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Influence of the operation time on the performance of a new SCR monolithic catalyst

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Abstract

The effect of the time in operation on the performance of a novel monolithic catalyst was studied in a life test carried out with real effluent gases from a coal fired power plant. Although deposition of fly ash and ammonium sulphates were observed, the catalytic activity, physical and mechanical properties of the catalyst remained largely unchanged after 5000 h of operation.

Keywords: SCR monolithic catalyst

1. Introduction

Selective catalytic reduction (SCR) is a well established process for NO_x removal from power plants. The process is widely used due to its high efficiency and selectivity [1]. Monolithic catalysts are utilised in these processes due to the advantages which they present over conventional pelleted catalysts with respect to: the low pressure drop across the catalyst bed, the large external surface, the uniform flow, the low axial dispersion and the radial heat flow [2].

The honeycomb shaped SCR catalysts currently employed for the treatment of gaseous effluents from stationary power plants are generally prepared by supporting vanadium and tungsten oxides on titania [1]. In commercial units, the high activity and selectivity of these materials must be balanced with the drawbacks of their low abrasion resistances and mechanical strengths.

In order to overcome the problems associated with the poor mechanical characteristics the utilization of binders has been proposed. Strong organic or mineral acids [3], although leading to much improved mechanical properties, cause severe reductions in the catalytic activities. However, the agglomeration phenomena is different when a natural magnesium silicate is employed as a binder. Studies have shown [4] that the use of α-sepiolite, a natural mineral of low cost and high abundance in Spain, not only aids the handling characteristics of the paste and provides a structure with enhanced porosity but also improves the mechanical resistance of the finished product with no detrimental effects on the activity and selectivity of the catalyst [5]. From kinetic studies with this catalyst an equation able to reproduce the experimental results, in the absence of mass transfer limitations, has been defined [6]. Under sim-

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ulated industrial conditions the influence of the physical shape of the catalyst has been studied [7] and the effective diffusion coefficient (De) determined [8]. The limitations of mass transfer phenomena were taken into account for the reactor modelling.

2. Experimental

The monolithic catalyst used in this study was produced from vanadium–tungsten/titanium oxides and α-sepiolite, following a method reported elsewhere [9]. The α-sepiolite constituted 50 wt.-% while the atomic composition of titania:vanadia:tungsta was 92:7.5:0.5 respectively. The monolithic catalyst was produced with a square cell shape at a cell density of 8 cells/cm^2. The wall thickness was 0.089 cm with an open section of 0.070 cm^2 and cross section of 0.1253 cm^2, giving a geometric surface area of 846 m^2/m^3 and a bulk density of 0.64 g/cm^3.

In the present study, units of this monolithic catalyst were placed in parallel with the SCR installation of a coal fired power plant operating in a 'low dust' configuration at 320°C. However, the test was conducted with the addition of fly ash in order to simulate a 'high dust' configuration. Thus, the gas composition at the entrance to the catalyst bed was the following: $[NO_x] = 1300$–2400 mg N m^{-3}, $SO_2 = 150$–220 mg N m^{-3}, $SO_3 < 4$ mg N m^{-3}, $O_2 = 3$–5%, $H_2O \leq 8\%$, fly ash = 8–12 g N m^{-3}. Samples of the catalyst were recovered from the installation after 500, 1000, 1500, 3000 and 5000 h and variations in their physical characteristics and catalytic activities were determined.

The porosities were measured by mercury intrusion porosimetry (MIP) using a Micromeritics Poresizer 9320, taking the contact angle and surface tension of mercury as 140°C and 480 mN m^{-1}, respectively. Nitrogen adsorption isotherms were determined using a Micromeritics 1310 ASAP on samples previously outgassed at 140°C. The surface areas were calculated using the BET method from the linear part of the graph, usually located between 0.05 and 0.30 p/p°, taking the area of the nitrogen molecule as 0.162 nm^2.

