Micro-kinetics of NO_x storage and reduction with $\text{H}_2/\text{CO}/\text{C}_3\text{H}_6$ on $\text{Pt}/\text{BaO}/\text{Al}_2\text{O}_3$ monolith catalysts

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Abstract

Isothermal steady state NO_x storage and reduction on $\text{Pt}/\text{BaO}/\text{Al}_2\text{O}_3$ by $\text{H}_2/\text{CO}/\text{C}_3\text{H}_6$ reactant mixtures is studied using, 1+1 dimensional two-phase model that accounts for washcoat diffusional limitations. It predicts the storage and reduction performance over a wide range of inlet feed concentrations and temperatures. A major limitation of global kinetic models is not being able to predict accurately the performance of the catalyst with changing feed composition. Micro-kinetic models elucidating the role of individual reductants can account for such variations. The temperature dependence of the rate constants has been quantified so that the surface chemistry is consistent with experimental observations. Inclusion of washcoat diffusion enables the model to accurately predict the NO_x conversion and scale-up performance of the catalyst over a wide temperature range. The sensitivity of the estimated kinetic parameters to the effective diffusivities in the washcoat is analyzed. Results indicate that the estimated micro-kinetic parameters are influenced by the washcoat pore structure as well as the properties of the catalytic and storage components.

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1 Introduction

Reducing NO_x emissions from diesel engines remains a challenge due to the high air to fuel ratio in the engine feed. The excessive oxygen renders the conventional three-way catalysts inefficient in reducing NO_x in the lean-burn engine exhaust. NO_x storage and reduction has evolved to be a promising technology in reducing NO_x under lean conditions. It consists of treating NO_x over a bifunctional catalyst to form N_2 and H_2O . The catalyst is composed of precious metals, storage and support components. A typical NO_x storage and reduction (NSR) catalyst contains precious metals such as Pt/Pd/Rh to enhance the uptake of NO_x and facilitate the oxidation/reduction processes. NO_x is adsorbed onto the storage materials comprising oxides, carbonates and hydroxides of alkaline earth metals such as Ba, Mg, Ca or on alkali metals such as K, Cs etc. The most widely studied formulation of NSR catalyst is Pt/BaO/ Al_2O_3 .

Various groups have confirmed the existence of several underlying pathways in the NSR, which include oxidation of NO to NO_2 , NO conversion to N_2O and N_2 , formation of NH_3 , reaction of NH_3 with NO_x to form N_2 and H_2O etc. A general consensus is that oxidation of NO to NO_2 over the precious metal is an essential precursor to NO_x storage [1, 2, 3] and that NO_2 is subsequently stored on the trapping material in the form of nitrites/nitrates. Various factors affect the stability of nitrates and in turn influence the NO_x conversion performance. It has been suggested that the stability of the nitrates is increased by the presence of oxygen [4], which otherwise are decomposed resulting in the release of NO_x . The presence of carbon oxides and water in the vehicular exhaust complicates the catalytic chemistry in the NSR catalyst [5]. They also affect the stability of the surface nitrates, as CO_2 can compete for the storage sites to form carbonates and thus negatively impacting the performance [6] while H_2O can either enhance or diminish the de NO_x efficiency of the NSR catalyst [7].

The main products of the stored NO_x regeneration are NH_3 , N_2 , N_2O , H_2O and CO_2 . NH_3 is an essential intermediate which reacts with stored NO_x . NH_3 is produced when H_2 is used as the sole reductant and also when CO is the reductant in the presence of H_2O , either

through isocyanate intermediates or through water–gas shift mechanism. Precious metals play a prominent role during NO_x reduction. The Pt/BaO interface enables reverse spillover of the NO_x onto the Pt and is subsequently reduced by the H_2 , CO or HC (hydrocarbon; C_3H_6 in the current study) species. Several studies indicate that H_2 is a better reductant compared to CO and C_3H_6 , while a precious metal is necessary to activate H_2 , CO can be active even on BaO/ Al_2O_3 [8].

The motivation to investigate the performance of the NSR with mixed reductants arises because real exhaust gas is comprised of various species such as H_2 , CO, HC, CO_2 , H_2O , NO_x , NH_3 , O_2 , N_2 , N_2O etc. Such complex mixture can influence the optimum operation of the NSR and the SCR catalysts. The main objective of this work is to construct a micro–kinetic model that elucidates the complexities introduced by the combined feed of $\text{H}_2/\text{CO}/\text{C}_3\text{H}_6$. We also aim to provide a wider understanding of the influence that individual reductants exert on the de NO_x activity of the catalysts. To realize this objective we have initially developed a kinetic model for each individual reductant. We then use these models to predict the isothermal NSR performance under various operating conditions. We present the approach towards a reaction mechanism that is corroborated by several UHV and flow reactor investigations. The models are used to fine tune the extracted parameters and test their consistency with observations of prior experimental studies. In the present work, we focus on the NO_x storage and reduction on Pt/BaO/ Al_2O_3 in the presence of $\text{H}_2/\text{CO}/\text{C}_3\text{H}_6$.

2 Model development

Several models describe the NO_x storage and reduction processes. Global kinetic schemes have been proposed by Hepburn et al. [9], Olsson et al. [10], and Tuttles et al. [11] based on the shrinking core model. Scholz et al. [12] developed a global reaction kinetic model based on multiple storage sites. Bhatia et al. [13] proposed a micro–kinetic scheme for NO oxidation on Pt and a global kinetic model [14] for both NO_x storage and reduction that

is based on the NO oxidation model. They considered two types of NO_x storage sites in the global model named ‘fast’ and ‘slow’ sites based on their proximity to the Pt. Olsson et al. [15] presented a detailed model of NO_x storage and reduction over a Pt/BaO/Al₂O₃ catalyst. Earlier research studies focused exclusively on the individual stages of the NSR such as NO oxidation, or nitrate formation, or the effect of specific reductants on the NO_x release during the regeneration. We attempt to develop a wider understanding of the NSR in the presence of feed consisting of H₂/CO/C₃H₆ by a detailed model that encompasses all the essential stages. The Pt/BaO/Al₂O₃ catalyst and monolith properties used in this work are listed in Appendices A1 and A2.

