

Mean field modeling of NO oxidation over Pt/Al₂O₃ catalyst under oxygen-rich conditions

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Abstract

This paper deals with catalytic NO oxidation into NO₂ over Pt/Al₂O₃ in oxygen-rich exhaust. Based upon kinetic measurements performed in a gradient free loop reactor and DRIFTS examinations, a mean field model is established to simulate catalytic data and calculate surface coverages. The kinetic model includes a network of 16 elementary reactions whereby NO oxidation is described by an Eley–Rideal-type mechanism. A comparison of measured and simulated data shows that the experimental results of the NO/O₂ reaction are well described by the model. Kinetic parameters for the elementary reactions were taken from the literature or determined from a fit of the model to experimental data. To reduce the number of free parameters, we estimated the activation energy of O desorption for zero coverage and the corresponding linear constant α_2 by numerically simulating the O₂ TPD pattern. For the kinetic model of NO oxidation, the preexponential factors for NO₂ adsorption ($68 \text{ m}^3 \text{ s}^{-1} \text{ m}^{-2}$) and NO oxidation ($104 \text{ m}^3 \text{ s}^{-1} \text{ m}^{-2}$); the activation energies for NO desorption (114 kJ mol^{-1}), NO₂ desorption (72 kJ mol^{-1}), NO oxidation (35 kJ mol^{-1}), and NO₂ dissociation (51 kJ mol^{-1}); and the linear constant α_{13} (14 kJ mol^{-1}) are fitted. Furthermore, the calculated surface coverages provide evidence for the effect of CO, CO₂, and H₂O on the rate of NO oxidation. © 2004 Elsevier Inc. All rights reserved.

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1. Introduction

Diesel engines with direct fuel injection exhibit the highest efficiency for automotive applications. As a consequence, the low fuel consumption of diesel vehicles leads to reduced emissions of the greenhouse gas carbon dioxide (CO₂). However, a serious constraint of diesel engines is the production of the pollutants nitric oxide (NO) and soot. Three-way catalyst (TWC) technology is not suitable for the removal of NO from diesel exhaust [1]. TWC systems have been successfully applied to the simultaneous conversion of NO, hydrocarbons (HC), and carbon monoxide (CO) in gasoline cars since the 1980s. In the exhaust gas of diesel engines only insufficient NO conversion takes place, as the reducing agents HC and CO react mainly with oxygen present

in a large excess. Hence, new catalytic procedures were developed to convert NO under oxidizing conditions [1]. Currently, selective catalytic reduction (SCR) and NO_x storage catalyst (NSC) are the most favored techniques for this application. To reduce the emissions of soot, the use of diesel particulate filters (DPF) is taken into account. Such filter systems are already being applied in passenger cars and buses, for instance, as part of CRT (Continuously Regenerating Trap) systems.

The exhaust after-treatment procedures mentioned above include the oxidation of NO into NO₂ over platinum as a key reaction. In SCR, nitrogen oxides are continuously reduced by ammonia over TiO₂-supported WO₃/V₂O₅ catalysts [2], whereby the NO reduction rate is substantially accelerated in the presence of NO₂ [3]. Nitrogen dioxide is produced here with the use of a Pt/Al₂O₃ pre-catalyst. The NO_x storage catalysts contain platinum and basic adsorbents, such as Ba(OH)₂/BaCO₃. Nitric oxide is catalytically oxidized on the Pt component, and then the formed NO₂ is stored by the

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adsorbents. When the storage capacity is reached, NSC is regenerated by engine management, resulting in the conversion of the chemisorbed nitrogen oxides into nitrogen [4–6]. The CRT technique is based on mechanical filtration and subsequent oxidation of the soot with the use of NO₂ [7]. In the first processing step the soot is separated by the DPF systems, and in the second step the oxidation of the deposited soot is initiated by NO₂ [8]. In this reaction, soot is mainly converted into CO₂, and NO₂ is reduced to NO. In CRT, NO₂ is also formed over a Pt/Al₂O₃ pre-catalyst.

Despite the technical importance of the Pt-catalyzed NO/O₂ reaction under oxygen-rich conditions, very little is available on the details of the mechanism or kinetic modeling of this reaction in the literature. Burch and co-workers [9] have shown that NO oxidation can be described with an Eley–Rideal-type mechanism. They assume the oxygen to be the dominating species on the active Pt sites, whereas NO reacts from the gas phase. This mechanism was confirmed by Olsson et al. [10], Chatterjee [11], and Deutschmann [12]. The latter authors [10–12] have studied the kinetics of NO oxidation over Pt in detail and defined a complex network of the respective elementary reactions.

