

# Chemical deactivation of $V_2O_5/WO_3-TiO_2$ SCR catalysts by additives and impurities from fuels, lubrication oils and urea solution

## Part II. Characterization study of the effect of alkali and alkaline earth metals

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Received 23 May 2007; received in revised form 26 July 2007; accepted 27 July 2007

Available online 2 August 2007

### Abstract

A characterization study on a practice-oriented  $V_2O_5/WO_3-TiO_2$  SCR catalyst deactivated by Ca and K, respectively, was carried out using  $NH_3$ -TPD, DRIFT spectroscopy, and XPS as well as theoretical DFT calculations. It was found from  $NH_3$ -TPD experiments that strongly basic elements like K or Ca drastically affect the acidity of the catalysts. Detailed DRIFT spectroscopy experiments revealed that these poisoning agents mostly interact with the Brønsted acid sites of the  $V_2O_5$  active phase, thus affecting the  $NH_3$  adsorption. Moreover, these experiments also indicated that the  $V^{5+} = O$  sites are much less reactive on the poisoned catalysts. XPS investigations of the O 1s binding energies showed that the oxygen atoms of the  $V^{5+} = O$  sites are affected by the presence of the poisoning agents. Based on these results and on DFT calculations with model clusters of the vanadia surface, the poisoning mechanism is explained by the stabilization of the non atomic holes of the (0 1 0)  $V_2O_5$  phase as a result of the deactivation element. Consequently, V–OH Brønsted acid sites and  $V^{5+} = O$  sites are inhibited, which are both of crucial importance in the SCR process. The deactivation model also gives an explanation to the very low concentrations of potassium needed to deactivate the SCR catalyst, since one metal atom sitting on such a non-atomic hole site deactivates up to four active vanadium centers.

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**Keywords:** Catalyst deactivation; SCR catalyst; Ammonia adsorption; DRIFT; XPS; DFT

### 1. Introduction

Selective catalytic reduction (SCR) of  $NO_x$  is a wide-spread process for the abatement of  $NO_x$  from the flue gas of stationary emission sources and the exhaust gas of Diesel trucks. In this process  $NO_x$  reacts with the reducing agent  $NH_3$ , which might be fed either directly or in the form of harmless  $NH_3$  precursors, such as urea solution [1]. The catalysts used for this process contain 1.0–2.5 wt.%  $V_2O_5$  supported on anatase- $TiO_2$ . This system is promoted by 8 wt.% tungsta ( $WO_3$ ), which increases the acidity of the catalyst surface [2,3], promotes the spreading of the vanadia on the surface and inhibits the transformation of anatase to rutile.

The mechanism of the  $NH_3$ -SCR reaction over  $V_2O_5/WO_3-TiO_2$  and the way in which the catalytic sites are involved has been extensively investigated over the last few decades. Most of the authors working on this topic came to the conclusion that the V–OH Brønsted acid sites play a key-role during the SCR reaction. One of the first to support this theory was Inomata et al. who proposed an activation mechanism for  $NH_3$  on the V–OH Brønsted acid sites, and tentatively proposed a role of the  $V^{5+} = O$  sites adjacent to the Brønsted acid sites [4,5]. This model was further supported and validated by Jansen et al. who gave more emphasis to the role of the  $V^{5+} = O$  sites as the easiest reducible species on the catalyst surface that could trap  $NH_3$  as V–O– $NH_2$  and subsequently reduce the adjacent V=O site to V–OH [6]. Beside these theories, Ramis et al. proposed a mechanism that involves only Lewis acid sites on vanadia [7–9]. However, recently published results of DFT calculations on a  $V_2O_9H_8$  cluster showed that the adsorption of  $NH_3$  on Lewis

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acid sites is highly unfavorable [10]. Based on their results these authors proposed a mechanism where, on first instance  $\text{NH}_3$  is activated on the V–OH Brønsted acid sites, and then it reacts with NO to finally form  $\text{H}_2\text{N-NO}$ . These authors also found that  $\text{V}^{5+}=\text{O}$  is the most favorable site where decomposition of  $\text{H}_2\text{N-NO}$  takes place. This decomposition mechanism would be achieved by a push–pull hydrogen transfer between the  $\text{V}^{5+}=\text{O}$  and V–OH sites.

Due to the presence of significant amounts of additives in engine lubrication oils and in the fuel and due to the presence of impurities in the urea solution, combusted as well as uncombusted deactivating agents are deposited on the SCR catalyst. These deposits can strongly affect the catalytic performance, as shown in part I of this study for the elements Ca, K, Mg, Zn, P, B, Mo, and their combinations [11]. The most important results of the catalytic tests are summarized in Table 1.

It is obvious from these results and the literature that the deactivation of SCR catalysts is an important issue, which requires explanations in the context of the proposed mechanisms. Structural characterization studies on the deactivation mechanism on tungsta-free SCR catalysts have been performed by several authors. It was shown that strong deactivation agents like K cause a decrease of acidity and prevent an effective activation of  $\text{NH}_3$  on the surface [12–14]. However, only a few studies were performed on tungsta-containing catalysts [3,15–19] and we are unaware of any investigations dealing with the chemical deactivation of SCR catalysts for Diesel vehicles. Moreover, no clear evidence was supplied about how these strong deactivation agents act on a molecular level. Only recently, a clearer picture was provided by means of a DFT calculation of the  $\text{V}_2\text{O}_5$  (0 1 0) surface represented by a  $\text{V}_{10}\text{O}_{31}\text{H}_{12}$  cluster containing one atom of an alkali metal [20]. According to this model, the deactivation agent preferentially occupies a non-atomic hole site of the (0 1 0)  $\text{V}_2\text{O}_5$  surface, and blocks the oxygen centers that are involved in the SCR process.