2.1 Species balance equations

Steady state 1+1 dimensional two phase model is used to simulate the storage and reduction of NO_x in a single monolith channel. The model incorporates washcoat diffusional limitations. The basic assumptions are a) fully developed laminar flow; b) axial dispersion is negligible compared to convection; c) physical properties are independent of the species concentration; d) concentrations are low so that heat effects can be neglected and the system can be treated as isothermal; e) pressure drop in the channel is negligible; f) the reaction mixture is dilute so that gas expansion effects can be neglected. The balance equations are, *Species balance in the channel:*

$$\frac{\partial X_{jm}}{\partial t} = -\bar{u} \frac{\partial X_{jm}}{\partial z} - \frac{k_c(j, z)}{R_\Omega} (X_{jm} - X_{js}), \quad (1)$$

where X_{jm} and X_{js} are the mole fractions of species j in the bulk fluid and at fluid–washcoat interface respectively, $\bar{u}$ is the average velocity, $k_c(j, z) = D_{m,j} Sh_e(z)/4R_\Omega$ the position dependent mass transfer coefficient accounts for the transverse gradients in the gas phase, R_Ω is the channel hydraulic radius, $D_{m,j}$ is the gas phase diffusivity of species j in the bulk fluid, $Sh_e(z)$ is the position dependent external Sherwood number [16]. The gas phase

diffusivities calculated using Lennard–Jones potentials are reported in Appendix A2.

Species balance in the washcoat:

$$\varepsilon_{wc} \frac{\partial X_{jwc}}{\partial t} = D_{ewc} \frac{\partial^2 X_{jwc}}{\partial y^2} + \frac{1}{C_{Tm}} \left(\sum_{r=1}^{M_g} \hat{\nu}_{jr} R_r^S(\underline{X}_{wc}, \underline{\theta}_S) + \sum_{r=1}^{M_g} \hat{\nu}_{jr}^* R_r^Y(\underline{X}_{wc}, \underline{\theta}_Y) \right) \quad (2)$$

here, X_{jwc} is the mole fraction of species j in the washcoat, ε_{wc} is the washcoat porosity, D_{ewc} is the effective species diffusivity inside the washcoat, C_{Tm} the total molar concentration, $(\underline{X}_{wc}, \underline{\theta}_S)$, $(\underline{X}_{wc}, \underline{\theta}_Y)$ are the species mole fraction and fractional surface coverage vector on S=Pt and Y=BaO, M_g is the number of gas species, $\hat{\nu}_{jr}$, $\hat{\nu}_{jr}^*$ are the stoichiometric coefficients and $R_r^S(\underline{X}_{wc}, \underline{\theta}_S)$, $R_r^Y(\underline{X}_{wc}, \underline{\theta}_Y)$ are the reaction rates involving diffusing (gas phase) species on S and Y sites, respectively. In this work, we assume that only Pt interacts with gas phase species and take the second summation term to be zero.

Adsorbed/Surface species balance:

$$C_S \frac{\partial \theta_{Sj}}{\partial t} = \sum_{r=1}^{M_s} \nu_{jl} R_{Sl}(\underline{X}_{wc}, \underline{\theta}_S) \quad (3)$$

$$C_Y \frac{\partial \theta_{Yj}}{\partial t} = \sum_{r=1}^{M_s} \nu_{jl}^* R_{Yl}(\underline{X}_{wc}, \underline{\theta}_S, \underline{\theta}_Y), \quad (4)$$

where, $(S = Pt, Y = BaO)$ are the total molar concentration of Pt and BaO sites, R_l is the rate of reaction that involves the adsorbed species, ν_{jl} , ν_{jl}^* are the stoichiometric coefficient and $(\underline{\theta}_S, \underline{\theta}_Y)$ are the fractional surface coverage vectors for sites of type S and Y , respectively.

Initial and Boundary conditions:

$$(i) \quad X_{jm}(z, 0) = 0 \quad @ \ t = 0 \quad (5)$$

$$X_{jwc}(y, z, 0) = 0 \quad @ \ t = 0 \quad (6)$$

$$\theta_j(y, z, 0) = 0 \quad @ \ t = 0 \quad (7)$$

$$(ii) \quad X_{jm}(0, t) = X_{inlet}(t) \quad @ \ z = 0 \quad (8)$$

$$k_c(j, z)(X_{jm} - X_{js}) = -D_{ewc} \frac{\partial X_{jwc}}{\partial y}; \quad X_{js} = X_{jwc} \quad @ \ y = 0 \quad (9)$$

$$-D_{ewc} \frac{\partial X_{jwc}}{\partial y} = 0 \quad @ \ y = \delta_{wc} \quad (10)$$

The transient equations were solved until steady state conditions prevailed. Initial conditions consist of zero initial concentrations and coverages along with simultaneous inflow of species in the feed. Inlet boundary conditions are as prescribed in Eq 8 while flux continuity and zero flux conditions are applied at the fluid–washcoat interface (@ $y = 0$) and washcoat–wall interface (@ $y = \delta_{wc}$), respectively. The balance equations were discretized in the axial direction using upwind scheme for the convection term in Eq 1 and central differencing for the diffusion term in Eq 2. We have considered a total of 81 grid points in the axial direction and 11 in the transverse direction inside the washcoat, and the integration is performed for 11 gas phase species in the channel and in the washcoat, along with 18 surface species in the washcoat. A total of $\sim 27,000$ variables obtained after discretization were then solved using the method of lines approach where the system of ODEs is integrated in time with the corresponding initial conditions using Livermore solver (LSODE).

2.2 Kinetic model

Typical diesel engine exhaust consists of NO, NO₂, O₂, H₂, CO, CO₂, HC, H₂O etc. The presence of various species increases the complexity of analyzing the mechanism of the reactions occurring on the catalyst surface. We present here a micro–kinetic model that captures the main features of isothermal NO reduction by H₂/CO/C₃H₆ on a Pt/BaO/Al₂O₃ catalyst (Appendix A3).

