

# INTERNATIONAL JOURNAL OF CHEMICAL REACTOR ENGINEERING

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*Volume 5*

2007

*Article A1*

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## **Micro-Kinetic Study of Reduction of NO on Pt Group Catalysts**

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ISSN 1542-6580

# Micro-Kinetic Study of Reduction of NO on Pt Group Catalysts

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## Abstract

Catalytic reduction using CO has significant potential for the control of NO<sub>x</sub> using Pt group catalysts as CO is already present in the exhausts and Pt group catalysts have high durability in the presence of SO<sub>2</sub> and H<sub>2</sub>O. Different reaction mechanisms are given in the literature for this reaction based on NO dissociation, -NCO formation and so on, but the exact reaction mechanism capable of capturing experimentally observed features is as yet unavailable. To determine the kinetics and reaction mechanism, we propose here an elementary reaction mechanism based on NO dissociation applicable to Pt group catalysts and simulated with CHEMKIN 4.0.2 using single and multiple PSR (Perfectly Stirred Reactor) model. The activation energies of the elementary steps are found from the Unity Bond Index-Quadratic Exponential Potential (UBI-QEP) method. Excellent agreement between literature experiments and our simulation results are observed for the NO-CO reaction on Pt and Rh catalysts and for the NO-CO-O<sub>2</sub> reaction on Ir catalyst. The effect of temperature on the NO reduction activity is captured well by the model. Additionally the simulations can also point towards importance of particular reactions, selectivity to N<sub>2</sub>, effects of surface coverage, effects of residence time and catalytic surface area on NO reduction.

**KEYWORDS:** NO, CO, Pt, surface reaction mechanism, CHEMKIN, PSR

## 1. INTRODUCTION

Oxides of nitrogen ( $\text{NO}_x$ ) are common atmospheric pollutants arising from both stationary sources and automobile engines. They are harmful and toxic for human and aquatic life, leading to photochemical smog and acid rain. Different technologies are used or proposed to control the emissions of  $\text{NO}_x$  from automobiles (e.g. Three-way catalytic converter,  $\text{NO}_x$  storage catalyst, Selective Catalytic Reduction (SCR)).

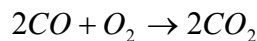
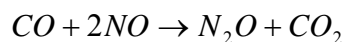
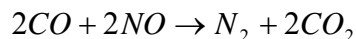
Researchers are focusing attention on selective catalytic reduction of  $\text{NO}_x$  by hydrocarbons (HC-SCR) in which hydrocarbons act as reductants to convert  $\text{NO}_x$  selectively to  $\text{N}_2$ , in the presence of significant oxygen. As Pt group catalysts (Pt, Pd, and Rh) are already used in the catalytic converter and are known to have high durability in the presence of  $\text{H}_2\text{O}$  and  $\text{SO}_2$  (Ciambelli et al., 2000; Zhang et al., 1992), these catalysts are proposed for SCR as well. Several review papers discussing various aspects of HC-SCR are available in the literature (Fritz and Pitchon, 1997; Amiridis et al., 1996; Burch et al., 2002).

Surface reactions for HC-SCR will necessarily include the steps for reduction of NO by CO, and its corresponding oxidation to  $\text{CO}_2$ , as a sub-set of the total reaction mechanism. The reduction of NO by CO is well-studied in the literature - due in part to its importance in the catalytic converter and the NO-HC reaction (Parvulescu et al., 1998; Kobylinski and Taylor, 1974; Hecker and Bell, 1983; Chambers et al., 2001; Harmsen et al., 2001; Bera et al., 2001). Also, CO is a regulated pollutant, and typically present in automobile exhaust. Considering all these facts, several surface reaction mechanisms (for Pt and Rh catalysts) are proposed in the literature for the reduction of NO by CO (Hecker and Bell, 1983; Oh et al., 1986; Chatterjee et al., 2001; Fink et al., 1992; Granger et al., 1998a; Sarkar and Khanra, 2004). In the presence of  $\text{O}_2$  (under lean burn condition), Ir catalyst is found to be more effective than other Pt group catalysts. However, a reliable, quantitative reaction mechanism capable of capturing experimentally observed features is not available for NO-CO and NO-CO- $\text{O}_2$  reactions.

In this work, a quantitative elementary reactions mechanism is proposed for the NO-CO and NO-CO- $\text{O}_2$  reactions on Pt group catalysts. Various reactor models like PSR (Perfectly Stirred Reactor), series of 10 and 20 PSRs are considered and the simulation results are compared to literature experiments. Excellent agreement in the variation of reactant conversions and product selectivities with reaction temperature is obtained. Complete information about the rate constants of the involved elementary reactions is provided. The roles of adsorbed species concentrations in determining the product composition are analysed in detail. Importance of each elementary reaction is examined using sensitivity analysis.

## 2. SURFACE REACTION MECHANISM

The reaction between CO and NO yields  $\text{CO}_2$  and  $\text{N}_2$  as main products and  $\text{N}_2\text{O}$  as an important side product. In the presence of  $\text{O}_2$  (lean burn conditions), CO is oxidized to give  $\text{CO}_2$  by the free oxygen as well. The following global reactions are suggested for this system (Hahn and Lintz, 1989):



However, such global reaction sets rarely serve as good predictive tools due to the limitations that the kinetic parameters associated with them are fitted to a narrow range of operating conditions. Detailed reaction mechanisms based on elementary steps are a better option, as they are able to capture the underlying science from a fundamental standpoint. Furthermore, the microkinetic approach (Braun et al., 2001) possesses the additional advantage that it does not require any assumptions about the rate determining step and is thus likely to be valid over a large range of operating conditions.

Granger and co-workers (1998a; 1998b; 1999; 2002) have proposed a surface reaction mechanism for the reduction of NO by CO, on Pt group catalysts, involving NO dissociation, and N<sub>2</sub> and N<sub>2</sub>O formation. An estimate of the pre-exponential and activation energy for the overall (global) reaction rate expression derived from this reaction mechanism has been obtained by fitting to experimental data. However, since the information regarding the rates of individual reactions in the mechanism is not provided, the validity range of this kinetic data is small. Similarly, other authors have estimated overall reaction orders, activation energies, and so on from experimental data (Hecker and Bell, 1983; Permana et al., 1995; Na-Ranong et al., 2002) which are valid within narrow ranges of operating conditions.

Shustorovich and Bell (1993) have proposed a detailed reaction mechanism involving the formation of N<sub>2</sub>, N<sub>2</sub>O and NH<sub>3</sub> (in the presence of H<sub>2</sub> in the feed) and provided information regarding the activation energies of individual, elementary reaction steps, for various transition metal catalysts. Some of the observed features can be explained by analysis of the activation energies. However, pre-exponential factors are not provided, and quantitative comparisons with experiments are not shown. There are some issues with respect to the steps involving N<sub>2</sub>O formation proposed in this work, as discussed further below. Our work is in close accord with this article but addresses some of these drawbacks.

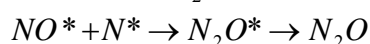
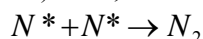
Oh et al. (1986) have proposed a reaction mechanism for the reduction of NO by CO on Rh(111) catalysts. The formation of N<sub>2</sub>O is ignored. An N-CO "interaction energy" value, and the NO desorption pre-exponential are fitted in order that the simulation results match the CO<sub>2</sub> formation rates measured in the experiments. In the model, the fractional coverage of oxygen is ignored in the site conservation equation (assuming it is negligibly small), which may not always be valid. Some of the other drawbacks of this reaction mechanism are discussed in detail in section 3.2.

Chatterjee et al. (2001) propose a quantitative detailed reaction mechanism, which includes several steps for the reduction of NO by CO for Pt and Rh, relevant for catalytic converter conditions, and couple it with CFD simulations, while other researchers use a simple reaction mechanism for the NO-CO system on Pt(100), at low pressures, and perform bifurcation analysis (Fink et al., 1992; Makeeva and Kevrekidis, 2004; Imbihl et al., 1992; Frank and Renken, 1998). However, the formation of N<sub>2</sub>O is not considered in any of these mechanisms.

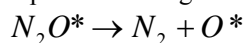
The literature on the NO-CO system indicates a fair consensus on some of the reaction steps – molecular NO adsorption, dissociation of adsorbed NO to form adsorbed N and O species, and the

oxidation of molecularly adsorbed CO to form CO<sub>2</sub>. The steps involving the formation of the products N<sub>2</sub> and N<sub>2</sub>O are however, under contention. On the one hand, several articles point to the reaction  $2N^* \rightarrow N_2 + 2^*$  as the only source of N<sub>2</sub> (Permana et al., 1995; Belton et al., 1995; Holles et al., 2000; Ohno et al., 2003), while on the other hand, the intermediacy of N<sub>2</sub>O in the formation of N<sub>2</sub> is strongly proposed by other researchers (Hecker and Bell, 1983; Oh et al., 1986; Shustorovich and Bell, 1993; Cho et al., 1989; Taylor and Schlatter, 1980). NCO has been proposed as an intermediate by some others (Silva and Schmal, 2003).

