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Journal of Catalysis 229 (2005) 480-489

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

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

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Received 16 July 2004; revised 27 October 2004; accepted 24 November 2004

Available online 12 January 2005

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 m³ s⁻¹ m⁻²) and NO oxidation (104 m³ s⁻¹ 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.

Keywords: Kinetics; Mean field modeling; Mechanism; Catalytic oxidation; Nitric oxide; Nitrogen dioxide; Platinum; Diesel exhaust

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 places, as the reducing agents HC and CO react mainly with oxygen present

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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 O_2 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). N_2 physisorption was carried out by with a Sorptomatic 1990 from Porotec. The sample was pretreated at 400 °C for 12 h in vacuum (3 \times 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 2 θ 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 analyzator (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.

Table 1 Composition of the feed gas used in the kinetic studies

Mixture	NO	СО	CO ₂	H ₂ O	O ₂
	(ppm)	(ppm)	(vol%)	(vol%)	(vol%)
1	500				1.5, 3.0,
					6.0, 15
2	500	500			6.0
3	500		6.0		6.0
4	500			6.0	6.0
5	500	500	6.0	6.0	6.0

Mass transfer limitations were estimated by Mears [15] and Weisz criteria [15,16]; the estimations indicated that neither film diffusion nor pore diffusion affects the catalytic oxidation of NO or CO. The effect of pore diffusion is also experimentally excluded. In these measurements different particle sizes of the Pt/Al₂O₃ catalyst are used, whereby the realistic diesel model exhaust gas is fed. The results show that the same reaction rate for CO and NO oxidation is obtained for the different catalyst sizes.

Temperature-programmed desorption (TPD) of O_2 was performed with the reactor system described above after the external gas loop was separated. The catalyst (5.0 g) was heated in a N₂ flow at 700 °C for 1 h, cooled to 350 °C, and then treated with a gas mixture that consisted of 2 vol% O_2 and 98 vol% N₂. After saturation, the catalyst was flushed with N₂, and then TPD was started, with nitrogen as a carrier gas (500 cm³ min⁻¹). In TPD the sample was heated to 700 °C at a rate of 14 K min⁻¹. Here O₂ was analyzed by CIMS (Airsense 500, V & F).

The surface compounds formed from reaction of Pt with NO, NO₂, CO, and CO₂ were studied by vibrational spectroscopy. The analyses were performed on an ATI Mattson Galaxy 5020 FTIR spectrometer equipped with a MCT detector (Thermo Mattson) and DRIFTS optics (Graseby Specac). The stainless-steel IR cell contained a ZnSe window and was attached to a gas handling system. The spectra were recorded in the range of 500 to 4000 cm^{-1} with an instrument resolution of 4 cm⁻¹. Fifteen thousand scans were accumulated for a spectrum. The temperature of the sample was monitored with a K-type thermocouple placed ca. 3 mm beneath the sample surface. Before the spectra were collected, the catalyst was ground to powder in an agate mortar for several minutes, charged in the sample holder, and then heated for 5 h at 500 °C in a nitrogen flow of 500 cm³ min⁻¹. We exposed the catalyst to the reactive gases at 30 °C by passing a mixture (20 cm³ min⁻¹) of 500 ppm NO in N₂ or 500 ppm NO_2 in N_2 through the cell. A dose of a mixture that consisted of 500 ppm CO, 2 vol% CO₂ and N₂ as balance was also passed through the cell. We did not expose the catalyst to O_2 because respective bands are expected in the spectral region of the strong lattice vibrations of the Al₂O₃ support. After 20 min of adsorption the cell was purged with nitrogen, and then the analysis was started. The unreacted catalyst was taken as a reference for the spectra (presented in Kubelka-Munk units). Background scans were conducted in a N₂ atmosphere after the same pretreatment as described above. The DRIFTS data are only displayed in the region from 1200 to 1900 cm⁻¹, because at lower wavenumbers a relatively high noise was observed that was associated with strong lattice vibrations. At higher frequencies no features of species adsorbed on Pt were detected.

