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Redox behaviour of vanadium during hydrogen–oxygen exposure of the V_2O_5-WO_3/TiO_2 SCR catalyst at 250 °C

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ABSTRACT

A series of experiments was conducted to reveal the impact on the catalyst and NH_3-SCR activity of an industrial deNO$_x$ catalyst from Haldor Topsøe A/S (V_2O_5-WO_3/TiO_2) by exposure to H_2 and H_2/O_2. Treatment of the SCR catalyst was done by exposure for 60 min with three different concentrations of H_2 (0–2%) in an 8% O_2/N_2 mixture, where the SCR activity was measured before and after the hydrogen treatment. The results show that the activity of the SCR catalyst is only negligibly affected during exposure to the H_2/O_2 gas and in all cases it returned reversibly to the initial NO_x conversion rate after reexposure to the standard NH_3-SCR gas. *In situ* electron paramagnetic resonance (EPR) and UV–vis spectroscopy at 250 °C suggest that a significant part of V^{4+} present during SCR conditions was oxidized to V^{5+} during exposure to 2% H_2 + 8% O_2. However, the distribution of vanadium in oxidation states V^{4+} and V^{5+} returned to the initial redox equilibrium in less than an hour after the hydrogen–oxygen treatment, emphasizing the reversibility of the V^{4+}-V^{5+} system.

1. Introduction

Vanadium oxide based catalysts are widely used in catalysis and especially when supported on other metal oxides they exhibit remarkable properties. Among others, vanadium oxide surface sites are very active in adsorption of organic molecules. This process follows a Mars van Krevelen mechanism, where the adsorbed organic molecule is oxidized via reduction of the superficial metal cation [1–3]. Ammonia is also easily and strongly adsorbed on vanadium active sites. Centi et al. described competitive adsorption phenomena between ammonia and oxygen in propane ammoxidation reaction to acrylonitrile on bulk VPO catalysts [4]. The commercial V_2O_5-WO_3/TiO_2 catalyst is widely employed for the selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with ammonia as reductant.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

SCR is used for NO_x removal from flue gases from stationary sources, and more recently also for exhaust gases from diesel trucks [5]. The chemical and mechanistic aspects of the NH_3-SCR processes have been reviewed previously by Busca et al. [6]. Most authors agree that the SCR reaction for vanadia-based systems takes place according to an Eley-Rideal mechanism, involving strongly adsorbed ammonia species and gaseous or weakly adsorbed NO species. Wachs et al. observed that the vanadium turnover frequency of sub-monolayer V_2O_5/TiO_2 catalysts is enhanced either by increasing the vanadium coverage or by adding tungsten oxide [7,8]. The SCR reaction is believed to preferentially take place on two adjacent vanadium sites, and/or a vanadium site next to a tungsten site [9]. This also complies with the dual-site mechanism proposed by Topsøe et al., involving an acid/base and a redox function [10].

The vanadium–hydrogen system has been subject of many investigations because vanadium is capable of storing relative large amounts of hydrogen [11]. Also the vanadia–titania system has been subject of numerous studies, due to its wide applicability for important industrial processes, such as NH_3-SCR, VOC-oxidation, oxidation of o-xylene to phtalic anhydride [12] and acetic acid production from ethanol [13]. In a study of V_2O_5/TiO_2 catalysts with different loading of vanadia by Boghosian et al. [14], the reducing

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effect of various reducing gases was investigated. The effect of H_2 was shown to be more pronounced at high temperature (>400 °C) and low vanadium surface coverage.

Special interest has been given to the WO_3-promoted catalyst optimized for the SCR reaction, where a combined acid/base and redox cycle accounts for the selective reduction of NO with ammonia via the reaction (Eq. (1)). It is well established that at the relevant oxygen concentration and reaction temperature of conventional installations (350–420 °C), the reaction order of oxygen becomes quasi zero order [15] due to the fast reoxidation of the intermediate vanadium (IV) species formed in the redox cycle, very characteristic for vanadium oxide based catalysts [16]. Retro-fitting the technology to lower temperatures (e.g. 250 °C) is possible, however, the kinetics are more complicated, since the lower reoxidation rate triggers a certain dependence on the O_2 concentration in the gas phase [17]. Operating deNO$_x$ catalysts at this temperature is becoming an attractive solution for many types of installations, especially in relative small scale installations, like e.g. NO elimination units in municipal waste plant etc.

Municipal waste flue gas was previously found to deactivate the Pt-based CO oxidation catalyst severely. In the specific case studied, siloxanes were found to cause the deactivation [18] of the active Pt/PtO centers. An on-site method for complete regeneration of the catalysts activity was found without necessity of shutdown of the flue gas stream, i.e. by *in situ* treatment of the Pt-catalyst by reductive H_2 gas. The process works both in the absence and the presence of oxygen. However, the introduction of H_2 gas in the gas stream could also affect other units in the tail pipe gas cleaning system. Of special interest in this study is the effect of hydrogen gas on the performance of the selective catalytic reduction (SCR) process, i.e. the catalytic removal of NO$_x$ from the flue gas. The SCR unit is often placed directly after the CO oxidation catalyst in municipal waste burning facilities. Based on the literature mentioned above, it is expected that the vanadium system is resistant toward hydrogen treatment at normal incineration conditions, especially if oxygen also would be present along with hydrogen in the regeneration gas.

