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Utilization of low-grade iron ore in ammonia decomposition

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Abstract

Due to its cleanliness, fast energy cycle, and convenience of energy conversion, hydrogen has been regarded as the new energy source. Conventional process to produce hydrogen yield large amount of CO as byproduct. Moreover, the hydrogen storage and transportation have become the drawbacks in hydrogen economy. Thus, there has been increased interest in the hydrogen transportation medium as alternatives from the conventional process to produce and transport hydrogen. Ammonia has drawn worldwide attention as the most reliable hydrogen transportation medium. Through the decomposition of ammonia, hydrogen and nitrogen gas were produced as the byproduct without any CO or CO₂ emission. In this experiment, the ore were introduced as the medium for ammonia decomposition. The ore were put into quartz tube reactor and were dehydrated at 400°C for 1 hour, then hydrogen reduced for 2 hours before and undergone ammonia decomposition at 500-700°C for 3 hours. The effects of temperature to the % conversion of ammonia decomposition were also studied. Ammonia decomposition at higher temperature gives higher conversion. As seen in the results, the NH₃ conversion decreased with increasing time and the value after 3 hours of reaction increased in the sequence of 500°C < 600°C < 700°C. During ammonia decomposition, nitriding of iron occurred. The relation between temperature and the nitriding potential, K_N is also investigated. The purpose of this study is to investigate the utilization of low-grade ore as medium for ammonia decomposition to produce hydrogen.

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1. Introduction

Hydrogen is conventionally produced from fossil fuel either by steam reforming, methane cracking, and carbon dioxide decomposition methods¹. Conventional processes such as steam reforming, autothermal reforming and partial oxidation yield large amount of CO as a byproduct^{2, 3} which would cause problems of poisoning of the reforming catalyst². Studies in the generation of clean hydrogen have become recent interest in developing polyelectrolyte membrane fuel cells car for fuel cell application^{4, 5}. However, one of the main problems is of hydrogen supply. Some proposed ways to transport hydrogen are by using liquid hydrogen directly, hydrogen storage materials, or reformation of chemical hydrides such as hydrocarbon. Ammonia, NH_3 has drawn worldwide attention as hydrogen transportation medium⁶. The operated process produces no carbon monoxide, CO or carbon dioxide, CO_2 gasses however, nitrogen, N_2 gas is produced instead as the only co-product⁴. Primary iron resources in Malaysia, hematite, is expected to be in shortage in the near future. Low-grade iron ore is an attractive alternative domestic iron ore resource however it contains low Fe content, high amount of gangue material and combined water^{7, 8}. Since Malaysia has low-grade iron ore resources such as goethite, it could be utilized and become good alternative for iron resources through some treatment processes via dehydration of iron ore⁹. The removal of combined water via dehydration process would create pores within it and increased the surface area of ore. Ammonia decomposition with low-grade ore produced hydrogen and nitrogen. The nitriding of metal is also associated with the ammonia decomposition reaction. During ammonia decomposition, the ammonia gas will react with the iron ore at the iron surface, yielding hydrogen and nitrogen gasses to atmosphere. However, due to the surface reaction between ammonia gas and iron phase, it is necessary that the dissolution of nitrogen in iron phase occurs via the dissociation of ammonia at the surface, followed by the dissolution of nitrogen in iron and the formation of nitrogen gas to the atmosphere. The schematic diagram of ammonia decomposition process with ore is illustrated in Fig.1.