3. Results and discussion

Based upon the N₂ isotherm, the BET surface of the Pt/Al₂O₃ catalyst was calculated to be 175 m² g⁻¹, and total pore volume was 0.70 cm³ g⁻¹. The mean BJH pore diameter was determined to be 8.6 nm. The active Pt surface area (A_{act}) and the dispersion of Pt [17,18] were deduced from the CO adsorption isotherm with the use of Eqs. (1) and (2). The CO:Pt stoichiometry (*n*) is assumed to be 0.7 [19], whereas the surface area per Pt site (a_m) is taken as 8.07 Å² [17]. Eq. (1) leads to an active Pt surface of 5.3 m² g⁻¹, and the dispersion of Pt is calculated to be 2.1% (Eq. (2)).

$$a_{\rm Pt} = \frac{V_{\rm ads} N_{\rm A} n a_{\rm m}}{V_{\rm m} m w} \times 100,\tag{1}$$

$$D_{\rm Pt} = \frac{a_{\rm Pt}M}{a_{\rm m}N_{\rm A}} \times 100. \tag{2}$$

The denotations used in Eqs. (1) and (2) are as follows: V_{ads} , volume of chemisorbed CO; V_m , molar volume; N_A , Avogadro's number; m, mass of catalyst; w, weight percentage of Pt. The SEM micrograph shows that the mean size of the Pt particles is about 200 nm. Furthermore, the PXRD data prove the existence of crystalline Pt, which is indicated by the respective (111) and (200) reflexes.

The effect of the O_2 concentration on the kinetics of the NO oxidation over the Pt/Al₂O₃ catalyst is displayed in Fig. 1. The conversion of NO into NO₂ rises in the whole temperature range if the concentration of O₂ is increased from 1.5 to 6.0 vol%. However, a further increase in the O₂



Fig. 1. Effect of O_2 on the concentration of NO_2 ((\spadesuit) 1.5 vol% O_2 , (\square) 3.0 vol% O_2 , (\blacktriangle) 6.0 vol% O_2) in the oxidation of NO over the Pt/ Al₂O₃ catalyst. With 6.0 and 15 vol% O_2 the same results are obtained. In all the measurements gas mixture 1 was used (Table 1).



Fig. 2. Effect of CO (500 ppm) on the concentration of NO (\Box) and NO₂ (\blacksquare) in the oxidation of NO over the Pt/Al₂O₃ catalyst. In this measurement gas mixture 2 was used (Table 1).



Fig. 3. Effect of H_2O (6.0 vol%) on the concentration of NO (\Box) and NO₂ (\blacksquare) in the oxidation of NO over the Pt/Al₂O₃ catalyst. In this measurement gas mixture 4 was used (Table 1).

concentration to 15 vol% does not result in a higher yield of NO₂. Concentrations of O₂ exceeding 15 vol% are not established because of a relatively high blank of NO₂ associated with NO oxidation in the gas phase. With 500 ppm CO in the feed, the NO/O₂ reaction is inhibited below $350 \,^{\circ}$ C (Fig. 2). In this measurement no oscillations of the concentration of the product CO₂ are observed as the molar ratio of CO to O₂ is very small, amounting to 0.008. From the literature it is known that the oscillatory region starts from a CO/O₂ ratio of about 0.015 [20,21].

In presence of 6.0 vol% CO₂ the rate of NO₂ formation does not change (not depicted). As compared with CO, a weaker decrease in NO conversion is observed when H₂O (6.0 vol%) is supplied (Fig. 3). With dosing of the realistic diesel model exhaust that contains all of the gas components, a stronger decrease in NO oxidation rate is obtained than in the case where only CO is fed (Fig. 4). In all of the kinetic measurements the outlet concentration of NO_x is always found to be 500 ppm. Hence, we conclude that no NO_x reduction takes place in these studies. Furthermore,



Fig. 4. Concentration of NO (\Box) and NO₂ (\blacksquare) in the oxidation of NO over the Pt/Al₂O₃ catalyst in the realistic diesel exhaust. In this measurement gas mixture 5 was used (Table 1).



Fig. 5. O_2 TPD data of the Pt/Al₂O₃ catalyst. The saturation with O_2 was carried out at 350 °C.

the formation of N_2O , a potential product on thermodynamic grounds, is not observed.

The profile of O_2 TPD is presented in Fig. 5. The pattern exhibits a maximum at about 487 °C (55 ppm) and a shoulder at ca. 590 °C (30 ppm). The first TPD peak is assigned to the oxygen desorption from defect sites (e.g., steps), and the latter one is associated with oxygen bonded to Pt terrace sites [10,37].

