

A New Class of Environmental Friendly Vanadate Based NH₃ SCR Catalysts Exhibiting Good Low Temperature Activity and High Temperature Stability

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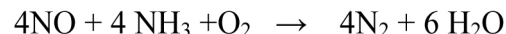
ABSTRACT

For the removal of NO_x from the oxygen-rich diesel exhaust in mobile applications the selective catalytic reduction (SCR) is one of the most favoured technologies. Well established NH₃-SCR technique uses either V₂O₅/WO₃-TiO₂ or Zeolite based catalysts, NO_x being continuously reduced by NH₃ resulting in the selective formation of nitrogen and water. A major drawback of V₂O₅ based formulations is their lower thermal stability and low temperature activity, in addition, V₂O₅ release poses serious environmental and toxicity problems. In active filter regeneration performed by post-injection of fuel the temperature may increase up to 800°C resulting in drastic loss of activity (due to poor stability of V₂O₅ based formulations) as well as discharge of V₂O₅. Zeolite-based catalysts promoted by transition metal such as Fe and Cu represent an excellent solution to overcome the stability problems of V₂O₅-based catalysts with only a small activity penalty and cost raise issues but may show disadvantages in stability after hydrothermal ageing. In the present study a new class of rare earth modified Fe vanadates are shown to be valid substitutes of V₂O₅ in SCR catalyst providing i) good activity in the low temperature window (180°C-300°C) ii) high temperature stability up to 850°C,

with no major associated activity loss, iii) absence of toxicological and environmental concern.

INTRODUCTION

The most widely employed technology for removal of NO_x out of exhaust gases of stationary sources is the so called *standard*-SCR (selective catalytic reduction) process. Accordingly, NO_x is converted by ammonia into nitrogen and water in line with the reaction:



The application of this technique to the mobile sources has to overcome some difficulties, such as dynamic operating conditions, the broadening of the operational window, improvement of the low-temperature activity and high-temperature stability.

A typical SCR system in mobile applications consists of a reduction catalyst, urea injection (as an ammonia source), dosing components, pipes and a storage tank. A huge number of modern catalysts are extruded or coated substrates based on titanium /tungsten (TiO₂/WO₃) with vanadium pentoxide (V₂O₅) as the catalytically active component. Normally, in a conventional vanadia-based SCR catalyst the active phase is

referred to as V_2O_5 but actually, as demonstrated by Raman analyses [1], it consists of polyvanadate species and isolated vanadyl centers [2].

With increasing stringent automobile exhaust emission regulations for diesel vehicles (e.g. EURO 6 regulations) after-treatment systems comprising both a diesel particulate filter (DPF) and a SCR catalyst will be required in future [3].

Such systems will demand a higher temperature stability of the SCR catalyst and V_2O_5 based systems are not considered viable for such applications. In addition, due to the toxicological concern of the V_2O_5 component of currently used vanadia-based catalysts its possible release into environment represents a problem. Significant discharges of various components of automotive catalysts have been proven to take place due to fracture and abrasion effects during operation [4, 5, 6, 7].

There were reported maximum operation temperatures for a $TiO_2/WO_3/V_2O_5$ catalyst of 550°C and 580°C for short term basis [8]. In view of the application under EURO 6 an improvement in thermal stability of a V_2O_5 containing TiO_2/WO_3 based catalyst is required [8]. Accordingly a catalyst containing V_2O_5 as active component and a support material consisting of TiO_2/WO_3 and additionally containing Si may be operated at the maximum temperature of 600°C and 650°C on a short term basis. However, the system may be not operated at higher temperatures.

In diesel applications the catalytic activity in the low temperature range (180°C-300°C) must be enhanced in respect to what currently applied in stationary applications. This has been achieved by means of different techniques.

A commonly used method for improving the SCR catalytic activity in removing nitrogen oxides at low temperatures is that of increasing the NO_2/NO molar ratio in the exhaust gases. It is well known that the reaction between ammonia and nitrogen oxides with an optimum NO_2/NO unit molar ratio, called *fast*-SCR proceeds according to the following stoichiometry [9, 10, 11]:



In the case of SCR applications to vehicles, the promoting action associated with NO_2 is achieved by positioning a diesel oxidation catalyst upstream of the onboard SCR unit to partially convert NO to NO_2 ; the DOC is typically based on Pt or other precious metals [12].

An improvement in terms of the thermal stability of a V-containing $TiO_2/WO_3/SiO_2$ SCR catalyst has been already reported [13]. According to a preferred embodiment the

vanadium is present not in the form of vanadium pentoxide but in form of a rare-earth vanadate ($REVO_4$). The catalysts prepared according to [13] exhibit high NOx conversion after being thermally treated at 750°C for 10 hours, in contrast with the reference material made of V_2O_5 on $TiO_2/WO_3/SiO_2$ which was almost inactive after undergoing the same thermal treatment [14]. Further investigation on this catalyst showed that in the low temperature range, that is 200°C - 230°C, it did not show any catalytic activity; its NO conversion at 250°C was 25% for the sample calcined at 650°C for 2 hours. After aging the catalyst at 700°C for 10 hours an increase of catalytic activity was found, but still very low conversion rates were measured (6%, 20% and 55% respectively at 200°C, 230°C and 250°C). Despite its low NO SCR activity values, this catalyst still exhibits higher conversion rates than a state of the art catalysts currently applied in heavy-duty diesel SCR, based on formulation of vanadium pentoxide on $TiO_2/WO_3/SiO_2$ after heat treatment at 700°C for 10 h.

