

A study of the selective catalytic reduction of NO_x by NH₃ over an oxide-based catalyst for a Diesel application.

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In the last decades, researches about the treatment of NO_x compounds have increased. Several sources are responsible of their emission. One of them is the exhaust gases from automobiles which also contain CO, hydrocarbons, particulates... The conversion of these pollutants to CO₂, N₂ and H₂O using catalysts is a challenge for lean-burn engine, especially for NO_x due to the oxidizing media of such engines. There are two main processes to eliminate NO_x in excess of oxygen. One possible way is the NO_x storage reduction (NSR) process. Another possibility is the selective catalytic reduction (SCR) of NO_x [1], which is well-known for stationary source application, using NH₃ as reductant in order to produce N₂ [2-4]. Nevertheless, the direct use of liquid/gaseous NH₃ is not acceptable for an automotive application due to the dangerousness of this molecule. However, substitution of ammonia by a precursor such as urea is a most conceivable and secure path. In the selective catalytic reduction of NO_x (SCR) with urea, the urea solution decomposes in the hot exhaust gas and on the catalyst to yield the actual reducing agent: ammonia (NH₃). According to the mechanism reported in Fig 1, urea decomposition starts by a first step of thermolysis into NH₃ and isocyanic acid (HNCO) in a non-catalytic reaction (1). HNCO is transformed in a second step by hydrolysis which can be catalytically assisted (2). Direct urea hydrolysis is also possible in presence of water (3) [5].

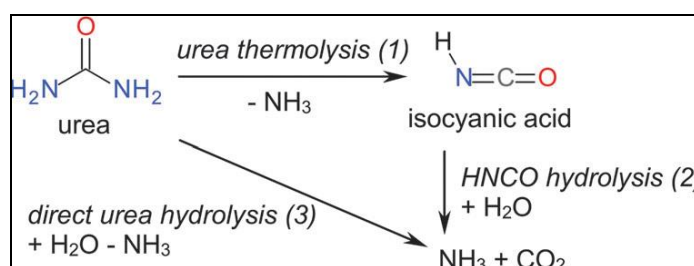


Fig.1: Reaction scheme of catalytic urea decomposition [5].

For automotive application, urea-SCR over V₂O₅-WO₃/TiO₂ catalysts is used from approximately one decade in Europe for heavy duties. However, these catalysts are not suitable for exhaust pipe equipped with a Diesel particulate filter (DPF) since its regeneration induces high temperature (>600°C) leading to a possible vanadium sublimation. Then, highly stabilized zeolites, exchanged with Fe or Cu, were proposed. In order to optimize the exhaust

gas treatment, the integration of the NSR catalyst in the DPF porosity is a great challenge, but it appears quite difficult with zeolites and it may be easier with oxide based catalysts.

In this work, the NO_x SCR with NH₃ was studied over an oxide SCR catalyst (powder) which was provided by Solvay. It was hydro-treated for 5h under air containing 10 % H₂O at 600°C or 850°C and evaluated in the NH₃-SCR reaction. The aim of this work was to study the catalytic behavior of this catalyst depending on the catalytic test condition.

The “reference” NH₃-SCR test was performed in light-off mode, in the 120-600°C temperature range (5°C/min). The gas mixture was composed of 400 ppm NO, 400 ppm NH₃, 10 % O₂, 10 % CO₂, 10 % H₂O + N₂ balanced. The GHSV was fixed at 160 000 h⁻¹. Most gases (NO, NO₂, N₂O, NH₃, CO₂, H₂O) were analyzed using a Multigas FTIR detector (MKS 2030). The N₂ selectivity is calculated assuming no other nitrogen compounds than NO, NO₂, N₂O, NH₃ and HNCO.

Examples of NO_x conversions over this catalyst depending on the temperature ageing are reported in Fig. 2.

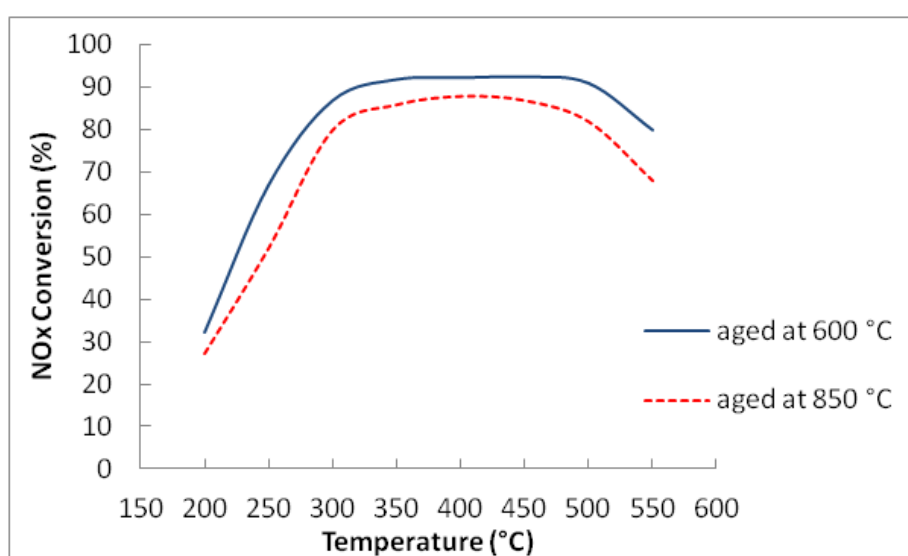


Fig.2: NH₃-SCR reaction for two catalysts

Fig 2 shows a slight deactivation of the catalyst after ageing at 850°C. 50 % of NO_x conversion is obtained at 225 °C and 250°C for catalyst aged at 600 °C 850 °C, respectively. Maximum NO_x conversions are obtained in the 300-500°C temperature range for both catalysts. The decrease of the NO_x conversion up to 500°C is not correlated with a decrease of the NH₃ conversion, which tends to 100%. It indicates that the ammonia oxidation by O₂ takes place for temperature higher than approximately 500°C.

Other preliminary tests also show an increase of the N₂O selectivity with the increase of the NO₂/NO ratio in the inlet gas.

From these previous results, different reaction parameters were examined with special consideration to the NO_x conversion, the selectivity of the reaction with possible N₂O formation, and the NH₃ oxidation by O₂.

With this aim different parameters were varied:

- The inlet NO₂/NO ratio
- The NH₃-NO_x concentration (1000 ppm NO, 1000 ppm NH₃, 10 % O₂, 10 % CO₂, 10 % H₂O)
- The impact of NH₃ pre-adsorption at low temperature
- The NH₃/NO_x ratio at fixed temperatures. The urea decomposition behavior (the amount of obtained NH₃ can change during the urea decomposition process) and the possible ammonia storage should induce significant changes in the NH₃/NO_x ratio depending on the temperature test.
- The NH₃-O₂ reactivity

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