Full Length Article

Investigation of ammonia removal from the simulated producer gas of biomass gasification by H_2-reduced titanomagnetite

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ABSTRACT

Catalytic removal of NH_3 by both unprocessed and H_2-reduced titanomagnetites ($Fe_{2.9}Ti_{0.1}O_4$) from two gases has been experimentally investigated in a lab-scale fluidised bed reactor. The test gases include Ar gas as control and simulated producer gas from biomass steam gasification (H_2, CO, CO_2 and CH_4). In the test gases, the NH_3 concentration was 2300 ± 100 ppmv and the operation temperatures were varied from 500 to 850 °C.

The experimental results show that in the control Ar gas, the H_2-reduced titanomagnetite had much higher activity than the unprocessed titanomagnetite to decompose NH_3 at all of the temperatures tested, and the efficiency of NH_3 removal increased with reaction temperature. The NH_3 decomposition by the reduced titanomagnetite was 97.8% at 500 °C, 99.7% at 600 °C, and 100% at 750 and 850 °C, in comparison with corresponding values of 31.6%, 34.0%, 83.9% and 93.2% for the unprocessed titanomagnetite. Therefore, the H_2-reduced titanomagnetite was then employed to remove NH_3 in the simulated producer gas in which the NH_3 decomposition was $28.4 \pm 3.4\%$, $94.7 \pm 2.8\%$ and $98.4 \pm 0.4\%$, respectively, at 500, 750 and 850 °C. In NH_3 decomposition in the simulated gas, side reactions have been identified and analysed which played different roles at different temperatures and also affected the gas composition. At 500 °C, the carbon formation from the Boudouard reaction significantly suppressed the activity of the reduced titanomagnetite for NH_3 decomposition.

1. Introduction

The producer gas from steam biomass gasification mainly consists of H_2, CO, CO_2 and CH_4 which can be used for power generation, synthesis of liquid fuel, pure hydrogen or chemicals. However, undesirable contaminants are also present in the producer gas including particles and alkalis, tars, N-containing compounds (NH_3 and HCN), S-containing compounds (H_2S and COS) and chlorine (HCl) [1]. The contaminants severely impact the applications of the producer gas, therefore, these contaminants must be decomposed or removed stringently to acceptable concentration levels to meet the downstream application requirements.

Concentrations of N-containing compounds in the producer gas are strongly dependent on the N content in the feedstock, gasifier type and gasification operating conditions [2,3]. It has been found that 60–80% of nitrogen in the feedstock was liberated as ammonia which is the major N-containing compound and the primary gaseous contaminant in the producer gas of biomass gasification [4]. It is also reported that the NH_3 concentration ranges from 100 to 5000 ppmv in the producer gas of woody biomass gasification but, in most cases, the NH_3 concentration

is lower than 2300 ppmv [2,3,5,6]. Ammonia is known as the toxin for catalysts used in downstream processes and the precursor of NO_x when oxidation process occurs [7]. However, when the producer gas is used for power generation, chemical synthesis and liquid fuel production, the concentration of ammonia in the producer gas should meet stringent specifications which are shown in Table 1.

To remove NH_3 in the producer gas of biomass gasification, both physical and chemical methods can be used. Among the physical methods, wet scrubber is the most attractive method and has been investigated extensively, from which different NH_3 removal efficiencies have been reported. Boerrigter et al. [10] reported that a water scrubber following the "OLGA" system had NH_3 removal efficiency of 99.3% which reduced the NH_3 concentration from 1304 to 8.5 ppmv. Pino et al. [11] used a scrubber system to cool down the producer gas and, at the same time, to remove NH_3 in the producer gas using the condensed water, and they found that the NH_3 removal efficiency could be higher than 90%. Loipersböck et al. [12] also found that a biodiesel scrubber at low temperatures with assistance of condensed water from the producer gas from a DFB steam blown gasifier had a remarkable capacity to absorb NH_3 in the producer gas with removal efficiency of

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Downstream application	NH$_3$ concentration requirement (ppmv)	Reference
Gas turbine	< 50	[3]
Methanol synthesis	< 10	[8]
Fischer-Tropsch (FT) process	< 1	[9]

99.7%. However, in a separate study by Pröll et al. [13], only 50% of 500 ppmv NH$_3$ in the producer gas of biomass gasification was removed by using a wet scrubber using mixture of an organic solvent with condensed water from the same producer gas. In the study of Pröll et al. [13], when the NH$_3$ concentration was increased to 2000 ppmv, the NH$_3$ removal efficiency was reduced to 30%. The wet scrubber method has disadvantages of waste solution generation and low NH$_3$ removal efficiency if the inlet NH$_3$ concentration was high [14]. Therefore, an alternative hot-catalytic method was investigated in this research.

Catalytic hot-gas cleaning technology is an effective method for ammonia removal in biomass gasification. Its advantages include low energy consumption, high NH$_3$ removal efficiency, and no waste liquid being generated and effective processes available for catalyst regeneration. In previous studies, some commonly used catalysts have been tested for ammonia removal, and it is reported that alkaline earth metal oxides such as limestone and dolomite showed high activity to remove ammonia in an inert gas [2,15,16]. However, these catalysts are easily deactivated when species of producer gas are present such as H$_2$, CO, CO$_2$ and CH$_4$ [15,17,18]. Fe-based catalysts, such as iron sinter, ferrous dolomite, limonite and magnetite, have attracted increasing attention in the past decades because of their desirable performance and low cost. Tsubouchi et al. [19] reported that reduced limonite (α-FeOOH) showed effective NH$_3$ removal in helium gas (99.9% NH$_3$) at 500 °C. However, its NH$_3$ removal efficiency was reduced by the presence of CO and H$_2$ [20] or H$_2$S [21] which were resulted from carbon deposition through the Boudouard reaction, equilibrium reduction and sulphur poisoning. On the other hand, Tsubouchi et al. [19], in the subsequent studies, found that addition of CO$_2$ and H$_2$O on the syngas (CO and H$_2$ mixture) improved the catalytic performance by reducing the carbon deposition. For further improvement of the NH$_3$ removal, the limonite was reformed by adding 3 wt% Mg on the catalyst, which showed significant increase in efficiency and stability for NH$_3$ removal [22]. In a separate study at a 5 MW updraft gasifier, Leppälahti et al. [23] found that iron based materials (ferrous dolomite, iron sinter and iron pellet) showed that the NH$_3$ removal efficiency of these catalytic materials was higher than dolomite and limestone but lower than commercial Ni-based catalysts.