Preliminary DRIFTS investigations show qualitatively the same spectra for the catalysts that exhibit 2 and 10 wt% Pt. As the latter sample provides a better signal-to-noise ratio, this catalyst is employed in the following IR examinations. The DRIFT spectrum recorded after NO exposure exhibits a very prominent band at 1714 cm⁻¹ and two less intense bands located at 1764 and 1787 cm⁻¹ (Fig. 6). These features are associated with the stretching vibration of NO, which is linearly coordinated by its N atom to Pt particles of different sizes [22–25]. The weak peaks observed at wavenumbers between 1200 and 1650 cm⁻¹ are referred to nitrite and nitrato species originating from the reaction with the Al₂O₃ support [26]. The exposure to nitric oxide is also carried out at 175 and 200 °C to examine the adsorption of



Fig. 6. DRIFT spectrum of the Pt/Al_2O_3 catalyst (10 wt% Pt) exposed to NO at 30 $^\circ\text{C}.$



Fig. 7. DRIFT spectrum of the Pt/Al_2O_3 catalyst (10 wt% Pt) exposed to NO at 175 °C (bottom) and 200 °C (top).

NO on Pt. From the DRIFT spectrum recorded at 175 °C (Fig. 7) it is obvious that the same type of NO species is produced on the Pt surface as in the case of adsorption performed at 30 °C. However, at 200 °C respective bands are no longer observed in the spectrum. We therefore conclude that the existence of NO bonded to Pt sites is rather unlikely above 200 °C. Furthermore, for NO₂ adsorption the same qualitative results are obtained as for NO exposure (not depicted). The absence of NO₂ adsorbed on Pt sites is also in agreement with the literature and is associated with its fast desorption at ambient temperature [27]. After exposure to the CO/CO₂ mixture, an intense band is observed at 2092 cm^{-1} with a shoulder at 2050 cm^{-1} (Fig. 8). These features are attributed to the stretching vibration of CO species linearly bonded to different Pt sites [24,28,29]. Furthermore, a weak signal is found at 1849 cm^{-1} , which is interpreted as ν (CO) vibration of CO molecules bridging two Pt sites. The bands located at lower wavenumbers are associated with carbonato surface complexes [28].

To describe the mechanism of the NO oxidation in the realistic model exhaust, a network of 6 surface species and 16



Fig. 8. DRIFT spectrum of the Pt/Al_2O_3 catalyst (10 wt% Pt) exposed to CO and CO_2 at 30 $^\circ\text{C}.$

elementary reactions is defined. In Eqs. (3)–(8), an asterisk (*) labels a free Pt site and r_i the respective reaction rate. Reactions (3)–(8) represent the adsorption/desorption equilibrium of each component, whereby dissociative adsorption of O₂ is included according to methods described in the literature [10,13].

$$O_{2(g)} + 2* \stackrel{r_1}{\underset{r_2}{\longleftrightarrow}} 2O*, \tag{3}$$

$$NO_{(g)} + * \stackrel{r_3}{\underset{r_4}{\longleftrightarrow}} NO*, \tag{4}$$

$$NO_{2(g)} + * \stackrel{r_5}{\underset{r_6}{\longleftrightarrow}} NO_2 *, \tag{5}$$

$$\operatorname{CO}_{(\mathrm{g})} + * \stackrel{r_7}{\underset{r_8}{\longleftrightarrow}} \operatorname{CO*},$$
 (6)

$$\operatorname{CO}_{2(g)} + * \stackrel{r_9}{\underset{r_{10}}{\overset{r_9}{\leftrightarrow}}} \operatorname{CO}_2 *, \tag{7}$$

$$\mathrm{H}_{2}\mathrm{O}_{(\mathrm{g})} + * \stackrel{r_{11}}{\underset{r_{12}}{\overset{\sim}{\mapsto}}} \mathrm{H}_{2}\mathrm{O}*, \tag{8}$$

$$NO_{(g)} + O* \stackrel{r_{13}}{\underset{r_{14}}{\longrightarrow}} NO_2*, \tag{9}$$

$$\operatorname{CO}_{*} + \operatorname{O}_{*} \stackrel{r_{15}}{\underset{r_{16}}{\longrightarrow}} \operatorname{CO}_{2}_{*}.$$
(10)

Reactions (9) and (10) show the reversible oxidation of NO and CO, respectively. The formation of N₂ and N₂O is neglected in the reaction network, since neither species is formed in the kinetic experiments. For oxidation of NO the Eley–Rideal-type mechanism is postulated (Eq. (9)), including the reaction of dissociatively adsorbed oxygen with gas-phase NO. This mechanism is supported by the literature [9] and by our kinetic and spectroscopic studies. The kinetic results indicate first an increase and then a constancy in the NO oxidation rate with increasing O₂ concentration, and in DRIFTS no further bands associated with NO adsorbed on Pt are observed above 200 °C. For CO oxidation,