Based on our initial analysis of the reaction mechanism, the dissociation of molecularly adsorbed NO is a crucial step (in concurrence with literature results (Granger et al., 2002; Burch et al., 1994). Also, the formation of N<sub>2</sub> and N<sub>2</sub>O are as follows:



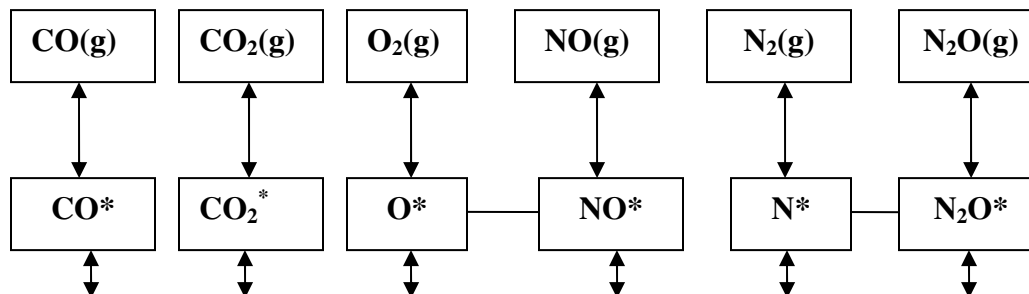
This implies that we ignore the following pathway for N<sub>2</sub> formation from N<sub>2</sub>O:



First of all, we believe that the experiments of Belton et al. (1995) conclusively eliminate this pathway. Secondly, the activation energy for the above step is given to be zero by Shustorovich and Bell (1993). From this we expect that as soon as N<sub>2</sub>O\* is formed, it will convert to N<sub>2</sub>. The activation energy for desorption of N<sub>2</sub>O\* being 5.6 kcal/mol on Pt(111) and 10 kcal/mol on Rh(111), we can expect to never see N<sub>2</sub>O as a gaseous product on Pt and Rh catalysts, due to the highly competitive parallel path consuming N<sub>2</sub>O\* to N<sub>2</sub> (assuming that the pre-exponentials for both pathways are comparable in magnitude). Needless to say, considerable N<sub>2</sub>O has been observed as a product, at low temperatures, for Pt (Chambers et al., 2001; Granger et al., 1998a) and for Rh (Chambers et al., 2001; Hecker and Bell, 1983; Kondarides et al., 2000; Belton and Schmiege, 1993). We believe that the one way to explain this feature is to follow the work of Belton (1995) and eliminate this pathway from reaction mechanisms, at least pending further quantitative information about the rate constant. Regarding -NCO and -CN as intermediates, it is found that only 5% of NO is consumed to -CN and -NCO species and also that they have very low stability in the NO-CO reaction (Lorimer and Bell, 1979), so these pathways are also not included in our reaction mechanism.

Considering all of these facts, the schematic representation of the surface reaction mechanism we propose is given in Table 1. The main features are: molecular adsorption of reactants NO and CO, dissociation of adsorbed NO\* to N\* and O\*, recombination of N\* to form N<sub>2</sub>, reaction of adsorbed NO and N\* to form N<sub>2</sub>O and finally, the reaction of adsorbed CO with O\* to form CO<sub>2</sub>. In the presence of O<sub>2</sub> (NO-CO-O<sub>2</sub> system), additional steps for the dissociative O<sub>2</sub> adsorption (first order) and desorption of O\* are also considered. All the reactions are considered as reversible including N<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub> adsorption. The set of elementary reactions is assumed to remain the same for all the catalysts studied: Pt, Rh and Ir, with only the activation energies and sticking coefficient values being different on different catalysts.

Table 1. Schematic representation of proposed surface reaction mechanism (\* and (g) refer to adsorbed species and gas species respectively).



## 2.1 Reactor Model

Since the length/diameter ratio of the reactors used in experimental studies (Chambers et al., 2001; Ogura et al., 2000) is small, we assume that there are no significant concentration and temperature gradients in the reactor, thus we consider a steady state isothermal catalytic PSR (Perfectly Stirred Reactor) for the mass balance of gas species. Since no real reactors behave as ideal PSRs, multiple (10 and 20) PSRs (same total volume as a single PSR) in series are considered as well. Simulation results with all these models are compared with literature experimental data. For the series of PSRs, the total volume, surface area and residence time for all the reactors together is assumed to be equal to that in case of the single PSR.

The surface intermediates are assumed to be in steady state, which implies that their rate of formation is equal to their rate of disappearance. The conservation of surface sites demands that the summation of all the fractional surface coverages is one. Detailed explanations of the model equations for the PSR are given in the CHEMKIN manual (CHEMKIN 4.0.2, 2005).

Information regarding the activation energy and the pre-exponential factor/sticking coefficient is required for each catalyst, for each reaction. To avoid the various discrepancies found in literature, we have calculated all the activation energies for the NO sub-chemistry using a semi-empirical method called the Unity Bond Index-Quadratic Exponential Potential (UBI-QEP) method (Shustorovich and Sellers, 1998). These calculations are based on inputs of atomic/molecular heat of adsorption, relevant for the (111) surface of various metal catalysts. The atomic/molecular heats of adsorption and gas phase bond energies required for this method are taken from literature (Shustorovich and Bell, 1993; Hie et al., 1998). Thus it is to be understood that our proposed surface reaction mechanism is for Pt(111), Rh(111) and Ir(111) surfaces. The pre-exponential factors are maintained at the approximate levels determined by transition state theory as in earlier literature (Aghalayam et al., 2000). The values of 0.89 on Pt (Aghalayam et al., 2000), 0.67 on Rh (Bowker et al., 1999), and 0.92 on Ir (Burghaus et al., 1997) are considered for the CO adsorption sticking coefficient. For NO adsorption, a sticking coefficient of 0.6 on Pt, 0.67 on Rh and 0.6 on Ir are assumed whereas a sticking coefficient of 0.03 is used for the dissociative adsorption (first order) of O<sub>2</sub> on Ir catalyst. The sticking coefficient for CO<sub>2</sub> adsorption is taken to be 0.005 (Crocoll et al., 2005) while for N<sub>2</sub> and N<sub>2</sub>O, sticking coefficients are assumed to be 0.001 for all the catalysts. Pre-exponential factors/sticking coefficients and activation energies

corresponding to each of the elementary reactions for the different catalysts (Pt, Rh, and Ir) used in this study are also shown in Table 2.

Table 2. Surface reaction mechanism in CHEMKIN format for the NO-CO reaction on Pt, Rh catalysts and the NO-CO-O<sub>2</sub> reaction on Ir catalyst.

No	!Reactions	!A (mole-cm-sec-K)	!b	!Ea (kJ/mol)
	!(k = A T**b exp(-Ea/RT))			
	!*****			
	!**** SURFACE MECHANISM FOR NO-CO REACTIONS ON Pt			
	!-----			
1	NO +Pt (S) =>NO (S) STICK	6.000E-01	0.0	0.0
2	NO (S) =>NO +Pt (S)	1.000E+13	0.0	109.085
3b	!NO (S) +Pt (S) =>N (S) +O (S)	4.818E+19	0.0	52.565
3n	NO (S) +Pt (S) =>N (S) +O (S)	4.818E+19	0.0	61.000
4	N (S) +O (S) => NO (S) +Pt (S)	4.818E+19	0.0	152.68
5	N (S) +N (S) =>N <sub>2</sub> +Pt (S) +Pt (S)	4.818E+19	0.0	111.276
6	N <sub>2</sub> +Pt (S) +Pt (S) =>N (S) +N (S) STICK	1.000E-03	0.0	0.0
7	NO (S) +N (S) =>N <sub>2</sub> O (S) +Pt (S)	4.818E+19	0.0	89.066
8	N <sub>2</sub> O (S) +Pt (S) =>NO (S) +N (S)	4.818E+19	0.0	15.094
9	N <sub>2</sub> O (S) =>N <sub>2</sub> O +Pt (S)	1.000E+13	0.0	23.430
10	N <sub>2</sub> O +Pt (S) =>N <sub>2</sub> O (S) STICK	1.000E-03	0.0	0.0
11	CO +Pt (S) =>CO (S) STICK	8.900E-01	0.0	0.0
12	CO (S) =>CO +Pt (S)	1.000E+13	0.0	133.880
13	CO (S) +O (S) =>CO <sub>2</sub> (S) +Pt (S)	4.818E+19	0.0	97.269
14	CO <sub>2</sub> (S) +Pt (S) =>CO (S) +O (S)	4.818E+19	0.0	77.147
15	CO <sub>2</sub> (S) => CO <sub>2</sub> + Pt (S)	1.000E+13	0.0	15.185
16	CO <sub>2</sub> + Pt (S) => CO <sub>2</sub> (S) STICK	0.0050000	0.0	0.0
	!*****			
	!**** SURFACE MECHANISM FOR NO-CO REACTIONS ON Rh			
	!*****			
1	NO +Rh (S) =>NO (S) STICK	6.700E-01	0.0	0.0
2	NO (S) =>NO +Rh (S)	1.000E+13	0.0	109.085
3	NO (S) +Rh (S) =>N (S) +O (S)	4.818E+19	0.0	27.922
4	N (S) +O (S) => NO (S) +Rh (S)	4.818E+19	0.0	199.166
5	N (S) +N (S) =>N <sub>2</sub> +Rh (S) +Rh (S)	4.818E+19	0.0	111.276
6	N <sub>2</sub> +Rh (S) +Rh (S) =>N (S) +N (S) STICK	1.000E-03	0.0	0.0
7b	NO (S) +N (S) =>N <sub>2</sub> O (S) +Rh (S)	4.818E+19	0.0	89.066
7n	!NO (S) +N (S) =>N <sub>2</sub> O (S) +Rh (S)	4.818E+19	0.0	76.0
8	N <sub>2</sub> O (S) +Rh (S) =>NO (S) +N (S)	4.818E+19	0.0	8.818
9	N <sub>2</sub> O (S) =>N <sub>2</sub> O +Rh (S)	1.000E+13	0.0	41.84
10	N <sub>2</sub> O +Rh (S) =>N <sub>2</sub> O (S) STICK	1.000E-03	0.0	0.0
11	CO +Rh (S) =>CO (S)	6.700E-01	0.0	0.0

