Molecular Catalysis 436 (2017) 43–52

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

MCAT

Editor's choice paper

Micro-calorimetric studies of NO_2 adsorption on Pt/BaO-supported on γ-Al_2O_3 NO_x storage and reduction (NSR) catalysts—Impact of CO_2

Stanislava Andonova [a,c], Valentina Marchionni [b], Luca Lietti [b], Louise Olsson [a,*]

[a] *Competence Centre for Catalysis, Chemical Engineering, Chalmers University, 412 96 Gothenburg, Sweden*
[b] *Dipartimento di Energia, Laboratory of Catalysis and Catalytic Processes and NEMAS, Centre of Excellence, Politecnico di Milano, via La Masa 34, 20156 Milano, Italy*
[c] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

ARTICLE INFO

Article history:
Received 16 November 2016
Received in revised form 27 March 2017
Accepted 28 March 2017
Available online 21 April 2017

Keywords:
NO_x storage/reduction
NO_x removal
Pt/BaO/Al_2O_3 catalysts
NO_2 adsorption
Micro- calorimetric measurements
TPD
NO_x coverages
Heat of NO_2 adsorption

ABSTRACT

The adsorption of NO_2 on Pt/BaO/γAl_2O_3 catalyst has been investigated by micro calorimetry at atmospheric pressure, NO_x storage tests and temperature-programmed desorption (TPD). The heat of adsorption of NO_2 ($\Delta H_{ads}(NO_2)$) was determined over a wide range of NO_x coverages, as the catalyst was exposed to 500/900 ppm NO_2 in the absence/presence of 5% CO_2 in the range of 423–773 K. The temperature dependent changes of $\Delta H_{ads}(NO_2)$ verified the presence of energetically different NO_x storage sites with different binding strength. The $\Delta H_{ads}(NO_2)$ was found to follow a linear correlation versus temperature, ranging for example from −134.5 to −178.8 kJ/mol for NO_x storage over Pt/BaO/γAl_2O_3 at 423–673 K. Thus, at high temperature mostly strongly bound nitrates were formed, while at lower temperature more loosely bound species were also present. Interestingly, the heat of adsorption was higher when using higher NO_2 concentration, indicating more bulk barium nitrate formation. This is consistent with the TPD data where a clear high temperature peak was visible after adsorption using 900 ppm NO_2 at 423 and 473 K, which was not the case for 500 ppm NO_2. Moreover, the micro-calorimetric data also provided evidence in support of the detrimental effect of CO_2 on the NO_x uptake process. The heat released during the NO_x storage in 500 ppm NO_2 + 5% CO_2 was determined to be significantly reduced *ca.* −97.8 kJ mol^{-1} at 423 K, but *ca.* −134.5 kJ mol^{-1} without CO_2. Furthermore, our results show that it is critical to measure heat of adsorption for surface compounds since they are significantly different compared to thermodynamic data for bulk materials.

1. Introduction

The need to find innovative ways to deal with exhaust emissions of nitrogen oxides (NO_x) and the high environmental standards [1] restricting the NO_x emissions in particular from diesel-equipped vehicles have driven the development of different technologies of NO_x reduction in oxygen rich conditions [2,3]. Thus, over the past several years, the NO_x storage-reduction (NSR) technology originally developed by Toyota Motor Corporation [3–5] has received considerable attention as an economical and effective solution for catalytic abatement of NO_x pollutants in excess oxygen. The typical NSR catalytic systems [6,7] consist of noble metals (Pt, Rh, Pd) for oxidation/reduction purposes, a material for storage, e.g., metal oxides like BaO (or $BaCO_3$ in the presence of CO_2, as under actual conditions), and γ-Al_2O_3 as high surface area support. The concept [6,7] is based on the alternating cycles of lean (abundant in oxygen) and rich (abundant in reductants such as unburned hydrocarbons, H_2 and CO) regimes of the diesel-fuel vehicles. Under typical lean exhaust conditions, NO is oxidized to NO_2 over precious metal sites and reversibly stored as nitrates/nitrites on the storage component and on the support material. Stored NO_x species are subsequently decomposed, released and reduced to N_2 during short periodic excursions to rich (i.e., net reducing) conditions. The storage ability of the NSR catalyst is thus restored after every lean-rich cycle. One of the key factor of this approach [8,9] is thus the presence of a NO_x storage compound and the BaO surfaces play a crucial role for the stability of stored NO_x species and their subsequent reduction in the overall NSR performance of the Pt/BaO/γ-Al_2O_3 catalyst.

