PRELIMINARY STUDIES FOR THE DEVELOPMENT OF A PERIODIC STORAGE-DECOMPOSITION PROCESS FOR NO_X ABATEMENT

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Abstract
A novel cyclic catalytic process based on adsorption and subsequent decomposition of NO on LaCu-ZSM-5 catalyst has been proposed as alternative to the traditional SCR technique for nitric oxides abatement. The process was simulated with experiments consisting of three main steps: i) NO adsorption at 50°C until zeolite saturation; ii) heating of the reactor up to 480°C for 1 h (decomposition of NO into N_2 and O_2) and iii) system cooling back to 50°C. At the end of step iii) the zeolite was regenerated and ready for a new cycle. The investigation was carried out over zeolite-coated monoliths located in a stainless steel reactor. No nitrogen oxides have been detected in the gas phase during all the steps of the periodic process, NO_x being completely adsorbed in phase I and N_2 and O_2 being the only products at the end of decomposition phase.
The process has been tested also in the presence of O_2 in the feed (2.5 vol.%) obtaining similar performance. This represents a very promising result for a potential novel application under real conditions.

Introduction

SCR (Selective Catalytic Reduction) is presently the most common technique for NO_x control from stationary sources. Nitrogen oxides are reduced by ammonia or urea in the presence of oxygen over V_2O_5-WO_3/TiO_2 catalysts. The main drawbacks are safety issues and high costs related to the use of the reducing agent. [1]. SCR has been also proposed for mobile sources as Diesel or CNG engines where the traditional three-way catalyst cannot operate due to the typical lean conditions [2].
Various alternative processes have been recently proposed for both stationary and mobile sources, however, the catalytic decomposition of NO into N_2 and O_2 still remains an ideal reaction since it does not require the addition of any reducing agent. Cu-ZSM-5 shows unique properties in the direct decomposition of nitric

oxide, although its kinetics is not fast enough for practical applications and the presence of oxygen partially inhibits the reaction [3].
In this paper a preliminary study for the development of a novel cyclic catalytic process for nitric oxides abatement based on adsorption and subsequent decomposition of NO has been reported. This process would overcome the kinetics limitations of Cu-ZSM-5 through the storage of significant amounts of NO on the zeolite and the subsequent occurrence of the decomposition reaction under static conditions in the presence of a NO partial pressure much higher than that typical of the gas stream to be treated and, at the same time, with a suitable reaction time.
The work has been carried out over La-doped Cu-ZSM-5 coated monoliths by studying both the adsorption and the decomposition/regeneration step, with the aim of assessing the feasibility of this innovative approach.

Experimental
The LaCu-ZSM5 powder was prepared by ion-exchange of a commercial H-ZSM5 zeolite (Zeolyst CBU-5020, Si/Al = 25, BET surface area=350 m^2/g). Cu and La concentrations, determined by an Agilent 7500 ICP-MS, were 1.8 and 0.16 wt% respectively.
Structured catalysts were prepared according to the procedure reported in [4] using ceramic monoliths (Corning, 400 cpsi). The procedure was repeated four times for each monolith until the target weight (about 0.6g) of zeolite was reached.
The test rig was designed to perform experiments under unsteady state conditions. The feeding mixture was obtained by mixing high purity He and O_2 and 1 vol% NO/He mixture. The flow-rate of the feed stream was controlled by mass flow-controllers (BROOKS MFC SLA5850S).
The reactor used for the NO_x Storage Decomposition (NSD) tests consists of a stainless steel tube (length = 28 cm; diameter = 2.54 cm) where monoliths are located. The reactor was filled up with 14 monoliths; two of them were coated with the LaCu-ZSM-5 (about 1.2g LaCu-ZSM-5 total load) and placed in the 5cm middle zone of the reactor, identified as isothermal zone by preliminary measurements, while the others (uncoated cordierite) were symmetrically placed in the side zones of the reactor providing the reduction of the void volume and blocking the coated monoliths in the central position. The reactor can be isolated from the gas stream using two three-ways valves. At the reactor outlet, before the second 3-way valve, a pressure transducer (Dwyer series 628, range 0-300 psig) was positioned in order to monitor the pressure during the different phases of the experiment. A heating jacket (Tyco Thermal Controls) equipped with a PID controller provided for the external heating of the reactor at the desired temperature. The two internal thermocouples were placed inside the reactor to measure the temperature at the catalytic zone inlet and into the catalytic bed respectively. A scheme of the reactor is shown in Fig. 1.