	STICK					
12	CO(S)	=>CO	+Rh(S)	1.000E+13	0.0	133.880
13	CO(S)	+O(S) =>CO2(S)	+Rh(S)	4.818E+19	0.0	101.91
14	CO2(S)	+Rh(S) =>CO(S)	+O(S)	4.818E+19	0.0	47.144
15	CO2(S)	=> CO2 + Rh(S)		1.000E+13	0.0	21.661
16	CO2 + Rh(S)	=> CO2(S)		0.0050000	0.0	0.0
	STICK					
	!*****					
	!**** SURFACE MECHANISM FOR NO-CO-O2 REACTIONS ON Ir					
	!*****					
1	NO	+Ir(S) =>NO(S)		6.000E-01	0.0	0.0
	STICK					
2	NO(S)	=>NO	+Ir(S)	1.000E+13	0.0	128.473
3	NO(S)	+Ir(S) =>N(S)	+O(S)	4.818E+19	0.0	32.200
4	N(S)	+O(S) => NO(S)	+Ir(S)	4.818E+19	0.0	192.424
5	N(S)	+N(S) =>N2	+Ir(S) +Ir(S)	4.818E+19	0.0	164.578
6	N2	+Ir(S) +Ir(S) =>N(S)	+N(S)	1.000E-03	0.0	0.0
	STICK					
7	NO(S)	+N(S) =>N2O(S)	+Ir(S)	4.818E+19	0.0	120.100
8	N2O(S)	+Ir(S) =>NO(S)	+N(S)	4.818E+19	0.0	0.0
9	N2O(S)	=>N2O	+Ir(S)	1.000E+13	0.0	58.576
10	N2O +Ir(S)	=>N2O(S)		1.000E-03	0.0	0.0
	STICK					
11	CO	+Ir(S) =>CO(S)		8.900E-01	0.0	0.0
	STICK					
12	CO(S)	=>CO	+Ir(S)	1.000E+13	0.0	142.256
13	CO(S)	+O(S) =>CO2(S)	+Ir(S)	4.818E+19	0.0	104.172
14	CO2(S)	+Ir(S) =>CO(S)	+O(S)	4.818E+19	0.0	61.130
15	CO2(S)	=> CO2 + Ir(S)		1.000E+13	0.0	18.097
16	CO2 + Ir(S)	=> CO2(S)		0.0050000	0.0	0.0
	STICK					
17	O2	+Ir(S) +Ir(S) =>O(S)	+O(S)	3.000E-02	0.0	0.0
	STICK					
	FORD/Ir(S) 1/					
18	O(S)	+O(S) =>Ir(S)	+Ir(S) +O2	4.818E+21	0.0	280.320

## 2.2 Solution Methodology

Reaction mechanisms with kinetic data for Pt and Rh (NO-CO) and Ir (NO-CO-O<sub>2</sub>) catalysts, in CHEMKIN format, are given in Table 2. Feed concentrations and catalyst characteristics used in the various experiments differ slightly. Chambers and co-workers (2001) carried out the experiments on SiO<sub>2</sub> supported Pt group catalysts (Pt/SiO<sub>2</sub> and Rh/SiO<sub>2</sub>). Ikeda and co-workers (2001) performed experiments on Pt/Al<sub>2</sub>O<sub>3</sub> whereas Ogura et al. (2000) carried out experiments for the NO-CO-O<sub>2</sub> reaction on three different supported Ir catalysts. The parameters used in these experiments are given in Table 3. Since support effects are not included in our model, input data corresponding to these experiments for our simulations only differ in terms of parameters such as inlet concentration, reactor dimensions and catalytic surface area.



Table 3. Parameters used in the reactor model for Pt and Rh catalysts.

Parameters		Chambers et al. (2001)	Ikeda et al. (2001)	Ogura et al. (2000)
Diameter of the reactor (cm)		0.4	-	1.0
Length (cm)		1.4 <sup>a</sup>	-	2.0
Volume of reactor (cm <sup>3</sup> )		0.1756	0.4647	1.5714
Flow rate (V <sub>0</sub> ) (cm <sup>3</sup> /min)		100	100	100
Catalyst support		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /silicalite
Catalytic surface area (cm <sup>2</sup> )	Pt <sup>a</sup>	827	3120	-
	Rh <sup>a</sup>	669	-	-
	Ir	-	-	1476
NO in feed (ppm)	Pt	3000	10000	-
	Rh	2900	-	-
	Ir	-	-	1000
CO in feed (ppm)	Pt	3400	10000	-
	Rh	3500	-	-
	Ir	-	-	7500
O <sub>2</sub> in feed (%)	Ir	-	-	1

<sup>a</sup> Personal communication with W.C. Noel

### 3. NO-CO REACTION: RESULTS AND DISCUSSIONS

Incorporating the parameters given in Table 3 and the proposed quantitative surface reaction mechanism given in Table 2 into the steady state isothermal PSR model, we have performed numerical simulations using CHEMKIN 4.0.2 on Pt, Rh and Ir catalysts and studied the effect of reactor temperature on the concentration of various gas and surface species.

#### 3.1. Pt Catalyst

The concentrations obtained from our simulations with two different activation energies (52.565 kJ/mol (base value, calculated using the UBI-QEP method), and 61 kJ/mol (new value)) for NO\* dissociation are plotted versus reactor temperature on Pt catalyst in Figure 1 (as lines). It is found that at low temperatures (<250<sup>o</sup>C), there is no reaction between NO and CO. As the temperature increases, the conversions of both NO and CO increase and NO conversion reaches 100% at higher temperatures (~400<sup>o</sup>C).

To validate our model, we compare our simulation results with the experiments carried out by Chambers and co-workers (2001) for the NO-CO reaction on a 1.1% Pt/SiO<sub>2</sub> catalyst. In this experiment, 75 mg of catalyst was placed in a pyrex tube of 0.4 cm diameter and a standard NO-CO mixture (3000 ppm NO + 3400 ppm CO) was passed through the catalyst bed at a rate of 100 cm<sup>3</sup>/min (Details of the parameters are given in Table 3). Reactor temperature was varied between 155<sup>o</sup>C and 430<sup>o</sup>C.

The concentration profiles with respect to reactor temperature for the above experiment are shown in Figure 1 (experimental results are shown by symbols). It was found that at lower

temperatures ( $<250^{\circ}\text{C}$ ), there is no reduction of NO. NO conversion starts at  $250^{\circ}\text{C}$  and reaches 100% at  $420^{\circ}\text{C}$ . At lower temperatures, selectivity to  $\text{N}_2\text{O}$  was found to be higher than that of  $\text{N}_2$  and a peak was observed at  $330^{\circ}\text{C}$  for the  $\text{N}_2\text{O}$  concentration. As the temperature is increased above  $330^{\circ}\text{C}$ ,  $\text{N}_2$  selectivity was found to increase sharply. Concentration of CO was found to decrease with temperature and remain constant at high temperatures. Our simulation results with the simple reactor model using the base value of 52.565 kJ/mol for  $\text{NO}^*$  dissociation (shown with dashed lines in Figure 1) shows qualitative match with the literature experiments in terms of concentrations of all species and the peak in  $\text{N}_2\text{O}$  concentration, however a difference in the temperature range of  $\sim 15^{\circ}\text{C}$  is observed. Sensitivity analysis (discussed in section 5) suggests that  $\text{NO}^*$  dissociation is a critical reaction in the NO-CO system. Considering this fact, the  $\text{NO}^*$  dissociation activation energy value is changed from 52.565 to 61 kJ/mol and the simulated results are shown in Figure 1 (solid lines). Results show that with this new value, an excellent quantitative match for exit gas concentrations is obtained between simulations and experiments. In particular, the temperature dependence of NO, CO concentrations and the peak in  $\text{N}_2\text{O}$  formation match well.

The good match between our simulations and the experimental results (Figure 1) serves as a validation of our surface reaction mechanism. Such a quantitative match between experimental results and simulations for this system is reported for the first time. Considering the simplicity of the reactor-scale model used here, it is fair to assume that the surface reaction mechanism is the critical component of this model. Thus, the notions that the dissociation of adsorbed NO is the primary path for its reduction, formation of  $\text{N}_2$  is only from the recombination of  $\text{N}^*$  and the formation of  $\text{N}_2\text{O}$  is from the combination of  $\text{NO}^*$ - $\text{N}^*$  species, are found to be valid.

We must mention here that our reaction mechanism has not been fitted or tuned (except the  $\text{NO}^*$  dissociation value as discussed above) to make the results agree with experiments. The kinetic data as reported in Table 2 are taken from calculations/literature sources with no modifications. Furthermore, the calculations are based on the assumption of a (111) surface, while the experimental results are for supported Pt. We believe that the agreement between experiments and simulations despite this difference indicates that either Pt/SiO<sub>2</sub> behaves similar to Pt(111) as far as the NO-CO reaction is concerned, as also proposed earlier for Rh(111) and Rh/SiO<sub>2</sub> (Belton and Schmiege, 1993; Peden et al., 1995), or that support effects are minimal in this system as discussed below.

