

The influence of Ni load and support material on catalysts for the selective catalytic oxidation of ammonia in gasified biomass

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Abstract

The effect of nickel (Ni) load (0, 5 and 10 wt.%) and support material ($\text{Ce}_{0.9}\text{La}_{0.1}\text{O}_2$, $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ and $\gamma\text{-Al}_2\text{O}_3$), together the amount of oxygen ($\lambda = 0.25$ and $\lambda = 0.5$) and gas hourly space velocity (50 000, 100 000 and 150 000 h^{-1}) were investigated for the selective catalytic oxidation of ammonia in gasified biomass. The mixed metal oxide support materials were prepared by microemulsion, whereas the alumina was a commercial product. Ni was added to the different supports by incipient wetness. All the obtained catalysts were characterised by BET and XRD analysis. Cordierite monoliths coated with 20 wt.% catalytic material were tested in a tubular quartz reactor. For simulating the gasified biomass fuel, 500 ppm of NH_3 was added to the fuel. Water was also present during the activity tests, which were carried out between 500 and 750 °C.

The results from the activity tests at $\lambda = 0.25$ and gas hourly space velocity of 100 000 h^{-1} indicated that the 10 wt.% Ni on $\text{Ce}_{0.9}\text{La}_{0.1}\text{O}_2$ was the best catalyst obtaining 65 and 97% N_2 yield at 500 and 750 °C, respectively. By increasing λ to 0.5 and decreasing the gas hourly space velocity, the N_2 yield improved considerably at low temperature level (500 °C). Moreover, NO_x emissions maintained at low levels depending on the experimental conditions. Constant conversion and negligible carbon deposition were also two other important observations from the mixed metal oxide supported catalysts. On the contrary, all the alumina-based catalysts displayed the lowest performance.

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Keywords: Selective catalytic oxidation; Biomass; Microemulsion; Mixed metal oxides; Nitrogen yield; Lambda; Gas hourly space velocity

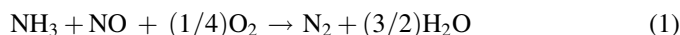
1. Introduction

The continuously increase of fossil fuel consumption in order to fulfil the growing energy demand has led to an emerging interest in the use of renewable energy sources for power production. Additionally, strict environmental legislation which control all the emissions such as NO_x , CO and hydrocarbons, has contributed to the development of catalytic combustion as a very promising technology for power production with potential of achieving ultra-low emissions [1,2].

Biomass is an abundant renewable energy source, and its gasification is an environmentally attractive fuel that can be used for energy production, for example in a gas turbine cycle. The main components of gasification gas are CO, H_2 , CO_2 , CH_4 and H_2O . In case of air used as an oxidising agent, N_2 is also

present. Biomass-derived gasification gas also contains harmful components from the gasifier, such as tar (polyaromatic hydrocarbons), solid particles, char, nitrogen- and sulphur-bound compounds [3], which need to be removed from the fuel. Particularly, the nitrogen-containing compounds are responsible for fuel- NO_x formation.

Nowadays, most large-scale combustion plants use the selective catalytic reduction (SCR) process to reduce the already-formed NO_x from the combustion process. According to this technology, ammonia is added to the exhaust gases as a reductive component in order to form nitrogen, with the overall reaction:

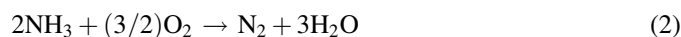


One the other hand, various technologies have been applied in order to treat the fuel at an early stage, before entering the gas turbine cycle. Catalytic decomposition of NH_3 at high temperature and pressure [4] is one technique that is often used. Additionally, catalytic combustion could offer the unique opportunity to directly selectively oxidise the fuel-bound

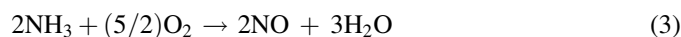
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nitrogen (mainly NH_3) into N_2 [5] according the following reaction:



This process is well-known as the selective catalytic oxidation (SCO) of ammonia to nitrogen. However, attention is necessary since the fact that if the catalyst is too strongly oxidising, NO will easily be formed through the reaction:



It is beneficial for the overall thermal efficiency of the process to operate the SCO at a temperature approximately as high as the temperature of the gas leaving the gasifier. This means that it would have been a great advantage to use catalysts that can cope at temperatures as high as 800–900 °C for energy conservation purposes. For that reason, a lot of research is focused on the development of high performance catalysts at these high temperatures, which is the key issue in the process.

Alumina-based catalysts have been extensively tested [6–8] over the past years for the SCO of ammonia. A variety of transition metals such as Ni, Mn, Fe, Cu, including some noble metals (Pt, Ru or Ag) have been supported on alumina (mainly $\gamma\text{-Al}_2\text{O}_3$) at different compositions and the catalysts have been tested mainly at limited temperature range (200–600 °C), at fuel-rich conditions and with space velocities between 61 000 and 250 000 h^{-1} . So far N_2 yield obtained from these tests ranges between 82 and 98%. However, it is commonly observed that selectivity to N_2 decreases with increasing temperature.

