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Control of NO_x storage and reduction in NSR bed for designing combined NSR–SCR systems

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ABSTRACT

A detailed analysis of the catalytic behavior in the storage and reduction of NO_x of a homemade Pt–BaO/Al_2O_3 NSR monolith catalyst determining the N_2/NH_3 production surface in response to operational variables, namely temperature and hydrogen concentration during rich conditions was obtained. The production response curves are used to design the optimal operation, with high NO_x removal efficiency and maximum production of nitrogen, when running the single NSR catalyst and the combined NSR–SCR configuration with Fe-beta zeolite catalyst placed downstream the Pt–BaO/Al_2O_3 monolith. Optimal operation of the single NSR monolith was attained at 300 °C and 1% H_2, which showed NO_x removal of 74% with 64% of nitrogen production (both related to the total amount of NO in the feedstream, difference was mainly ammonia). The double NSR–SCR configuration allowed the Fe-beta catalyst storing ammonia to react with NO_x leaving the NSR during the subsequent lean phase. This has a benefit on both the NO_x removal efficiency and the N_2 production. The amount of ammonia needed for total NO_x removal efficiency and N_2 production can be supplied by tuning temperature and H_2 concentration. Temperature of 300 °C and 3% H_2 during rich conditions, produced 23% of ammonia at the exit of NSR. The SCR reaction between this amount of ammonia adsorbed on Fe-beta and the untrapped NO in NSR, resulted in practical total NO_x removal efficiency (98%) and N_2 production of 97% when the double NSR–SCR system is operated.

1. Introduction

It is now well recognized that diesel and lean burn engines improve fuel efficiency, consequently reducing emissions of carbon dioxide. However, the NO_x abatement from these engines is difficult to achieve since they work mainly under excess of oxygen. In the last decade, two main approaches towards NO_x reduction have been proposed: the NO_x storage and reduction (NSR) technology and the selective catalytic reduction (SCR) of NO_x.

The NSR catalysts consist of a cordierite monolith wash coated with a porous alumina on which alkali or alkali-earth oxide (e.g. BaO) and a noble metal (Pt) are deposited. These catalysts operate alternatively under lean and rich conditions [1,2]. During the lean period, when oxygen is in excess, the platinum oxidizes NO to a mixture of NO and NO_2 (NO_x), which is adsorbed (stored) on Ba as various species (nitrite, nitrate). Before that an unacceptable amount of NO_x slips through the catalyst, the engine switches to rich condition (excess of reductant) for a short period where the stored NO_x are released and reduced into N_2 over Pt. Different types of reducing agents such as hydrocarbon, CO, and H_2 have been used in NSR catalyst studies [3–6], and hydrogen has been found to be the most effective reductant.

On a commercial NSR system, the efficiency to transforming the emitted NO_x to N_2 should be as high as possible. This is remarkable, as the Pt itself is selective for the formation of N_2 from NO and H_2 only in a narrow range of NO to H_2 ratio. Nova et al. [7] concluded that the ammonia formation over Pt/Ba/Al was dependent on the amount of stored NO_x, temperature and hydrogen concentration. The reduction by H_2 of nitrates stored proceeds according to a two-step mechanism in which the first step is the fast reaction of hydrogen with nitrates producing ammonia, followed by the slower reaction of the latter with nitrate species leading selectivity to N_2 [8,9]. Accordingly a good tuning of the operating conditions of both the adsorption rate and the reduction phases can drive selectively to N_2 and/or NH_3.

The second approach, NH_3-SCR, is based on the selective catalytic reduction of NO_x by NH_3 generated by a urea solution stored in a special tank, or by NH_3 directly. This approach was originally developed for stationary emission sources, mainly power plants, but now is also a well established technique for truck and heavy duty vehicles, under the oxygen rich environment of diesel exhaust. In the urea-SCR technology, urea is injected in the flue gases where

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it decomposes and hydrolyzes to CO_2 and NH_3. The ammonia then reacts selectively with NO_x under lean (oxidizing) conditions, giving N_2 as the final product [10,11]. Non-noble metals like Cu, Fe and Ce over ZSM-5, are among the most active catalysts for the urea/NH_3-SCR process [12–14].

The performance of model Pt–BaO/Al_2O_3 NSR monolith catalyst under different operating conditions, including the duration of the regeneration and storage times, regeneration feed composition and temperature, and monolith temperature, has been recently reported in literature [6,15,16]. The cycled-averaged NO_x conversion exhibited a maximum at about 300–330 °C corresponding to the NO_x storage maximum. The N_2 selectivity exhibited a maximum at a somewhat higher temperature, at which point the NH_3 exhibited a minimum. We studied recently the influence of the duration of the storage and reduction periods, and the H_2 concentration on the NSR performance of a Pt–BaO/Al_2O_3 monolith catalyst [16]. Then, we defined the NSR efficiency as the moles of N_2 at the reactor outlet related to the total amount of NO_x entering the trap, expressed as percentage. Maintaining this efficiency as high as possible should be the aim of the NSR technology. At the studied conditions the minimum H_2 concentration to obtain total NO_x reduction during regeneration was experimentally determined (1.1% H_2), and also corresponded to the highest NSR efficiency, around 70%. If the H_2 concentration is lower or the reducing pulse is too short, the regeneration of storage sites is incomplete and thus the activity of NO_x trap decreases. On the contrary, if the H_2 concentration is higher or the pulse is too long undesirable product as ammonia is produced.

To avoid the NH_3 break-out, one possibility is to combine the NSR catalyst with a SCR system. Corbos et al. [14,17] found that the presence of a SCR catalyst placed downstream the NSR catalyst bed (double-bed configuration) allows the storage of ammonia released during the rich phase on the NO_x trap. The adsorbed ammonia is then converted to N_2 in the subsequent lean phase, according to the occurrence of a SCR reaction involving the stored ammonia and NO/NO_2 released from the front trap catalyst layer.