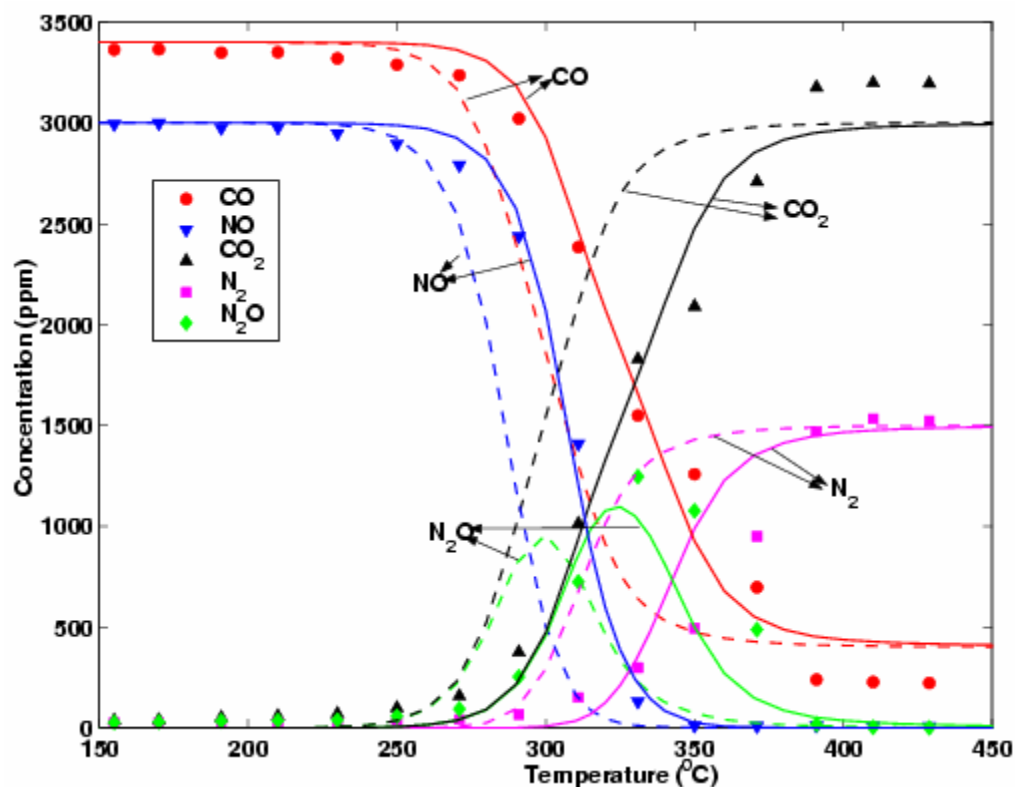


Figure 1. Effect of temperature on outlet gas concentrations for NO-CO reaction on Pt catalyst. Comparison between model (single PSR) results (dashed line: base value (52.565 kJ/mol), solid line: new value (61 kJ/mol) of activation energy for NO\* dissociation) and experimental results (symbols) of Chambers et al. (2001).

Ikeda and co-workers (2001) carried out experiments on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst for the NO-CO system. The details of the parameters used in this experiment are also shown in Table 3. Figure 2 shows the NO conversion as a function of reactor temperature obtained from the experiments of Chambers et al. (2001) for Pt/SiO<sub>2</sub> and Ikeda et al. (2001) for Pt/Al<sub>2</sub>O<sub>3</sub> (as symbols) along with our corresponding simulation results (as lines). From Figure 2, it is observed that the NO conversion at any given temperature is nearly same for both the experiments. The important parameters for this set-up, based on our analysis are: catalyst active site density, catalytic surface area and ratio of inlet concentrations of NO and CO. The values of these parameters are nearly the same for the two experiments (see Table 3). Therefore, we can intuitively expect that, if the effect of the support is not strong, the conversion versus temperature graph will more or less coincide for the two experiments. The results of our simulations for the two cases are also shown in Figure 2 (as lines). Good agreement between experiments and simulations is observed again. The slight difference between the simulation results for the two cases is due to the difference in the values of the parameters mentioned in Table 3.

Overall it is possible to conclude from Figures 1 and 2 that the effect of the material of the catalyst support on the NO-CO reaction is minimal, and that our reaction mechanism based on rate constant values for Pt(111) can capture observed trends in conversions and selectivities for supported Pt catalysts. An analysis of the simulation results with the aim of comprehending the

phenomenon of NO reduction by CO will be provided in a later section using the information on surface coverages.

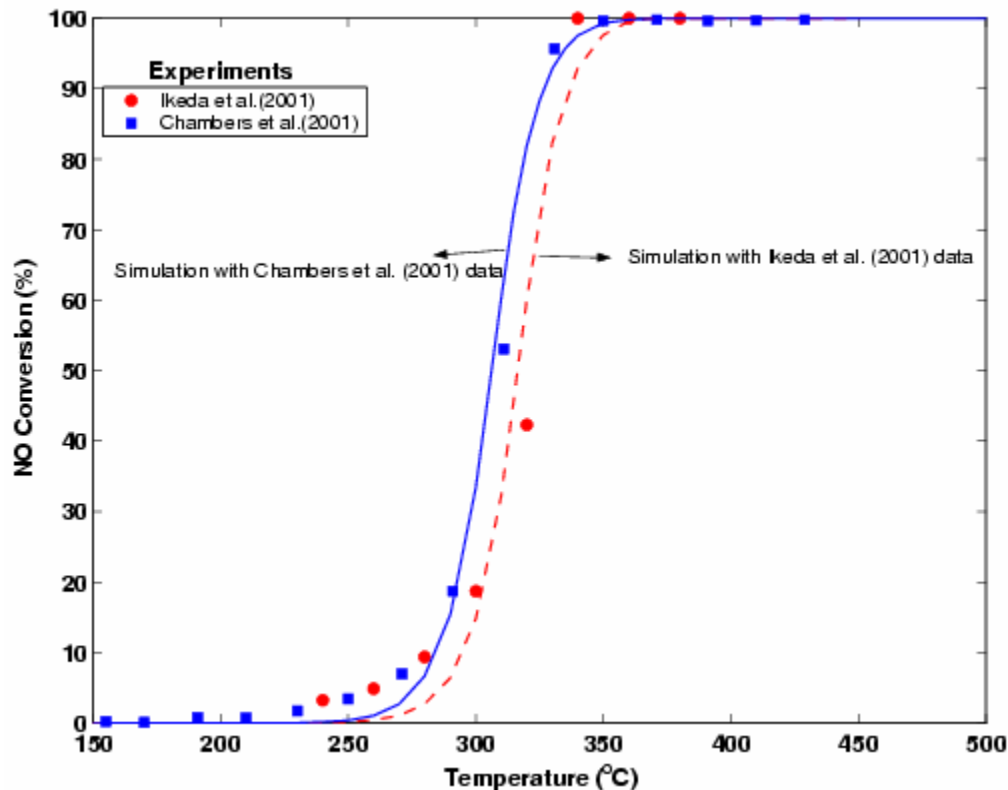


Figure 2. Effect of temperature on NO conversion for NO-CO reaction on Pt catalyst. Comparison between literature experimental results (symbols) and simulation results (lines). ■ and solid line (Chambers et al., 2001), ● and dashed line (Ikeda et al., 2001).

### 3.2 Rh Catalyst

Chambers and co-workers (2001) also performed experiments on a 1.1% Rh/SiO<sub>2</sub> catalyst for the NO-CO system (2900 ppm NO + 3500 ppm CO). The concentration profile as a function of reactor temperature for this experiment is shown in Figure 3(a) (as symbols). NO conversion starts at 200°C and completes at 300°C for the Rh/SiO<sub>2</sub> catalyst (for the Pt/SiO<sub>2</sub> catalyst 100% conversion occurs at ~400°C). Qualitatively, similar type of behavior is observed for both Pt and Rh catalysts but the NO conversions are obtained at lower temperatures on Rh.

The simulation results obtained for the Rh catalyst (shown as lines in Figure 3) agree well with the experimental results for Rh/SiO<sub>2</sub> (shown by symbols in Figure 3). In particular, the temperature at which the catalyst becomes active matches well. However, we predict a lower concentration of N<sub>2</sub>O as compared to the experiments. This probably indicates that our activation energy values for N<sub>2</sub>O formation on Rh are not as good as for Pt. On the other hand, various experimental results (Oh et al., 1986; Hendershot and Hansen, 1986) show very small/negligible amount of N<sub>2</sub>O on the Rh catalyst (as we observed in our simulation). Based on our studies,

varying the activation energy for the  $\text{NO}^*\text{-N}^*$  recombination step (reaction 7 in Table 2) can result in a better match between our simulations and the experimental results. We have changed the activation energy of this reaction from 89.066 (base value, calculated using UBI-QEP method) to 76.0 (new value) kJ/mol. Simulation results with these two activation energies are shown in Figure 3(a) with dashed lines and solid lines respectively. We are able to get an exact match for  $\text{N}_2\text{O}$  concentration in our simulation as in the literature experiments with the new value of 76 kJ/mol for the activation energy of this reaction. Note that in addition to  $\text{N}_2\text{O}$  concentration, the NO and CO concentrations are also better predicted at the changed activation energy, indicating the importance of the  $\text{NO}^*\text{-N}^*$  recombination reaction, in this mechanism.

Comparison of activation energies (Table 2) for Pt and Rh shows that the NO dissociation activation energy is lower on Rh. This is why the NO conversion occurs at lower temperatures on Rh than on Pt, as observed in both the literature experiment and our simulations (see Figure 3).

