Long-term stability of the V_2O_5/Al_2O_3 catalyst for the selective reduction of nitrogen oxides

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Changes of the V_2O_5/Al_2O_3 catalyst aged for up to 10 years under real conditions of the selective catalytic reduction of NO_x by ammonia (SCR) at the tail gases of the nitric acid plant were characterized by ^{51}V NMR spectroscopy, porosimetry, temperature programmed reduction (TPR) and catalytic activity measurements. The catalytic activity and the redox properties of the catalyst were found intact. Only small variations of the ratio of the octahedral and tetrahedral vanadia species were documented by ^{51}V NMR on aged catalyst.

Keywords: vanadia / alumina; stability; NO_x selective reduction

1. Introduction

Since the first industrial installations of the SCR systems at the beginning of the seventies, supported vanadia still remains the most important and widely used catalytic system for this environmentally important process.

The long-term behavior of the catalyst and its resistance to deactivation is one of the most important parameters. This strongly influences the commercial value of the catalyst and the economy of the SCR process. Due to the basic limitations of the accelerated deactivation studies [1], information gathered during a real long-term test should still be useful for optimization of the catalyst life.

There are several potential mechanisms bringing about the deterioration of an industrial catalyst, nevertheless transformation of the surface active species and changes of their intrinsic activity are probably of the highest importance.

It is well established that the catalytic activity of vanadium oxides is significantly influenced by the interaction of the active vanadium oxide phase with the support and the formation of oxovanadium species stabilized on the support [2]. This interaction is the result of very complex processes, initiated during the impregnation of the support [3] and continuing during the heat treatment [4]. The development of the active surface of the fresh catalyst is further accomplished during the first several hours under the reaction conditions [5].

In this study we report the changes of the V_2O_5/Al_2O_3 catalyst used in the SCR industrial process for up to 10 years using several physicochemical techniques.

2. Experimental

2.1. CATALYST PREPARATION

In principle, the catalyst was prepared by the usual preparation method. Thus extrudates of γ-Al_2O_3 (diameter approximately 6 mm and length 15–25 mm) were impregnated by an aqueous solution of vanadyl oxalate. Then the extrudates were dried and calcined in air. The vanadia content of the prepared catalyst was 12–14 wt% of V_2O_5. Details of the preparation procedure are subject of the know-how of the producer of the catalyst.

2.2. WORKING CONDITIONS OF THE SCR INDUSTRIAL PROCESS

The catalyst was used on tail gases of a nitric acid production plant. The typical conditions of the reactor operated with one batch of catalyst without replacement were as follows:

reaction temperature: 220–270°C;
reaction pressure: nearly atmospheric;
space velocity: approx. 10 000 h^{-1};
NO_x content: inlet 0.2–0.4 vol%, outlet <200 ppm.

The catalyst samples for the tests were taken from the upper layer about 10 cm beneath the surface of the catalytic bed after 4, 8 and 10 years of plant operation. Catalyst samples withdrawn from the industrial reactor were preserved in sealed containers and kept in dark.

To compensate for a random fluctuation of the vanadium oxidation state caused by accidental variations of the actual conditions during the long-term SCR test and samples preservation, all catalysts were oxidized before characterization by calcination at 450°C for 2 h in air. It could be expected that some minor characteristics of the aged catalysts were altered by such procedure and thus the irreversible changes of the aged catalysts were monitored at the following tests.