However, since fairly little *in situ* spectroscopy regarding the reducibility of the V_2O_5-WO_3/TiO_2 system for NH_3-SCR can be found in the literature and since using hydrogen as a probe molecule provides fundamental insight of the redox behavior of this important redox system, the present study is focused on the structural properties of vanadium oxides combined with the SCR activity of the $3V_2O_5$-$7WO_3$/TiO_2 catalyst during exposure to hydrogen–oxygen mixtures and normal NH_3-SCR gases.

2. Experimental

2.1. Catalyst preparation

Commercial SCR catalyst samples were obtained from Haldor Topsøe A/S, and consist of 3 wt% V_2O_5, 7 wt% WO_3 on a TiO_2 anatase carrier ($3V_2O_5$-$7WO_3$/TiO_2). The precursors were co-impregnated onto TiO_2 using the conventional incipient wetness method followed by calcination in air at 450 °C. The DNX catalyst has a specific surface area around 60 $m^2\,g^{-1}$ and is shaped as a fiber reinforced monolithic system. Preparation of the samples for activity measurements demanded that the active material was extracted from the monolith surface, excluding the fiber matter, and then pressed into tablets (Ø = 13 mm, 5 tonne), crushed, and sieved to obtain the 180–295 μm fraction.

2.2. NH_3-SCR with ammonia

The SCR activity measurements were carried out in a fixed-bed quartz reactor. Around 50 mg of the catalyst was loaded between two layers of inert quartz wool. The reactant gas composition for SCR was: 1000 ppm NO, 1100 ppm NH_3, 3.5% O_2, 2.7% H_2O, and balance N_2. The total flow rate was maintained at 300 Nml/min. The NO concentration was continuously monitored by a Thermo Electron's Model 10A Rack-Mounted Chemiluminescent NO-NO$_x$ Gas Analyzer.

Exposure of the catalyst to $H_2/O_2/N_2$ or H_2/N_2 was done through a bypass to the feed gas. The impact of hydrogen/oxygen on the catalytic activity of the V_2O_5-WO_3/TiO_2 catalyst at 250 °C was investigated in two steps. First, the effect of hydrogen on the catalytic activity at steady state was studied vs. time by 10% H_2/N_2 exposure. The activity was measured when the system, re-exposed to the SCR-gas, returned to steady-state (minimum 20 min after hydrogen exposure). Secondly, a diluted mixture of hydrogen and oxygen was applied. Three experiments were performed with several hydrogen concentration values: 0, 0.5 and 2.0% H_2 in 8% O_2/N_2. The catalyst was subjected to the $H_2/O_2/N_2$ gas for 60 min, followed by re-exposure for up to 45 min to the operating NH_3-SCR gas.

2.3. EPR Spectroscopy

The influence of the SCR and $H_2/O_2/N_2$ gas on the catalytic system was studied by *in situ* electron paramagnetic resonance (EPR) spectroscopy. For the EPR measurements, particles with a size of 180–295 μm were used. The sample was placed into a reactor cell specially designed for high temperature EPR measurements using a Bruker standard ER4102ST cavity equipped with an ER 4141VT unit with added air-cooling of the Teflon nuts placed outside the cavity. Spectra were recorded *in situ* at 250 °C (conditions similar those during activity measurements, but without dilution of the sample) using a Bruker EMX EPR spectrometer. Thus, conversion degree is expected to be similar or slightly less (due to possible internal diffusion limitations) compared to the activity measurements described above.

2.4. In situ UV–vis spectroscopy

Redox properties of the catalyst were studied by *in situ* UV–vis DRS Spectroscopy. UV–vis spectra were recorded after equilibration in dry air for at least 30 min in the range 200–1100 nm on an AvaSpec 2048TEC spectrophotometer equipped with a diffuse-reflectance attachment using halon as a reference. The quartz reactor was filled with 0.5 grams of the catalyst with the particle size between 180 and 295 μm. Spectra were collected every third minute at 250 °C. A 100 ml/min gas flow was added in the sequence as follows: a) 3.5% O_2/N_2, b) 2.7% H_2 + 8% O_2 in N_2, c) 3.5% O_2/N_2, d) 2.7% H_2/N_2. Finally, the catalyst was heated to 500 °C in 2.7% H_2/N_2.

2.5. In situ Raman spectroscopy

The Raman spectra were run under *in situ* conditions with a single monochromator Renishaw System 1000 equipped with a cooled CCD detector (−70 °C) and holographic super-Notch filter. The samples were excited with the 488 nm Ar^+ beam, operated at 15 mW; spectral resolution was approx. 3 cm^{-1}. The Raman spectra were run at 250 °C under dehydrated conditions after the catalyst had been oxidized in dry air at 400 °C for an hour. The *in situ* Raman study during hydrogen oxidation were obtained under reaction conditions (in a gas mixture of 8 ml/min O_2, 90 ml/min N_2 and 2.7 ml/min H_2) in a home-made reaction cell, using quartz tubing connected to an optical quality quartz cuvette [19]. Essentially, it is a fixed-bed catalytic reactor with walls that are optically appropriate for in situ Raman spectroscopy. Tests were made using 0.5 g of sample with particle dimensions in the 0.25–0.125 mm range.