Thermal gravimetric analysis (TGA) was carried out on a Netzsch STA409EP in an air flow of 75 ml min^{-1} with a heating rate of 5°C min^{-1}. Powder X-ray diffraction (XRD) was recorded on a Philips PW1710 powder diffractometer using CuK$_\alpha$ radiation ($\lambda = 0.1518$ nm). The axial strengths of the monoliths were measured with a Chatillon LTCM Universal Tensile and Spring Tester. The compositions of the catalyst surfaces were determined by energy dispersive X-ray analysis (EDX), using a LINK EXL detector.

The laboratory scale catalytic activities were measured in a monolithic reactor described elsewhere [9], working in isothermal conditions. The analyses of NO and NO_2 at the reactor's inlet and outlet were made by chemiluminescence in a Luminox 201 B (BOC) and the NH_3 concentration was determined by nondispersive infrared spectroscopy in a Luft model (ADC). The oxidation of SO_2 to SO_3 was determined by the ASTM method 711. In this technique the SO_3 is condensed as a sulphuric acid mist by controlled cooling of the flue gas. The condensate collected over a period of 4 h is then titrated to determine the acid content.

3. Results and discussion

The fresh sample had a pore volume of approximately 0.5 cm^3 g^{-1} and a BET surface area of about 90 m^2 g^{-1}. However, during the first 1000 h there was a progressive reduction in both the total pore volumes (TPV) and surface areas compared to the original material conditioned at 500°C for 4 h. With longer exposure times these values remained at the levels reached after the first 1000 h. The variations in the TPV and BET area with operation time compared to that of the fresh catalyst are shown in Fig. 1.

The XRD spectroscopy results are shown in Fig. 2, where the diffractogram designated S-T obtained with the monolith made from sepiolite conditioned at 500°C for 4 h is also included for

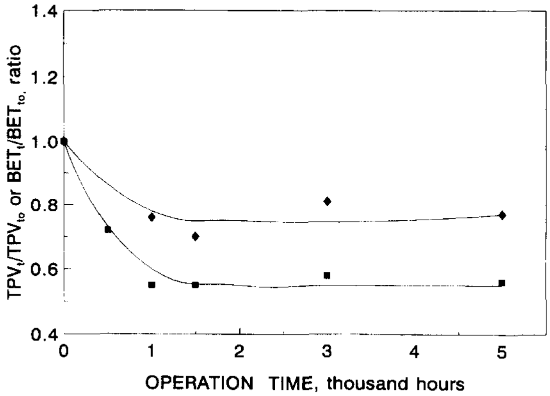

Fig. 1. Variation in the TPV ■ and BET Area ◆ vs. operation time.

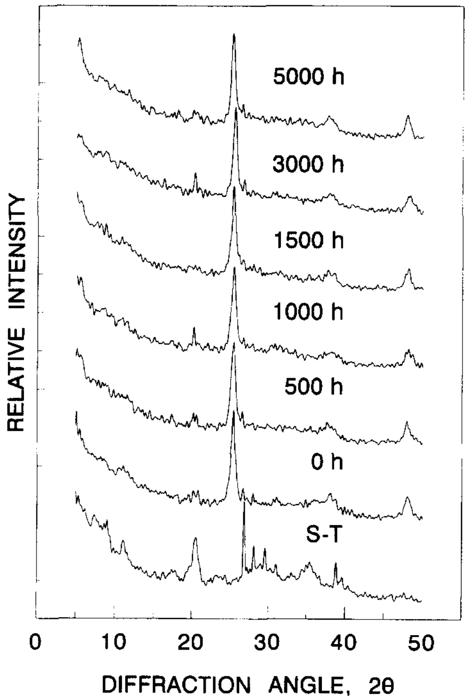

Fig. 2. X-ray analyses after various exposure periods.

comparison. From the diffractograms of the exposed samples it may be concluded that no important variations in the nature of the phases of the catalysts were produced during the life test, with the titania remaining as the anatase phase. The peaks observed at $2\theta = 20.74$, 26.6, 28.0 and 31.1, which could have been assigned to V_2O_5, clearly belonged to the α-sepiolite treated at 500°C. The high dispersion of the V_2O_5 component in the catalyst was confirmed through the absence of the corresponding peaks from FT-Laser Raman spectroscopy.