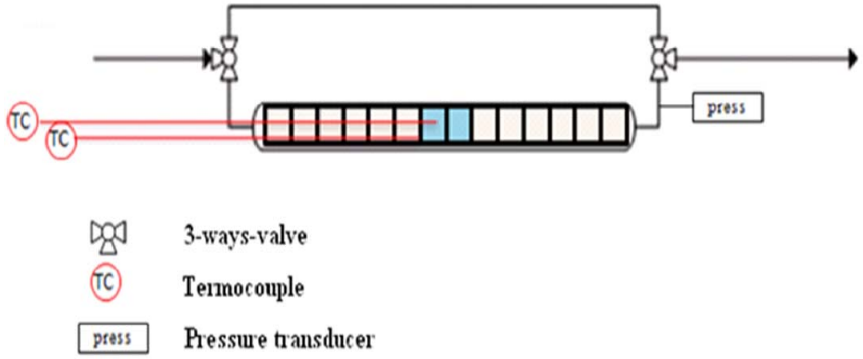

Figure 1. Scheme of the reactor for cyclic NO adsorption/decomposition tests.

The NO and NO_2 concentration was measured by a continuous analyzer (ABB AO2020), equipped with two UV channels. A second analyzer (Hartmann & Braun) equipped with a NDIR channel was used to measure N_2O concentration. The analysis of N_2 and O_2 was performed using a Micro Gas Chromatograph (Agilent 3000A Micro GC), in parallel to the analyzers and equipped with a Mol Sieve 5 Å (MS5A) column with back-flash. The short time-length of the Micro GC analysis (about 60 s) allowed us to consider also this response as continuous.
The experimental tests were carried out according to a cyclic procedure consisting of a sequence of adsorption, decomposition and purging stages. A flowing mixture containing 800 ppm NO and, in some cases, O_2 (2.5vol.%), was fed to the pre-oxidized catalyst at 50°C. Under these conditions, LaCu-ZSM-5 reactivity was negligible and only NO adsorption on the catalyst surface takes place. At the end of the adsorption phase the reactor was by-passed (closed system), heated up to 480°C under static conditions and kept at this temperature for a fixed period of time. At the end of the decomposition stage, the reactor was rapidly cooled down back to 50°C and evacuated re-opening valves under pure He flow (purging phase). Gases exiting the reactor were analyzed. In preliminary experiments a temperature programmed desorption (TPD) was carried out after purging (heating rate = 10°C/min; He flow rate = 20 Nl/h). When a sequence of NSD cycles was performed, a TPD was carried out only after the last cycle.

Results and Discussion

A typical NSD test is represented in Fig. 2, where the gas phase composition, as analysed at the reactor outlet, is reported as a function of time during the adsorption and purging phase following decomposition and reactor cooling.

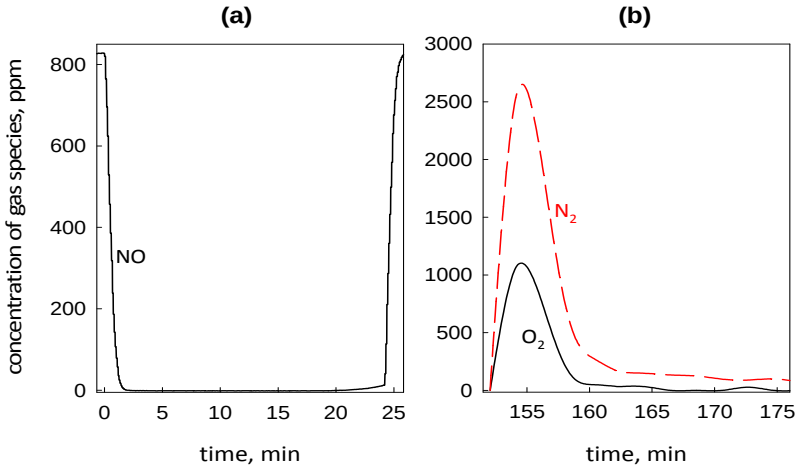

Figure 2. Concentration profiles as functions of elapsing time of: (a) NO during the adsorption phase; (b) N_2 (– –) and O_2 (——) during the purging phase.

