



A complete reaction mechanism for standard and fast selective catalytic reduction of nitrogen oxides on low coverage VO_x/TiO₂(001) catalysts



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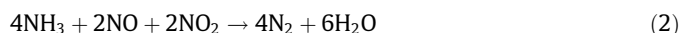
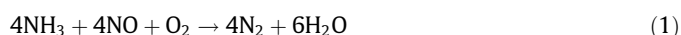
ABSTRACT

We present a complete catalytic mechanism describing both the Standard and the Fast selective catalytic reduction (SCR) reactions in their correct stoichiometric form on a vanadia titania (anatase 001 facet) based catalyst model. It consists of two cycles, a NO-activation cycle and a Fast SCR cycle that share the same reduction part but use NO + O₂ and NO₂ respectively for the reoxidation. The stoichiometry of the Standard SCR reaction is obtained by coupling the two cycles and the stoichiometry of the Fast SCR reaction is represented by the Fast SCR cycle. We establish structures and energetics for each elementary reaction allowing us to calculate the rate for the two reactions by microkinetic modeling. We find at low temperatures the rate for the Standard SCR reaction is determined by H₂O formation and desorption as neither NO nor O₂ reacts exothermically with the reduced site prior to H₂O desorption. On the contrary NO₂ reacts directly with the reduced site resulting in higher rate for the Fast SCR reaction at low temperatures. The rate for the two reactions is the same at higher temperatures as the rate determining step is in the reduction part which is common to both reactions.

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1. Introduction

The selective catalytic reduction (SCR) of NO and NO₂ (NO_x) by NH₃ to N₂ and H₂O is a well-established technology to control the emission of NO_x formed during combustion in diesel engines, power plants and other pollution sources. The three-way catalyst (TWC) used in gasoline vehicles removes more than 99% of the NO_x formed but requires a near-stoichiometric gas mixture and no oxygen. Diesel engines are on the contrary lean burn and the catalyst has to work in excess of oxygen. With the SCR technology subsequent NO_x removal is possible using NH₃ as a reducing agent according to the following:



Reaction (1) is the so-called Standard SCR reaction where equimolar amounts of NH₃ and NO form N₂ and H₂O. When NO₂ is present the SCR process can run according to reaction (2) which is inherently faster than reaction (1) and therefore referred to as the “Fast SCR” reaction [1]. In automotive applications ~90–95% of the NO_x in diesel exhaust is NO, and Fast SCR is promoted by

the oxidizing catalyst upstream to the SCR catalyst that forms NO₂ from NO, to yield a near optimum of NO/NO₂ = 1 [2]. Due to legislation requiring more stringent emission control on NO_x gasses targeting a reduction in their negative impact on the environment in form of contribution to air pollution, acid rain formation and depletion of the ozone layer [3–5], it is important to improve the performance of the commercially available catalysts used today. In order to achieve that goal a fundamental understanding of the underlying mechanism governing the SCR chemistry is needed. The most widely used catalyst for the SCR process is vanadium oxide (vanadia) dispersed on titania oxide (anatase), but also copper- and iron-zeolites are available on the market. Additionally, vanadia based catalysts are used for several oxidation reactions such as dehydrogenation of propane and oxidation of ethanol, mercury oxidation and o-xylene to phthalic anhydride [6–10]. The VO_x/TiO₂ system for SCR has been studied extensively in the past and a number of reaction mechanism have been proposed e.g. Takagi [11], Inomata [12], Jansen et al. [13], Ramis et al. [14], Went et al. [15] and Topsøe [16]. However, no clear conclusion about a catalytic mechanism, especially on the atomic level has been made which demonstrates the complexity of the catalytic chemistry of the SCR process. The general agreement is that the SCR reaction is a redox process where NO and NH₃ participate in the reduction and O₂ is needed for the reoxidation. In the first few decades the main motivation for studying the

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SCR reaction was for stationary applications where the working temperature is relatively stable. More recently the focus has been on mobile applications where efficient SCR activity is needed in a larger temperature window. Today it is well established that at low temperatures the reoxidation with O_2 is the rate determining part [17–22] whereas at higher temperatures it is the reduction part [12,14,16,23,24]. However, at high temperatures the catalyst also becomes diffusion limited, so improvements of intrinsic activities are mainly of interest in the low temperature regime. This has motivated the study of the Fast SCR since NO_2 is a better oxidizing agent than O_2 [17–22].

What is missing is a consistent reaction mechanism which reproduces the stoichiometry of the Standard and Fast SCR reactions and explains the transition between reoxidation and reduction being the rate determining steps as the temperature is increased. Additionally, a complete mechanism should be able to identify key intermediates and structural changes on the active site observed by different experimental techniques or serve as an inspiration for interpreting these data and link to structural changes and activity.

In a recent publication we have studied the reduction part of the SCR reaction separately and highlighted the influence of Brønsted acidity on this part of the total reaction [25]. In this paper we link the reduction part to the total reaction mechanism and reveal the more complicated reoxidation reactions of both the Standard and Fast SCR. This is done for a model of low coverage vanadia consisting of a monomeric VO_3H species on the (001) facet of anatase TiO_2 as the starting structure. We then construct a complete reaction mechanism for both the Standard and Fast SCR reactions and provide energetics and structures of the active site, transition states and intermediates along with a microkinetic model comparing the rates of the two SCR reactions under industrial conditions.