The microkinetic model is based on 25 elementary and quasi–elementary steps. It includes two irreversible steps involving N₂, N₂O generation. The model follows some of the mechanistic steps described in the literature along with the deviations based on experimental

findings by various investigations. The approach is consistent with established surface chemistry. We include storage steps following the generally accepted NO_x spill-over mechanism, where NO is oxidized to NO_2 on Pt and depending on the proximity of BaO sites, it spills over to the storage sites forming nitrates. The reactions sequence is shown below, where '*' denotes a vacant Pt site,

Reactions R1–R5 comprise NO oxidation reaction on Pt. It is well known by now that Pt plays a crucial role in oxidizing NO to NO_2 , which is an important precursor in the NO_x storage[18]. Medhekar et. al. [22] suggested that Pt assists NO decomposition and that a significant portion of the NO_x storage and nitrates reduction occurs at the Pt–BaO interface. There is a significant evidence of $\text{Ba}(\text{NO}_3)_2$ formation during the NO_x storage. Steps R1, R3, R4 and R8 are consistent with the generally accepted and experimentally verified stoichiometry of the storage reaction where 1 mole of NO is released for every 3 moles of NO_2 consumed ,

Reactions R3 and R8 are consistent with a number of studies that suggest the role of O

adatom in the formation of nitrates [18, 23, 24, 25]. It is to be noted that R8 is applicable to both ‘*fast (f)*’ and ‘*slow (s)*’ storage sites. Though broadly ‘*f*’ and ‘*s*’ sites are categorized based on their proximity to Pt, phenomenologically their functionality differs through the interaction of BaO with the surface and gas species during the storage process. While BaO(*f*) sites close to Pt enable spillover/reverse-spillover of O*, NO*, NO₂* species during storage [26], remote BaO(*s*) sites carry out direct interaction with the species from gas phase and diffusion through Ba phase thus representing the difference in time scales. As stated earlier, in this work we ignore the direct adsorption of gas phase NO₂ or any other species with Ba sites and hence take the second summation term in Eq 2 to be zero.

The reduction of stored NO_x occurs through a Pt catalyzed pathway, forming NH₃ as the intermediate which again reacts with NO_x to form N₂ and H₂O. Regeneration has been studied by several groups focusing on the effects of type and amount of the reductant, and that of the lean and rich times. Commonly studied reductants are H₂, CO, C₃H₆ and it has been suggested that H₂ is a better reductant than CO [27, 28, 29, 30], especially at low temperatures (T < 250°C). At high temperatures the performance of H₂ and CO is similar. H₂ and CO are known to be more efficient reductants than C₃H₆. We study the kinetic mechanism of the reactions involving NO and H₂/CO/C₃H₆ and compare the predictions with experimental data and evaluate the key parameters involved in the NSR process. The impact of H₂O on the NO_x reduction has practical significance because of its presence in the exhaust gas during the combustion. The model accounts for adsorption and desorption of H₂O and for the inhibiting effect of H₂O on NO adsorption, suggested in the literature [32]:

R1, R2, R9–R17, comprise the overall reaction for NH_3 formation. Based on experimental observations by Clayton et al. [31], we propose that NH is one of the key intermediates in the formation of N_2O , N_2 and NH_3 . It reacts with the surface isocyanates to form N_2O and N_2 , and is easily hydrolyzed by water to form NH_3 .

CO is a well known inhibitor on Pt metal catalyst [33]. Studies indicate that NCO is an intermediate in the formation of N_2 and NH_3 during the regeneration [34, 35]. Szailer et. al. [36] reported significant formation of NCO species on Pt/Al_2O_3 between 200–400°C with a maximum at around 300°C. The reaction steps are as follows:

Reaction steps R18–R20 comprise CO oxidation reaction, and along with steps R9–R12 represent the water–gas shift reaction. The overall reactions for both CO oxidation and water–gas shift reactions are:

Reactions R8(*f,s*) and R23(*f,s*) represent the storage of NO_x and CO₂ on BaO. These are in line with the various literature studies that suggest the existence of different storage sites [17, 18, 19]. The storage sites considered in this study are those pertaining to the proximity of BaO to Pt and to the activity of BaO towards NO_x and CO₂. Lindholm et. al. [20] have presented the direct interaction of Ba(NO₃)₂ and BaCO₃ during the storage. In contrast we consider such interaction only through vacant BaO sites. Such representation keeps the model simple and takes care of all the intermediate steps present during the storage.

Through isotopic labeling experiments Unland [37] suggested the presence of surface NCO species on Pt/Al₂O₃ and described its importance as a reaction intermediate in the formation of NH₃ in the presence of H₂O. The following were reported to be the possible reaction routes, along with the water–gas shift reaction, in the formation of NH₃ for NO/CO/H₂O reaction system:

The reaction mechanism is consistent with the above steps, R11, R14–R22 represent NH₃ formation from NCO, while the other two steps are already described earlier.

Several reaction schemes have been proposed for selective reduction of NO_x using propylene (C₃H₆). Reduction of NO_x with propene (C₃H₆) generates complex surface species. To keep the model simple we consider only the following reactions:

Reaction R24 and R25 are inline with the experimental observations reported by Kotsifa

et al. [40], who suggested that the reduction of NO by C₃H₆ always occurs in parallel to propylene oxidation and that the surface O adatoms, formed either by NO bond dissociation or dissociative O₂ adsorption, is dominant in oxidizing the hydrocarbon intermediates.

Some kinetic parameters were kept constant during the estimation process, using values provided by Xu et al. [21]. The activation energies for some of the adsorption steps are set to 0 kJ/mol assuming them to be non-activated processes. When diffusion in the pores of the washcoat is in the bulk regime, the adsorption rate constants may be expressed as,

$$k_j = S_{0j} C_{Tm} \alpha_v \sqrt{\frac{RT}{2\pi M_{wj}}} \quad (11a)$$

where S_{0j} is the sticking coefficient of species j at zero coverage, C_{Tm} is the total molar concentration of the gas, R is the universal gas constant, T is the absolute temperature, M_{wj} is the molecular weight of the species and α_v is the exposed Pt surface area per unit volume of washcoat. When diffusion in the pores of the washcoat is in the Knudsen regime, it is more convenient to express the adsorption rate constant as,

$$k_j = k_{0j} C_{Tm} C_{Pt} \quad (11b)$$

where C_{Pt} is the concentration of active Pt sites for unit volume of washcoat. Since C_{Pt} and α_v are linearly related for a fixed Pt dispersion, the difference between Eqs. (11a) and (11b) is rather small, we have adopted Eq.(11a) in what follows. A conventional Arrhenius relation is used to describe the temperature dependent rate constants for surface reactions,

$$k_i = A_i e^{-E_i/RT} \quad (12)$$

where, k_i is the rate constant in step i , A_i and E_i are the corresponding pre-exponential factors and activation energies. The values of the pre-exponential factors and activation energies for all the reactions are listed in Appendix A5. The parameter estimates have been

obtained by minimizing the residual sum of squares from the experimental and calculated conversions and selectivities. Orthogonal distance regression solver package (ODRPACK) was employed to perform the multi-response nonlinear regression [39]. [Remarks: (i) the 25 step micro-kinetic scheme listed above corresponds to 9 overall independent reactions between 14 species (ii) In general, all the micro-kinetics constants are not independent and need to satisfy the enthalpic and entropic constraints imposed by thermodynamics which is discussed in section 4].

