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Catalysis Today 42 (1998) 85–92

CATALYSIS TODAY

Two-bed catalytic system for NO_x/SO_x removal

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Abstract

A combined monolithic catalytic system has been developed by which NO_x and SO_x are successively removed from flue gases produced by the combustion of coal and other fossil fuels. The honeycomb catalysts used in this study have been manufactured at industrial scale by extrusion of pastes which contain all the precursors or their components. Nitrogen oxides are removed in the first stage of this combined process by selective catalytic reduction with ammonia, using a $DeNO_x$ monolithic catalyst based on Ti–V–W oxides dispersed in the structure of a natural magnesium silicate. The outlet gases pass through a second monolithic bed which oxidizes SO_2 to SO_3; this $DeSO_x$ monolithic catalyst is based on vanadium oxides and alkali pyrosulfates supported on diatomaceous earth. Laboratory scale activity tests were carried out using small honeycomb sections cut from the industrial catalysts. At a temperature of 450°C, molar conversions of 90% and 80% for NO_x and SO_x were achieved respectively, without any ammonia slip. The monolithic structure, and mechanical properties of both catalysts allows their operation in high dust configurations. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Catalyst; Monolith; Selective catalytic reduction; $DeNO_x$; Sulfur dioxide oxidation; $DeSO_x$; TiO_2; V_2O_5; Magnesium silicate; Diatomaceous earth

1. Introduction

Public health and acid rain control considerations have led to worldwide action to reduce SO_x and NO_x emissions from coal-fired boilers. Nowadays, the current global emphasis on environmental protection is being directed towards the development of technologies for NO_x and SO_x removal, where further reductions in their emission levels are required in accordance with the application of more stringent regulations.

Latterly, emission control techniques from coal and other fossil fuels have been developed with significant improvements in pre, post and in-combustion.

Wet lime/limestone scrubbers for flue gas desulfuration (FGD) and selective catalytic reduction (SCR) of nitrogen oxides with ammonia are the most widespread post-combustion methods. Limestone injection multi-stage burners (LIMB) are an example of in-combustion technology [1] which reduces simultaneously SO_2 and NO_x emissions by a relatively simple method, although the required levels are not achieved. Similar processes, where sorbent injection is followed by selective noncatalytic reduction [2] or selective catalytic reduction [3] have been also proposed.

Some efforts have been carried out carbon catalyst technology [4,5]; the process developed by Bergbau–

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PII S0920-5861(98)00079-0

Forschung GmbH [6] uses active coke as adsorbent for SO_2 (first stage), and as catalyst for nitrogen oxides removal by ammonia (second stage). In the RTI-Waterloo low temperature process [7] SO_2 is oxidized to SO_3 which is removed as sulfuric acid in a series of periodically flushed trickle-bed reactors, the SO_2 free-gas is reheated to 150°C and mixed with ammonia for NO_x removal by a SCR process; both catalytic steps employ different types of activated carbon-based catalyst.

Other advanced systems for SO_x/NO_x removal such as the NOXSO® process [8] uses, as regenerable sorbent a high specific surface area γ-alumina support impregnated with sodium carbonate. In other studies a series of materials featuring copper and/or vanadium oxide supported on titania, alumina or a composite alumina-titania carrier were tested for suitability as sorbent/catalysts for the simultaneous removal of SO_2 and NO_x [9].

In the process reported by Mitsubishi in the early 1980s [10] the catalyst, a mixture of vanadium oxide with potassium, copper or cesium sulfate supported on titania, operates at 380°C for the simultaneous SCR of NO_x and SO_2 oxidation processes. The SO_3 generated is adsorbed on the fly ash which is easily collected by the electrostatic precipitator. At the same time, a similar simultaneous process was registered by Hitachi and Babcock-Hitachi K.K., [11] using a vanadium oxide (with or without iron oxide) on titania support at 400°C and CaO or $CaCO_3$ particles for the SO_3 collection.