a Langmuir-Hinshelwood-type mechanism is implemented, as reported by Ertl and co-workers [30]. Furthermore, it must be noted that in our mean field model the different types of active Pt sites (e.g., terraces and steps) are supposed to be equivalent. For every forward and backward reaction an Arrhenius-based rate expression is defined (Eq. (11) to (26)), where A_i is the preexponential factor, E_i is the activation energy, $E_i(0)$ is the activation energy at zero coverage, c_i is the gas-phase concentration of species i, θ_i is the respective coverage, and θ_* is the number of free Pt sites. Because of repulsion of adsorbed species, a linear decrease in activation energy with increasing oxygen coverage is assumed for the desorption of O, NO, and NO₂ (Eqs. (12), (14), (16)) [10, 12]. For this purpose the constant α is introduced. A similar relationship is used for desorption and oxidation of CO [31], where activation energy decreases with the growth of CO coverage (Eqs. (18) and (25)). However, oxygen is known to inhibit the dissociation of CO_2 (Eq. (26)), and hence it must be taken into account that the activation energy increases when oxygen coverage grows [12].

$$r_1 = A_1 \exp\left(-\frac{E_1}{RT}\right) c_{\mathcal{O}_{2(g)}} \theta_*^2, \tag{11}$$

$$r_2 = A_2 \exp\left(-\frac{E_2(0)(1-\alpha_2\theta_{\rm O})}{RT}\right)\theta_{\rm O}^2,\tag{12}$$

$$r_3 = A_3 \exp\left(-\frac{E_3}{RT}\right) c_{\mathrm{NO}_{(g)}} \theta_*,\tag{13}$$

$$r_4 = A_4 \exp\left(-\frac{E_4(0) - \alpha_4 \theta_0}{RT}\right) \theta_{\rm NO},\tag{14}$$

$$r_5 = A_5 \exp\left(-\frac{E_5}{RT}\right) c_{\mathrm{NO}_{2(g)}} \theta_*,\tag{15}$$

$$r_6 = A_6 \exp\left(-\frac{E_6(0)(1-\alpha_6\theta_{\rm O})}{RT}\right)\theta_{\rm NO_2},\tag{16}$$

$$r_7 = A_7 \exp\left(-\frac{E_7}{RT}\right) c_{\mathrm{CO}_{(g)}}\theta_*,\tag{17}$$

$$r_8 = A_8 \exp\left(-\frac{E_8(0) - \alpha_8 \theta_{\rm CO}}{RT}\right) \theta_{\rm CO},\tag{18}$$

$$r_9 = A_9 \exp\left(-\frac{E_9}{RT}\right) c_{\text{CO}_{2(g)}} \theta_*,\tag{19}$$

$$r_{10} = A_{10} \exp\left(-\frac{E_{10}}{RT}\right) \theta_{\rm CO_2},$$
 (20)

$$r_{11} = A_{11} \exp\left(-\frac{E_{11}}{RT}\right) c_{\rm H_2O_{(g)}}\theta_*,$$
(21)

$$r_{12} = A_{12} \exp\left(-\frac{E_{12}}{RT}\right) \theta_{\rm H_2O},$$
 (22)

$$r_{13} = A_{13} \exp\left(-\frac{E_{13}(0) - \alpha_{13}\theta_{\rm O}}{RT}\right) c_{\rm NO_{(g)}}\theta_{\rm O},\tag{23}$$

$$r_{14} = A_{14} \exp\left(-\frac{E_{14}}{RT}\right) \theta_{\text{NO}_2},$$
 (24)

$$r_{15} = A_{15} \exp\left(-\frac{E_{15}(0) - \alpha_{15}\theta_{\rm CO}}{RT}\right)\theta_{\rm CO}\theta_{\rm O},\tag{25}$$

$$r_{16} = A_{16} \exp\left(-\frac{E_{16}(0) + \alpha_{16}\theta_{\rm O}}{RT}\right) \theta_{{\rm CO}_2} \theta_*.$$
 (26)

For the modeling of the NO/O₂ reaction and the calculation of the surface coverage, some kinetic parameters are determined from literature sources and some are calculated in order to reduce the number of free parameters in the estimation procedure. The numeric simulation is based upon a combination of the mass balance of each gas phase (Eq. (27)) and adsorbed species (Eq. (28)), leading to a system of six algebraic and six nonlinear differential equations. The respective surface coverages depending on the temperature are then calculated with Matlab tool ods15s. The free parameters, that is, activation energies and preexponential factors, are estimated with a nonlinear regression method (Matlab tool Isqcurvefit)

$$\dot{V}c_{i,\text{in}} - \dot{V}c_{i,\text{out}} + A_{\text{act}} \sum_{j}^{N_j} v_{ij}r_{ij} = 0,$$
 (27)

$$A_{\rm act}\Gamma_{\rm cat}\frac{d\theta}{dt} = A_{\rm act}\sum_{j}^{N_j} v_{ij}r_{ij}.$$
(28)