Ni-based catalysts were also investigated because of its high capability of removing tar and NH$_3$ simultaneously. A catalyst named Ni-3, which is composed of 4.0 wt% NiO, 14.3 wt% MoO$_3$ and Al$_2$O$_3$, showed high efficiency to remove NH$_3$ and model tar compound of 1-Methylnaphthalene [24]. Ozawa et al. [25] also found that the Ni-based catalyst supported on ZSM-5 had high efficiency and selectivity to decompose NH$_3$ as well as the ability to inhibit carbon formation at temperature of 250–400 °C. Similar results have been reported by Simell et al. [26] who found that the Ni-based catalyst decomposed tar and NH$_3$ effectively from the biomass gasification producer gas at operation conditions of 900 °C and 5 bar with residence time of 1 s. At these conditions, carbon deposition and sulphur poisoning were prevented. Mojtahedi and Abbasian [27] found that the NH$_3$ removal efficiency by Ni-based catalysts was strongly dependent on the Ni content, and the catalysts with high Ni content could effectively decompose NH$_3$ in the simulated producer gas consisting of CO, CO$_2$, CH$_4$, H$_2$, H$_2$O and N$_2$. However, the Ni-based catalysts are expensive, which is the key barrier for their commercial applications.

Previous study by Hongrapipat et al. [23] investigated the performance of Fe-based catalyst, named titanomagnetite, in decomposition of NH$_3$ in Ar gas which showed high efficiency for NH$_3$ removal. Titanomagnetite is cheap and can be found in natural form, therefore, it has promising future in commercial applications. However, its performance in the simulated producer gas and the effects of the gas composition are unknown. The objective of this research aims to investigate the NH$_3$ removal efficiency of titanomagnetite both in the original form and in the reduced form in an inert gas, Ar, and then to investigate the performance of the selected titanomagnetite in simulated producer gas from biomass gasification. Influence of producer gas composition will also be examined and possible reactions in the NH$_3$ removal will be explored.

2. Materials and methods

2.1. Catalyst material and preparation

Fe-based sand, namely titanomagnetite, was purchased from a local supplier in New Zealand and used as the catalyst in the experiments. The composition of titanomagnetite was determined using X-ray Fluorescence (XRF) analyser, which was found to contain 86.2 wt% Fe$_2$O$_3$, 7.4 wt% TiO$_2$, 3.5 wt% Al$_2$O$_3$, 2.7 wt% MgO and 1.7 wt% SiO$_2$. The BET surface area, BJH, as well as sorption cumulative pore volume and average pore diameter of the titanomagnetite were also measured which values are, respectively, 1.1 m^2/g, 0.002 cm^3/g and 10.6 nm. Particle density and bulk density of the titanomagnetite are 4540 and 2810 kg/m^3. Other properties of the titanomagnetite can be found elsewhere [28]. After being received, the unprocessed titanomagnetite was sieved to size range of 180–250 μm and was then dried in an oven at 105 °C for 2 h. Separate titanomagnetite samples in the same size range were reduced at 810 °C in a gas mixture of 36.5 vol.% H$_2$ in Ar gas for 6 h for further tests.

2.2. Gases

Pure industry grade Ar gas and simulated producer gas were tested in this study in which NH$_3$ was introduced at controlled low flow rate based on required NH$_3$ concentration of 2300 ± 100 ppmv in all of the test gases. In practical gasification of woody biomass, NH$_3$ concentrations in most of producer gases are lower than 2300 ppmv, therefore, the selected NH$_3$ concentration in this research represents the worst case [29].

The simulated producer gas was purchased from the BOC group, Australia, and its composition was 18.9 ± 0.4 vol.% CO, 19.1 ± 0.4 vol.% CO$_2$, 14.4 ± 0.3 vol.% CH$_4$ and 47.6 ± 0.4 vol.% H$_2$. This composition was chosen based on reported studies by this research group on biomass steam gasification on a dual fluidised bed (DFB) gasifier [30,31], and this was also close to that from other studies although it was affected by operation conditions and application of catalytic bed materials [12,13,32,33].

2.3. Equipment setup

The hot catalytic gas cleaning system used in this study is shown in Fig. 1 in which a vertical quartz tube placed in the centre of a furnace was used as the fluidized reactor for NH$_3$ removal study. Dimensions of the reactor are 40 mm in inner diameter and 815 mm in length. A Lenton tube furnace was used to provide heat and control the temperature inside the reactor. For each run, Ar gas was firstly introduced to pre-heat the reactor with the temperature ramping rate of 10 °C/min until the target temperature was reached. After this the Ar gas was switched off (except that Ar was used as test gas), test gas as well as NH$_3$ containing gas were switched on and introduced into the reactor. In each run, 100 g dried titanomagnetite was directly applied to the quartz tube as a bubbling fluidised bed reactor and the bed depth at static state was 28.3 mm.