The catalytic activities of vanadium oxide or chromia supported on titania (with or without activated carbon) in the simultaneous removal of NO and SO_2 were studied by Kasaoka et al. [12]. In this process, the SO_3 produced is fixed on the catalyst surface as ammonium sulfate and the NO is reduced via SCR process at 130°C. The sulfate deposited on the catalyst must be periodically removed for regeneration and repeated use of the catalyst.

Some other NO_x/SO_x removal technologies combine the SCR process with catalytic sulfur dioxide oxidation to sulfur trioxide which is further converted to sulfuric acid. In the SNO_x® process [13,14], after dust removal, the flue gas is preheated to 370°C for NO_x reduction via conventional SCR technology using ammonia as a reductant over a monolithic catalyst (Tøpsoe DNX catalyst); the products heated to 420°C pass over an oxidation bed of a V_2O_5 based catalyst conformed in ring shapes, where SO_2 is oxidized to SO_3 which is recovered in a WSA condenser, as concentrated sulfuric acid (94–97%) [15,16]. Dust deposited on the catalyst rings increases the pressure drop across the converter and therefore the catalyst has to be cleaned by mechanical screening at regular intervals.

The $DeSONO_x$® process (Degussa) [17] is similar to the SNO_x® process, although the sulfuric acid is obtained at a lower concentration (70%). However, in this system both catalysts are installed in a two bed reactor which operates at 450°C, eliminating the need of a preheater between the SCR and SO_2 oxidation units [18].

Recently, Combustion Engineering [19] has registered a process of analogous operational characteristics to those described in the above mentioned SNO_x® and $DeSONO_x$® processes, which includes a heat recovery system.

In this work, a $DeNO_x$–$DeSO_x$ two-bed combined monolithic reactor is presented. In the first bed the nitrogen oxides are selectively reduced by ammonia, to nitrogen and water; and in the second, the sulfur dioxide is oxidized to sulfur trioxide, which can be further converted to sulfuric acid. The monolithic structure, mechanical properties of both catalysts allows their operation in high dust configurations. The reactor runs at 450°C without heating between the two catalyst beds, with the subsequent technical simplicity and low operation cost.

2. Experimental

2.1. Monolithic catalysts

The two proprietary catalysts used in this study were manufactured by extrusion of pastes which contained all the components or precursors of the final catalysts.

The $DeNO_x$ catalyst was prepared with a mixture of V, W and Ti compounds together with a natural magnesium silicate, following a method similar to described elsewhere [20]. This monolithic catalyst was manufactured in a square-cell shape with a cell density of 7.5 cells cm^{-2}, pitch of 0.37 cm, wall thickness of 0.09 cm, geometric surface area of

806 m^2 m^{-3}, and a bulk density of 0.5 g cm^{-3}. The axial crushing strength values of the monoliths, measured with a Chatillon LTCM Universal Tensile and Spring Tester, were about 190 kg cm^{-2}.

The $DeSO_x$ catalyst, based on vanadium oxides and potassium pyrosulfates supported on diatomaceous earth and shaped as a honeycomb structure, was prepared according to a procedure reported elsewhere [21]. The $DeSO_x$ square-cell monoliths, have a cell density of 4.5 cells cm^{-2}, pitch of 0.47 cm, wall thickness of 0.09 cm, geometric surface area of 690 m^2 m^{-3}, bulk density of 0.7 g cm^{-3} and a crushing strength of around 470 kg cm^{-2}.

2.2. *Activity tests*

Catalytic activity measurements were carried out in a monolithic reactor working close to the isothermal axial profile, at the following operation conditions: temperature=450°C, pressure=120 kPa and GHSV (gas hourly space velocity, at normal conditions) from 4000 to 12 000 h^{-1}.

Two different sets of experiments were undertaken. Firstly, the behavior of each monolithic catalyst was studied separately in their corresponding reaction. Secondly, a monolithic two-bed catalytic reactor was designed in which NO_x and SO_x were successively removed from the flue gases.