To compare our mechanism with other reaction mechanisms in literature, we have used the reaction mechanism proposed by Oh et al. (1986) with the PSR model in CHEMKIN and compared the results with our model and the experimental data on Rh/ $\text{SiO}_2$  catalyst of Chambers et al. (2001). Figure 3(b) shows the effect of reactor temperature on outlet concentrations of NO and CO for both the simulations along with experimental data. Feed conditions used in the simulations are same as of Chambers et al. (2001) (Table 3). Results with the mechanism of Oh et al. (1986) are far away from the experimental data where as our model is able to present a good match with the experiments as already seen. In addition to the poor prediction of NO and CO conversions, the reaction mechanism proposed by Oh et al. (1986) has the limitation of ignoring  $\text{N}_2\text{O}$  formation.

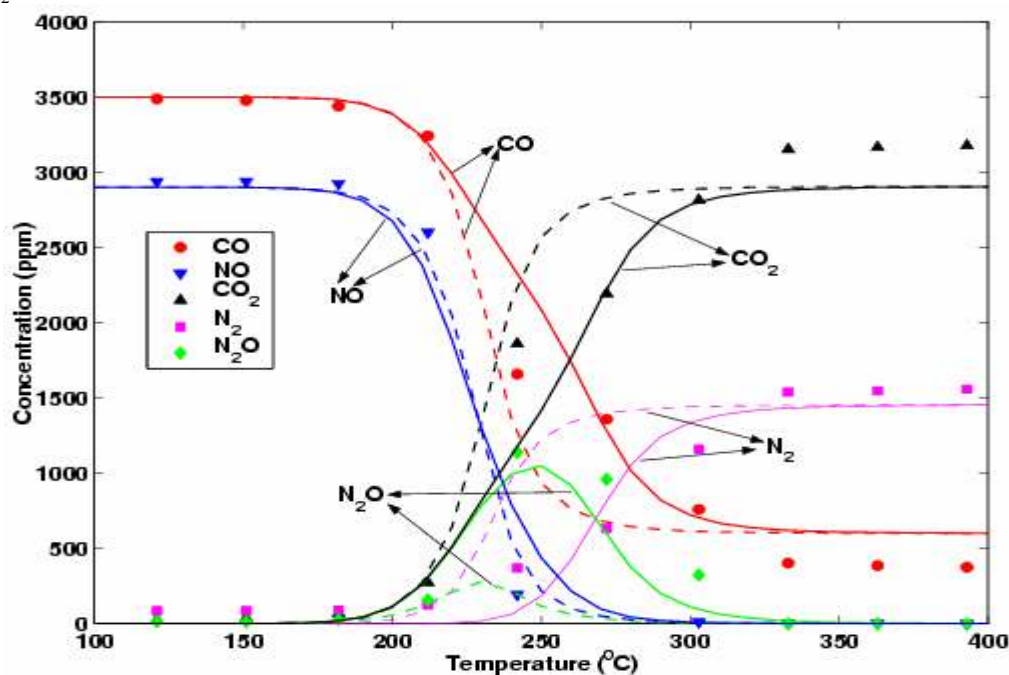


Figure 3(a). Effect of temperature on exit gas concentration for NO-CO reaction on Rh catalyst. Comparison between model (single PSR) results (dashed line: base value (89.066 kJ/mol), solid line: new value (76 kJ/mol) of activation energy for  $\text{NO}^*\text{-N}^*$  recombination) and experimental results (symbols) of Chambers et al. (2001).

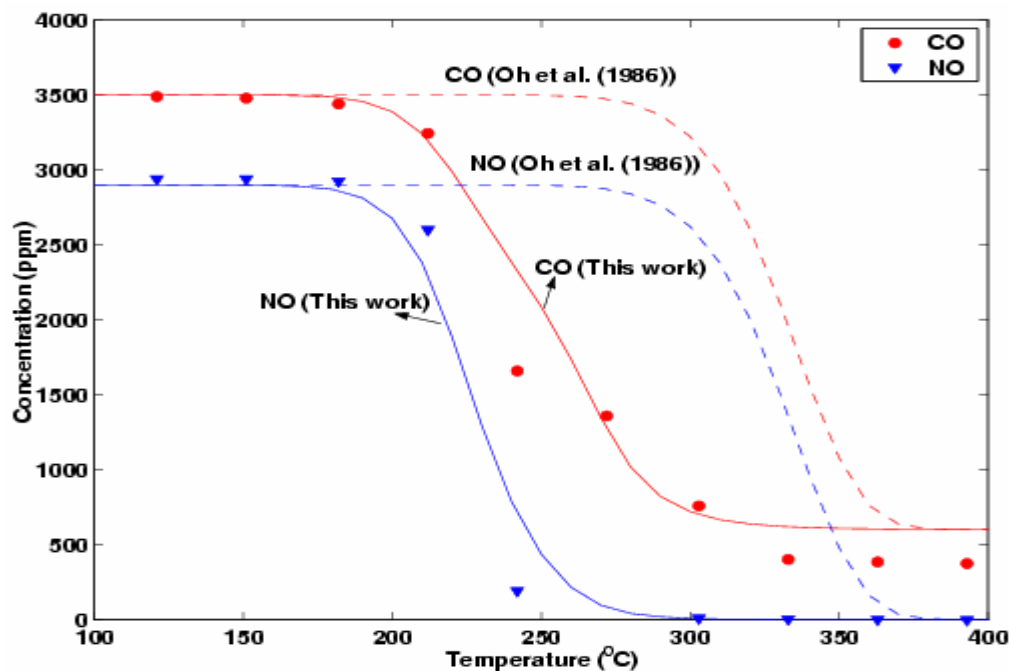


Figure 3(b). Effect of temperature on exit gas concentrations for NO-CO reaction on Rh catalyst. Comparison between our mechanism (solid line), Oh et al. (1986)'s mechanism (dashed line) and experimental results (symbols) of Chambers et al. (2001).

### 3.3 Influence of Reactor Model

The results presented above are considering the single PSR model (as the experimental reactor beds have a small L/D ratio). In a PSR, we assume complete mixing of the reactants. Considering the non-ideality of the experimental reactor, we also performed simulations using the new activation energies for NO\* dissociation on Pt catalyst (61 kJ/mol) and NO\*-N\* recombination reaction on Rh catalyst (76 kJ/mol) using CHEMKIN 4.0.2 with the PSRs in series model (10 and 20 PSR in series) for validation of the results. Effect of number of PSRs in series for Pt and Rh catalysts is shown in Figure 4(a) and Figure 4(b) respectively. Results suggest that the behavior for NO reduction does not change with the reactor model and only a small temperature difference is observed with single PSR and 20-PSR in series for the same volume of reactor. Addition of energy equations in model (results not shown) does not have much effect (only a difference of 5-10 °C) on the behavior of NO reduction, which validates our isothermal assumption for this system.

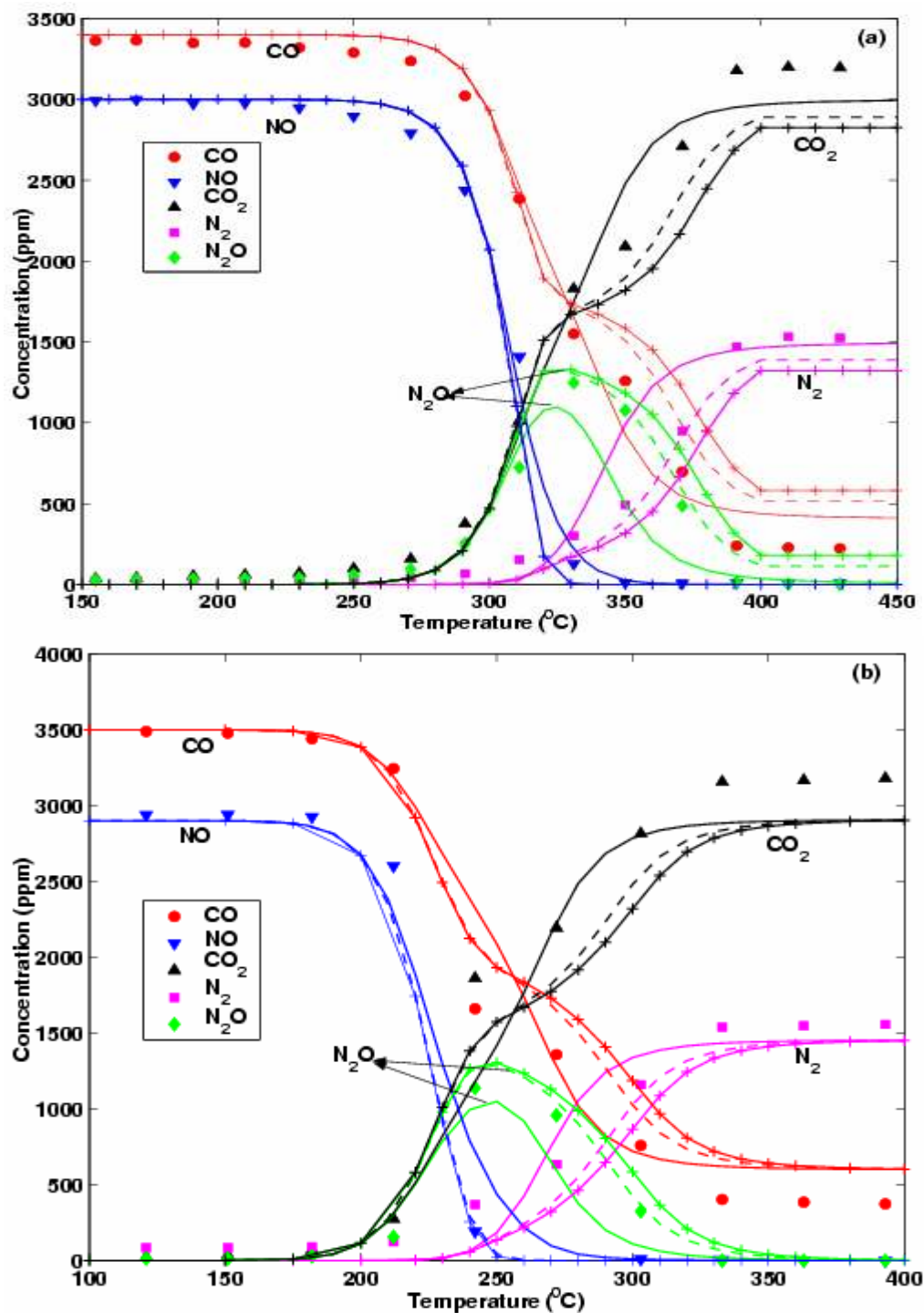


Figure 4. Effect of reactor model (single and series in PSR) on exit gas concentration with temperature for NO-CO reaction on (a) Pt catalyst and (b) Rh catalyst. Single PSR (solid lines), 10-PSR in series (dashed lines), 20-PSR in series (+ lines) and experimental results (symbols).