The preexponential factor for the adsorption of NO, O₂, CO, CO₂, and H₂O is calculated with Eq. (29), and the corresponding sticking coefficient for zero coverage (S^0) is taken from the literature [12,31–33]. Γ_{Pt} denotes the Pt site density and is simply calculated from CO chemisorption data, that is, a_{Pt} , n, and the CO monolayer volume. In Eq. (29) we neglect the temperature dependence by using an average temperature of 325 °C

$$A_{i} = \frac{N_{\rm A} R T}{(2\pi M_{i} R T)^{1/2}} a_{\rm m} \Gamma_{\rm Pt} S^{0}.$$
 (29)

Furthermore, we neglect the activation energy for the adsorption of all of the gaseous species, $E_1 = E_3 = E_5 =$ $E_7 = E_9 = E_{11} = 0$ kJ mol⁻¹, which is in good correspondence with the literature [12,33–35]. The preexponential factor of O_2 desorption (A_2) is taken from the literature [13,34]. For NO desorption the preexponential factor (A_4) and correction factor of the activation energy (α_4) are assumed to be 10^{16} s⁻¹ [12,34,35] and 10 kJ mol⁻¹ [12], respectively. Moreover, the preexponential factor of NO2 desorption $(A_6 = 10^{13} \text{ s}^{-1})$ and α_6 (0.075) are from other authors [10,12,36]. The preexponential factor of NO₂ decomposition (A_{14}) , that is, the backward reaction of NO oxidation, is supposed to be 10^{13} s⁻¹ [10,12]. The kinetic parameters of CO desorption, A_8 (10¹⁶ s⁻¹), $E_8(0)$ (146 kJ mol⁻¹), and α_8 (33 kJ mol^{-1}) , are taken completely from Zerkle et al. [31]. For the activation energy of CO oxidation (E_{15}) , values in the range of 100 kJ mol^{-1} are reported in literature [12,30, 31,37]. In our kinetic model we have used the value determined by Deutschmann (108 kJ mol⁻¹), with α_{15} amounting to 33 kJ mol⁻¹, and A_{15} is 10⁹ s⁻¹ [12]. The activation energy of the CO₂ decomposition (E_{16}) is from Campbell et al., who calculated the value as 155 kJ mol^{-1} [30,37]. The further kinetic parameters of this reaction, α_{16} (45 kJ mol⁻¹) and A_{16} (10¹³ s⁻¹), are also taken from Deutschmann [12]. The preexponential factors of the desorption of CO₂ (A_{10}) and H₂O (A_{12}) are shown to be in the range of 10¹³ s⁻¹ [12,31], and the corresponding activation energies are found to be 27 (E_{10}) and 40 kJ mol⁻¹ (E_{12}), respectively.

To obtain independent kinetic parameters for the adsorption and desorption of oxygen (Eq. (3)), we numerically simulated the spectrum of O_2 TPD (Fig. 5). The interaction of oxygen with the active Pt sites is expected to be a dominating process in the NO/O₂ reaction. The simulation is performed in the same way as NO oxidation, whereby the mass balance of the gas phase and adsorbed oxygen (Eqs. (30) and (31)) results in a system of one algebraic (Eq. (32)) and one nonlinear differential equation (Eq. (33)).

$$\dot{V}c_{O_{2(g)},in} - \dot{V}c_{O_{2(g)},out} - A_{act}r_1 + 2A_{act}r_2 = 0,$$
 (30)

$$A_{\rm act}\Gamma_{\rm cat}\frac{d\theta_{\rm O}}{dt} = 2A_{\rm act}r_1 - 2A_{\rm act}r_2,\tag{31}$$

$$c_{O_{2(g)}} = \frac{A_{act}A_2 \exp(-\frac{E_2(0)(1-\alpha_2\theta_O)}{RT})\theta_O^2}{\dot{V} + A_{act}A_1 \exp(-\frac{E_1}{ET})(1-\theta_0)^2},$$
(32)

$$A_{\text{act}}\Gamma_{\text{cat}}\beta \frac{d\theta}{dT} = 2A_{\text{act}}A_1 \exp\left(-\frac{E_1}{RT}\right)c_{\text{O}_{2(\text{g})}}(1-\theta_0)^2 -2A_{\text{act}}A_2 \exp\left(-\frac{E_2(0)(1-\alpha_2\theta_0)}{RT}\right)\theta_0^2.$$
(33)