In attempt to clarify the mechanism of NO_x storage, extensive studies have been conducted by several research groups [10–16] and the results can be classified into two main categories. Accord-

---

* Corresponding author at: Chemical Engineering, Competence Center for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden.
E-mail address: louise.olsson@chalmers.se (L. Olsson).

http://dx.doi.org/10.1016/j.mcat.2017.03.030
2468-8231/

ingly, the NO_x storage process is described [10,12] to occur initially via oxidation of NO to NO_2 and then the process occurs via a mechanism of disproportionation [11] with Ba nitrate formation and a release of NO in the gas phase. The second storage mechanism [14–16] is based on the so called: “nitrite” route where NO is effectively adsorbed on a Ba site in proximity of a Pt site through stepwise oxidation to form at first a nitrite species that is progressively oxidized into a nitrate. Different experimental [17–25] and theoretical [23,26] studies were focused on the elucidation of the interaction of NO_2 with the storage Ba component, and on the nature of the NO_x absorbed species formed on the surface of the $Pt/BaO/\gamma\text{-}Al_2O_3$ catalyst. Among the numerous studies reported up to date, there is a general agreement for the existence of energetically different NO_x storage active sites that can be differentiated by the mechanism of adsorption. For instance, the storage of NO_x on alumina-supported BaO has been studied extensively in the past several years by Lietti et al. [17] who proposed that the storage of NO_x occurs preferentially more efficiently in the order of BaO, $Ba(OH)_2$ and $BaCO_3$. The abundance of the different Ba sites at the catalyst surface was found to depend on the composition of the exhaust gas and extent of reduction. Similar results were also obtained by Nova et al. [18], who reported that NO_x storage occurs first on BaO and then on $BaCO_3$, which are the most abundant sites following regeneration of the catalyst. Additionally, the presence of two kinds of adsorption sites was also reported by Rodrigues et al. [19], either in the form of large barium carbonate crystals or in the form of highly dispersed barium species on the alumina support. Similarly, it has been indicated by Piacentini et al. [20] where depending on the Ba loading, three different NO_x storage sites were found to exist on the catalyst surface: amorphous BaO, LT-$BaCO_3$ (low thermal stability) and HT-$BaCO_3$ (high thermal stability). Further evidence of multiple NO_x sorption sites, most likely based on the proximity of Ba and Pt components, was obtained in the studies performed by Epling et al. [21].

The nature of the NO_x adsorbed – species on the $BaO/\gamma\text{-}Al_2O_3$ system has been thoroughly discussed in various former studies in the literature [22–27]. Using primarily vibrational spectroscopic techniques and TPD analysis, Szanyi et al. [9,22] have found the existence of two distinctly different nitrate species: NO_x adsorbed more loosely bounded to the surface BaO monomers/dimers strongly interacting with the support and NO_x strongly bounded to the bulk BaO particles, existing in the form of three-dimensional BaO clusters.

There are several kinetic models published in the literature describing the NO_x storage process. A detailed kinetic model was developed by Olsson et al. [28] for a monolithic $Pt/BaO/Al_2O_3$ system. The proposed kinetic model considered that NO is oxidized to NO_2 on Pt sites and that NO_2 is then stored on the Ba component. It was successfully validated by comparing model predictions with experimental data obtained during NO_2 adsorption and TPD experiments. Moreover, there are some models that considers NO_x storage on fast and slow sites, respectively, like the studies by Scholz et al. [32] and by Kočí et al. [33]. In the study by Scholz et al. [32], the model considers that fast NO_x storage occurs at surface barium sites, as determined by the reaction kinetics. Slow NO_x storage occurs at the semi-bulk and bulk barium sites, where diffusion plays a major role. It is assumed that surface, bulk, and semi-bulk sites differ not only in physical appearance, but also in chemical reactivity. Mass-transfer inside the storage particles was also considered in shrinking core-type of models by Tuttlies et al. [30] and Olsson et al. [29,31,34]. Moreover, multiple storage sites have been added to kinetic models to reflect storage on different materials, such as alumina barium and potassium [34–36].