The interaction between oxygen and active Pt surface under atmospheric pressure conditions was examined by Olsson and co-workers [10] and by Zhdanov et al. [13]. The rates of adsorption and desorption of oxygen were defined with an Arrhenius-type equation, whereby a dissociative adsorption of O₂ is postulated. Furthermore, the activation energy for oxygen desorption was assumed to depend on the oxygen coverage [14].

The aim of this work has been to study the mechanism and kinetics of catalytic NO oxidation over Pt in a realistic diesel model exhaust. Based on the experimental data, a kinetic mean field model, including all elementary reactions, was established to simulate catalytic results and calculate surface coverages.

2. Experimental

2.1. Catalyst preparation

The catalyst used in this study was a Pt/Al₂O₃ system. We prepared the sample by coating γ -Al₂O₃ balls ($d = 0.61$ mm, Sasol) with an aqueous solution of Pt(NO₃)₂ (ChemPur). For impregnation an incipient wetness method was used, that is, a defined volume of the solution was taken such that it was completely absorbed. With this technique the load of platinum could be calculated in a simple way. The coated alumina was dried at 20 °C for 24 h and subsequently at 65 °C for 2 h. After this, a gas mixture consisting of 10 vol% H₂ and 90 vol% N₂ (1000 cm³ min⁻¹) was passed over the sample to reduce the Pt precursor. The catalyst was heated at a rate of 1.7 K min⁻¹ to 300 °C and was held at this temperature for 30 min. The sample was conditioned at 500 °C for 2 h in air. For kinetic studies and TPD the Pt load

was established to be 2 wt%, whereas for DRIFTS analysis a catalyst with a Pt content of 10 wt% was also used. The loading of platinum was confirmed by AAS (AAS 4100, Perkin–Elmer).

2.2. Catalyst characterization

The catalyst that contained 2 wt% Pt was characterized by N₂ physisorption, CO chemisorption, scanning electron microscopy (SEM), and powder X-ray diffraction (PXRD). N₂ physisorption was carried out by with a Sorptomatic 1990 from Porotec. The sample was pretreated at 400 °C for 12 h in vacuum (3×10^{-4} mbar) and cooled to -196 °C, and then the N₂ isotherm was recorded. Based upon these data, the BET surface area, total pore volume, and mean BJH pore diameter were determined. For CO chemisorption also performed on the Sorptomatic 1990, the sample was reduced in pure H₂ at 300 °C for 90 min and then evacuated overnight in vacuum (10^{-7} mbar). After the sample was cooled to 40 °C, the CO adsorption isotherm was measured. The chemisorption of CO was carried out to evaluate both the active Pt surface area and the dispersion of Pt. SEM pictures (LEO Gemini) were taken to determine the size of the Pt particles. PXRD analysis was conducted on a D501 from Siemens with Ni filtered Cu-K α radiation. A 2θ step size was employed with an integration time of 3 s. The sample was measured with a rotation frequency of 2 Hz.

2.3. Kinetic studies

Kinetic studies were performed with a gradient free loop reactor with an external gas cycle. The catalyst (1 g) was fixed in a quartz glass tube (i.d. 11 mm) by a glass frit. The feed gas flowed downward and was a blend of pure components and synthetic air (Messer Griesheim). The latter was added at the reactor inlet to avoid NO oxidation in the stainless-steel lines that were heated to 150 °C. All of the gases were fed from independent flow controllers (MKS Instruments). Water was dosed to the gas stream with a liquid flow controller from Bronkhorst. The temperature was monitored by two K-type thermocouples located directly in front of and behind the catalyst bed. The total volume flow was 400 cm³ min⁻¹ with a recycle ratio ϕ ($\phi = F_{\text{loop}}/F_{\text{out}}$) of 80. The temperature was increased in steps of 25 °C from 150 to 500 °C. The reactor effluents were analyzed after they reached steady state. NO_x was monitored with a chemiluminescence detector (CLD El-ht, Eco Physics), and N₂O, CO, and CO₂ were measured by NDIR (Ultramat 5E from Siemens for N₂O; Binos 5 for CO and Binos 4b.1 for CO₂, both from Leybold Heraeus). Oxygen was detected with a magnetomechanic analyzer (Magnos 6G, Hartmann & Braun). To investigate the effect of O₂, CO, CO₂, and H₂O on the kinetics of the NO oxidation, several gas mixtures were used (Table 1). Before the measurements were made, the catalyst was pretreated in nitrogen flow at 500 °C to remove possible impurities.

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