In the estimation procedure the parameters A_1 , E_1 , and A_2 are kept fixed, and $E_2(0)$ and α_2 are fitted. The fit leads to an activation energy for the O_2 desorption of 200 kJ mol⁻¹, whereby α_2 is determined to be 0.10 (Table 2). These results are consistent with data found in the literature. $E_2(0)$ obtained from experiments on a Pt(111) single crystal surface [38] and polycrystalline Pt [34] is reported to be 213 and 200 kJ mol⁻¹, respectively. Furthermore, Olsson et al. [10,34] have reported a value of 0.1 for α_2 . The calculated O coverage depending on temperature is displayed in Fig. 9. The coverage is relatively high at the beginning of TPD (0.75) but decreases continuously with increasing temperature. At 700 °C only 1% of the active Pt site is covered with oxygen. Fig. 10 proves that the TPD curve is reasonably well fitted by the kinetic data implemented in the O₂ adsorption/desorption model. As a result of the mean field model, the TPD pattern is approximated by one peak only.

The kinetic parameters used for the modeling of the NO oxidation are summarized in Table 2. In the estimation procedure these parameters are kept fixed, whereas the preexponential factors for the NO₂ adsorption (A_5) and NO oxidation (A_{13}); the activation energies for NO desorption ($E_4(0)$), NO₂ desorption ($E_6(0)$), NO oxidation ($E_{13}(0)$), and NO₂ dissociation (E_{14}); and the linear constant α_{13} are fitted. The modeled results, including the respective 95% confidence interval, are also presented in Table 2. Fig. 11 shows the comparison of the measured and simulated concentrations of NO and NO₂. It is evident that the simulated results correspond well with the experimental data, and



Fig. 9. Calculated surface coverage of oxygen in O_2 TPD of the $\mathrm{Pt}/\mathrm{Al}_2\mathrm{O}_3$ catalyst.



Fig. 10. Comparison of measured (—) and fitted O_2 TPD data (—) of the Pt/Al₂O₃ catalyst.



Fig. 11. Comparison of measured and fitted concentration of NO ((\Box) measured, (-) fitted) and NO₂ ((\blacksquare) measured, (-) fitted) in NO oxidation over the Pt/Al₂O₃ catalyst in the diesel model exhaust. In this measurement gas mixture 5 was used (Table 1).