Inlet and outlet nitrogen oxides and ammonia contents were analyzed using a Chemiluminescence NO/NO_x analyzer (Signal Series 400), with an ammonia converter; SO_2 contents were analyzed by Gas Chromatography (Varian 3400), using a photometric detector, and SO_3 measurements were carried out by volumetric analysis [22].

2.3. *Characterization studies*

Samples of monolithic catalysts before and after use in the reaction were studied by the following characterization techniques: BET surfaces areas were measured by nitrogen adsorption–desorption in a Micromeritics ASAP 2000; the pore size distribution was determined by mercury-intrusion using Thermo Quest Pascal 140/240 Porosimeters. The $DeNO_x$ catalyst was analyzed by a Brucker Model RFS 100 FT-Raman spectrometer, with a NdYAG excitation laser. Thermal gravimetric analysis was carried out on a Netzsch STA409EP with an air flow of 75 ml min^{-1} and a heating rate of 5°C min^{-1}.

3. Results and discussion

3.1. $DeNO_x$ *process*

Conventional SCR catalysts operate at temperatures between 300°C and 380°C, trying to avoid undesirable reactions of ammonia or sulfur dioxide with the oxygen present in the inlet-gases. As the operation temperature of the $DeSO_x$ process is about 450°C, it was necessary to develop a monolithic SCR catalyst with activity and selectivity at this temperature in the presence of SO_2 in order to achieve the denitrification and desulfuration of the gases in an unique reactor.

The finally selected catalyst has 5 wt% tungsten oxide in its composition, because tungsta–titania is characterized by both a larger number and stronger Lewis and Brønsted acid sites compared to vanadia–titania, thus, ensuring higher surface ammonia coverage even at high temperatures [23]. However, the catalyst has a low vanadia content (1 wt%) in order to minimize its activity for the ammonia oxidation reactions. Less attention was given to the oxidation of sulfur dioxide in this $DeNO_x$ step of the combined process, since sulfur trioxide may be considered as the product of the overall process.

Establishing the working temperature of this $DeNO_x$ catalyst at 450°C, the influence of space velocity and oxygen concentration on the NO_x conversion were studied to predefined some of the operating conditions for the $DeNO_x$–$DeSO_x$ combined process.

The influence of the residence time, 1/GHSV (h), on the nitric oxide conversion and ammonia slip at a temperature of 450°C and a total pressure of 120 kPa is shown in Fig. 1. The gas-inlet composition was: NO=NH_3=SO_2=1000 ppm; O_2=5 vol%; N_2=balance. At a GHSV of around 10 000 h^{-1}, nitric oxide conversions of 90% were obtained without ammonia slip. No formation of nitrous oxide was detected.

The inlet oxygen concentration was also studied since this parameter affects the performance of sulfur dioxide oxidation catalysts. At 450°C no influence on the reduction of nitric oxide was observed for oxygen concentrations from 1 to 10 vol%, hence this value