3 Washcoat diffusion coefficients

An important part of the model is accounting for the washcoat diffusion, specifically how the various species diffusivities are calculated. These values, in turn, influence the values of the kinetic parameters that are estimated from the experimental data. In the literature, various models are available for calculating the effective diffusivities based on the washcoat structure (i.e. micro and macro porosity, pore size distribution, pore connectivity, etc.). However, most of these models do not consider the presence of storage or catalytic materials within the pores of the washcoat. For example, in Pt/BaO/Al₂O₃ catalysts, the Pt crystallite size is not uniform and can vary widely (typical values being 3 to 20nm depending on the dispersion and/or aging of the catalyst) while the barium particle size varies with the amount of NO_x stored. Both sizes are strongly dependent on the catalyst temperature history. Further, the presence of these active materials influences the pore connectivity and hence the species effective diffusivities profoundly (e.g. crystallite size could be of the same order of magnitude or larger than the diameter of some pores). Further, unlike the case for traditional catalysts, the porosity (as well as tortuosity) in the dual function catalysts such as Pt/BaO/Al₂O₃ varies with the amount of NO_x stored. Since our focus here is not on the detailed washcoat structure, we use a simpler model for estimating the effective diffusivities. We assume an effective average pore radius (r_{eff}) and diffusion in the partially blocked pores

Figure 1: Comparison of experimental and model results for NO and CO conversions at different values of D_{e0} at 270°C. The feed consists of NO (500 ppm) + CO (15–1200 ppm) over Pt/BaO/Al₂O₃ catalyst.

of the washcoat can be described by a modified form of the Knudsen diffusion formula:

$$D_{ewc} = \left(\frac{\varepsilon_{wc}}{\tau}\right) 97 r_{eff} \sqrt{\left(\frac{T_s}{M_{wj}}\right)} = D_{e0} \sqrt{\left(\frac{T_s}{T_r}\right) \left(\frac{M_{wr}}{M_{wj}}\right)},$$

where $D_{e0} = \left(\frac{\varepsilon_{wc}}{\tau}\right) 97 r_{eff} \sqrt{\left(\frac{T_r}{M_{wr}}\right)}$ is the diffusivity at the reference temperature T_r and molecular weight M_{wr} . It accounts for the changes in porosity, tortuosity and the effective average pore radius (r_{eff}). Here, T_s is the absolute temperature, and M_{wr} the molecular weight of the species. For the base case, we assume that $D_{e0} \sim 2.1 \times 10^{-7} \text{ m}^2/\text{s}$ at $T_r = 275^\circ\text{C}$ and $M_{wr} = 28$ and vary this parameter to study the sensitivity of the estimated kinetic parameters.

Figure 1 shows a comparison between the model predictions and experimental results,

Figure 2: Dependence of CO conversion on the effective diffusivity in the washcoat at 270°C with the feed consisting of NO (500 ppm) + CO (15–1200 ppm) over the Pt/BaO/Al₂O₃ catalyst.

while Figure 2 gives the sensitivity of CO conversion to various values of washcoat diffusivity. Using a much lower value for D_{eo} leads to lower than observed CO conversions, while at a sufficiently high D_{eo} value, the conversion (or kinetic parameters) become insensitive. We took the lowest D_{eo} value that gives the closest fit to the experimental data. An important consideration in the estimation of the intrinsic kinetic parameters is the diffusional disguise of the kinetics. The model already accounted for external mass transfer (gas phase diffusion) as well as diffusion in the washcoat. Thus diffusional disguise could exist only in the pore scale. The importance of pore scale diffusional effects on the estimated values of the micro-kinetic parameters can be estimated by comparing the characteristic times. The pore scale diffusion time of NO molecule, defined as $\frac{L_\mu^2}{D_{ewc}}$ (where L_μ is the characteristic pore length taken to be ~ 10 nanometers.) is estimated to be 10^{-10} s with the base value of D_{eo} . While the time constant for adsorption step $\frac{1}{(S_{0NO}\alpha_v(1-\theta_v)(\frac{RT}{2\pi M_{wj}})^{0.5})}$ is approximately 10^{-9} s. Based on these

estimates, it appears that the system is close to the transition region beyond which micro-kinetics could be disguised by pore scale diffusional effects. Similar comparison between the time constants of adsorption for CO, H₂, C₃H₆ revealed that the kinetic parameters are sensitive to the effective diffusivities of the species in NO/CO and NO/C₃H₆ systems. However, such sensitivity was not observed in NO/H₂ system. This is expected because the time constant for H₂ adsorption is $\sim 10^{-8}$ s which is about two orders of magnitude higher than the diffusion time constant indicating the presence of pore scale kinetic control.

It should be noted that on the scale of washcoat thickness, all the three systems considered NO/H₂, NO/CO and NO/C₃H₆ exhibit washcoat diffusion controlled regime because the washcoat scale diffusion time constant ($\frac{\delta_{wc}^2}{D_{ewc}}$) is estimated to be of the order of $\sim 10^{-3}$ s. Therefore, depending on the temperature and concentration of the reductants, the reaction can occur either within a thin layer of washcoat close to the fluid-washcoat interface or the entire washcoat. For example, Figure 3 shows the NO species concentration inside the washcoat at different temperatures. Due to high reactivity compared to CO and C₃H₆, the reaction of H₂ with NO is limited to a very small region close to the fluid-washcoat interface while that of CO and C₃H₆ is spread across the washcoat thickness. The figure also shows the existence of different regimes in the system from washcoat diffusion controlled to kinetic controlled regime. Clearly, the kinetic parameters are independent of washcoat properties only if the system is in kinetic controlled regime both on the scale of the washcoat and the (micro and macro) pores. The dependence of the micro-kinetic rate constants on pore scale parameters is generally neglected in most literature studies but could be important in high surface area catalysts such as Pt/BaO/Al₂O₃.