Table 2 Kinetic parameters of the NO oxidation over the Pt/Al₂O₃ catalyst

Reaction	Parameter	Value	95% confidence interval	Reference	Units
Adsorption					
$O_{2(g)} + 2* \rightarrow 2O*$	A_1	11		$S^0 = 0.07 [10,44]$	$(m^3 s^{-1} m^{-2})$
	E_1	0		[10,33]	$(kJ mol^{-1})$
$NO_{(g)} + * \rightarrow NO*$	A_3	138		$S^0 = 0.85$ [10]	$(m^3 s^{-1} m^{-2})$
	E_3	0		[10,33]	$(kJ mol^{-1})$
$\mathrm{NO}_{2(g)} + \ast \to \mathrm{NO}_2 \ast$	A_5	68	± 31	This work	$(m^3 s^{-1} m^{-2})$
	E_5	0		[10,33]	$(kJ mol^{-1})$
$CO_{(g)} + * \rightarrow CO*$	A_7	141		$S^0 = 0.84$ [28]	$(m^3 s^{-1} m^{-2})$
	E_7	0		[10,33]	$(kJ mol^{-1})$
$CO_{2(g)} + * \rightarrow CO_{2}*$	A_9	0.67		$S^0 = 0.005 [10,27]$	$(m^3 s^{-1} m^{-2})$
-	E_9	0		[10,33]	$(kJ mol^{-1})$
$H_2O_{(g)} + * \rightarrow H_2O*$	A_{11}	157		$S^0 = 0.75 [10, 27]$	$(m^3 s^{-1} m^{-2})$
-	E_{11}	0		[10,33]	$(kJ mol^{-1})$
Desorption					
$2O* \rightarrow O_{2(g)} + 2*$	A_2	2×10^{10}		[9,11]	$(mol s^{-1} m^{-2})$
	$E_{2}(0)$	200	± 1	This work [45]	$(kJ mol^{-1})$
	α_2	0.10	± 0.08	This work [45]	()
$NO* \rightarrow NO_{(g)} + *$	A_4	2×10^{11}		[9,31]	$(mol s^{-1} m^{-2})$
	$E_4(0)$	114	± 0.5	This work [45]	$(kJ mol^{-1})$
	α_4	10		[10]	$(kJ mol^{-1})$
$NO_2 * \rightarrow NO_{2(g)} + *$	A_6	2×10^8		[8,10,32]	$(mol s^{-1} m^{-2})$
	$E_{6}(0)$	72	± 2	This work [41]	$(kJ mol^{-1})$
	α_6	0.075		[8]	(-)
$\mathrm{CO}* \to \mathrm{CO}_{(g)} + *$	A_8	2×10^{11}		[27]	$(mol s^{-1} m^{-2})$
	$E_{8}(0)$	146		[27]	$(kJ mol^{-1})$
	α8	33		[27]	$(kJ mol^{-1})$
$CO_2 * \rightarrow CO_{2(g)} + *$	A_{10}	2×10^{8}		[10]	$(mol s^{-1} m^{-2})$
	E_{10}	27		[10]	$(kJ mol^{-1})$
$H_2O* \rightarrow H_2O_{(g)} + *$	A ₁₂	2×10^{8}		[10]	$(mol s^{-1} m^{-2})$
	E_{12}	40		[10]	$(kJ mol^{-1})$
Surface reactions					
$NO_{(g)} + O_* \rightarrow NO_2*$	A ₁₃	104	± 68	This work [45]	$(m^3 s^{-1} m^{-2})$
	$E_{13}(0)$	35	± 2	This work [45]	$(kJ mol^{-1})$
	α ₁₃	14	± 3	This work	
$NO_2 * \rightarrow NO_{(g)} + O*$	A_{14}	2×10^{8}		[8,9]	$(mol s^{-1} m^{-2})$
	E_{14}	51	± 1	This work	$(kJ mol^{-1})$
$CO* + O* \rightarrow CO_2* + *$	A_{15}	4×10^{4}		[10]	$(mol s^{-1} m^{-2})$
	$E_{15}(0)$	108		[10,26,33]	$(kJ mol^{-1})$
	α_{15}	33		[10]	$(kJ mol^{-1})$
$\mathrm{CO}_{2}*+* \to \mathrm{CO}*+\mathrm{O}*$	A ₁₆	2×10^8		[10]	$(mol s^{-1} m^{-2})$
	$E_{16}(0)$	155		[26,33]	$(kJ mol^{-1})$
	α_{16}	45		[10]	$(kJ mol^{-1})$

hence we conclude that our kinetic model (Eqs. (3) to (15)) describes satisfactorily NO oxidation over a Pt catalyst in diesel model exhaust. The maximum difference between simulated and experimental results is about 10%.

In the estimation procedure the preexponential factor of the NO₂ adsorption (A_5) is determined to be 68 m³ s⁻¹ m⁻². For comparison, A_5 is also calculated according to kinetic gas theory (Eq. (29)), leading to an average value of 118 m³ s⁻¹ m⁻², which is somewhat higher than the fitted result.

The activation energy for NO desorption ($E_4(0)$) has been investigated by several groups that used platinum single crystals. Grote and co-workers report that $E_4(0)$ is found to be 105 kJ mol⁻¹ for a Pt(111) surface and 151 kJ mol⁻¹ for a Pt(100) surface [35], whereas Morris et al. report a value of 114 kJ mol⁻¹ for a Pt(111) surface [39]. Furthermore, Serri et al. have reported an activation energy for desorption of NO from Pt steps of 142 kJ mol⁻¹ [40]. A similar result (145 kJ mol⁻¹) has been determined by Altmann for polycrystalline Pt [41]. These results agree well with our fitted value (114 kJ mol⁻¹).

In this work we estimate a value of 72 kJ mol⁻¹ for the activation energy of the NO₂ desorption $E_6(0)$. Bartram et al. [42] have found $E_6(0)$ to be 80 kJ mol⁻¹ for a Pt(111) sur-



Fig. 12. Calculated surface coverage of the components of the diesel model exhaust present in NO oxidation over the Pt/Al_2O_3 catalyst. In the measurement gas mixture 5 was used (Table 1).

face, and in presence of oxygen it is lowered to 46 kJ mol⁻¹. Wickham et al. [43] studied the NO₂ desorption energy on polycrystalline Pt and report to a result ranging from 59 to 75 kJ mol⁻¹. From this comparison we deduce that our value is in good agreement with the data available in the literature.