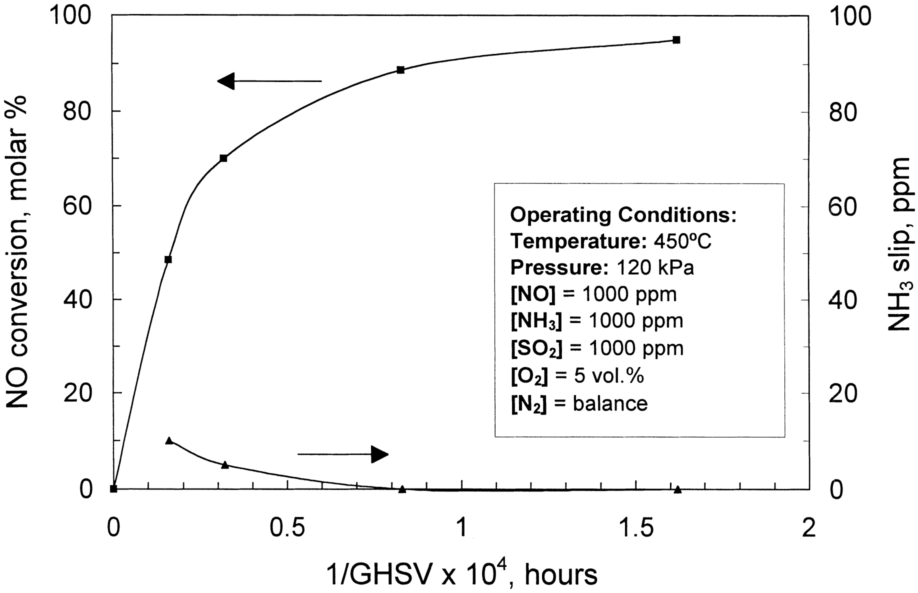

Fig. 1. Variation of the NO conversion and ammonia slip with the residence time. $DeNO_x$ catalyst.

would be defined by the requirements of the $DeSO_x$ process.

The textural properties of the fresh and used catalyst are listed in Table 1. It should be noted that the $DeNO_x$ catalyst exhibits an adequate bimodal pore-size distribution [24] and that the textural values for both samples do not significantly change.

By Laser-Raman spectroscopy of the $DeNO_x$ catalyst, signals of V_2O_5 were not detected, and only the typical peaks belonging to the anatase phase (638, 517, 394 cm^{-1}) were present, indicating that the vanadium oxide remains well dispersed on the titania surface. From SEM-EDX results [25] this catalyst may be described as supported vanadium and tungsten oxides on titania particles dispersed among the magnesium silicate fiber bunches, which enhance the porosity and mechanical properties and allow the configuration of the paste in monolithic form.

3.2. $DeSO_x$ *process*

Different formulations of the $DeSO_x$ catalyst in monolithic shape were prepared by modifying the paste components and the extrusion parameters looking for a compromise between the conformation procedure, and the mechanical properties and catalytic activity of the monoliths The selected active phase composition of the final catalyst corresponds to a mixture of vanadium oxides dissolved in alkali pyrosulfates which is partly or completely liquid under reaction conditions, similar to conventional sulfuric acid manufacturing catalysts [26]. These melted species are dispersed in the pores of a mixture of diatomaceous earth and natural alkali-earth silicates.

Good performance of this monolithic catalyst is obtained at temperatures above 430°C; lower reaction temperatures result in a loss of catalytic activity due to

Table 1
Textural properties of the $DeNO_x$ and $DeSO_x$ catalysts

	$DeNO_x$ catalyst	$DeNO_x$ used catalyst[a]	$DeSO_x$ catalyst (green)	$DeSO_x$ used catalyst[a]
BET surface area ($m^2 g^{-1}$)	97	81	27	<2
Total volume > 8 nm ($cm^3 g^{-1}$)	0.58	0.57	0.27	0.21
Average pore diameter (nm)	29 and 49	33 and 46	78	784

[a] After 300 h on stream.

dramatic changes in the chemical species (increase of the V^{4+}/V^{5+} ratio) and in the physical properties (solidification) of the catalyst active phase. Tests with water vapor present in the gas inlet, with concentrations up to 15 vol%, had no influence on the activity of the catalyst.

In Table 1 some textural properties of this monolithic catalyst are given. The "green catalyst" corresponds to the material dried at 110°C before being treated with SO_2 and O_2 to achieve its final chemical composition. After this treatment, a significant increase in the pore diameter with loss of specific surface area is observed, while the total pore volume remains almost constant. No conclusions concerning the pore structure can be drawn because the catalyst was cooled down to room temperature and the real pore distribution might have been modified during the liquid phase condensation processes.