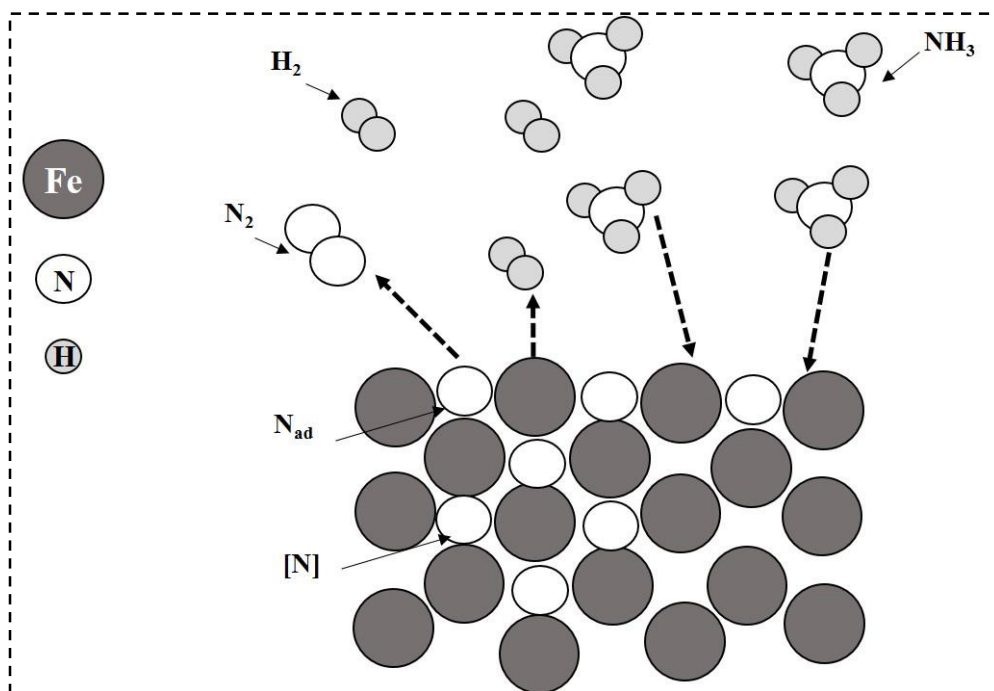


Fig. 1. Schematic diagram of ammonia decomposition process with iron ore

Nomenclature

N_{ad}	N adsorbed at the iron surface
[N]	Nitrogen that is dissolved in the iron surface
GC	Gas chromatography
HCL	Hydrochloric acid
XRD	X-ray diffraction
K_N	Nitriding potential

2. Experimental procedures*2.1. Iron ore samples and preparations*

Iron ore sample used for this experiment is taken from Tasik Chini area, Pahang state of Malaysia. The mineral composition of the ore exists is mainly in the form of goethite having FeOOH phase and iron content of 58.1% Fe with other gangue materials such as silica (0.8%), aluminum (1.3%), titanium (6.2%), mangan (0.4%) and calcium (0.3%) as impurities. The ore was crushed and sieved to obtain particle size below 106 μm . The ore was dehydrated at 400°C for 1 hour to obtain hematite phase. Then, the dehydrated ore was hydrogen reduced at temperature of 500°C for 2 hours. The hematite reagent of 99.999% purity was used as the reference sample in this experiment.

2.2. Ammonia decomposition

The ammonia decomposition experiment with iron ore is conducted in a quartz tube reactor. Ammonia decomposition took place succeeding the hydrogen reduction process at temperature of 500°C for 3 hours with the same heating rate during hydrogen reduction. The exhaust gas was analyzed using micro GC and the excess ammonia gas was flowed into HCL solution for dilution. This process was repeated by raising the temperatures to 600°C and 700°C to compare the effects of temperature to the ammonia conversions during ammonia decomposition. Conversion of NH_3 to N_2 can be estimated by using the amounts of NH_3 fed and N_2 formed on the assumption that NH_3 decomposition proceeds according to the following equation.

*2.3 Nitriding potential*

Iron nitridation is associated during ammonia decomposition. The nitrogen adsorption on the iron surface reaction can be expressed as the nitriding behavior. It can be estimated by the nitriding potential as defined as follows;

$$K_N = P_{\text{NH}_3} / P_{\text{H}_2}^{1/2} \quad (2)$$

Whereby P_{NH_3} and P_{H_2} are the partial pressures of the ammonia and hydrogen gases respectively. The nitriding potential of ore is calculated by gas analysis at temperature of 500-700°C to compare the nitridation behaviors of ore.