2.3. CATALYST CHARACTERIZATION

Specific surface area and porosimetry measurements were carried out on a Digisorb 2600 and an Auto-Pore 9200 (Micromeritics, USA). Temperature programmed reduction (TPR) data were obtained using a conventional flow apparatus with a thermal conductivity detector, heating rate of 20°C min^{-1}; a flow of 80 $\mathrm{ml\,min}^{-1}$ of a reaction mixture containing 10% of H_2 in purified nitrogen was used. In all experiments the amount of sample, calculated as V_2O_5 present, was about 10 mg. The catalytic activity in the NO–NH_3–O_2 reaction was determined on an integral isothermal reactor, using about 1.0 g of the catalyst and a flow (30 $\mathrm{Nl\,h}^{-1}$) of the reaction mixture, consisting of 0.4 vol% of NO, 0.4 vol% of NH_3, and 3 vol% of O_2, with nitrogen as a balance. The catalytic activity was expressed as conversion of the NO present in the feed. ^{51}V NMR spectra were measured using a Bruker MSL-400 spectrometer (magnetic field 9.39 T) at 105.2 MHz in the frequency range of 250 Hz. 1 µs radio frequency pulses were used with a pulse repetition rate of 10 Hz. The ^{51}V chemical shifts were measured relative to $VOCl_3$ external standard.

3. Results

Specific surface area and porosimetry. About 20% decrease of the original surface area, i.e. from about 200 $\mathrm{m^2\,g^{-1}}$ to about 155 $\mathrm{m^2\,g^{-1}}$ has been found for the catalyst after a 10 year run at the SCR process. As it was accompanied by an increase of the average pore radius (from 7.3×10^{-3} to 9.8×10^{-3} µm) but without any substantial change of the total pore volume (about 0.7 $\mathrm{cm^3\,g^{-1}}$ for all samples), the decrease of the surface of the aged samples could probably be explained by disappearance of the narrowest pores.

TPR. For all catalysts a similar TPR profile with only one maximum at about 470°C has been obtained. These results are illustrated in fig. 1, showing also the more complex profile typical of the unsupported V_2O_5.

Catalytic activity. The measurements under laboratory conditions over the temperature region of 200–350°C have shown that the catalytic activity has not changed substantially (see fig. 2). This is consistent with the stable performance of the SCR installation over the whole operation time of the catalyst.

^{51}V NMR spectroscopy. The spectra of the vanadia catalysts after various times of industrial utilization are presented in fig. 3. The spectra consist of several superimposed lines with changing proportion of the individual lines at the region of −350 to −1250 ppm.

4. Discussion

It has been shown that the catalytic performance of the V_2O_5/Al_2O_3 catalyst is very stable and even 10 years of industrial utilization at the SCR does not substan-

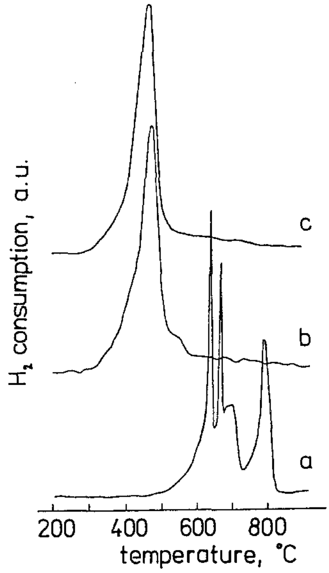

Fig. 1. TPR profiles of the pure V_2O_5 (a), the catalyst before (b) and after utilization at the SCR reactor for 10 years (c).

tially change its catalytic activity. It should be stressed that, according to the nature of the recommended operation of nitric acid production, the tail gases are completely free of either alkali metals and sulphur dioxide or dust particles. These characteristics are, according to literature, critical for deactivation of the vanadia catalysts [6,7].

Some sintering of the narrowest pores has been indicated but obviously with limited relevance to the catalytic activity.

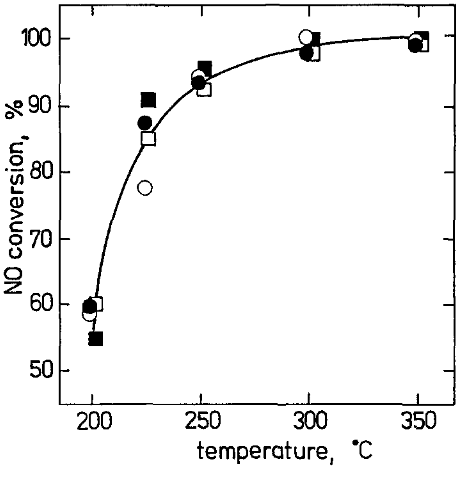

Fig. 2. The standard activity test of the catalyst before (○) and after 4 (●), 8 (□), and 10 years (■) of utilization at the SCR reactor.