The experiment confirms the capacity of the zeolite of adsorbing a significant amount of NO. At 50°C and 700 h^{-1} space time, the time needed to saturate the zeolitic monoliths with a 800ppm NO/He mixture is about 24 minutes (Fig. 2a).
After heating the reactor under static atmosphere (constant volume and closed system), the proper decomposition phase was carried out for 1h at 480°C (at this temperature the pressure inside the reactor reaches about 2.5 bar, as expected mainly for the increase of temperature, the increase of number of molecules in the gas phase being negligible) and is followed by the rapid reactor cooling back to 50°C. After valves opening the reactor was flushed with helium and the analysis of the exit gases was carried out. Only N_2 and O_2 were detected in significant amounts (Fig. 2b) whereas NO and NO_2 were detected only in trace amounts (NO_x desorbed < 0.5 μmol). This means that the idea of converting nitrogen oxides through this approach can be preliminary validated by these experimental results.
However, the production of N_2 was insufficient to balance the amount of nitrogen adsorbed on the zeolite. This effect is also more significant for oxygen (Fig. 2b). Nevertheless, the mass balance is closed within the experimental error for nitrogen if we take into account the amount of N atoms remained on the catalyst after the purging phase. In fact, by carrying out a TPD test, significant amounts of NO and NO_2 were detected in the gas phase, showing that they were been retained by the catalyst after decomposition and that their complete desorption took place only raising the temperature under He flow. The TPD profile (not shown) is in good agreement with our previous recent studies [5].
The oxygen amount desorbed in the TPD (both as NO_2 and O_2) is however still low indicating that an oxygen fraction was missing. This should be attributed to the

copper redox chemistry. Actually, it is well known that Cu(II) in Cu-ZSM-5 is spontaneously "self-reduced" to Cu(I) above 400°C due to O_2 desorption while Cu (I) is easily re-oxidized by molecular oxygen at low temperature [6]. Therefore, copper starts the cycle as Cu(II), it is reduced at high temperature and then oxygen produced by the decomposition reaction is partially consumed to oxidize the catalyst again.

If a suitable number of complete cycles were carried out without performing any TPD at the end of each cycle, constant values of NO adsorption and N_2 and O_2 emission were reached suggesting that the catalyst approached a similar initial condition at the end of each cycle.

In Tab. 1 the amount of NO adsorbed and reacted is reported for each cycle. It seems that the NO storage capacity of the catalyst apparently decreases with the number of consecutive cycles. At the same time, the NO conversion increases up to a value of about 100%. Actually, the unreacted NO_x re-adsorbed on the catalyst limit the amount of NO adsorbed after the first cycle and a steady-state condition is reached after few cycles. After 1 hour decomposition time a buffer fraction of adsorbed NO_x remains on the zeolite, which is then not completely regenerated. This fraction can potentially react prolonging the time-length but, on the other hand, it should be emphasized that it is not emitted in the purging phase. Therefore, although the reaction conditions preliminary explored in this work do not provide the total conversion of the adsorbed NO, the re-adsorption of the unreacted fraction assures zero NO emission also at the end of the reaction step. This means that also under conditions far from those required for an optimized process no NO_x emissions take place.

Table 1. Amount of NO adsorbed and converted in the different cycles in the absence of O_2 in the feed.

cycle	NO adsorbed, μmol	NO converted, %
1	75.2	69.0
2	49.8	84.2
3	42.7	100
4	42.0	100
5	38.3	100
6	38.8	100
7	35.1	100
8	37.9	100
9	34.9	100

The NSD process was also studied in the presence of 2.5% vol. O_2 (and constant value of NO concentration of 800 ppm). The results of cyclic tests are reported in Tab. 2. In the presence of oxygen, the amount of NO adsorbed in the first cycle was more than doubled, in agreement with previous findings on Cu-ZSM-5 powder

[5]. The promoting effect of lanthanum and/or the additive role of cordierite in adsorbing NO_2 results in an even larger NO adsorption compared to Cu-ZSM-5 powder, although this effect almost disappears by cycling the process. Indeed, starting from the second cycle, the amount of NO adsorbed is stabilized around values very similar to those obtained in the absence of O_2. However, the conversion estimated on the entire process, based on nitrogen species (oxygen is fed in large excess) still remained about 100%, a very promising and interesting result for the NO_x abatement process, because obtained with a more realistic gas composition (namely, in the presence of O_2 in the gas).

Table 2. Amount of NO adsorbed and converted in the different cycles in the presence of O_2 in the feed.

cycle	NO adsorbed, μmol	NO converted, %
1	189	28.7
2	40.7	83.0
3	37.2	100
4	37.4	100

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