In the present paper we report on the characterization of a practice-oriented  $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$  catalyst for Diesel SCR systems, deactivated by Ca and K, respectively, by means of  $\text{NH}_3$ -TPD, DRIFT spectroscopy, and XPS experiments. Additional theoretical calculations of the XPS binding energies helped to interpret the results in terms of the above mentioned interaction model. This paper follows up preliminary findings, reported in [21], and a detailed investigation of the effects of the poisoning additives on the catalytic performance of the  $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$  catalysts [11].

## 2. Experimental

### 2.1. Sample preparation

Samples containing Ca, and K, respectively, were prepared by incipient wetness impregnation of a  $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$  catalyst powder (Wacker Chemie GmbH). The formulation is based on a  $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$  catalyst, which was originally developed at the Paul Scherrer Institute with about 10 wt.%  $\text{WO}_3$ , >2%  $\text{V}_2\text{O}_5$  [22] and a specific surface area in the range  $S_{\text{BET}} = 55\text{--}60 \text{ m}^2/\text{g}$ . According to Bond and Tahir, the amount of  $\text{V}_2\text{O}_5$  is below the theoretical monolayer capacity relative to the measured surface area [23].

Firstly, the catalyst powder was dried at  $120^\circ\text{C}$  for 16 h, and cooled to RT in a desiccator. The K- and Ca-containing samples were prepared by impregnating the dry powder (0.7 ml/g water pore volume) with a 3.8 mg/mL aqueous solution of  $\text{K}_2\text{CO}_3$  (puriss, Fluka) and 9.4 mg/mL aqueous solution of  $\text{Ca}(\text{CH}_3\text{COO})_2$  (96%, Merck), respectively. The freshly impregnated powders were dried at ambient conditions for 4 h and at  $120^\circ\text{C}$  for 16 h. Finally the powders were calcined at  $500^\circ\text{C}$  for 4 h. A Ca +  $\text{PO}_4$  containing sample was prepared for the purpose of comparison by sequential impregnation, i.e. first,  $\text{PO}_4$  was spread by using a solution of 6.5 mg/ml of  $\text{H}_3\text{PO}_4$  (Merck) and then Ca by using a solution of 9.5 mg/ml of  $\text{Ca}(\text{CH}_3\text{COO})_2$ . Drying and calcination steps were applied after each impregnation step. The loading of each poisoning element was 0.4 mol% as confirmed by elemental analysis.

### 2.2. Temperature programmed desorption of $\text{NH}_3$ and DRIFT experiments

Temperature programmed desorption of ammonia ( $\text{NH}_3$ -TPD) was carried out by means of a Thermo TPDRO 1100 instrument, equipped with a TCD detector. About 0.2 g of powder catalyst were placed in a quartz tubular reactor and subjected to an oxidative pre-treatment prior to each  $\text{NH}_3$ -TPD experiment. For this purpose the sample was heated to  $500^\circ\text{C}$  at  $30^\circ\text{C}/\text{min}$  in a stream of 10%  $\text{O}_2$  in He (20 mL/min), held at  $500^\circ\text{C}$  for 5 min, and then cooled down to  $50^\circ\text{C}$ .

In the actual  $\text{NH}_3$ -TPD experiment the sample was saturated at  $50^\circ\text{C}$  with a gas mixture of 5%  $\text{NH}_3$  in  $\text{N}_2$  for 15 min. At the end of the saturation process, the sample was flushed with pure He at 20 mL/min until the TCD signal was stabilized. Then, the

Table 1  
Deactivation potential of different poisoning agents and their combinations on the SCR activity of  $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$  [11]

| Relative $\text{DeNO}_x$ at 10 ppm $\text{NH}_3$ slip | Element (0.4 mol% based on catalyst and $\approx 20$ mol% based on vanadium) |                            |                             |                             |                             | Influence of increasing amounts of K |
|---|--|----------------------------|-----------------------------|-----------------------------|-----------------------------|--------------------------------------|
| >95% moderate deactivation                            | P  | B                          | $\text{CaSO}_4$             | Mo                          | $\text{PO}_4 + \text{BO}_3$ |                                      |
| 75–85%  | Zn   | $\text{Zn} + \text{PO}_4$  | $\text{Zn} + \text{BO}_3$   | $\text{Ca} + \text{PO}_4^a$ |                             | K (0.1 mol%)                         |
| 40–70%  | $\text{Ca}^a$  | $\text{Ca} + \text{BO}_3$  | $\text{Zn} + \text{CaSO}_4$ |                             |                             | K (0.2 mol%)                         |
| 20–40%  | $\text{Ca} + \text{Zn}$  | $\text{K} + \text{CaSO}_4$ |                             |                             |                             |                                      |
| <20% strong deactivation                              | K  | $\text{K} + \text{PO}_4$   | $\text{K} + \text{BO}_3$    | $\text{K} + \text{Zn}$      | $\text{K} + \text{Ca}$      | K (0.4 mol%) <sup>a</sup>            |

The last column shows the influence of increasing amounts of K.

<sup>a</sup> Samples used for structural characterization in the present study.

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