



UTILIZATION OF MALAYSIAN LOW GRADE IRON ORE AS MEDIUM FOR AMMONIA DECOMPOSITION

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ABSTRACT

Hydrogen has been regarded as the new energy source due to its cleanliness, fast energy cycle and convenience of energy conversion. Hydrogen storage and transportation difficulties have become major drawbacks in hydrogen economy. Conventional process of steam reforming produces large amount of CO as byproduct. Thus, ammonia has attract worldwide attention as new alternative for hydrogen storage as ammonia decomposition yields H_2 and N_2 as byproduct without any CO emissions. Low grade ore is used as medium for enhancing ammonia decomposition. This paper presents the study of low-grade iron ore as medium for ammonia decomposition. Malaysian low-grade iron ore was taken as the raw material in this experiment. Ammonia decomposition over iron ore medium were studied at temperature of 500-700°C. The nitriding potential of ore was also studied.

Keywords: ammonia decomposition, hydrogen, low grade iron ore, ammonia conversions and nitriding potential.

INTRODUCTION

Ruthenium- based catalysts has been reported as the most active catalyst for ammonia decomposition so far due to it high conversion of NH_3 . However, due to its limited resources and high cost material, ruthenium catalyst becomes the obvious disadvantage especially for large scale applications. Ni- based catalyst is also widely used as catalyst; however, ammonia decomposition over Ni-catalyst requires operating temperature as high as 1000 °C [1]. In contrast, iron- based catalyst with availability and much lower cost demonstrates high reactivity of ammonia conversion at lower operating temperature. As stated by [2], they reported the use of limonite ore in catalytic ammonia decomposition for a hot gas clean up method. Earlier studies have also reported the used of ferrous dolomite and sintered iron ore were effective for decomposing a low concentration of NH_3 for ammonia decomposition at 900 °C [3]. Also, [4] reported that ammonia decomposition with hematite ore occurred at temperature of 430 °C which yield hydrogen and nitrogen. Ammonia had gained worldwide attention as new alternative for hydrogen transportation medium. Ammonia decomposition is endothermic process which produces hydrogen and nitrogen [4-5] with no CO emissions as byproduct [6]. This paper presents the study of low grade iron ore as medium for ammonia decomposition at temperature of 500-700 °C. The ammonia conversion to hydrogen and nitrogen were studied as well as the effect of temperature on the ammonia decomposition. Nitriding potential of ore were also investigated.

EXPERIMENTAL METHOD

The experiment was performed in a quartz tube reactor having internal diameter of 6 mm. Approximately 0.25 g of ore were charged into the fix bed reactor and

were dehydrated up to 400 °C and held for 1 hour with heating rate of 10 °C/min under nitrogen flow. Prior to ammonia decomposition, the dehydrated ore were then heated to 500 °C and then treated with H_2 reduction for 2 hours to enhance the catalytic performance of ore. The hydrogen flow was stopped after constant flow of gas for 2 hours had been achieved. Then, before subjected to NH_3 decomposition, the N_2 flow in the reactor was restored to into nitrogen flow for 5 to 10 minutes to remove the excess hydrogen in the reactor. Decomposition of NH_3 over ores was conducted under pure NH_3 flow for 3 hours. The gas product were analysed using online micro GC while the mineral composition and characterization were performed using the XRD measurement and SEM analysis. 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.

RESULTS AND DISCUSSIONS

The low grade ore used in this present study which was taken from Chini area from Pahang state Malaysia was employed as the raw material. Mineral composition of the original ore consists of iron oxide species of 58.1% with the existence of other gangue minerals such as alumina, silica, mangan oxide, calcium, vanadium and titanium are shown as tabulated in Table-1. Ammonia decomposition using low grade iron ore as medium took place in an 8mm fixed bed reactor. The iron ore was introduced into quartz tube and dehydrated at 400 °C. Dehydration of iron ore was conduct to remove the combine water present in the original ore. Thermal gravimetry analysis (TGA) was used to analyse the change in weight loss of original iron ore during dehydration process as shown in Figure-1. The total weight loss for



iron ore is 8%. From the graph, it can be observed that decomposition starts at temperature of 200 °C. Continuous weight loss were observed in the temperature range of 200-400 °C. The total weight loss indicates the high combine water presence in the ore.

Table-1. Mineral composition of iron ore.

Source of Iron ore	Fe	Si	Al	S	Mn	V	Ti	Ca
Chini (Pahang)	58.1	0.8	1.3	0.2	0.4	0.5	6.2	0.3

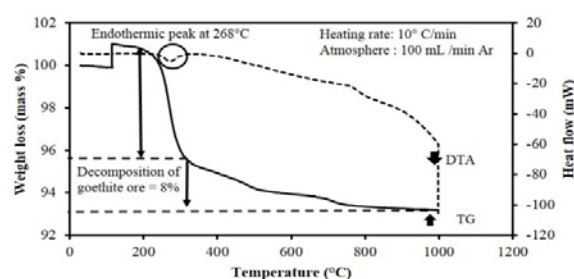


Figure-1. Thermal analysis of original iron ore.