Results obtained from all these models are compared with experimental data (symbols in Figure 4). In case of the Pt catalyst (Figure 4(a)), the 20 PSRs model is able capture the trend in  $N_2$  and  $N_2O$  formation at lower temperature ( $<400^\circ C$ ) better. However at higher temperatures, this trend is captured better with a single PSR model. The NO conversion is captured well with all the reactor models (10, 20 PSRs and single PSR). In case of Rh catalyst also (Figure 4(b)), results with single, 10 and 20-PSRs in series model show similar behavior and a very small difference is observed only at intermediate temperatures. It must be mentioned here that at high temperatures, there is some quantitative difference between the simulations and experiments for the CO and  $CO_2$  concentrations. It is possible that this is because of additional reactions for oxidizing CO, such as  $CO+N_2O \rightarrow CO_2+N_2$ . There is some evidence in literature pointing at such a reaction step (Cho, 1992), however, since our predictions of  $N_2O$  and  $N_2$  concentrations are in good agreement with experiments, we have not explored this aspect further.

It is fair to conclude that the surface reaction mechanism is the critical component of this model and other aspects including the reactor geometry and species transport are of minor significance in determining conversion and selectivity as a function of reactor temperature.

### 3.4 Analysis of Surface Coverages

The information on surface coverages of the adsorbed species helps us understand the various observed features. A plot of fractional surface coverages versus reactor temperature for the Pt catalyst using a single PSR model is shown in Figure 5. The coverages of all surface species compared to that of  $CO^*$  are small at the conditions studied here. At lower temperatures ( $<250^\circ C$ ), the catalyst is saturated with  $CO^*$  (fractional coverage  $\sim 1$ ), or CO renders the catalyst inert. This is the reason for the low conversions of NO and CO at these temperatures (see Figure 1).

As the coverage of  $CO^*$  decreases ( $>250^\circ C$ ), the coverages of  $NO^*$  and  $N^*$  correspondingly increase, leading to increased catalytic activity for the reduction of NO. In the intermediate range of temperatures ( $280-350^\circ C$ ),  $NO^*$  and  $N^*$  are both present in significant amounts, and therefore their combination to give  $N_2O^*$  occurs at a high rate, and this in turn leads to a high concentration of  $N_2O$ . Since  $NO^*$  coverage is decreasing and  $N^*$  coverage is increasing in this temperature range, at a certain temperature ( $\sim 320^\circ C$ ), the conditions for  $N_2O$  formation are optimal and a peak in  $N_2O$  concentration is observed (see Figure 1).

At higher temperatures ( $>370^\circ C$ ), the  $NO^*$  coverage is negligible, therefore the  $N_2O$  selectivity is found to be low. Below  $400^\circ C$ , there is a strong competition between  $CO^*$  and  $N^*$ , which means that as the  $CO^*$  coverage decreases, the  $N^*$  coverage correspondingly increases (surface coverages of all the other species are very low). At higher temperatures ( $>400^\circ C$ ), the  $N^*$  is no longer a competitor for the surface sites. Thus we can say that at  $400^\circ C$ , the surface is optimally used as far as NO is concerned, with the  $NO^*$  dissociating to form  $N^*$ , which immediately recombines to give  $N_2$ . The coverage of  $O^*$  is found to be low at all temperatures (not shown in Figure). This indicates that the catalyst surface is in reduced form throughout.

Overall, we can conclude that the catalyst site competition between the reacting species is important in determining the catalyst activity. Conditions under which NO adsorbs strongly on the surface and immediately dissociates are ideal in terms of high conversion and optimal selectivity.



Similar features are observed in case of the Rh catalyst (results not shown), with the temperature range being different. The coverage of  $N^*$  is found to be slightly higher in Rh catalyst as compared to Pt catalyst. Furthermore, larger rate of NO dissociation on Rh catalyst (Rh has a lower activation energy for  $NO^*$  dissociation than Pt) implies lower  $NO^*$  coverage at a given temperature, therefore the rate of  $N_2O$  formation would be lower on Rh than Pt, as also observed in the experiments and reactor simulations (shown in Figure 3).

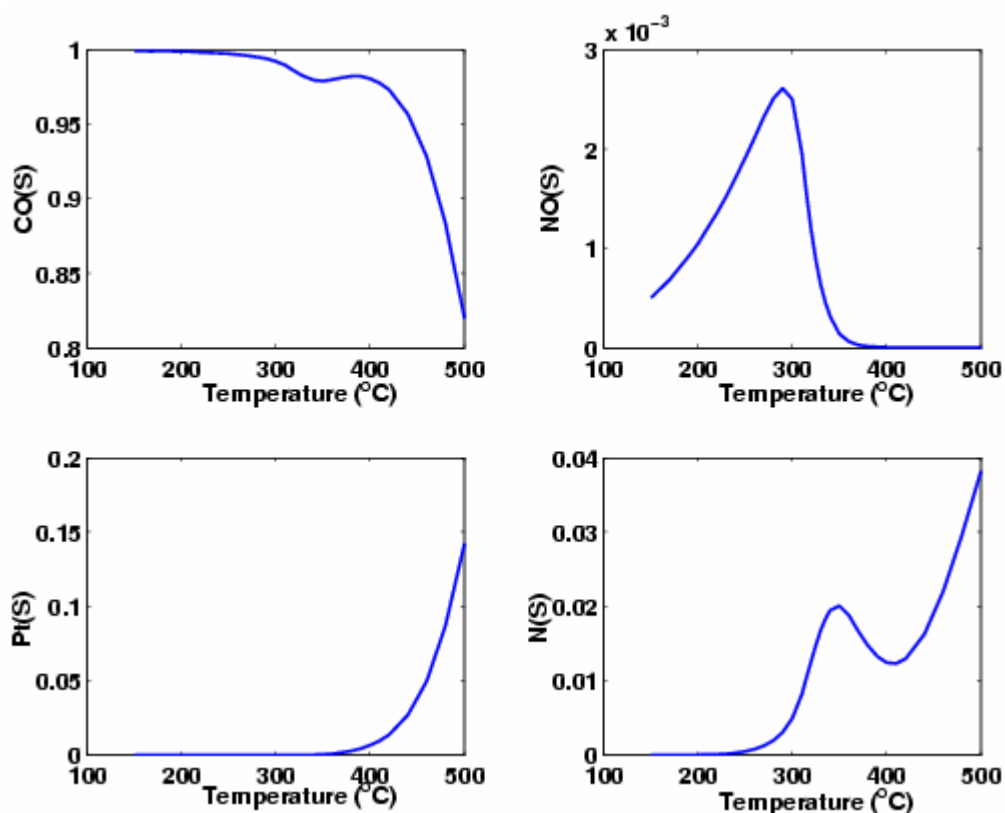


Figure 5. Fractional coverages of various surface intermediates versus reactor temperature on Pt catalyst.

### 3.5 Effects of Residence Time and Surface Area on NO Conversion

The model is employed to study the effects of residence time and catalytic surface area on NO conversion. The feed conditions used for the simulations are same as in Chambers et al., (2001) (see Table 3). Effect of residence time on NO conversion is investigated by varying the residence time from 0.001 to 100 s. Figure 6(a) shows these results (keeping reactor volume and catalytic surface area constant, changing the inlet volumetric flow rate) on NO conversion at different reactor temperatures on Pt catalyst. The results depict, as expected, that the NO conversion increases with residence time. The effect seems to be small at lower temperatures compared to intermediate temperatures. At 300°C, NO conversion increases from 29% to 70%, when the residence time increases from 0.1 sec to 1 sec, whereas increase in residence time from 1 sec to 10 sec, changes the NO conversion from 70% to 99% only.