3. Results and discussions

3.1. Ammonia decomposition of ore

The results show ammonia conversion (%) during ammonia decomposition for temperature ranging from 500-700°C. The hematite reagent was used as the reference material in this study. The ammonia decomposition was found highest at temperature of 700°C for hematite reagent with almost 64% of ammonia decomposed as shown in Fig. 2. However, the decomposition at 700°C for ore from Chini area is slightly lower than the hematite reagent, having 58% of ammonia decomposed. Fig. 3 depicts the ammonia conversion (%) during ammonia decomposition at 600°C with a yield of 27% for hematite reagent and 19% of ammonia decomposed for ore from Chini area. Fig. 4 shows the decomposition of ammonia at 500°C with 2% of ammonia decomposition for hematite reagent and 4% of ammonia conversion for ore from Chini area. As seen in the results, the NH_3 conversion decreased with increasing time and the value after 3 hours of reaction increased in the sequence of 500°C < 600°C < 700°C.

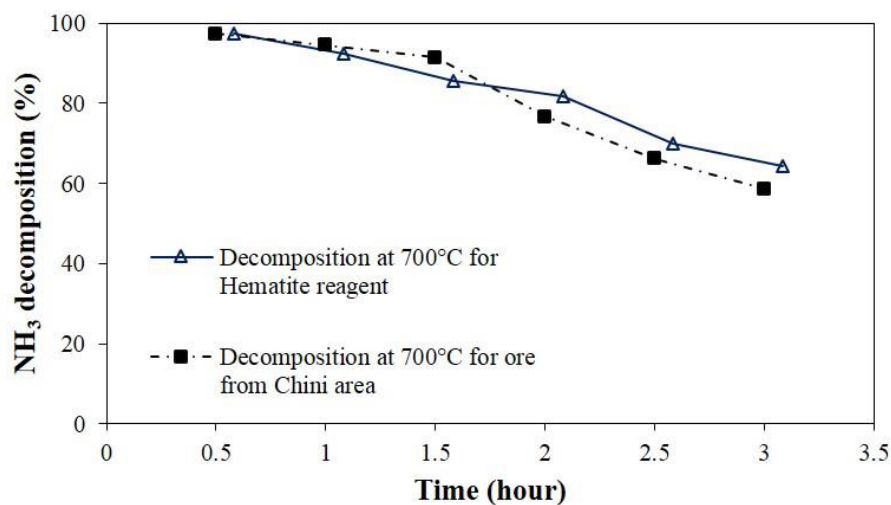


Fig. 2. Comparison of ore and hematite reagent for NH_3 decomposition (%) to N_2 at temperature of 700°C

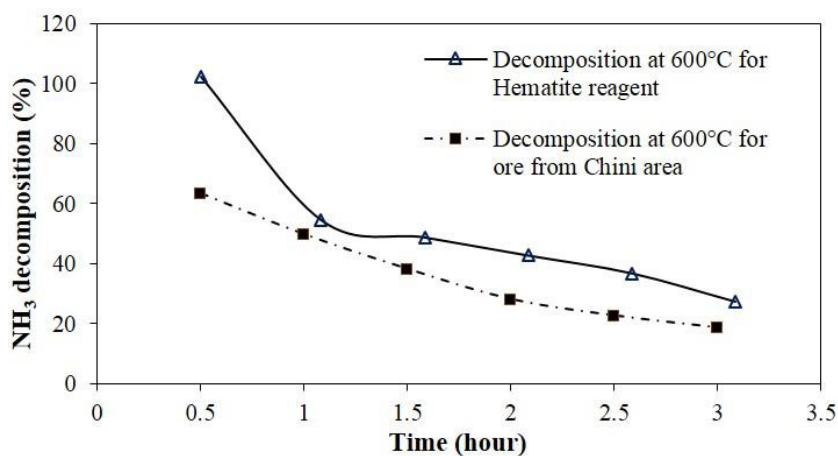


Fig. 3. Comparison of ore and hematite reagent for NH₃ decomposition (%) to N₂ at temperature of 600°C