The results of the thermal gravimetric analysis are shown in Table 2. In the "green catalyst", the loss observed in the first temperature range, 100–300°C, corresponds mainly to water, CO_2 and NH_3 liberation. Between 300°C and 800°C the weight losses are assigned to the decomposition of various impurities of the diatomaceous earth and the natural silicates used in the catalyst preparation. The used catalyst corresponds to a sample which was in operation for 6000 min at 450°C; the loss observed in the range 600–800°C, is mainly due to SO_2 from the pyrosulfates decomposition.

Table 2
Termogravimetric results of the $DeSO_x$ catalyst

Temperature range (°C)	Weight loss (%)	
	$DeSO_x$ catalyst (green)	$DeSO_x$ used catalyst
100–300	4.8	0.0
300–600	7.9	0.0
600–800	2.2	15.7

The activation of the catalyst was carried out feeding air to the reactor at a GHSV of 3500 h^{-1} and raising the reactor temperature at a rate of 10°C per minute up to 400°C. Once that temperature was reached, the inlet gas composition was changed to SO_2=1000 ppm; O_2=5 vol%; N_2=balance, the flow was increased to GHSV=4900 h^{-1} and the reactor temperature raised to 450°C, at a rate of 2°C min^{-1}. From this point, SO_2 concentration in the outlet gas was analyzed. The results are presented in Fig. 2 where two sections may be distinguished. During

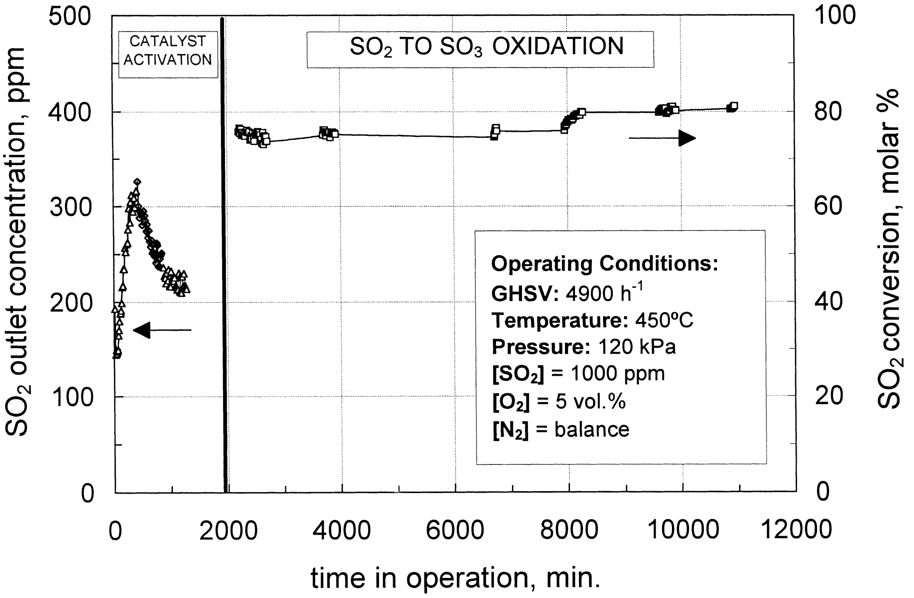

Fig. 2. Start up of the $DeSO_x$ catalyst at the indicated operation conditions.

