonite-catalyzed N<sub>2</sub> formation from C<sub>5</sub>H<sub>5</sub>N in the coexistence of fuel gas or COG components should be the subject of future work from a scientific point of view.

#### 4. Conclusions

Catalytic decomposition of 100 ppmv C<sub>5</sub>H<sub>5</sub>N in the presence of fuel gas or COG components with limonite rich in  $\alpha$ -FeOOH has been studied mainly with a cylindrical quartz reactor under the conditions of 0.1 MPa, 750–850°C and 51 000 h<sup>-1</sup>. The principal conclusions are summarized as follows:

(1) The limonite catalyst exhibits very high activity for the decomposition of C<sub>5</sub>H<sub>5</sub>N in inert He at 500–850°C, and C<sub>5</sub>H<sub>5</sub>N conversion and N<sub>2</sub> yield at 500°C reach almost 100% and more than 85 N%, respectively.

(2) In the coexistence of 20% CO/10% H<sub>2</sub> at 750°C or 50% H<sub>2</sub>/30% CH<sub>4</sub>/5% CO at 850°C, the limonite is considerably deactivated due to the remarkable occurrence of carbon deposition.

(3) On the other hand, the addition of 5–10% CO<sub>2</sub> to the syngas and main COG composition can suppress carbon formation and consequently improve the catalytic activity of the limonite significantly.

(4) The XRD analyses reveal the transformation of  $\alpha$ -FeOOH-derived active  $\alpha$ -Fe into Fe<sub>3</sub>C in the coexistence of 20% CO/10% H<sub>2</sub> alone or 50% H<sub>2</sub>/30% CH<sub>4</sub>/5% CO alone. When the H<sub>2</sub>O or CO<sub>2</sub> is added to the syngas at 750°C and the main COG composition at 850°C, on the other hand,  $\alpha$ -Fe is the only Fe form.

(5) On the basis of the above-mentioned results, it is likely that the two oxidizing gases can work for keeping the limonite surface as catalytically active  $\alpha$ -Fe.

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