In the above described models, the binding strength of stored NO_x has been tuned to flow reactor data. However, it is a large advantage to measure the heat of adsorption and use this data directly into the models. This will lead to less parameters that need to be fitted and thereby decreasing the correlation between the parameters, which gives stable and robust models. However, to our knowledge, no investigations have been reported in the literature where the heat of adsorption of NO_2 over $Pt/BaO/\gamma\text{-}Al_2O_3$ catalyst was measured.

The objective of the current work is therefore focused on measuring the binding strength of NO_2 on Pt/BaO-supported on $\gamma\text{-}Al_2O_3$ using micro calorimetric studies. The adsorption of NO_2 has been investigated by micro calorimetry, performed in parallel with the time-on-stream of the NO_x storage tests and subsequent TPD analysis. In addition to this, the impact of CO_2 on NO_x adsorption was also investigated, since the mechanism of the NO_x uptake in the presence of CO_2 is believed [37] to occur by competitive adsorption of CO_2 and NO_2 for the same adsorption sites. Thus, the heat of adsorption of NO_2 ($\Delta H_{ads}(NO_2)$) was determined over a wide range of surface NO_x coverages, as the $Pt/BaO/\gamma\text{-}Al_2O_3$ catalyst was exposed to 500/900 ppm NO_2 in the absence/presence of 5% CO_2 at five different temperatures in the range of 423–773 K. Based on these measurements in a combination with TPD analysis, it is possible to provide evidence, as calorimetric verification *(i)* for the presence of energetically different adsorption sites, producing NO_x adsorbed species with different bond strength, *(ii)* in support for the detrimental effect of CO_2 on the NO_x uptake performance and (iii) effect of NO_2 concentration on the binding strengths.

2. Experimental

2.1. Catalyst preparation

Conventional incipient wetness impregnation of $\gamma\text{-}Al_2O_3$ (171 m^2/g, Sasol Puralox SBa-200) was used for synthesis of the $Pt/BaO/\gamma\text{-}Al_2O_3$ and $BaO/\gamma\text{-}Al_2O_3$ samples. The procedure of preparation has been described in detail in Refs. [38,39]. Briefly, the $Pt/BaO/\gamma\text{-}Al_2O_3$ catalyst (1 wt% Pt and 16 wt% BaO) was prepared by consecutive impregnation of the support with aqueous solutions of $Pt(NO_3)_2$ (15.46 wt%, W.C. Heraeus) and $Ba(NO_3)_2$ (99 wt%, Sigma-Aldrich). The noble metal precursor solution was prepared separately and after complete dilution, $\gamma\text{-}Al_2O_3$ powder (pre-calcined at 1023 K for 2.5 h) was slowly added to the aqueous solution under constant stirring at room temperature. The slurry was continuously stirred and freeze dried in liquid nitrogen until the water from the suspension was completely removed. The product was then ground into a fine powder form and calcined at 773 K for 2 h. After that, the barium nitrate precursor solution was slowly added under vigorous stirring at room temperature to the pre-prepared solution of $Pt/\gamma\text{-}Al_2O_3$ sample dispersed in a certain amount of milli-q water. The mixture was continuously stirred for 1 h and then the slurry was again freeze dried and calcined at 873 K for 2 h. In similar way, the non-Pt containing $BaO/\gamma\text{-}Al_2O_3$ sample (the amount of BaO was kept constant at 16 wt% in both samples) was synthesized by incipient wetness impregnation of the $\gamma\text{-}Al_2O_3$ with the aqueous solution of $Ba(NO_3)_2$. Then, after continuously stirring for 1 h the mixture was freeze dried and calcined at 873 K for 2 h.

2.2. Micro – calorimetric and NO_x storage/TPD experiments

The NO_2 adsorption and TPD experiments have been performed using a gas flow-through differential scanning calorimeter (*DSC*) at atmospheric pressure. The design as well as the operation of the experimental set-up has been previously described in Ref. [38]. Briefly, the microcalorimetric cell comprises a pair of two vertical quartz tubes mounted in an electric furnace, part of the assembly of the heat-flux *DSC Setaram Sensys*. One contained the sample