In the present investigation the problem of the low-temperature NO conversion of vanadium pentoxide-free based catalysts and the toxicological and environmental behaving of the catalytically active metal-vanadate compounds are addressed. We have shown that changing the formulation of the $REVO_4$ -based catalyst by introducing a transition metal or a transition metal/rare-earth vanadate on the same $TiO_2/WO_3/SiO_2$ support, thermal resistance and low temperature NO conversion activity are considerably enhanced.

The transition metal and transition metal rare-earth vanadates applied for the preparation of the catalyst were investigated on their health risks and showed a significant improvement of the toxicological and environmental profile when compared with V_2O_5 .

EXPERIMENTAL

PREPARATION OF THE CATALYTICALLY ACTIVE COMPONENT (METAL-VANADATE) - $Fe_xEr_{(1-x)}VO_4$ ($x = 0 - 1$)

To prepare metal-vanadates of the general formula $Fe_xEr_{(1-x)}VO_4$ ($x = 0-1$) the calculated stoichiometric amount of iron(III)nitrate nonahydrate and erbium nitrate hexahydrate were dissolved in deionised water to yield a (mixed) metal nitrate solution. A second aqueous solution was prepared by dissolving ammonium metavanadate in deionised water at approximately 80°C. After the two solutions were mixed under continuous stirring, the pH was adjusted to 7.25 by adding ammonia solution. The precipitate so formed was stirred, filtered, washed and dried.

PREPARATION OF THE POWDER CATALYST

The metal-vanadate prepared was used to make an aqueous slurry which was mixed with a second slurry containing the titania/tungsta/silica (weight % ratio $\text{TiO}_2/\text{WO}_3/\text{SiO}_2 = 81/9/10$) support (TWS). The weight% ratio of metal vanadate/TWS typically was 8,4/91,6.

The combined slurries were evaporated to dryness and the solid obtained was dried at 120°C followed by calcination at 650°C for 2 hours to yield the so-called “fresh catalyst powder”. It was pressed into pellets, crushed and sieved in the range 355-425 μm to obtain the fresh powder catalyst.

AGING TREATMENTS

Aging treatments were carried out on the fresh catalyst in a muffle furnace at different temperatures in the range $700\text{-}800^\circ\text{C}$ for 10 hours. When more severe conditions were required, further thermal treatments of 50 or 100 hours at 700°C were made.

CATALYST CHARACTERIZATION

Surface areas of the catalysts were measured with the B.E.T. method by nitrogen adsorption at 77 K, using a Tristar 3000 gas adsorption analyzer (Micromeritics).

X-ray powder diffraction (XRD) patterns of the samples were collected in the range $10^\circ < 2\theta < 60^\circ$ using a Philips X'Pert diffractometer equipped with a Ni-filtered Cu K α radiation operated at 40 KV and 40 mA. Phase identification was conducted with the aim of the Philips X'Pert HighScore software.

TESTING OF POWDER CATALYSTS

Investigations on NH_3 -SCR activity were conducted by means of a laboratory equipment described in Figure 1. The powder catalyst was put in a down-flow tubular quartz microreactor inserted in a furnace; the temperature was controlled by a thermocouple inserted in the catalyst bed. The feed gas composition and the experimental conditions are reported in Table 1. High space velocities were used in order to obtain conversions typically in the range 40-90%. Mass flow meters were used to measure and control the single gaseous streams, while water was injected by using an injection pump. The feed stream was preheated and premixed with the exception of ammonia which was added to the gas mixture immediately before entering the microreactor in order to avoid side reactions. Activity of the samples was measured under stationary and dynamic conditions (ramp $3^\circ\text{C}/\text{min}$) in a temperature range of 200°C - 480°C . Results obtained with the two different methods were comparable on the entire temperature window investigated. Gas composition after SCR reaction was analyzed with an FT-IR spectrometer

(MKS Multigas Analyzer 2030) equipped with a heated multi-pass gas cell (5.11m length).

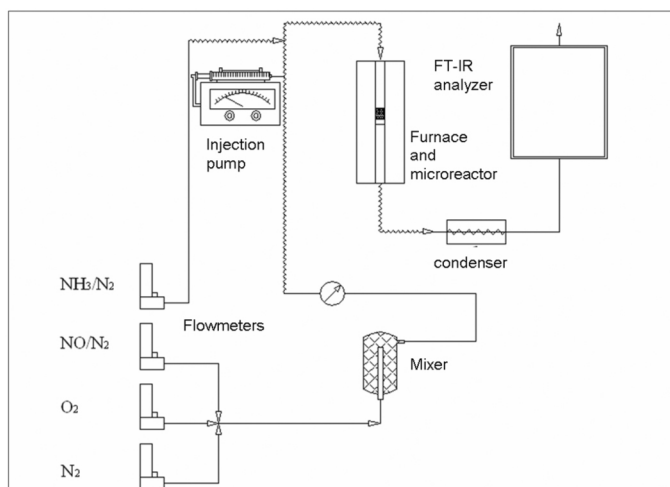


Fig. 1. schematic view of the experimental set-up for catalytic powder testing.