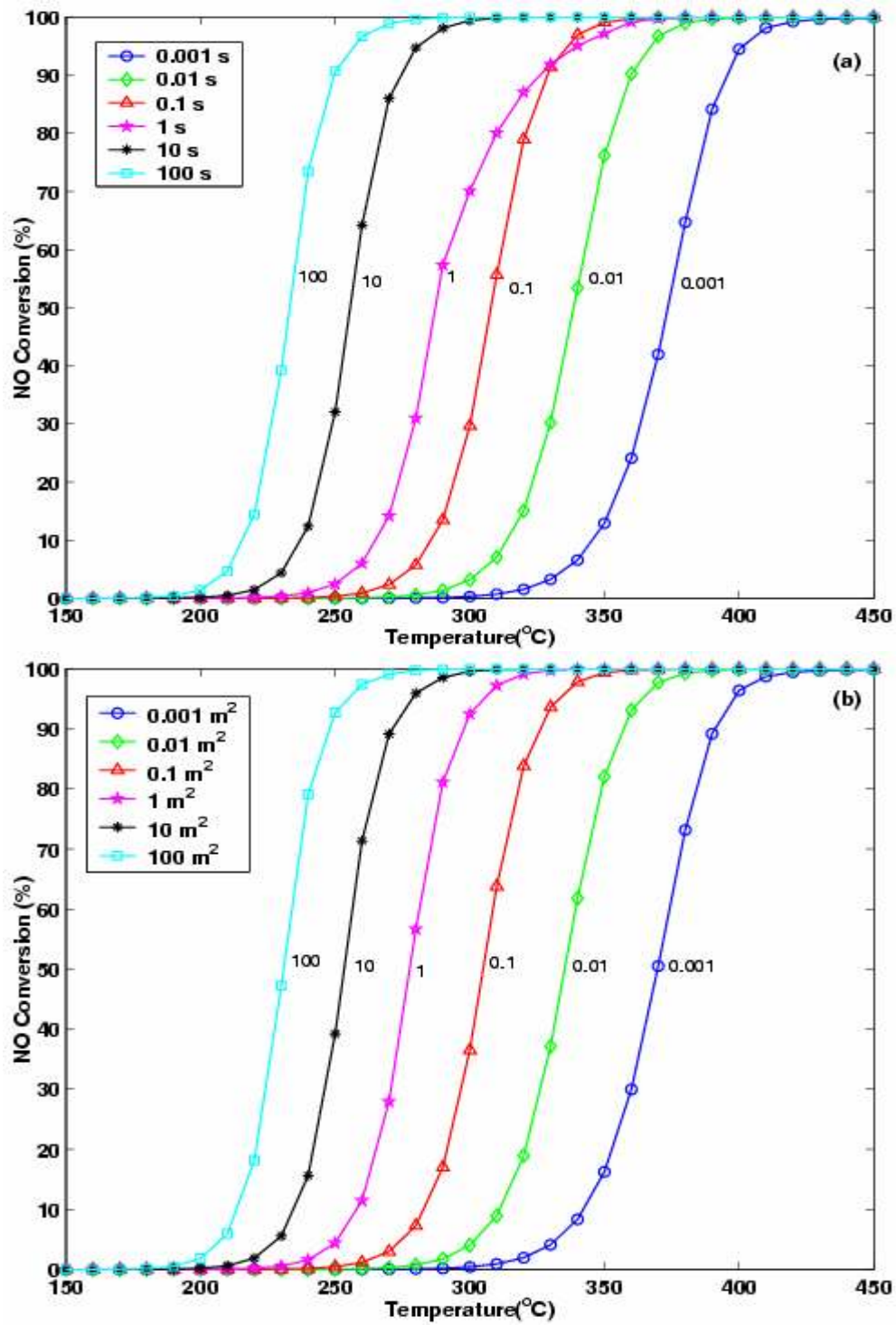


Figure 6. Effect of (a) residence time and (b) catalytic surface area on NO conversion for Pt catalyst.

The effect of catalytic surface area on NO conversion is examined by varying the catalytic surface area from 0.001 to 100 m<sup>2</sup>. Figure 6(b) shows effect of surface area (keeping reactor volume and residence time constant) on NO conversion for Pt catalyst at different reactor temperatures. The results show that the catalytic surface area does not have much effect on NO conversion at lower temperatures, however the NO conversion activity increases with surface area at higher temperatures. At 300°C, for an increase in surface area from 0.1 to 1 m<sup>2</sup>, NO conversion increases by 155%, whereas NO conversion increase only 8% with increase in surface area from 1 to 10 m<sup>2</sup>.

Overall we can conclude that at given temperature, NO conversion increases as the residence time and catalytic surface area increase. Also NO conversion can occur at lower temperatures with increase in surface area and residence time.

#### 4. NO-CO-O<sub>2</sub>: RESULTS AND DISCUSSIONS

Three-way-catalytic converters (TWC) have been successfully applied in gasoline engines since the 1980's for the simultaneous removal of NO<sub>x</sub>, hydrocarbon (HC) and carbon monoxide (CO), but they are ineffective under excess oxygen (lean burn) conditions since CO and HC have higher activity towards O<sub>2</sub> rather than NO. Compared to Pt, another active metal, Ir has two advantages, namely, higher selectivity towards N<sub>2</sub> versus N<sub>2</sub>O and higher activity under lean burn conditions (Liu et al., 2003; Iojoiu et al., 2004). Ir is found to be an effective catalyst compared to Pt, Rh and Pd for the NO-CO reaction under lean burn condition (Tauster and Murrell, 1976; Taylor and Schlatter, 1980; Wang et al., 2003). Various literature (Ogura et al., 2000; Haneda et al., 2003; Shimokawabe and Umeda, 2004) results are available for the NO-CO-O<sub>2</sub> reaction on Ir catalyst. To understand why the Ir catalysts exhibit such superior properties for the NO-CO-O<sub>2</sub> reaction, kinetics and surface reaction mechanism is considered necessary. However, to our knowledge, hardly any literature is available for the NO-CO-O<sub>2</sub> reaction on Ir catalyst, which proposes a validated, quantitative reaction mechanism.

Ogura et al. (2000) carried out experiments for the NO-CO-O<sub>2</sub> reaction on 0.02% Ir/SiO<sub>2</sub>, Ir/Al<sub>2</sub>O<sub>3</sub> and Ir/silicalite catalysts. In this experiment, 100 mg of catalyst was placed in a pyrex tube (10 mm diameter and 20 mm length) and a standard NO-CO-O<sub>2</sub> mixture (1000 ppm NO + 7500 ppm CO + 1% O<sub>2</sub>) was passed through the catalyst bed at a rate of 100 cm<sup>3</sup>/min. It was found that for all these catalysts, NO and CO conversion increases with an increase in temperature and once the CO conversion reaches its maximum value, NO conversion goes down with temperature (Results for all these three catalysts are shown in Figure 7 with symbols).

Incorporating the parameters listed in Table 3, with the elementary reaction mechanism (Table 2, considering first order dissociative adsorption of O<sub>2</sub>), we have performed simulations with CHEMKIN 4.0.2 with the single PSR model to obtain the conversion of NO and CO as a function of reactor temperature for Ir catalyst and compared it with literature experiments of Ogura et al. (2000) (lines in Figure 7 indicates the simulation results). It is found that same type of behavior is observed for both NO and CO conversion in our simulations as in experiments. NO conversion starts at ~250°C in experiments for all three catalysts and the same is observed in simulations. The peak for NO conversion for Ir/SiO<sub>2</sub>, Ir/Al<sub>2</sub>O<sub>3</sub> and Ir/silicalite catalysts are at 400°C, 365°C and 375°C respectively. In our simulations, the peak is observed at 381°C. As the support effect is not incorporated in our simulations, the results obtained can be considered to be in good agreement

with experiments. The important point here is that the simulation results match with experimental data without fitting any parameters. This verifies that the proposed mechanism is accurate for Ir catalyst. Typical volcano-type profile for NO conversion is mainly due to the presence of O<sub>2</sub> in the feed. While the NO conversion decreases after peak temperature, the CO conversion is found to be constant. The simulations have also been performed including the formation of NO<sub>2</sub> from oxidation of NO in the reaction mechanism (results not shown). Since significant concentrations of NO<sub>2</sub> were not noted, and there is no experimental measurement of NO<sub>2</sub> reported for this catalyst, these steps were not considered further. Overall, our contention is that the reduction of NO occurs through its dissociation on the catalyst surface, and not through the intermediacy of NO<sub>2</sub> or other such species. Effect of O<sub>2</sub> and the detailed explanations are given elsewhere (Mantri and Aghalayam, 2007).

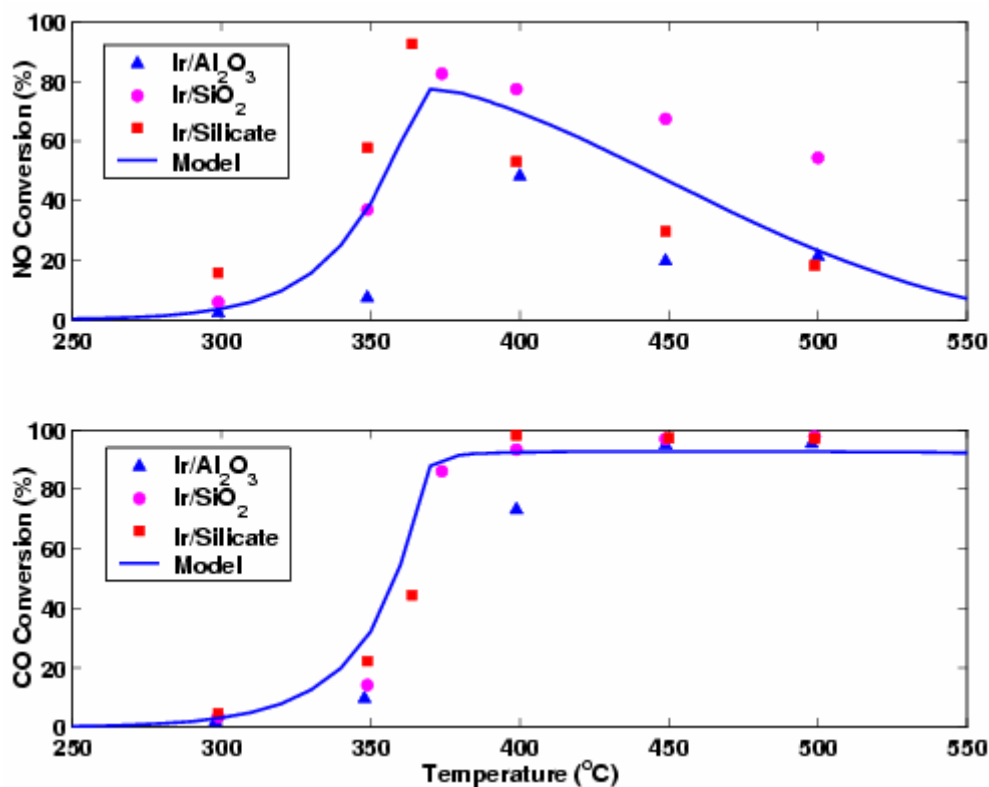


Figure 7. Effect of reactor temperature on NO and CO conversion for the NO-CO-O<sub>2</sub> reaction on Ir catalyst (Symbols correspond to experimental data of Ogura et al. (2000) and lines are our simulations results).