4 Results and discussion:

A typical NSR process comprises initial NO_x storage in the form of nitrates followed by reduction. NO_x breakthrough commences when the storage sites are nearly saturated.

Figure 3: NO concentration inside the washcoat at different temperatures for NO/H₂(1000ppm NO, 2500ppm H₂), NO/CO(500ppm NO, 500ppm CO), NO/C₃H₆(500ppm NO, 1000ppm C₃H₆, 5% O₂) system; GHSV = 60,000hr⁻¹, Pt loading = 2.2 wt%.

The distribution of products evolved during the regeneration is complex and depends on the temperature and the reductant to NO_x ratio. NH₃ is formed as an intermediate during the regeneration with H₂ that further reacts with stored NO_x to produce N₂ and H₂O. N₂O and N₂ are the primary products of the reduction reactions in the absence of H₂O using an NO/C₃H₆ feed or NO/CO feed, and these pairs are known to produce NH₃ in the presence of water. Various studies of the regeneration of stored NO_x reveal that H₂ is a better reductant than either CO or C₃H₆. The surface of the catalyst fields various parallel and consecutive pathways and several intermediates during the reduction of NO_x with H₂/CO/C₃H₆ as described in the following sections.

Heats of reactions for the gas phase are used in calculating the heats of surface reactions on the surface as shown below:

$$\Delta H_s = \Delta H_g + (Q_2 + Q_3 - Q_1)$$

Figure 4: Schematic for surface energetics.

Heats of adsorption for some of the diatomic molecules and monoatomic radicals are adopted from the experimental investigations based on UHV, calorimetric and TPR studies in the literature and are reported in Appendix A4. It can be easily verified that the overall reactions which are considered to be dominant in the system satisfy the enthalpic constraints. Using these values reduces the number of parameters to be estimated. The rest of the activation energy parameters along with the pre-exponentials were estimated and fine tuned using nonlinear orthogonal regression method mentioned earlier [39]. The experimental data obtained from the literature for the following studies correspond to the same catalyst composition, therefore the parameters were estimated for individual systems starting from NO/H₂ followed by NO/CO and NO/C₃H₆. The parameters of the prior system were held constant while estimating the parameters for the expanded system.

4.1 NO/H₂ reaction system:

The conversion/selectivity data for NO–H₂ reaction performed under isothermal conditions is obtained from the work of Xu et al.[19] over a range of temperatures and NO/H₂ ratios. All the data involve steady state measurements. The feed gas consists of 1000 ppm NO and variable amounts of H₂ in the absence of O₂. The properties of the catalyst used in simulations are given in Appendix A1 and A3.

NO oxidation and storage steps are the first set of reversible reactions in the kinetic model. There is a general consensus that NO is first oxidized to NO₂ which then is stored as nitrites/nitrates. Some authors argued that the initial step is nitrite formation which are later oxidized by NO₂ to nitrates [2]. Other authors argued that nitrates form by direct uptake of NO₂ on BaO [39].

Formation of NO₂ and its reversible spill-over onto the barium sites has been highlighted during the storage in many other studies [15]. Taking this into account and to maintain simplicity we have considered $R8(f, s)$ as the only set of steps representing the nitrate formation. Such interaction with the storage material was not considered by Xu et al. [21]. This also is consistent with the generally established notion that the presence of Pt facilitates the storage

Figure 5: Data fit obtained for the parameter estimation; NO, H₂ conversions for H₂/NO = 2.5 at different temperatures. Feed: 1000ppm NO, 2500 ppm H₂, GHSV = 60,000 hr⁻¹.

process. The surface reactions and their energetics in the NO–H₂ reaction system is sensitive to the catalyst surface structure and the coverages of NO, N, H species. Figure 5 shows the data used for parameter estimation. NO and H₂ conversions sharply increased in the low temperature (50–75°C) range. The formation of N₂O and NH₃ are strongly affected by the ratio of NO/H₂ and temperature. Both the experimental and modeling results show that at

low temperatures (<150°C) N₂O is the major product. The formation of N₂O is described by the following global reaction:

Figure 6 describes the model prediction for NO/H₂ system. Several mechanistic studies in the literature have indicated a higher selectivity to N₂O formation at lower temperatures compared to N₂ and NH₃ [41]. The reaction route for the formation of N₂O is still a matter of debate. Some authors proposed a combination of adsorbed NO and N species [41] while others have proposed the reaction between two adsorbed NO species, still others have suggested the role of adsorbed NH_x species in the formation of N₂O. In the present work we focus on two important routes with the assistance of the experimental results published in the literature.

The following are the two routes considered in this study for N₂O formation:

N* could be a product of NO* dissociation to N* and O*, or H* assisted NO* decomposition to form N* and OH* which also has a parallel route forming surface NH* species. Examining the kinetic parameters leading to the formation of N₂O indicates that at low temperatures the presence of abundant NO surface species results in rapid recombination of NO and N surface species compared to N–N adatoms, thus increasing the selectivity of N₂O. The reaction steps leading to the formation of nitrogen are influenced by the hydrogen concentration and temperature. The N₂ selectivity exhibited a local maximum at an intermediate temperature (100°C–200°C) which coincides with the progressive decrease in N₂O selectivity, due to the increase in the rate of NO dissociation. The selectivity of the reaction towards NH₃ gradually increases with subsequent hydrogenation of N adatom. This results in a shift of the product

distribution to a mixture of N_2 and NH_3 as the temperature increases.

Figure 6: Model prediction results for NO/H₂ system (a) NO and H₂ conversion for H₂/NO = 1.5 at different temperatures (Feed: 1000ppm NO, 1500ppm H₂, GHSV = 60,000hr⁻¹), (b) Selectivities of NH₃, N₂, N₂O for H₂/NO = 1.5 at different temperatures, (c) Selectivities of NH₃, N₂, N₂O for T = 360°C at different inlet H₂ concentrations (Feed: 500ppm NO, GHSV = 60,000hr⁻¹).

The overall reactions for the formation of N₂ and NH₃ are:

Formation of NH_3 increases with H_2/NO feed ratio and is consistent with the literature studies. Thus far the model reasonably predicts all the important steady state experimental observations, and since all the above mentioned surface phenomena are also present during transient operation, the model can also be applied for transient studies.