Table 1. experimental conditions and feed gas composition for catalyst powder test

Experimental conditions	
catalyst weight	100 mg
particle size	355-425 μm
total flow	0.3 l/min
GHSV	180000 h^{-1}
temperature range	$200\text{-}500^\circ\text{C}$
Gas composition	
NO	200 ppm
NH_3	220 ppm
O_2	20000 ppm
H_2O	10%
N_2	balance

PREPARATION OF A HONEYCOMB CATALYST (WASHCOATED CORDIERITE)

A cordierite honeycomb having a cell density of 400 cpsi, was coated with a slurry prepared of a mixture consisting of approximately 80 weight% of a catalyst composition $\text{TiO}_2/\text{WO}_3/\text{SiO}_2 : \text{Fe}_x\text{Er}_{(1-x)}\text{VO}_4$ ($x = 0\text{-}1$) and approximately 20 weight% Al_2O_3 as a binder. The washcoat loading is 120-160 g/L of catalyst with the suspension used for the coating containing approximately 170 g/L of solid.

After impregnation of the honeycomb with the slurry the catalyst was dried with a hot air stream (= fresh catalyst).

AGING TREATMENTS OF HONEYCOMB CATALYST (HYDROTHERMAL AGING)

The aging of the catalyst was performed under hydrothermal conditions at temperatures in the range from 680°C to 750°C for different periods in an air stream containing 10% water at an air flow rate of 200 L/h.

TESTING OF HONEYCOMB CATALYST

The catalytic test was performed according to the parameters disclosed in [Table 2](#).

Table 2. experimental conditions and feed gas compositions for catalytic test of honeycomb catalyst.

Reactor	2.54 cm
Catalyst	Cordierite honeycomb 400 cpsi, 2.54 cm diameter, h = 5.08 cm, Vol = 25 cm ³
Space velocity	30 000 h ⁻¹
Temperature	200-550°C / ramp of 5°C/ min
NO _x conc.	400 ppm at different conditions (a) NO, more than 90% (b) NO ₂ about 75% (c) NO:NO ₂ = 1:0.9-1.1
NH ₃ : NO _x	1
O ₂ conc.	6 %
H ₂ O conc.	7 %
N ₂ conc.	balance

TOXICOLOGICAL AND ENVIRONMENTAL BEHAVIOR OF METAL-VANADATES

Out of the group of Metal-Vanadates the ErVO₄, FeVO₄ and the Fe_{0.5}Er_{0.5}VO₄ were subjected to a “Bioeffect Screening” comprising in vitro tests to determine any cytotoxic, genotoxic, embryotoxic and estrogenic potential.

For the evaluation of cytotoxicity the XTT-Test, for the genotoxicity the UMU-Test, for the embryotoxicity the Modified EST-Test and for evaluating the estrogenic potential the so called E-Screen Assay method were applied.

The XTT test was performed in accordance with [15], the UMU-test was performed according to [16], the Modified EST-Test according to [17] and for the estrogenic potential (E-Screen Assay) the method according to [18] was applied.

Ecotoxicological effects were investigated by determination of the aquatic toxicity evaluating the EC50/48h against the microorganism “Daphnia magna” and the EC50/ 72h against the microorganism “Desmodesmus suspiciatus”.

The “Daphnia” and “Desmodesmus” tests were accomplished in accordance with the guidelines of OECD [19,20].

RESULTS AND DISCUSSION

As previously reported, a first generation of vanadium pentoxide-free catalysts containing REVO₄ as the de-NO_x active phase lead to an increase in the SCR activity after aging with respect to the vanadia-based catalyst [14]. The enhanced thermal resistance was attributed to the presence of the rare earth element chosen as the dopant. This was confirmed by the fact that the enhancement was promoted only by some of the elements belonging to the group of the rare-earths. [Figure 2](#) shows the relation between NO conversion increase/decrease after thermal treatment and the ionic radius of the rare earth element used as the dopant. All the rare earth vanadates containing catalysts could be broadly divided into two groups, the first one comprising La, Ce, Pr and Nd, which suffer deactivation after aging at 750°C for 10h, and the second one comprising Yb, Er, Dy, Tb, Gd and Sm, in which aging procedure shows a promoting effect. The RE-vanadate led to a SCR catalyst which catalytic activity even increased after thermal treatment at 700°C and 750°C for 10 hours. The drawback that could hinder the implementation of such catalysts in mobile applications was their low temperature SCR activity. In order to address this problem a change in the catalyst formulation was carried out to obtain standard-SCR catalyst with high activity in the 200°-300°C temperature range without losing the thermal stability benefits obtained with the RE doping.

The dopant formulation was modified by considering transition metal elements particularly Fe. Fe was introduced in the form of the single-metal vanadate or in combination with rare earths as mixed iron - rare earth vanadates.