The objective of this paper is to find how the temperature and the reductant concentration can play jointly on NO_x removal efficiency when the NSR runs as a single system or combined with an NH_3-SCR downstream the NSR in a double bed configuration. We try to establish a completed picture of the $N_2/N_2O/NH_3$ distribution at the exit of the lean NO_x trap (NSR) in the temperature–H_2 concentration operational region. The N_2/NH_3 response surfaces will allow tuning the operational conditions in the lean NO_x trap with the aim of getting the required amount of NH_3 to react with NO/NO_2 in the downstream SCR bed improving the total efficiency of the double NSR–SCR configuration towards the desired N_2 product. This will increase both the NO_x removal efficiency and the N_2 selectivity of the process as well.

2. Materials and methods

2.1. Catalysts

The Pt–BaO/Al_2O_3 NSR catalyst was prepared from a cordierite monolith, 20 mm in length and diameter, with a cell density of 400 cells per square inch and a wall thickness of 150 μm. The monolith was wash coated with γ-alumina (163 $m^2\,g^{-1}$ after stabilization at 700 °C, 4 h) by several immersions of the monolith into the alumina slurry until ≈1 g Al_2O_3 was deposited in the monolith structure. The incorporation of platinum was carried out by adsorption from tetraammine platinum (II) nitrate solution supplied by Alpha Aesar and the excess of liquid remaining in the channels was blown out with compressed air. After calcination in air (500 °C, 4 h) and subsequent reduction of the metallic phase in a 5% H_2/N_2 stream (500 °C, 1 h), the barium was incorporated by immersion of the monolith in a barium acetate solution supplied by Aldrich. Finally, the catalyst was calcined again (500 °C, 4 h). More details on the preparation of the Pt–Ba/Al_2O_3 monolith catalyst can be found in our previous work [18].

The SCR catalyst was a homemade, powdered 2% Fe-beta zeolite catalyst. The beta-zeolite was supplied by Zeolyst International, pelletized, crushed and sieved to 0.3–0.5 mm to avoid mass transfer limitations. The catalyst was synthesized by the traditional ion-exchange procedure. Fe-ion exchange was carried out by dissolving the required amount of $Fe(NO_3)_3{\cdot}9H_2O$ in water, later zeolite was added to the solution (8 g/l) and was stirred for 24 h at 60 °C. The ion exchanged samples were then filtered, dried and calcined at 650 °C for 4 h before use. In order to characterize the Fe-beta catalyst several techniques such as BET surface area analysis, TEM, TPR, NH_3-TPD and XRD were employed. The fresh zeolite had a surface area of 535 $m^2\,g^{-1}$, which after iron incorporation was reduced to 464 $m^2\,g^{-1}$, probably due to the fact that some iron particles blocked the pores of the support. No signals related to iron species were detected in XRD. Fe_2O_3 particles around 10 nm were observed in the external surface of the zeolite by TEM. The catalyst had a total acidity of 0.24 mmol NH_3/g (determined by TPD) dominated by Brønsted type sites. For testing in double bed NSR–SCR configuration, the SCR catalyst powder (2.5 g) was loaded in a second tubular reactor placed after the NSR trap; the outlet of the NSR trap entering the SCR reactor.

2.2. NO_x removal experiments

The NO_x storage–reduction experiments for the single NSR configuration were performed in a vertical downflow stainless steel reactor, inside which the Pt–BaO/Al_2O_3 monolith was placed. When testing the double NSR–SCR configuration, the Fe-beta zeolite powder catalyst was packed in a second reactor connected downstream the NSR reactor. Temperature was measured by thermocouples at the top and the bottom of the NSR monolith, and in the bed of SCR catalyst. Streams from either the exit of the NSR monolith or the exit of the double NSR–SCR system can be addressed to analyzers.

The composition of the lean gas mixture for NO_x storage was 350 ppm NO and 6% O_2 using Ar as the balance gas. During the rich period oxygen was replaced by hydrogen maintaining 350 ppm of NO in the feedstream. The duration of the lean and rich periods (t_L = 150 s and t_R = 20 s, respectively) was maintained constant and controlled by two solenoid valves. Gases were fed via mass flow controllers and the total flow rate was set at 3365 ml min^{-1}, which corresponded to a space velocity of 32,100 h^{-1} for the NSR and 50,400 h^{-1} for the SCR. NO_x storage and reduction tests were carried out varying the catalyst temperature and the hydrogen concentration fed during rich period in the following intervals T = [100 °C, 420 °C] and C_{H_2} = [0.4%, 3.0%]. The experimental design was defined with 9 different levels for each variable, leading to a total of 9^2 = 81 experiments. Analysis of products after the Pt–BaO/Al_2O_3 monolith allowed us to determine the influence of each variable independently, maintaining the other constant, but also to construct the product distribution response surfaces (by interpolation) in the domain of both variables, temperature and hydrogen concentration.

The outlet gas concentrations, after the NSR monolith and after the double NSR–SCR configuration were continuously measured using a MKS MultiGas 2030 FT-IR analyzer with a specific oxygen detector (ZrO_2) totally integrated and a MKS Cirrus quadrupole mass spectrometer in line. NO, NO_2, NH_3, N_2O and H_2O were quantitatively monitored by FT-IR, whereas O_2 was measured by the ZrO_2 detector. On the other hand, H_2 and N_2 were qualitatively monitored by QMS and also O_2, the latter used to match accurately the corresponding data obtained from each instrument (FT-IR and QMS) in the concentration vs. time plots.