4.2 NO/CO reaction system

A much more complicated behavior occurs using CO as a reductant. CO is known to poison the Pt surface. Lorimer et. al. [42] have reported a negative order dependence of the NO reduction with CO on Pt/SiO₂ catalyst. The competitive adsorption of CO₂ and NO₂ during the NSR catalysis has been suggested previously [43]. During the reduction by CO or C₃H₆, it is likely that some carbonates form on the catalyst surface. It is well established that carbonates are more stable than hydroxides of barium [44], hence our model neglected the Ba(OH)₂ formation. Of the other key parameters investigated the roles of the storage components and the reaction mechanism of carbonate formation are assessed. To reduce the complexity of the model due to the large number of possible reaction steps we assumed that equation R23 represents the CO₂ uptake. Figure 7 shows the overall CO and NO conversions on the Pt/Ba/Al₂O₃ catalyst at 270°C versus inlet CO concentration. The feed comprises 500 ppm NO and 15–1200 ppm CO as used in the experiments by Dasari et al. [45]. Initially, a steady increase in NO conversion is observed at low inlet CO concentrations, while the entire CO is converted to CO₂. NO conversion attains a maximum at CO feed concentration of ~ 300 ppm. As the CO concentration is further increased, its surface coverage increases thus inhibiting NO from adsorbing. NO conversion progressively declines to zero closely followed by CO conversion until the entire Pt surface is covered with CO species. Several schemes were proposed in the literature that describe CO conversion to CO₂ and NO to N₂O and N₂. Granger et al. [46] studied the NO/CO reaction on Pt catalysts using a Langmuir

Hinshelwood model.

We consider a non-dissociative adsorption of CO and NO on the adsorption sites according to equations *R1* and *R18*. The subsequent steps involve dissociation of adsorbed NO to form N and O adatoms. The selectivity of N₂/N₂O depends on the rate of recombination of N adatoms with N or NO on the surface. The difference in the reduction efficiency and the formation of NCO species on the catalyst surface suggest differing reduction mechanisms for H₂ and CO. However, it has been reported through FTIR investigations that the reduction occurs through Pt catalyzed pathway [47, 48]. On Pt the two main reactions of NO and CO involves N₂ and N₂O formation according to:

The presence of H₂O in the feed renders the analysis of NO/CO reaction slightly complicated due to the presence of surface species such as carboxylates, surface hydroxyl groups and N species. However, water is known to enhance the reduction of NO by CO and also results in the production of NH₃. Two major pathways have been suggested as active in NH₃ formation. One involves intermediate isocyanate species and the second involves the water-gas shift reaction. From reaction steps *R9* – *R12* and *R18* – *R20* show that the water-gas shift is inherent in the kinetic model. To account for the isocyanate pathway we introduced reaction step *R21*. Figure 7(b) shows the impact of H₂O on the conversions of NO and CO and that there is significant improvement in both conversions for CO feed concentration exceeding 300 ppm and containing 4% H₂O. For CO concentration lower than 300 ppm, the difference in the conversion behavior is small, suggesting an interaction of adsorbed CO with H₂O. H₂O is expected to clean the catalyst surface from adsorbed CO resulting in enhanced NO adsorption and subsequent reaction with CO and H surface species.

Figure 7: Effect of inlet CO concentration on the NO and CO conversion during the reaction of NO (500 ppm) + CO (15–1200 ppm) and NO (500 ppm) + CO (15–2500 ppm) + 4% H₂O at 270 °C over the Pt/BaO/Al₂O₃ catalyst.

4.3 NO/C₃H₆ reaction system

Several investigations have been made to evaluate propylene as a NO_x reducing agent. The steady-state performance of the catalyst with respect to NO/C₃H₆ system was examined by Kabin et al. [38] and their experimental results are used to evaluate the kinetic

Figure 8: Steady-state NO_x conversion and C_3H_6 conversion vs. Feed Temperature during the reaction between 500 ppm NO , 5% O_2 , 1000 ppm C_3H_6 .

modelproposed by equations $R1 - R8$ and $R18 - R22$. Figure 8 shows the NO_x conversion as a function of the feed temperature with a space velocity of $60,000 \text{ h}^{-1}$, for a gas feed containing 500 ppm NO , 1000 ppm C_3H_6 and 5% O_2 . The light off temperature is around 220°C which is close to that reported in the literature. The model gives a reasonably good prediction of both the NO and C_3H_6 conversions. At the lightoff the activation of propene is accompanied by the onset of NO reduction towards N_2 and N_2O . NO_x conversion reaches a maximum of 60% around $\sim 250^\circ\text{C}$ which is followed by a progressive decrease as the temperature is increased further. Kabin et al. have reported that the selectivity of N_2 was low under low concentrations of propene, confirming the role of propene as a scavenger [40] removing the O adatoms formed by NO bond scission. It was also pointed out that in the presence of excess O_2 , the O adatoms produced from NO and O_2 compete for the surface hydrocarbon species which as the temperature increases is dominated by the O_2 dissociation. This increases the surface coverage by O adatom inhibiting the NO adsorption and thereby reducing the NO conversion. For the given concentrations of reactants the temperature rise

could be as

Figure 9: Model predictions of NO, H₂, CO and C₃H₆ conversions during steady state operation. 300ppm NO, 1% O₂, 1%CO, 0.33% H₂, 0.33% C₃H₆.

high as 60°C and is not negligible, on the grounds of simplicity in terms of calculations the present model doesn't account for the non-isothermal effects. Such analysis will be presented in future work.

4.4 NO/H₂/CO/C₃H₆ reaction system

Real engine exhaust from the passenger vehicle is a mixture of various gas species as noted in the introduction. Consequently it is of practical importance to understand the behavior of NO_x storage and reduction process under the influence of such representative mixture (H₂/CO/C₃H₆). Previous sections all described and reasonably captured the reduction performance of NO_x with individual species. Here, the co-existence of H₂, CO, C₃H₆ results in a complicated series of reactions and reaction networks occurring in the NSR catalyst and the micro-kinetic modeling approach adapted in this work qualitatively represents such complexity and validates the key assumptions made in developing the kinetic model.

Figure 10: Model predictions of NO_x conversion and NH₃ selectivities in the cyclic reduction operation. Lean: 300ppm NO, 8% O₂, 60s; Rich: 1%CO, 0.33% H₂, 0.33% C₃H₆, 1% O₂ for 5s.