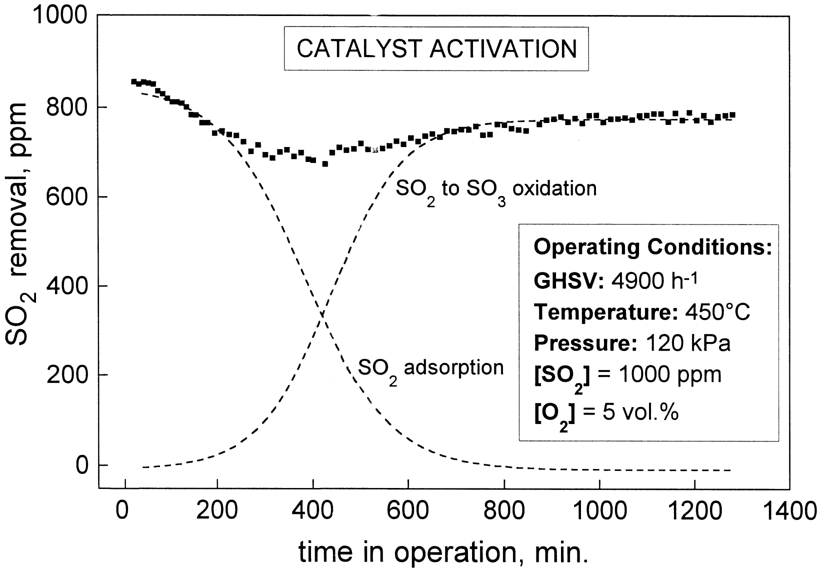

Fig. 3. Simultaneous SO_2 adsorption and SO_2 oxidation during the $DeSO_x$ catalyst activation.

the first 1400 min the monolith adsorbs SO_2 at a rate which decreases with the time in operation; simultaneously the catalyst active phase is being formed and starts to transform SO_2 to SO_3 at an increasing rate giving rise to the maximum observed in the left-hand side of Fig. 2; these two processes are represented in Fig. 3 where the above experimental data – expressed as SO_2 removal – may be considered as the sum of the

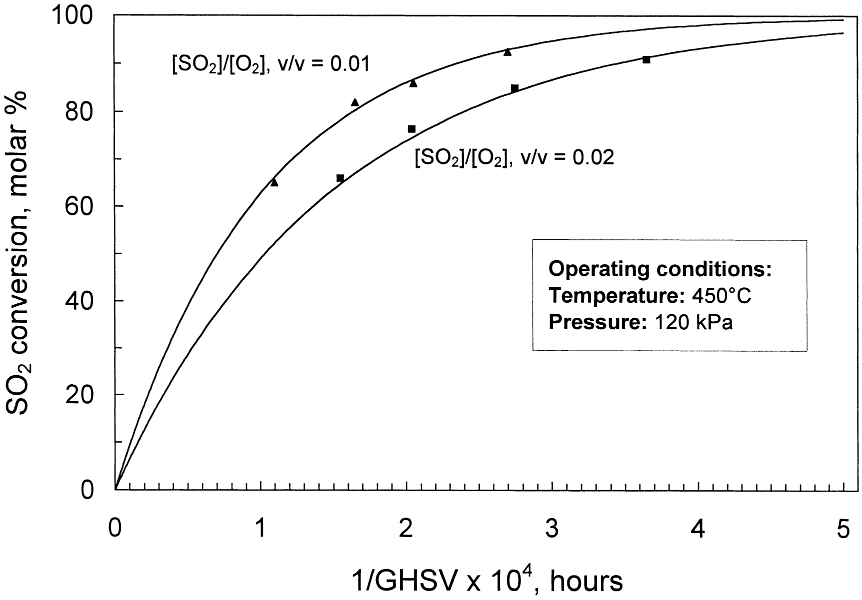

Fig. 4. Variation of the SO_2 conversion, at two SO_2/O_2 volume inlet ratios, $DeSO_x$ catalyst.

SO_2 adsorbed on the monolith and the SO_2 transformed to SO_3.

After the activation period the catalyst seems to reach steady state conditions – right-hand side of Fig. 2 – although a small increase in the conversion value is observed up to 8000 min in operation.

From kinetic experiments the controlling step of the whole process was found to be the chemical reaction on the active catalyst centers. The data fit satisfactorily to a first order kinetic equation with respect to SO_2, where the rate constant varies with the SO_2/O_2 feed ratio and is independent of the SO_3 concentration.

Fig. 4 shows the variation of the sulfur dioxide conversion to sulfur trioxide with the GHSV, at 450°C and two different SO_2/O_2 volume inlet ratios. The SO_2 conversion data were taken at 6000 min in operation. The experimental SO_2 and O_2 inlet concentrations were between 400 and 1000 ppm and 3–6 vol%, respectively.

