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Understanding Pt–Rh Synergy in a Three-Way Catalytic Converter

Abstract: NO reduction to N_2 is the key reaction for efficient operation of a three-way catalytic converter (TWC). It is reported that metal catalysts Pt and Rh co-exist as individual metals in a TWC to give synergistic performance. In this article, we have studied the NO + CO reaction for a 1:1 physical mixture of silica supported Pt and Rh catalysts using fixed bed experiments and microkinetic modeling. The microkinetic model [14] for the reaction on single metals Pt and Rh is simulated for the mixture case in CHEMKIN PRO[®]. It is observed that the mixture maintains the activity while producing less N_2O (by-product of NO + CO reaction) thus enhancing N_2 selectivity inspite of having only half amount of Rh. Analysis of surface coverages on individual metals in mixture shows that in the presence of Pt, CO poisoning of Rh is reduced at lower temperature leading to better overall conversion and selectivity. This has potential benefit in automotive catalysis, as it results in the formation of significantly lower amounts of N_2O , an undesirable side-product and greenhouse gas; at a lower cost than if pure Pt/Rh catalysts were used.

Keywords: NO reduction, Pt–Rh synergism, three-way catalytic converter, microkinetic modeling

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1 Introduction

The three-way catalytic converter (TWC) is an important device used in automobiles to treat exhaust gas emissions. The main chemical reactions occurring in the TWC are the oxidation of carbon monoxide and

hydrocarbons to CO_2 and H_2O ; and the reduction of nitrogen oxides to N_2 . The performance of the TWC is effective only in a narrow operating window around the stoichiometric fuel/air ratio.

The typical three-way converter consists of a cordierite (ceramic) honeycomb substrate, coated with a thin $\gamma-Al_2O_3$ washcoat as a carrier. The active catalyst components, i.e. the noble metals, Pt and Rh in a ratio of around 5:1, are incorporated into the washcoat. The oxygen storage material, ceria, is also a typical constituent of the TWC [1]. Although both Pt and Rh (and sometimes some other metals such as Pd) are present in the TWC, it is believed that alloying does not occur to a significant extent [2, 3]. However, the simultaneous presence of Pt and Rh is important, as the combination demonstrates higher overall catalytic activity under TWC conditions when compared with monometallic Pt- or Rh-based catalysts [4, 5, 6]. In general, it is known that Pt-based catalysts have higher HC/CO oxidation activities than Rh catalysts, whereas the Rh-based catalysts are more effective for NO reduction [3]. However, both Pt- and Rh-based catalysts are active toward the NO + CO reaction in different temperature ranges with Rh being active at lower temperatures. Rh is more expensive and scarce as compared with Pt, hence it is important to tune the bimetallic catalyst composition in catalytic converters in order to optimize performance and cost and to provide a wider operating temperature window for the NO + CO reaction. Due to the complex nature of the phenomenon of NO reduction and HC/CO oxidation in TWC, it is important to use detailed reaction models to understand the interactions between the various constituents.

In the literature, a number of detailed kinetic models are available for TWC chemistry. But they are either for single metal catalysts, i.e. only Pt [7], or, for multi-metallic TWC catalysts, they use average values for kinetic parameters, obtained from the fitting of experimental data. Such models consider a single representative catalytic site ([8] for Pt + Rh/Ce catalyst; [9] for Pd + Rh catalyst, and [10] for Pt + Rh catalyst) and do not distinguish between Pt and Rh. On the other hand, authors [11, 6] have used detailed kinetic model with separate

kinetic parameters for Pt and Rh, and our assumptions in this article are similar to theirs. However, they do not explicitly analyze their results from the view-point of the potential interactions between the chemistries occurring on Pt and Rh, which is the subject of this article.

In this study, we focus on understanding the synergy between Pt and Rh in the performance of TWC. Synergy for this system is defined as a non-linear (non-additive) effect of increasing activity, selectivity, product yields, and other reaction characteristics upon changing concentrations of the components of the catalytic systems (see previous reference to this phenomenon in literature [12]).