## 5. SENSITIVITY ANALYSIS

Sensitivity analysis allows quantitative understanding of how the solution depends on the various parameters. To determine the sensitive elementary reactions in the NO-CO mechanism, sensitivity analysis is performed using CHEMKIN 4.0.2.

The sensitivity coefficients (SC) represent the fractional change in conversion of NO caused by a fractional change of parameter  $k$  (rate constant).

$$SC = \frac{k}{X_{NO}} \frac{\partial X_{NO}}{\partial k} = \left( \frac{\partial \ln X_{NO}}{\partial \ln k} \right)$$

Where, SC = Sensitivity coefficient  
 $X_{NO}$  = NO conversion  
 $k$  = rate constant

A very small SC indicates that the reaction has almost no influence on the activity, no matter what the rate constant of the reaction and concentration of reactant species. Figure 8 shows the sensitivity coefficient (SC)s for NO conversion at different temperatures. The reactions having very small sensitivity coefficient are not shown in the Figure for Pt and Rh catalysts. For both the catalysts (Pt and Rh), at lower and higher temperatures, reactions 1 and 2 (NO adsorption and desorption), and 11 and 12 (CO adsorption and desorption) are more sensitive. Small change in the rate constant of these reactions will affect the NO conversion strongly. Increase in rate constant of reactions 2 and 12; increase the NO reduction while the opposite holds true for reactions 1 and 11. However at lower temperatures, overall NO conversion is found to be very less. At intermediate temperatures where the NO conversion is strongly dependent on the temperature, the reaction 3 (NO\* dissociation) has higher sensitivity coefficient and decrease in rate constant of this reaction increases the activity of catalyst for NO reduction. From this we can conclude that the adsorption/desorption of reactants are always important, but among surface reactions NO\* dissociation is the most critical in determining the NO reduction on both the catalysts for the NO-CO reaction. The NO conversion is not found to be sensitive to the other elementary reactions.

On Ir catalyst, for NO-CO-O<sub>2</sub> reaction, sensitivity coefficients are shown in Figure 8(c). Before the temperature of peak NO conversion, formation of N<sub>2</sub>, N<sub>2</sub>O\* formation and NO adsorption reactions are important while at the peak temperature, NO adsorption, NO\* dissociation and O<sub>2</sub> adsorption are important. At higher temperatures, O<sub>2</sub> adsorption is important. Overall we can say that O<sub>2</sub> adsorption plays a critical role for NO reduction in the NO-CO-O<sub>2</sub> reaction on Ir catalyst.

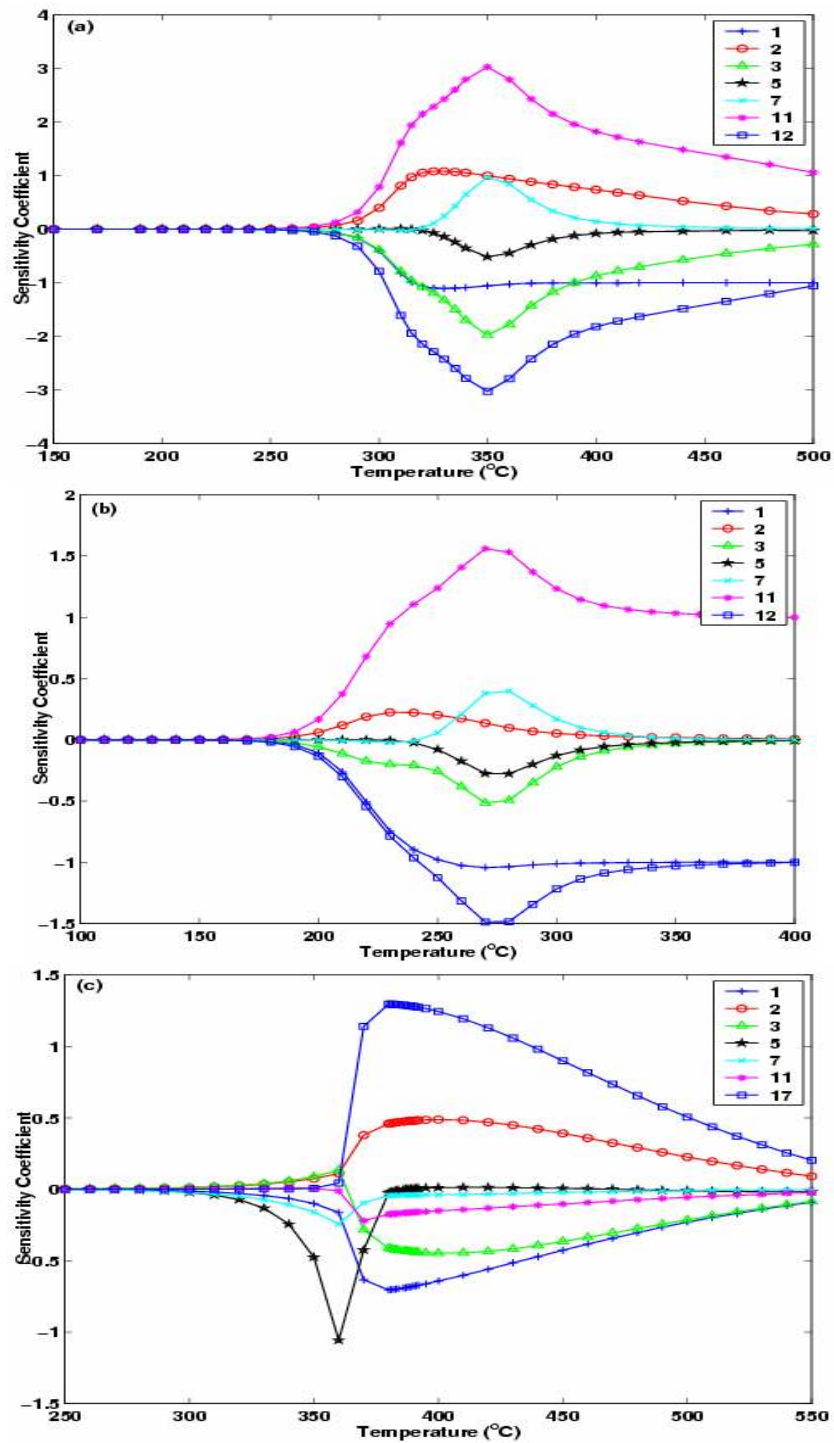


Figure 8. Sensitivity analysis for NO conversion with temperature on (a) Pt, (b) Rh catalyst for NO-CO reactions and (c) Ir catalyst for NO-CO-O<sub>2</sub> reaction. Numbers in legend shows the reaction number.

## CONCLUSIONS

An elementary-steps based detailed surface reaction mechanism is developed for the catalytic reduction of NO using CO as a reductant, over Pt group catalysts. Full quantitative details of the reaction steps are provided and incorporated in a Perfectly Stirred Reactor (PSR) model and solved using CHEMKIN 4.0.2. The rate constant values in the reaction mechanism are calculated here using a semi-empirical UBI-QEP technique. Excellent agreement between the results of the simulations performed here and literature experimental results, for both reactant conversions and product selectivities are shown for Pt and Rh catalysts for the NO-CO reaction and Ir catalyst for the NO-CO-O<sub>2</sub> reaction.

Catalyst site competition among the reacting species leads to a rich set of features. At low temperatures CO adsorbs strongly on the Pt catalyst, rendering it inert. As the temperature is increased, the desorption rate of CO increases, releasing catalyst sites for the reactions of NO. The condition where CO and NO can simultaneously adsorb on the catalyst, but adsorbed NO can dissociate at a high rate, is ideal for the catalytic reduction of NO by CO. Sensitivity analysis suggests that NO\* dissociation is crucial in the NO-CO system while O<sub>2</sub> adsorption is important in the NO-CO-O<sub>2</sub> system. Increase in surface area and residence time will advance the activity of NO reduction. Among the Pt group catalysts studied, Rh is found to perform better than Pt, showing lower temperature activity along with lower N<sub>2</sub>O emissions, while Ir shows better activity under lean burn conditions.

## ACKNOWLEDGEMENT

We are grateful to the Department of Science and Technology (DST), Govt. of India, for financial support through SERC (#03DS014).

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