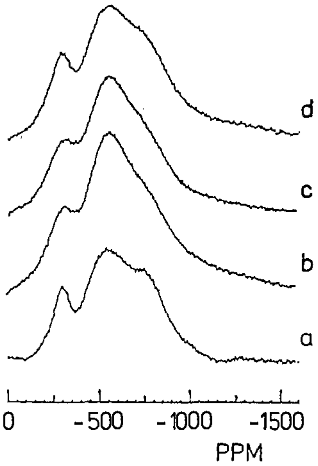

Fig. 3. ^{51}V NMR spectra of the catalyst before (a) and after 4 (b), 8 (c), and 10 (d) years of utilization at the SCR reactor.

The redox properties of the used catalyst were found intact (see fig. 1). In accordance with the previous results all catalysts displayed at the TPR experiment the same shift of the first peak to lower temperatures, if compared to the bulk V_2O_5, a feature characteristic of supported vanadia catalysts [8].

In the absence of any high extent of sintering or poisoning there is an opportunity to identify a possible slow solid-state interaction between vanadium oxide and the alumina support.

The stable catalytic activity during the whole span of the industrial exploitation may imply that the amount of the catalytically active centers on the catalyst surface is constant. Nevertheless, this could occur also if some transformation of the other vanadia surface species takes place due to the expected mobility of the various vanadia surface species [9] and the existence of an equilibrium of the individual surface species controlled by the vanadia content [10]. Accordingly for such evaluation the full identification of the various surface oxovanadium complexes, as provided by ^{51}V NMR spectroscopy is necessary [3,11].

The redistribution of the oxovanadium species as revealed by the ^{51}V NMR measurement is illustrated in fig. 3. In accordance with the previous results [3], several surface complexes with different coordination of the oxygen ligands have been identified at the V_2O_5/Al_2O_3 samples. Two kinds of tetrahedral VO_4 species, one with nearly regular tetrahedral coordination and loosely bound to the alumina surface (line A with $\delta = -550$ to -590 ppm with an isotropic line shape), and the other of isolated VO_4 species with higher number of V–O–Al bounds to the support (line B with $\delta = -750$ ppm and an isotropic line shape) have been identified at the samples. The third oxovanadium surface form was attributed to polynuclear species on the Al_2O_3 surface with a distorted octahedral environment of O atoms having one short V–O bond (line C with $\delta = -350$ ppm). The line belonging to the $AlVO_4$ phase and V_2O_5, both previously indicated in samples with higher vanadia content [3,10] were missing in our samples.

It is obvious that after some reconstruction of the vanadia surface species during the catalytic tests, as manifested by the change of the ratio of the isolated VO_4 species (line A) and the other oxovanadium forms, the samples were stabilized and the ^{51}V NMR spectrum displayed a rather high stability of the relative population of the individual surface vanadium forms. There is an indication of a relative decrease of the polynuclear form (line C) with the subsequent increase of the more strongly bound tetrahedral species (line B). This behavior probably reflects a partial transformation of the polynuclear species into isolated VO_4 species and an increase of the forms which are more strongly bound to the support. Nevertheless, this transformation process has taken place mostly during the transient period and no substantial changes have been found during several years of industrial exploitation.

Quite significantly formation of the $AlVO_4$ phase has not been found in any stage of the test. This is not surprising as these species are unstable under the conditions of the $NO–NH_3–O_2$ reaction [10].

5. Conclusions

No solid state and irreversible process between vanadia and alumina phases was identified under the conditions of the SCR process at temperature up to 270°C. The stability of the surface vanadia species under such conditions was found to be high enough to ensure the V_2O_5/Al_2O_3 catalyst to preserve its high activity for at least 10 years.

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