# Microemulsion-prepared Ni catalysts supported on cerium-lanthanum oxide for the selective catalytic oxidation of ammonia in gasified biomass

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## Abstract

Nickel (Ni) catalysts supported on cerium-lanthanum oxide were prepared by two different preparation techniques and have been tested in the temperature range of 500–750 °C for selective catalytic oxidation of ammonia to nitrogen in gasified biomass. The two different catalyst preparation methods used are the conventional and the microemulsion (water-in-oil). The effect on catalytic activity of different Ni loadings was also tested in combination with the preparation method.

Catalyst characterisation was focused on BET and XRD analysis. Cordierite monoliths were used in a tubular quartz reactor for the purpose of the activity tests. For simulating the gasified biomass fuel, 400 ppm $NH_3$ was added to the fuel. Water was also present during the activity tests, which were carried out at fuel rich conditions. Results showed that the microemulsion-prepared catalysts obtained higher performance than the conventional ones, with the best catalyst reaching 98% ammonia conversion and 99% nitrogen selectivity at 750 °C. The more the Ni supported on the catalyst, the higher the catalytic activity. Constant conversion and negligible carbon deposition were two other important characteristics for the microemulsion-prepared catalysts.

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## 1. Introduction

There is an increasing interest in the utilisation of renewable sources of energy for power production. Gasified biomass is considered to be a promising fuel for gas turbines. However, the gasified biomass usually contains considerable amounts of unwanted nitrogen-containing compounds predominantly ammonia, which during the combustion process in a gas turbine cycle can be converted into nitrogen oxides (fuel-$NO_x$ formation) affecting negatively health and environment [1,2]. The amount of these contaminants in the gasified fuel depends on the nitrogen content of the biomass feedstock (10–10,000 ppm $NH_3$) and the technology of the gasification process [3].

To meet the $NO_x$ emission standards and the strict environmental regulations while maintaining high thermal efficiency of the process, the gasified fuel should be sufficiently cleaned from the fuel-bound nitrogen compounds prior to entering the gas turbine. This can be achieved by various technologies, such as catalytic decomposition of $NH_3$ at high pressure and temperature [4], or selective catalytic oxidation (SCO) of $NH_3$ into nitrogen [5]. In the case of the SCO, the mechanism of $NH_3$ oxidation and nitrogen formation is complicated. At the moment, two mechanisms have been investigated and reported in literature. The first comprises the SCO by a direct route using a hydrazinium-type intermediate [6,7]. The second mechanism involves the internal selective catalytic reduction (iSCR) [8]. According to iSCR, $NH_3$ is first oxidised into $NO_x$ which are then reduced to nitrogen. As a conclusion, it is believed that good SCR catalysts can achieve high nitrogen selectivity in the SCO. This mechanism has been proposed without taking account the effect of the presence of other combustible components that might be present with

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ammonia in a gas mixture, such as CO, $H_2$, $CH_4$. In that case, the mechanism of iSCR of $NH_3$ is modified [9], where ammonia is completely oxidised to any nitrogen oxide species, which then are reduced by the reductive fuel components.

For long-term operation, contaminants in the raw gas from the gasifier, such as tar, solid particles, char, must be removed before the product gas enters the turbine. Cleaning the gas can be achieved by either hot or cool gas clean-up. The gas produced from the hot gas clean-up technology has approximately the same temperature with the gas leaving the gasifier, which is beneficial for the overall thermal efficiency of the process. It would have been an advantage to use catalysts that can cope at temperatures as high as 800–900 °C for energy conservation purposes.

During the past years, several catalysts have been developed and tested for their activity in the SCO reaction at mainly low temperatures (<500 °C). Several bulk metal oxides in excess oxygen were reported [1,10] to have high catalytic activity for $NH_3$ decomposition. Among these metal oxides, $Co_3O_4$, $MnO_2$ and NiO had high activity. Alumina ($Al_2O_3$)-supported catalysts containing different transition metals such as Ni, Cu, Cr and Mn were reported [5] to have substantially improved activity comparing to zeolites and heteropolyacids in temperatures as high as 800 °C. Further studies [11] show that the presence of small amounts of oxygen can improve the $NH_3$ decomposition, especially at high temperatures, when alumina is used as support material. On the other hand, presence of water causes significant decrease of nitrogen selectivity compared to the dry fuel [12]. Moreover, activity tests carried out on monoliths (honeycomb) give a more detailed idea of the ammonia decomposition mechanism by simulating real conditions.