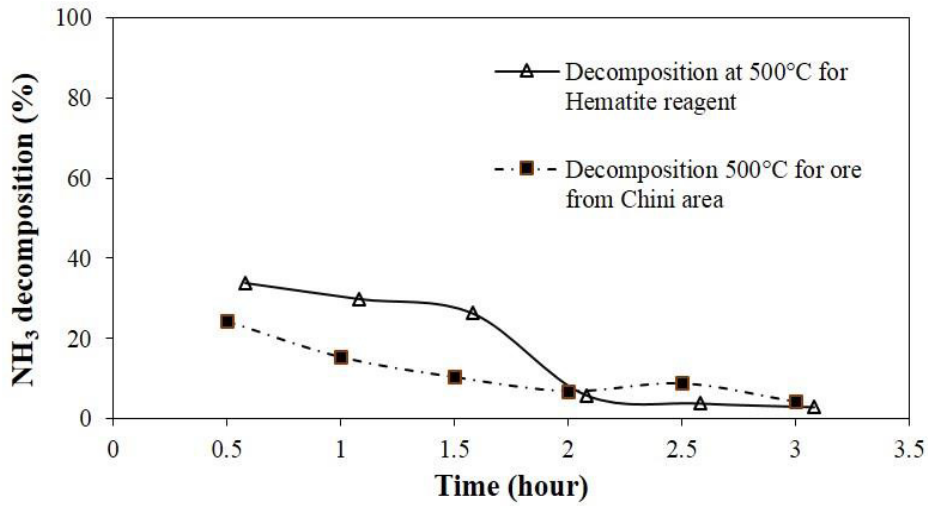


Fig. 4. Comparison of ore and hematite reagent for NH₃ decomposition (%) to N₂ at temperature of 500°C

3.2. Nitriding potential of ore

Figure 5 shows the comparison of nitriding potential of ore at different temperature of 500-700°C. Based on the results, ore decomposed at 500°C exhibit the highest nitriding potential, K_N followed by decomposed ore at 600°C and 700°C. Nitridation of iron is associated during ammonia decomposition. At lower temperature, the nitrogen absorption at the surface of iron is increased due to the high concentration of nitrogen on the surface thus formed iron nitrides. As the temperature is increased, the nitriding potential is decreased for the same reaction time. This might due to the formation of iron nitride took place at lower temperature compared to formation of iron nitride at higher temperature.

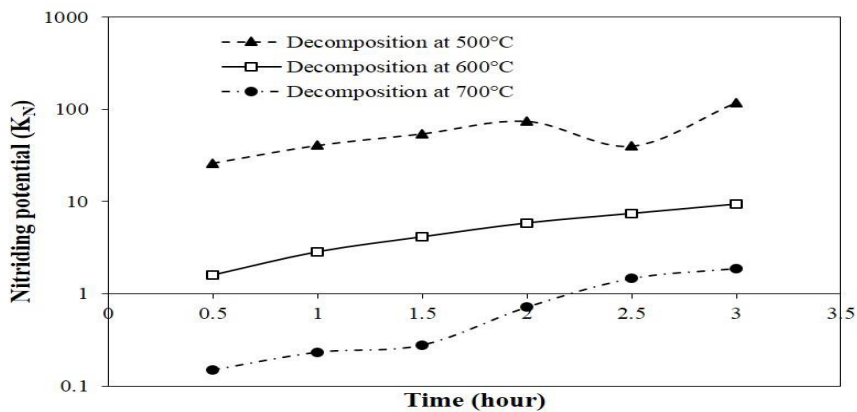


Fig. 5. Comparison of nitriding potential of ore at different temperature of 500-700°C

4. Conclusion

In conclusion, the ammonia conversion (%) to N_2 is increased as the temperature increased. At 700°C of reaction time, the conversion is up to 58%. Whilst, the nitriding of iron is associated during ammonia decomposition. Highest nitridation of iron occurred at reaction temperature of 500°C. These results indicate that the use of iron in ammonia decomposition would promote a higher conversion and the byproducts from the reaction are hydrogen, and nitrogen. Iron nitrides or metallic iron formed after reaction could be used in application such as in magnetic applications and steelmaking industries respectively.

Acknowledgements

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