In particular, we study the NO–CO reaction occurring on Pt- and Rh-based catalysts in detail, using a combination of laboratory experiments and microkinetic modeling. Although many such reactions occur simultaneously in the TWC, we focus entirely on this particular reaction as it is likely to be the most critical one in the system and throws up an important issue related to selectivity. CO is a priority pollutant present in the automobile exhaust in comparable amounts, and its reaction with NO takes care of both the pollutants. The importance of this reaction is emphasized in literature [13].

The overall reaction can be written as



This desirable reaction is accompanied by a side reaction forming N_2O at low temperatures



Our group [14] has developed a microkinetic model for the NO–CO reaction on Pt- and Rh-based catalysts. This reaction model is validated against experimental data from the literature for each of the pure metals, separately. In this work, the performance of a reactor in which Pt- and Rh-based catalysts are simultaneously present is examined in the context of the NO–CO reaction. Both laboratory-scale experiments and CHEMKIN PRO[®] based simulations using the validated microkinetic model are used to demonstrate the potential synergies. The results of this article are expected to closely mimic those in a commercial catalytic converter system and be of significant value in optimizing compositions of automotive catalytic converters.

2 Experiments

A fixed bed catalytic reactor setup was used to measure the conversions. The inlet feed mixture consisted of NO and CO at a fixed compositions. The catalysts used were

prepared in-house, as described below. The Rh/SiO₂ and Pt/SiO₂ catalysts were prepared separately, and for the reactor test on synergistic effects, a physical mixture of equal weights of each catalyst was used.

2.1 Catalyst synthesis

The wet impregnation technique was used for catalyst synthesis [15]. Pt salt, i.e. chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, SRL Pvt. Ltd), was used as the precursor for Pt. The required amount of chloroplatinic acid was dissolved in minimal quantity of deionized water. Then, silica (AEROSIL[®] 200, Evonik) was added to it. AEROSIL[®] 200 is a hydrophilic fumed silica (non-porous) with a specific surface area of $\sim 200 \text{ m}^2/\text{g}$. Additional quantity of distilled water was added, so that the mixture could be stirred. The resultant suspension was then stirred for 24 h using a magnetic stirrer. The mixture was then filtered. The filtered catalyst was dried at 110°C for 2 h and then calcined at 550°C for 6 h. The catalyst, thus, prepared was then used for fixed bed reactor experiments. Similarly for Rh/SiO₂, rhodium trichloride ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, Spectrochem Pvt. Ltd) was used as the precursor; and the rest of the preparation procedure was the same as for Pt.

2.2 Catalyst characterization

The prepared catalysts were characterized for the metal loading (ICP-AES), N_2 chemisorption for support surface area (BET surface area), CO chemisorption for active metal surface area, and HR-TEM for getting the metal crystallite size. This characterization was done in order to ensure that both the catalysts have similar physical characteristics. The details of the characterization methods can be found in [16].

The results of the characterization studies are summarized in Table 1. The important conclusion from here is that both the Pt and the Rh catalysts exhibit very similar properties, as far as the metal loading, surface area, and so on are concerned.

Table 1 Catalyst characterization results

Sample	BET surface area (m^2/g)	wt% metal (ICP-AES)	Metal crystallite size (nm)
Pt/SiO ₂	201	0.4	2–4
Rh/SiO ₂	195	0.4	

2.3 Catalyst activity testing

Fixed bed reactor experiments were conducted on SiO₂-supported noble metal catalysts (Pt and Rh) for the reduction of NO by CO. Two hundred milligrams of catalyst was placed in a quartz tube of 0.8-cm diameter, and a fixed composition NO–CO mixture (220 ppm NO + 1,800 ppm CO in N₂) was passed through the tube with a volumetric flow rate of 850 cm³/min (65,000 h⁻¹ GHSV). The catalyst bed was heated to 500°C at a rate of 3°C/min and then was cooled to room temperature at the same rate. The concentration of NO and CO at the exit was analyzed by the Kane-May Quintox gas analyzer at different temperatures during the cooling cycle. A similar exercise was repeated for a physical mixture of Rh/SiO₂ and Pt/SiO₂ (100 mg of each).

