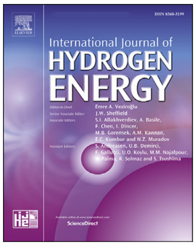
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



N-desorption or NH_3 generation of TiO_2-loaded Al-based nitrogen carrier during chemical looping ammonia generation technology

Yuan Gao [a,b], Ye Wu [a,b,*], Quan Zhang [a,b], Xiaoping Chen [c], Guodong Jiang [d], Dong Liu [a,b]

[a] MIIT Key Laboratory of Thermal Control of Electronic Equipment, School of Power Engineering, Nanjing University of Science & Technology, Jiangsu, 210094, China

[b] Advanced Combustion Laboratory, School of Energy and Power Engineering, Nanjing University of Science and Technology, Nanjing, 210094, Jiangsu, China

[c] Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing, 210096, Jiangsu, China

[d] College of Materials Science and Engineering, Nanjing Technology University, Nanjing, 210009, Jiangsu, China

ARTICLE INFO

Article history:
Received 31 May 2018
Received in revised form
29 June 2018
Accepted 9 July 2018
Available online xxx

Keywords:
NH_3
Chemical looping ammonia generation (CLAG)
N-desorption reaction
TiO_2

ABSTRACT

As a terrific hydrogen carrier, NH_3 can be wildly used as non-carbon gas fuel in energy area, because NH_3 can store a high density of H_2 and can be liquefied easily in ambient temperature and pressure. Chemical Looping Ammonia Generation (CLAG) is known to be a novel, efficient and environmentally friendly synthesis method for ammonia, in which the N-sorption/desorption of nitrogen carrier are included. The N-sorption step, which is known as the carbothermal reduction, is well studied while there are few reports on N-desorption step. Therefore, in this paper, stationary bed reactor and thermo-gravimetric analyzer (TGA) were used to study the N-desorption performance of the TiO_2-loaded Al-based N-carrier and the corresponding NH_3 generation during the N-desorption reaction. The results showed that, TiO_2 performed a good catalytic effect on the N-desorption reaction, which is due to the good dissociative adsorption performance of H_2O on TiO_2 surface, and the released hydroxyl (OH−) plays an important role in the N-desorption reaction. The conversion amount of aluminum nitride and the yield of NH_3 increased with the TiO_2 loading in the reactants, the reaction temperatures and the steam concentrations in the atmosphere, while the conversion efficiency of NH_3, which is significantly affected by temperature, didn't affected by the TiO_2 loadings.

Introduction

Ammonia (NH_3) is a promising hydrogen carrier [1,2] because NH_3 is easy to be liquefied in ambient temperature and pressure [3,4], which is beneficial to the storage and transformation of hydrogen as well as the energy containing [5,6] and so on. Also, NH_3 is an important raw material for chemicals in industrial and civil applications and wildly used to

---

* *Corresponding author*. MIIT Key Laboratory of Thermal Control of Electronic Equipment, School of Power Engineering, Nanjing University of Science & Technology, Xiaolingwei road No. 200, Jiangsu, 210094, China.
E-mail address: ywu@njust.edu.cn (Y. Wu).

https://doi.org/10.1016/j.ijhydene.2018.07.042

Please cite this article in press as: Gao Y, et al., N-desorption or NH_3 generation of TiO_2-loaded Al-based nitrogen carrier during chemical looping ammonia generation technology, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.07.042

synthesize explosive [7], chemical fertilizer [8,9], refrigerant [10], and medicine [11] and so on. Actually, the energy density of NH_3 is high, and the combustion products are water and nitrogen (in the absence of catalysts and pure oxygen), which have no harm to the environment. The combustion reaction is [4,12]:

$$NH_3 + \frac{3}{4}O_2 \rightarrow \frac{3}{2}H_2O + \frac{1}{2}N_2 \quad \Delta H^{\theta}_{298} = -317.5\ \text{kJ/mol} \qquad \text{R1}$$

Also, compared with H_2, a widely accepted clean energy, the energy density of NH_3 is higher (about 1.5 times that of H_2) [13]. Therefore, NH_3 could be regarded as a hydrogen carrier or a promising clean fuel and the corresponding synthetic technique needs to be further developed [14,15].

Nowadays, global production of NH_3 is about 130 million metric tons annually, and more than 90% of the world's ammonia are synthetized with the Haber–Bosch synthesis (HBS) process [13,16]. The reaction is shown as below:

$$N_2 + 3H_2 \xleftrightarrow{\text{catalyst}} 2NH_3 \qquad \text{R2}$$

Intensive studies were reported about the HBS process and various catalysts were used to reduce the energy barrier to fracture the N–N bonds, which is the speed control step of HBS [17–19]. In order to further improve HBS, Aziz M et al. integrate NH_3 synthesis with N_2 production to maximize the energy efficiency [6]. However, due to the limitation of the unfavorable thermodynamic equilibrium of NH_3, the conversion efficiency per pass of NH_3 in HBS is only around 25%–30% [20]. Accordingly, people are trying to find a better method to synthesis NH_3 with a higher NH_3 yield. Ankur J et al. found NH_3 could be produced easily through hydrolysis of metal nitrides while the metal nitrides could be reproduced to make a close cycle [19]. Based on this situation, a two-stage thermochemical process or chemical looping ammonia generation (CLAG) was proposed to decrease the cost needed for NH_3 production [20,21], and it consists of two reactions:

$$3C + N_2 + Al_2O_3 \xrightarrow{>1300^{o}C,k_{R3},K_{R3}} 2AlN + 3CO \quad \Delta H^{\theta}_{25^{\circ}C} = 708.1\text{kJ/mol} \qquad \text{R3}$$

$$2AlN + 3H_2O \xrightarrow{>900^{o}C,k_{R4},K_{R4}} Al_2O_3 + 2NH_3 \quad \Delta H^{\theta}_{25^{\circ}C} = -274.1\text{kJ/mol} \qquad \text{R4}$$

where R3 is N-sorption step or carbothermal reduction [22–25], R4 is N-desorption step. Compared with HBS, the source of raw materials (coal and N_2) for CLAG is extensive, and the raw material utilization efficiency of CLAG is higher.

Intensive studies including influence of the carbon agent and catalysts have been well reported to decrease the synthesis temperature and increase the AlN conversion of R3 [23–27]. For example, Forslund B et al. found AlN can be converted from Al_2O_3 in graphite furnace with flowing nitrogen gas between 1200 °C and 1500 °C using powder mixture with Al_2O_3:C molar ratio of 1:3 [24,25]. The structure and existing form of Al_2O_3 affect its reactivity in R3, while the reactivity of Al_2O_3 is of the order of γ-$Al_2O_3 > Al(OH)_3 > \alpha$-$Al_2O_3$ [26]. In order to further increase the yield of AlN and lower the reaction temperature, several catalysts, such as CaF_2, Y_2O_3 and Na_2CO_3, were added to the compound [23,27]. However, there are few reports on how to enhance the N-desorption reaction or R4 because AlN is widely used as ceramic material and semiconductor and the mechanisms of R4 are intensively studied to inhibit the hydrolysis of AlN or promote the stability of AlN (R4). C.J. Bartel et al. reported that the fracture of the Al–N bonds is the speed control step of N-desorption reaction and the reduction of hydroxyl (OH^-) on the AlN surface can well increase the activation energy of N-desorption reaction or inhibit the hydrolysis of AlN [28]. So, the addition of hydroxyl on the AlN surface is supposed to enhance the reaction kinetics of R4. How to increase the hydroxyl on the AlN surface is considered in our researches. Our previous studies found that Fe_2O_3 is a good catalyst to decompose H_2O and enhance R4 by reducing the activation energy by 30% [20]. However, the yield of NH_3 is low because Fe_2O_3 also promotes the decomposition of NH_3. Therefore, other kinds of catalyst should be used to accelerate R4. In fact, it has wildly reported that TiO_2 performs an excellent H_2O dissociative adsorption ability to release hydroxyl. For example, Zhao W et al. found H_2O is easy to be captured on TiO_2 surface [29]. Furthermore, density functional theory (DFT) also shows H_2O is easy to be dissociated on the TiO_2 (1 0 0) surface [30,31]. The reaction is shown as R5:

$$TiO_2 + H_2O \leftrightarrow TiO(OH)^{+} + OH^{-} \qquad \text{R5}$$

Based on this situation, we tried to use TiO_2 as a catalyst to enhance the N-desorption reaction and NH_3 generation. The results in our work show it really performs a good catalytic property. In this paper, N-desorption performances of AlN under different conditions including reaction temperatures, TiO_2 loadings and steam concentrations were studied with stationary bed reactor and thermo-gravimetric analyzer (TGA). Also, characterization methods, such as The X-ray diffraction (XRD), Scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS) were used to evaluate the catalyst.

Materials and methods

Sample preparation and characterization

The aluminum nitride (AlN) powder was obtained from Advanced Technology & Materials Co. Ltd. (N>32.5%, 2 μm of partial size), and the titanium dioxide (TiO_2) powder was obtained from Sinopharm Chemical Reagent Co., Ltd (purity>99.0%). Considering the impurity of TiO_2 and the N-desorption reaction temperature is over 800 °C, the fresh TiO_2 powder was calcined under the atmosphere of Ar at 900 °C for 1 h to remove the water and volatiles in the powder. After that, each sample was prepared by mixing predetermined amounts of AlN and TiO_2 in a mortar and grinded for 30 min, the resulting powder is the TiO_2-loaded AlN sample (hereafter called "TAN sample"). Target weight percentages were 20, 40, 50, 60, 70, 80 wt % of TiO_2 in samples and the corresponding names are 20 wt % of TAN, 40 wt % of TAN, 50 wt % of TAN, 60 wt % of TAN, 70 wt % of TAN and 80 wt % of TAN respectively. XRD data for mixed sample before and after reaction

Please cite this article in press as: Gao Y, et al., N-desorption or NH_3 generation of TiO_2-loaded Al-based nitrogen carrier during chemical looping ammonia generation technology, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.07.042