SCO performance (activity, selectivity and durability) has been also studied using zeolites as catalysts [9–13], such as Fe-exchanged ZSM-5 (Fe-ZSM-5), Cu-ZSM-5, Pd-ZSM-5, Pt-ZSM-5 and Ru-ZSM-5. The N_2 yield observed was very high (89–99%) and it was obtained at fuel-rich conditions, low temperatures (250–450 °C) and very high space velocities (230 000 h^{-1}). Particularly, Fe-ZSM-5 catalysts are favourable among all the zeolite catalysts for operations with low ammonia concentration and low space velocity. Long and Yang [9,10] have observed though that the activity of the zeolite catalysts is limited usually by the high content of water in the fuel which results in decrease of ammonia conversion, comparing to dry fuel.

A third group of catalysts used to investigate the SCO of ammonia to N_2 is mixed metal oxides, containing Fe, Ni, Cu and Co at various compositions and tested at different conditions [14]. Cerium and zirconium oxides have been reported to be promising supports as well for other catalytic oxidation processes, such as partial catalytic oxidation of methane under fuel-rich conditions, due to the high O_2 mobility that they promote [15]. In addition, previous work [16] has shown that Ni catalysts supported on cerium–lanthanum oxide reached 98% ammonia conversion and 99% N_2 selectivity at 750 °C. Additionally, Ni supported on alumina were the most active at 550–650 °C in excess oxygen, with selectivity to N_2 exceeding 90% [6].

In this paper we are focused on the synthesis and activity tests of Ni catalysts supported on three materials for the SCO of ammonia in gasified biomass. The aim of this work is to

investigate the effect of Ni load and the nature of the support (mixed oxides and alumina) on the SCO of ammonia in gasified biomass under fuel-rich environment, i.e. before the gasified biomass would enter the fuel–air mixing section in a catalytic combustion gas turbine.

Furthermore, the influence of the reaction conditions, such as air-to-fuel ratio (λ) and gas hourly space velocity is also investigated. For this study, Ni is supported on cerium–lanthanum, cerium–zirconium and γ -alumina. Based on the promising results previously achieved [16], the mixed oxide supports are synthesised by precipitation in water-in-oil (w/o) microemulsion (ME) and the Ni is added on all the supports by incipient wetness impregnation (IW).

The activity tests are carried out between 500 and 750 °C, testing two different lambda values, i.e. 0.25 and 0.5. Space velocity is also changed from low (50 000 h^{-1}) to medium (100 000 h^{-1}) and high (150 000 h^{-1}). All the tests are carried out under atmospheric pressure. The catalytic activity is determined using simulated gasified biomass as a fuel in presence of water. Moreover, monoliths (honeycomb) are used to all the tests in order to approach the SCO of ammonia under realistic conditions.

2. Experimental

2.1. Catalyst preparation

2.1.1. Co-precipitation in ME and IW

Three different catalyst support materials were synthesised; the two mixed metal oxides supports, $\text{Ce}_{0.9}\text{La}_{0.1}\text{O}_2$ and $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ were prepared from microemulsion (ME) and γ -alumina ($\gamma\text{-Al}_2\text{O}_3$) was supplied by SASOL Germany GmbH (Puralox hp-14/150).

Synthesis by co-precipitation in water is carried out by adding an aqueous solutions of Ce, La and Zr nitrates to another aqueous solution which contains the precipitating agent (e.g. ammonia). As a result, Ce, La and Zr form insoluble salts that precipitate. This synthesis can easily take place in a w/o ME system instead. The ME system [17] used for this work consists of CTAB/1-butanol as surfactant/co-surfactant and isooctane as oil, with the following composition (wt.%) [18]: CTAB/1-butanol–isooctane–water: 14.5/12–52.9–20.6 (CTAB:cetyl trimethyl ammonium bromide). This ME composition has been successfully used previously [16,19] for the preparation of catalyst nanoparticles. All chemicals were provided by Sigma–Aldrich.

Particularly, the synthesis in ME was carried out in the following way: aqueous solutions of the metal nitrates [cerium(III) nitrate hexahydrate— $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, zirconyl nitrate hydrate— $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ and lanthanum nitrate hydrate— $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, provided by Sigma–Aldrich], were contained in one ME system (ME_1). The other ME system (ME_2) contained the precipitating agent (ammonia). Then, ME_1 was added drop-wise to the ME_2 under vigorous stirring. The reaction (ageing) time was set to 24 h. The precipitated particles were then collected by centrifugation and then calcined.

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