Kinetic parameters estimated in the prior sections are used without any further tuning to calculate NO_x conversion in the presence of combined feed H₂/CO/C₃H₆. Figure 9 shows the conversions of NO_x, H₂, CO and C₃H₆ as a function of temperature. It can be observed that H₂ conversion is significant while that of CO and C₃H₆ are negligible for the operation conditions considered.

As is known from prior studies, H₂ is a more effective reductant than CO and C₃H₆. Similar behavior is predicted by the model as shown in Figure 9. However, it is to be noted that the conversion of propylene is negligible compared to CO and H₂, this highlights the competition of reductant species to react with the surface O adatom. We also attempt to predict the cyclic studies performed by Wang et. al. [59] using a fully formulated NSR catalyst that

contained ceria in addition to BaO as the storage material. The model predicts reasonably the NO_x conversion and selectivities of NH_3 with the mixed feed containing $\text{H}_2/\text{CO}/\text{C}_3\text{H}_6$. However the comparison is made with the catalyst based on ceria/zirconia support, hence the model prediction is only a qualitative representation. Both the periods contain 5% CO_2 and 5% H_2O ; GHSV of 30000 hr^{-1} and length of the catalyst ($\text{Pt}/\text{BaO}/\text{CeO}_2/\text{Zr}/\text{Al}_2\text{O}_3$) is 7.5cm [59].

5 Conclusions

The existing global kinetic models are unable to represent the feed composition dependency of the catalyst performance. We presented a detailed kinetic analysis of the NO_x storage and reduction on $\text{Pt}/\text{BaO}/\text{Al}_2\text{O}_3$ using 1+1 dimensional two phase model accounting for washcoat diffusional limitations.

The isothermal model developed is able to satisfactorily predict NO_x conversions observed in the experimental studies and also predict the N_2 and NH_3 selectivities qualitatively. Performance of the catalyst in the presence of complex feed $\text{H}_2/\text{CO}/\text{C}_3\text{H}_6$ over a range of temperatures and inlet feed concentrations is evaluated under varying feed compositions. Prior experimental and computational evidence has shown the non-negligible impact of washcoat diffusion on de NO_x efficiency of the monolith reactors which results in over predicting the NO_x conversion and inaccurately representing the scale-up performance. The kinetic scheme proposed in this work agrees with experimentally observed CO inhibition effects on NO_x conversion and is consistent with prior investigations performed by various groups. Complicated pathways suggested by experimental results are successfully captured by the model for example, water-gas shift and isocyanate pathways to form NH_3 in the $\text{NO}/\text{CO} + \text{H}_2\text{O}$ system. The washcoat diffusion scheme incorporated into our model enabled an accurate representation of onboard and experimental conditions. The effect of diffusivities on the estimated parameters indicate that the true kinetics is dependent on the washcoat structure, nature

and dispersion of the active materials.

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Notation

a = uncoated width/height of monolith channel (square)

A = pre-exponential factor (for units see Appendix)

C_X = total concentration of X sites ($X = \text{Pt}$ or BaO , mol of BaO/m^3 washcoat)

C_{ref} = reference concentration (mol/m^3)

C_{Tm} = total concentration in fluid phase (mol/m^3)

$D_{m,j}$ = diffusivity of species j in gas phase (m^2/s)

D_{eo} = effective diffusivity at reference temperature

$D_{e,wc}$ = effective diffusivity of species j in washcoat (m^2/s)

E = activation energy (kJ/mol)

ΔH = heat of reaction

$k_c(j,z)$ = mass transfer coefficient of species j at axial position 'z' (m/s)

k = reaction rate constant (for units refer to Appendices)

L = length of the monolith (m)

M_{wj} = Molecular weight of species j

OR = overall reaction

Q = heat of adsorption/desorption

r_{eff} = average pore radius

R_{vj} = rate of adsorption/desorption of species j (mol/m³washcoat/s)

R_l = rate of reaction on the catalyst surface (mol/m³washcoat/s)

R_Ω = effective transverse length scale (m)

t = time (s)

T = temperature (K)

T_r = reference temperature (K)

$\bar{u}$ = average fluid velocity in the fluid phase(m/s)

X_{jm} = cup mixing mole fraction of species j

X_{jwc} = mole fraction of species j in washcoat

z = axial coordinate (m)

Greek Letters

α_v = platinum surface area per unit washcoat volume (m²/m³)

δ_{wc} = washcoat thickness (m)

ε_{wc} = porosity of washcoat

θ_j = fractional coverage of surface species on the catalyst surface

v_{jr} = stoichiometric coefficient of surface species j in reaction r

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Appendix

A1: Constant parameters

<i>Parameter</i>	<i>Value</i>
a	1.1 mm
R_{Ω}	261 μm
L	2 cm
Sh_{e0}	3.608
α_v	$1.5 \times 10^6 \text{ m}^2 Pt / \text{m}^3 \text{ washcoat}$
δ_{wc}	30 μm
ϵ_{wc}	0.4
C_{Pt}	8 mol/m ³
$C_{BaO}(f), C_{BaO}(s)$	66.2, 272 mol/m ³

A2: Temperature dependent parameters

<i>Parameter</i>	<i>Value/Expression</i>
$\bar{u}$	$u_{ref}(\frac{T}{T_{ref}}); u_{ref} = 1m/s, T_{ref} = 548.15^\circ K (275^\circ C)$
C_{Tm}	$P_{atm}/RT \text{ (mol/m}^3\text{)}$
$D_{m,NO}$	$1.33 \times 10^{-9} (T)^{1.696}$
D_{m,NO_2}	$1.03 \times 10^{-9} (T)^{1.682}$
D_{m,O_2}	$0.8 \times 10^{-9} \times T^{1.7037}$
D_{m,N_2O}	$0.81 \times 10^{-9} (T)^{1.690}$
D_{m,N_2}	$1.34 \times 10^{-9} (T)^{1.690}$
D_{m,NH_3}	$1.22 \times 10^{-9} (T)^{1.739}$
D_{m,H_2}	$5.8 \times 10^{-9} (T)^{1.666}$
D_{m,H_2O}	$0.95 \times 10^{-9} (T)^{1.778}$
$D_{m,CO}$	$1.35 \times 10^{-9} (T)^{1.701}$
D_{m,CO_2}	$0.89 \times 10^{-9} (T)^{1.686}$
D_{m,C_3H_6}	$1.35 \times 10^{-9} (T)^{1.695}$