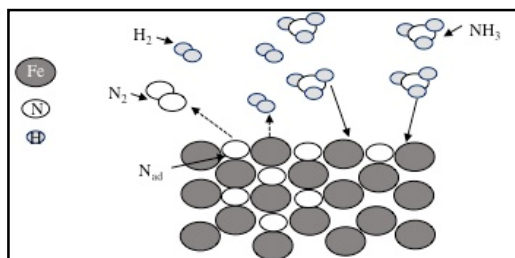


Figure-2. Mechanism during ammonia decomposition.

Figure-2 illustrates the mechanism during ammonia decomposition. NH_3 gas will come in contact with the medium (iron) thus, decomposed into hydrogen and nitrogen gas. Nitrogen adsorption, N_{ad} happened when the nitrogen concentration $[\text{N}]$ is higher at the surface of the iron ore thus forms iron nitride phase. Figure-3 shows the ammonia decomposition into hydrogen and nitrogen using iron ore as medium at temperature of 500 °C -700 °C. The graph shows that as time increased, the ammonia conversion decreased indicating decomposition of ammonia. At 700 °C, the ammonia conversion reaches 63% of ammonia decomposed, followed by ammonia conversion at 600 °C for 30% decomposed. At 500 °C, the conversion reaches 6%. These results show that at higher temperature, the ammonia conversion into hydrogen and nitrogen is prominent compared to ammonia conversion at lower temperature.

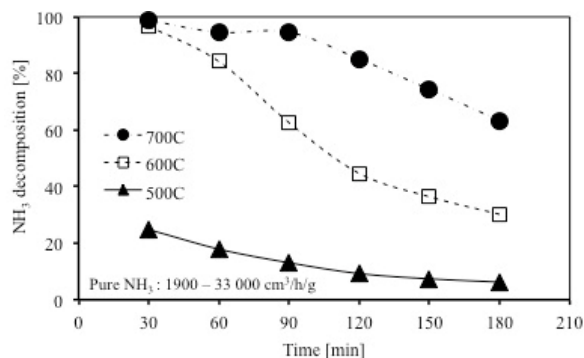


Figure-3. Ammonia decomposition using ore as medium at 500 °C -700 °C.

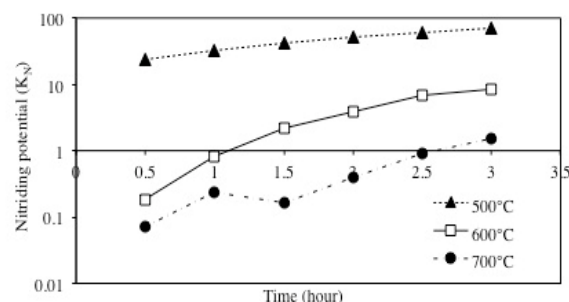


Figure-4. Nitriding potential of ore at 500 °C -700 °C.

CONCLUSIONS

Figure-4 shows the nitriding potential of ore at 500 °C -700 °C. Decomposition of ammonia is associated with the nitriding of iron on the surface of the ore. This would result in the formation of iron nitride phase. As the operating temperature during ammonia decomposition is lower, the nitriding potential is higher. This is due to the higher concentration of nitrogen on the surface of ore during low temperature operation, which contributes to the formation of iron nitride.

REFERENCES

- [1] S. F. Yin, B. Q. Xu, X. P. Zhou, and C. T. Au. 2004. A mini-review on ammonia decomposition catalysts for on-site generation of hydrogen for fuel cell applications. *Journal of Applied Catalysis A: General*. 277: 1-9.
- [2] N. Tsubouchi, H. Hashimoto, and Y. Ohtsuka. 2005. High catalytic performance of fine particles of metallic iron formed from limonite in the decomposition of a low concentration of ammonia. *Journal of Catalysis Letters*. 105: 203-207.



- [3] C. Xu, N. Tsubouchi, H. Hashimoto, and Y. Otsuka. 2005. Catalytic decomposition of ammonia gas with metal cations present naturally in low rank coals. *Journal of Fuel*. 84: 1957-1967.
- [4] S. Hosokai, Y. Kashiwaya, K. Matsui, N. Okinaka, T. Akiyama. 2011. Ironmaking with ammonia at low temperature. *Journal of Environmental Science and Technology*. 45: 821-826.
- [5] M. Itoh, M. Masuda, K. Machida. 2002. Hydrogen generation by ammonia cracking with iron metal-rare earth oxide composite catalyst. *Journal of Materials Transaction*. 43: 2763-2767.
- [6] T.V. Choudhary, C. Sivadinarayan, D.W. Goodman. 2001. Catalytic ammonia decomposition: CO_x-free hydrogen production for fuel cell applications. *Journal of Catalysis Letters*. 72: 197-201.