The technique followed for the preparation of the catalysts is a key issue in the process. Conventional co-precipitation and incipient wetness (IW) are widely used. For the scope of this work, microemulsion (ME) technique [13–16] is introduced as an alternative preparation method for producing catalysts. MEs are thermodynamically stable solutions of two immiscible liquids such as oil and water in the presence of a surfactant. In water-in-oil (w/o) ME, water droplets are dispersed in a continuous oil phase forming micelles typically in the size range of 5–25 nm, giving the ME its characteristic transparency. Metal nanoparticles can be synthesised in a ME by the use of water-soluble metal precursors. Furthermore, the presence of surfactant inhibits the excess of particle aggregation resulting in catalyst particles with narrow size distribution.

In this paper, we are focusing on the challenge of the technique applied for the preparation of catalysts for the SCO of ammonia. The aim of this work is to observe and report how the ME method affects the catalytic activity when comparing it with the conventionally prepared catalysts. For the scope of this work, Ni supported on cerium-lanthanum oxide catalysts were prepared and tested for their activity towards the SCO of ammonia primarily for obtaining as high as possible $NH_3$ conversion and simultaneously decreasing as much as possible the $NO_x$ emissions. The two techniques used for the preparation of the support and catalysts are the conventional and the (w/o)

ME method. Nickel was then added on the support by either IW or co-precipitation. The catalysts produced by the two alternative methods were characterised and then compared. The catalytic activity was determined using simulated gasified biomass over cordierite monoliths in the presence of oxygen (fuel rich conditions) and water.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. The conventional co-precipitation and IW method

This conventional method of catalyst synthesis utilises the fact that Ce, La and Ni forms insoluble salts that precipitate, when their corresponding nitrates dissolved in water are slowly added to an ammonia-containing water solution. In this work, the $Ce_{0.9}La_{0.1}O_2$ support material was prepared by that method. The metal nitrates [cerium(III) nitrate hexahydrate—$Ce(NO_3)_3 \cdot 6H_2O$ and lanthanum nitrate hydrate—$La(NO_3)_3 \cdot xH_2O$, all provided by Sigma–Aldrich] were dissolved in deionised water and added drop-wise to the ammonia-containing water solution under vigorous stirring. To ensure complete precipitation, the pH value was monitored by a digital pH-meter and controlled by adding extra ammonia when necessary. The reaction (ageing) time was set at 24 h. The precipitated particles were then collected by centrifugation and calcined.

Once the support material was synthesised, at the next step of the preparation, IW was used to impregnate the support material with 5 and 10 at.% Ni [Ni nitrate, $Ni(NO_3)_2 \cdot 6H_2O$, Sigma–Aldrich]. In a similar way of preparation with the support material, $Ni_{0.05}Ce_{0.86}La_{0.09}O_2$ and $Ni_{0.1}Ce_{0.82}La_{0.08}O_2$ were also synthesised by the co-precipitation method. This time, Ni was introduced during the synthesis together with the cerium and lanthanum metal precursors. Pre-reduction was not performed for any of the nickel catalysts.

#### 2.1.2. The w/o ME method

The second catalyst preparation technique under investigation was the w/o ME method. At the first stage of the preparation, the $Ce_{0.9}La_{0.1}O_2$ support was synthesised by co-precipitation but this time in a ME system. The same cerium and lanthanum metal precursors were used for the synthesis. The ME system [17] used for this work comprises CTAB/1-butanol as surfactant/co-surfactant and isooctane as oil, with the following composition (wt.%): CTAB/1-butanol–isooctane–water: 14.5/12–52.9–20.6 (CTAB: cetyltrimethyl ammonium bromide). All chemical were provided by Sigma–Aldrich. The reaction time (ageing) was set at 24 h followed by particle recovery and calcination.

Thereafter, 5 and 10 at.% Ni (Ni nitrate) was impregnated on the support by IW. As the conventional ones, $Ni_{0.05}Ce_{0.86}La_{0.09}O_2$ and $Ni_{0.1}Ce_{0.82}La_{0.08}O_2$ were also synthesised by co-precipitation of the corresponding nitrates in the same ME system used for the preparation of the support material. Table 1 summarises all the catalysts prepared for the purpose of this work.