3.3. DeNO$_x$–DeSO$_x$ *process*

Taking into account the performance of each catalyst, DeNO$_x$ and DeSO$_x$, in their separate processes, a combined two-bed reactor has been designed where molar conversion values higher than 90% and 80% for nitrogen oxide and sulfur oxide, respectively, were obtained.

Fig. 5 gives the activity results for this combined DeNO$_x$–DeSO$_x$ system. It is observed that the NO$_x$ molar conversion is maintained constant at around 90–92% throughout the time in operation. The sulfur dioxide in the inlet gases performs as an effective promoter for the selective reduction of nitrogen oxides with ammonia, leading to increases in the nitrogen oxides molar conversions, probably due to the presence of traces of SO_3 [27] produced by SO_2 oxidation on the DeNO$_x$ catalyst.

The DeSO$_x$ catalyst seems not to be affected by the presence of traces of nitrogen oxides in the gas to be treated, and shows high activity in the removal by oxi-dation of ammonia giving rise to null ammonia slip.

The SO_2 conversion slightly increases with time on line reaching a stable value of 80–82% after 10 000 min in operation.

From the work carried out in this study the following considerations may be derived:

- Molar conversions of 90% and 80% for NO and

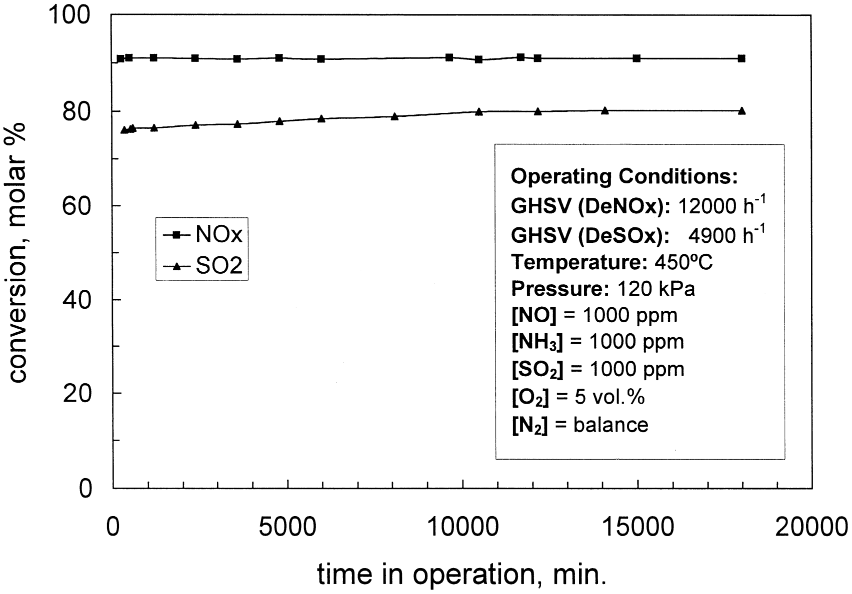

Fig. 5. Variation of the NO$_x$ and SO$_x$ conversion values with the time operation in the two-bed monolithic reactor. DeNO$_x$ and DeSO$_x$ catalysts.

SO_2 were obtained, respectively, with null ammonia slip and no N_2O formation.
- The use of a monolithic two-bed catalytic reactor presents the advantage of low pressure drop, two orders of magnitude lower than that obtained with conventional pelleted catalysts.
- The monolithic structure, mechanical properties and low sticking wall characteristics of both catalysts, allows their operation in high dust configuration.
- The reactor runs without heating between the two catalyst beds, with the subsequent technical simplicity and low operation cost.

Acknowledgements

This work was supported by the CAM (Comunidad Autonoma de Madrid). Project 0057/94. We are also grateful to Dr. M. Yates and Mr. C. Knapp for valuable discussions.

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