Chemical analysis of each sample was carried out by SEM-EDX at the bulk (I) and external (E) surfaces. Quantitative differences in the spectra of samples exposed for different periods of operation were displayed. The V_2O_5/TiO_2 ratio and the weight percent of SO_3 and SiO_2 in relation to the operation time are presented in Fig. 3. The V_2O_5/TiO_2 ratio in the bulk and external surfaces remained constant throughout the test; the line profiles of Ti, V and Si demonstrated [4] that the vanadium component was only associated with the titania particles and not the sepiolite fibres.

The SO_3 concentration in the bulk increased during the first 1000 h, then was maintained almost constant with operation time. However, a continuous rise in the SO_3 concentration on the external surface versus operation time was observed. This same pattern was repeated with the SiO_2 content. The slight increases of SO_3 and SiO_2 on the external surface, and the stabilization of both concentrations in the interior of the catalyst, indicated that the deposition of siliceous fly ash and ammonium sulphates largely took place on the external surfaces.

The EDX analysis of the deposits present on the surfaces of the catalyst after exposure to exhaust gases is presented in Fig. 4. The existence of Si, Al, Ca, K, Fe and S compounds, together with small amounts of phosphorous compounds confirmed that these deposits were mainly due to fly ash and ammonium sulphates [10].

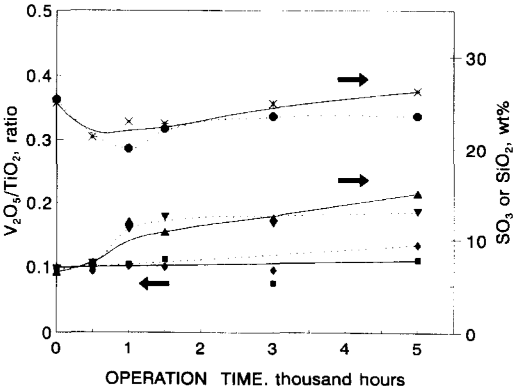

Fig. 3. EDX analysis of the external (E) and internal (I) catalyst surfaces versus operation time. V_2O_5/TiO_2 (E) ■, V_2O_5/TiO_2 (I) ◆, SiO_2 (E) ▲, SiO_2 (I) ▼, So_3 (E) *, So_3 (I) ●.

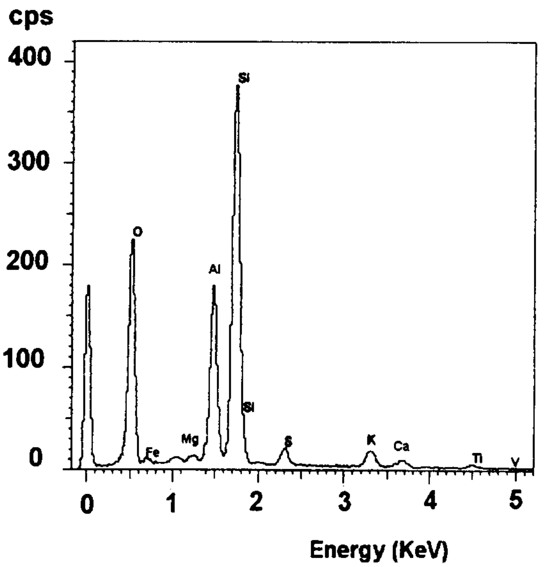

Fig. 4. EDX spectra of the deposits observed on the catalyst surface.