For the forward reaction of the NO oxidation, Olsson and co-workers [10] have estimated an activation energy (E_{13}) of 41 kJ mol⁻¹, and for the backward reaction the activation energy (E_{14}) is 142 kJ mol⁻¹. Deutschmann [12] has presented results that differ significantly from those published by Olsson. He has determined E_{13} and E_{14} to be 98 and 99 kJ mol⁻¹, respectively. Our modeled result for $E_{13}(0)$ (35 kJ mol⁻¹) agrees well with Olsson's, whereas E_{14} (51 kJ mol⁻¹) corresponds to the data estimated by Deutschmann. The fitted linear constant α_{13} was found to be 14 kJ mol⁻¹. For comparison, Deutschmann's simulation leads to a value of 45 kJ mol⁻¹.

Furthermore, the preexponential factor for NO oxidation (A_{13}), which we have estimated to be 104 m³ s⁻¹ m⁻², differs clearly from the values given by Olsson (3.36 m³ s⁻¹ m⁻²) and Deutschmann (0.38 m³ s⁻¹ m⁻²).

The result of the calculation of the surface coverages in the realistic model exhaust is presented in Fig. 12. The data show that the Pt surface is dominated by CO and O species in the whole temperature range. Up to $185 \,^{\circ}$ C CO is the most prominent surface species, and at higher temperatures CO coverage decreases continuously. At 500 $\,^{\circ}$ C only 0.1% of the Pt sites is covered by CO. In contrast, the amount of the O surface species increases with rising temperature. At $185 \,^{\circ}$ C oxygen becomes the dominant surface species, and above $300 \,^{\circ}$ C 99% of the Pt sites are covered by O. The coverage of NO amounts initially to 7% and decreases drastically with temperature. In contrast to this, NO₂ and H₂O adsorb to the Pt surface only to a small extent. For NO₂ the coverage ranges from 10^{-7} to 10^{-6} , whereas for H₂O it is about 10^{-5} . Furthermore, CO₂ shows values smaller than 10^{-8} .

The calculation of the surface coverages provides evidence for the effect of CO, CO_2 , and H_2O on the rate of NO oxidation. The kinetic experiments show that CO_2 does not



Fig. 13. Comparison of thermodynamic (--) and measured (--) concentration of NO₂ in NO oxidation over the Pt/Al₂O₃ catalyst. In this measurement the diesel model exhaust was used (mixture 5, Table 1).

affect the NO oxidation rate. The reason for this observation is the extremely low CO₂ coverage ($< 10^{-8}$ %) indicated by the surface calculation. This result is also supported by the DRIFTS data, which show no bands of CO₂ adsorbed to Pt (Fig. 8). In contrast to CO₂, CO leads to a clear decrease in the oxidation rate, especially at temperatures below 250 °C (Fig. 2). In this temperature range CO surface species compete strongly with oxygen, resulting in reduced O coverage and deceleration of the NO oxidation, respectively. The high carbon monoxide coverage is principally confirmed by the DRIFTS results (Fig. 8), which indicate a very intense band of CO coordinated with Pt. A much lower inhibition of the NO/O₂ reaction is caused by water (Fig. 3), as the H₂O coverage is about four magnitudes smaller than for CO.

The NO₂ concentration recorded in diesel model gas is compared with the thermodynamic concentration (Fig. 13) calculated with HSC Chemistry Software from Outokumpu Research. The formation of N₂ and N₂O is neglected, as these species are not observed in the measurements (Fig. 4). The experimental data show that thermodynamic NO₂ concentrations are obtained above 375 °C. At lower temperatures the oxidation of NO is kinetically limited.

4. Conclusion

The simulations show that the experimental data for catalytic NO oxidation over Pt/Al₂O₃ are well fitted by our postulated reaction network. The network consists of eight surface reactions, including forward and backward reactions. In addition to reversible adsorption of all of the components present in the feed, the NO/O and CO/O surface reaction is implemented in the model. DRIFTS and kinetic experiments indicate an Eley–Rideal-type mechanism for NO oxidation involving dissociative adsorption of O₂ and reaction of NO from gas phase. To reduce the number of free kinetic parameters in the fitting procedure, $E_2(0)$ and α_2 are determined by numerical simulation of O₂ TPD. For description of the NO oxidation, A_5 , A_{13} , $E_4(0)$, $E_6(0)$, $E_{13}(0)$, E_{14} , and α_{13} I other kinetic data are taken from the liter-
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are estimated, and other kinetic data are taken from the literature. Furthermore, the calculated surface coverages confirm the rather low activity of the Pt/Al_2O_3 catalyst in the presence of CO and H_2O .

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