A3: Catalyst properties

<i>Catalyst Composition</i>	<i>Pt(wt%)</i>	<i>BaO(wt%)</i>	<i>Pt Dispersion(%)</i>	<i>Pt Area(m²/g)</i>
<i>Pt/BaO/Al₂O₃</i>	2.2	16.3	21.9	1.19

A4: Surface energetics

<i>Reaction</i>	$\Delta H_g(kJ/mol)$	$Q_1(kJ/mol)$	$Q_2(kJ/mol)$	$Q_3(kJ/mol)$	$\Delta H_s(kJ/mol)$
$NO* \rightarrow N* + O*$	634.2[53]	109[51]	487.2[54]	357.2[54]	-100.8
$NO_2* \rightarrow NO* + O*$	306[52]	80[50]	109	357.2	-80
$OH* \rightarrow O* + H*$	428[52]	201[56]	357.2	254[55]	18
$H_2O* \rightarrow OH* + H*$	498[52]	45[56]	201	254	88
$O_2 \rightarrow 2O*$	498[52]	—	357.2	357.2	-216.4
$H_2 \rightarrow 2H*$	436[52]	—	254	254	-72
$N_2 \leftarrow 2N*$	945.4[52]	—	487.2	487.2	29
$N_2O \leftarrow NO* + N*$	481[52]	—	109	487.2	115
$CO_2* \rightarrow CO* + O*$	532[52]	20[57]	134[58]	357	61

A5: Rate expressions and kinetic constants

Rate Expression	$A_f(\text{mol}/\text{m}^3/\text{s})/S_0$	$A_r(\text{mol}/\text{m}^3/\text{s})/S_0$	$E_f(\text{kJ}/\text{mol})$	$E_r(\text{kJ}/\text{mol})$
$R1 : k_{1f}X_{NO}\theta_v - k_{1r}\theta_{NO}$	0.85	2.5×10^{16}	—	109
$R2 : k_{2f}\theta_{NO}\theta_v - k_{2r}\theta_N\theta_O$	3×10^{11}	4×10^{13}	63	163
$R3 : k_{3f}\theta_{NO}\theta_O - k_{3r}\theta_{NO_2}$	4×10^8	2.5×10^{13}	80.5	160
$R4 : k_{4f}\theta_{NO_2} - k_{4r}X_{NO_2}\theta_v$	5.7×10^{11}	1.0	80.1	—
$R5 : k_{5f}X_{O_2}\theta_v - k_{5r}\theta_O^2$	0.07	4×10^{14}	—	214
$R6 : k_{6f}\theta_N^2$	1×10^{12}	—	60	—
$R7 : k_{7f}\theta_{NO}\theta_N$	7×10^{12}	—	72.2	—
$R8 : k_{8f}\theta_{BaO}\theta_{NO_2} - k_{8r}\theta_v\theta_{Ba(NO_3)_2}(f)$	2×10^{12}	5×10^{13}	62	210
$R8 : k_{8f}\theta_{BaO}\theta_{NO_2} - k_{8r}\theta_v\theta_{Ba(NO_3)_2}(s)$	2×10^{11}	2×10^{12}	81	230
$R9 : k_{9f}X_{H_2}\theta_v - k_{9r}\theta_H^2$	0.046	4×10^{11}	—	72
$R10 : k_{10f}\theta_H\theta_O - k_{10r}\theta_{OH}$	4×10^{12}	6.28×10^{13}	73.5	91
$R11 : k_{11f}\theta_{OH}\theta_H - k_{11r}\theta_{H_2O}$	1×10^{13}	4×10^{13}	22.4	110
$R12 : k_{12f}\theta_{H_2O} - k_{12r}X_{H_2O}\theta_v$	3×10^{13}	0.3	45	—
$R13 : k_{13f}\theta_{NO}\theta_H - k_{13r}\theta_N\theta_{OH}$	4×10^{13}	4×10^{11}	62	180
$R14 : k_{14f}\theta_N\theta_H - k_{14r}\theta_{NH}\theta_v$	2×10^{13}	2×10^{12}	112	70.6
$R15 : k_{15f}\theta_{NH}\theta_H - k_{15r}\theta_v\theta_{NH_2}$	4×10^{12}	4×10^{12}	61.3	90
$R16 : k_{16f}\theta_{NH_2}\theta_H - k_{16r}\theta_{NH_3}\theta_v$	4×10^{12}	2×10^{12}	74.2	60
$R17 : k_{17f}\theta_{NH_3} - k_{17r}X_{NH_3}\theta_v$	2×10^{13}	0.73	51	—
$R18 : k_{18f}X_{CO}\theta_v - k_{18r}\theta_{CO}$	1.0	1.6×10^{13}	—	134
$R19 : k_{19f}\theta_{CO}\theta_O - k_{19r}\theta_{CO_2}\theta_v$	6×10^{11}	4×10^{12}	68	129
$R20 : k_{20f}\theta_{CO_2} - k_{20r}X_{CO_2}\theta_v$	9×10^{10}	0.5	20	—
$R21 : k_{21f}\theta_{CO}\theta_N - k_{21r}\theta_{NCO}\theta_v$	4×10^{12}	4×10^{14}	85	120
$R22 : k_{22f}\theta_{NCO}\theta_{H_2O} - k_{22r}\theta_{NH_2}\theta_{CO_2}$	4×10^{14}	4×10^{14}	72	110
$R23 : k_{23f}\theta_{BaO}\theta_{CO_2} - k_{23r}\theta_v\theta_{BaCO_3}(f)$	5×10^{10}	2×10^{13}	47	307
$R23 : k_{23f}\theta_{BaO}\theta_{CO_2} - k_{23r}\theta_v\theta_{BaCO_3}(s)$	5×10^8	2×10^{12}	80	340

$R24 : k_{24f}X_{C_3H_6}\theta_v - k_{24r}\theta_{CH_2}$	0.3	4×10^{12}	—	105
$R25 : k_{25f}\theta_{CH_2}\theta_O - k_{25r}\theta_{CO}\theta_{H_2O}$	4×10^{13}	4×10^{12}	90	380