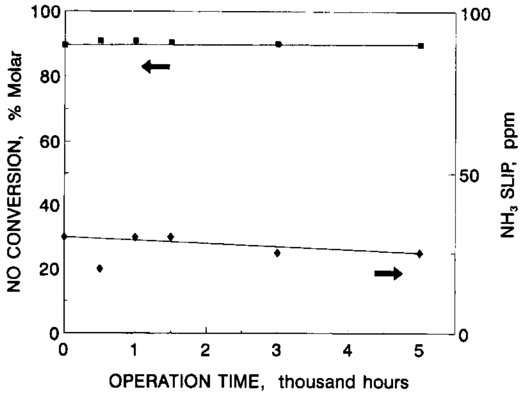

Fig. 5. Catalytic activity vs. operation time.

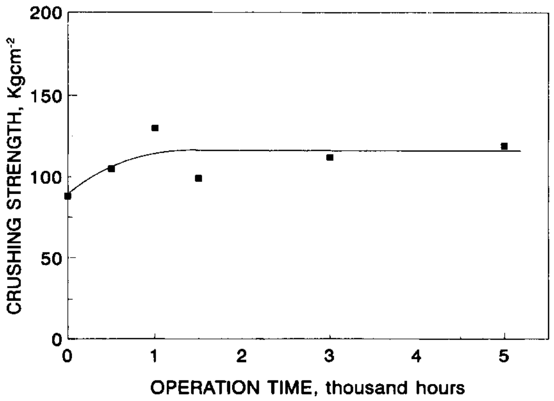

Fig. 6. Crushing strength vs. operation time.

The weight losses observed by thermal gravimetric analysis of the exposed samples between 700° and 1000°C were attributed to the decomposition of sulphates deposited on the monolith, produced by the reaction between SO_x and NH_3 present in the flue gases. The quantities were in good agreement with the afore mentioned EDX analysis.

Laboratory scale activity tests were performed at 320°C, 120 KPa, $AV = 7.9\ N\,m\,h^{-1}$, with a feed composition of $[NO] = [NH_3] = 1000$ ppm, $[O_2] = 3\%$, and N_2 as balance. At the end of the experiment SO_2 was added in place of NH_3 to determine its possible oxidation under simulated reaction conditions.

The NO conversion values, obtained with the samples of catalyst during the test are given in Fig. 5, as a function of the operation time. It may be observed that NO reduction values of the samples exposed for 500 and 1000 h were slightly higher than that corresponding to the fresh catalyst. After 1500 h, the NO conversion values remained constant.

The fresh monolithic catalyst gave an ammonia slip of less than 10 ppm at 350°C under the laboratory conditions, however during the life test, carried out at 320°C, this value was ca. 25 ppm. These levels were maintained constant for the whole 5000 h exposure period. The SO_2 oxidation reaction remained negligible over the 5000 h test period, at below 0.01%.

In Fig. 6 the crushing strength is plotted versus the operation time. The strength increased during the initial 1000 h and then remained constant with longer exposure periods.

4. Conclusions

The results demonstrated that during a life test of 5000 h exposure to real exhaust gases this novel monolithic catalyst maintained excellent performance characteristics in the reduction reaction of nitrogen oxides with ammonia.

In relation to the textural properties, it should first be noted that up to 1000 h there was a progressive reduction in both the total pore volume and the surface area. However, with longer exposure times, some of the total pore volume was recovered and the surface area values were maintained almost constant. Evaluation of porosimetry data showed that exposure to real gases did not greatly modify the pore size distribution.

Although quantities of fly ash and ammonium sulphate were deposited on the exposed catalyst surface, the activity remained unaffected during the 5000 h test. It should be emphasised that the activity of this catalyst towards the undesirable SO_2 oxidation was always less than 0.01 mol-%.

These results clearly demonstrate the high potential for this monolithic catalyst to be used commercially for the control of NO_x emissions from power plants. Not only because of its excellent activity and mechanical properties shown over the 5000 h test but also due to the much lower cost of the finished product in comparison to the commercial catalysts presently in use.

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