2. Computational methodology

All calculations were performed with the Grid-based Projector Augmented Wave (GPAW) program [26,27] with the general gradient approximation (GGA) BEEF-vdW functional [28] and grid spacing of $h = 0.20\text{Å}$. A particular hybrid exchange correlation (XC) functional (HSE06) has been proposed for SCR over Cu ions in zeolites [29–32] based on a better fit of the gas phase energetics. However, even though hybrid and also DFT + U based XC functionals may improve some energetics this does not imply that they are transferable to all energetics [33–37]. BEEF-vdW functional is generated using several training data sets of quantities that represent chemistry, solid-state physics, surface chemistry and vdW dominated interactions. Furthermore, BEEF-vdW has been successfully applied for the description of the interaction between zeolites and molecules [38,39]. This should ensure that BEEF-vdW has a high transferability and makes BEEF-vdW well suited for describing the different chemical interactions present in the NO oxidation reaction but not that it is necessarily better than HSE06. Because we use the BEEF-vdW functional we can establish the uncertainty due to the choice of XC functional and e.g. the intrinsic uncertainty of the activation energy in the reduction part is $E_{act} = 0.59 \pm 0.12$ eV and can therefore give rise to a shift in temperature by 100 K. The lattice parameters of the TiO_2 anatase crystal structure were optimized using the stress tensor method available in the Atomic Simulation Environment (ASE) package [40] to be $a = 3.80\text{Å}$ and $c = 9.67\text{Å}$, deviating from the experimental values by 0.54% and 1.6%, respectively [41]. The unit cell was periodic in the xy plane with a minimum of 10Å between successive slabs in the z-direction containing three layers of TiO_2 and the bottom layer fixed at bulk position. The coverage of V on the

$TiO_2(001)$ surface is 1.7V/nm^2 corresponding to one V in a (2×2) supercell.

Formation energies with respect to the states i and j and a molecule in the gas phase are calculated as

$$\Delta E_{ij} = E_j - E_i - E_{Mol(g)} \quad (3)$$

where a negative value corresponds to an exothermic process. For the corresponding Gibbs free energies the same method is used where gas phase free energies are obtained from the Shomate equations [42] and the harmonic approximation used for calculating the free energy of adsorbed species and transition state intermediates as implemented in ASE [40]

$$\Delta G_{ij}(T) = G_j(T) - G_i(T) - G_{Mol(g)}(T) \quad (4)$$

$$= (H_j(T) - TS_j(T)) - (H_i(T) - TS_i(T)) - (H_{Mol(g)}(T) - TS_{Mol(g)}(T)) \quad (5)$$

$$\cong \left(E_j^{DFT} + E_j^{ZPE} + \int_0^T C_{p_j} dT - TS_j(T) \right) - \left(E_i^{DFT} + E_i^{ZPE} + \int_0^T C_{p_i} dT - TS_i(T) \right) - \left(E_{Mol(g)}^{DFT} + E_{Mol(g)}^{ZPE} + \int_0^T C_{p_{Mol(g)}} dT - TS_{Mol(g)}(T) \right) \quad (6)$$

where E^{DFT} are DFT energies obtained at 0 K, E^{ZPE} are zero point energies, C_p are constant pressure heat capacities and S are entropies. The SCR rates were obtained by microkinetic modeling using CATMAP [43] from the series of elementary reaction equations described in the next section. CATMAP solves a mean-field microkinetic model to steady state using as input the Gibbs free energies calculated according to Eq. (6). The approximations used in this study mean that mainly qualitative conclusions can be drawn as e.g. absolute rates are prone to error due to the exponential dependence on the activation energy while relative rates can be compared. For analyzing the SCR rates and relating to different steps and structures in the mechanism we have used both sensitivity analysis also known as degree of rate control [44] and the apparent activation energy. The degree of rate control is given by

$$X_i = \frac{d \ln R}{d(-G_i/k_B T)}$$

where X_i is a number between -1 and 1 describing the sensitivity of step i . A positive value indicates the rate increases if G_i , the Gibbs free energy for step i decreases i.e. the final state is more stable. A negative value indicates the opposite. The apparent activation energy is defined as

$$E_{App} = - \frac{d \ln R}{d(1/k_B T)}$$

which shows how the rate depends on the surface reaction activation energies and the heats of adsorption of the reactants.

3. Results and discussion

Our analysis here is based on the mechanism in Ref. [45] where Janssens et al. constructed a consistent reaction mechanism for the NH_3 -SCR process on Cu-zeolites. Following the same guidelines, we construct a reaction mechanism on a monomeric $VO_3H/TiO_2(001)$ catalytic model (Fig. 1). It can be regarded as the simplest possible reaction path for the SCR reaction that reproduces the correct stoichiometry of the reaction. The mechanism is presented in Fig. 1, and consists of a reduction part and two separate reoxidation pathways. The initial site, represented by VO_3H attached to the anatase TiO_2 surface, is named A. During the reduction, NH_3 and NO react

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