The conversion of NO in the catalyst bed is calculated from the following formula:

$$\%NO, \text{ conversion} = \left(\frac{NO_{in} - NO_{out}}{NO_{in}} \right) \times 100 \quad [3]$$

$$\%N_2, \text{ selectivity} = \left(\frac{N_{2,out}}{N_{2,out} + N_2O_{out}} \right) \times 100 \quad [4]$$

3 Mathematical simulations

Detailed mathematical simulations corresponding to the experiments were performed using the perfectly stirred

reactor (PSR) module in CHEMKIN PRO[®], incorporating the microkinetic model that was earlier developed and validated in the group [14]. The PSR model was also demonstrated to be suitable for the modeling of such experiments in earlier work [14].

The elementary reactions as shown in Table 2 are molecular adsorption of reactants NO and CO, dissociation of adsorbed NO_s to N_s and O_s, recombination of N_s to form N₂, reaction of adsorbed NO and N_s to form N₂O, and finally, the reaction of adsorbed CO with O_s to form CO₂. All the reactions are considered as reversible including N₂, N₂O, and CO₂ adsorption. The set of elementary reactions is assumed to remain the same for both the catalysts studied: Pt and Rh with only the activation energies and sticking coefficient values being different on different catalysts. Pre-exponential factors/sticking coefficients and activation energies corresponding to each of the elementary reactions for the different catalysts (Pt and Rh) used in this study are also shown in Table 2.

The reaction rate parameters of this model were obtained from independent sources and not fitted to the experiment. As shown in earlier work [14] in the group, this reaction mechanism is able to predict the experimental data [17] to good accuracy. In our previous article, we have also proposed that slight modifications in a couple of the activation energies can lead to a quantitatively improved match with these experiments. However, we use the original mechanism without the fitted

Table 2 Microkinetic model for NO + CO reaction on Pt and Rh

Reaction number	Reaction steps	Pre-exponentials (s ⁻¹)/ sticking coefficient	Activation energy (kcal/mol)	
			Pt	Rh
1	NO + S → NO _s	0.6 (0.67)	0	0
2	NO _s → NO + S	1 × 10 ¹³	26	26
3	NO _s + S → N _s + O _s	1 × 10 ¹¹	12.4	6.7
4	N _s + O _s → NO _s + S	1 × 10 ¹¹	36.5	47.6
5	N _s + N _s → N ₂ + 2S	1 × 10 ¹¹	27	27
6	N ₂ + 2S → N _s + N _s	0.001	0	0
7	NO _s + N _s → N ₂ O _s + S	1 × 10 ¹¹	21.5	21.5
8	N ₂ O _s + S → NO _s + N _s	1 × 10 ¹¹	3.6	2.1
9	N ₂ O _s → N ₂ O + S	1 × 10 ¹³	5.6	10
10	N ₂ O + S → N ₂ O _s	0.001	0	0
11	CO + S → CO _s	0.89 (0.67)	0	0
12	CO _s → CO + S	1 × 10 ¹³	32	32
13	CO _s + O _s → CO _{2s} + S	1 × 10 ¹¹	23.2	24.4
14	CO _{2s} + S → CO _s + O _s	1 × 10 ¹¹	18.4	11.3
15	CO _{2s} → CO ₂ + S	1 × 10 ¹³	3.6	5.17
16	CO ₂ + S → CO _{2s}	0.005	0	0

Source: Ref. [14 pp. 5–6].

Notes: S denotes a vacant site; the values in the bracket are sticking coefficient values of respective gases on Rh.

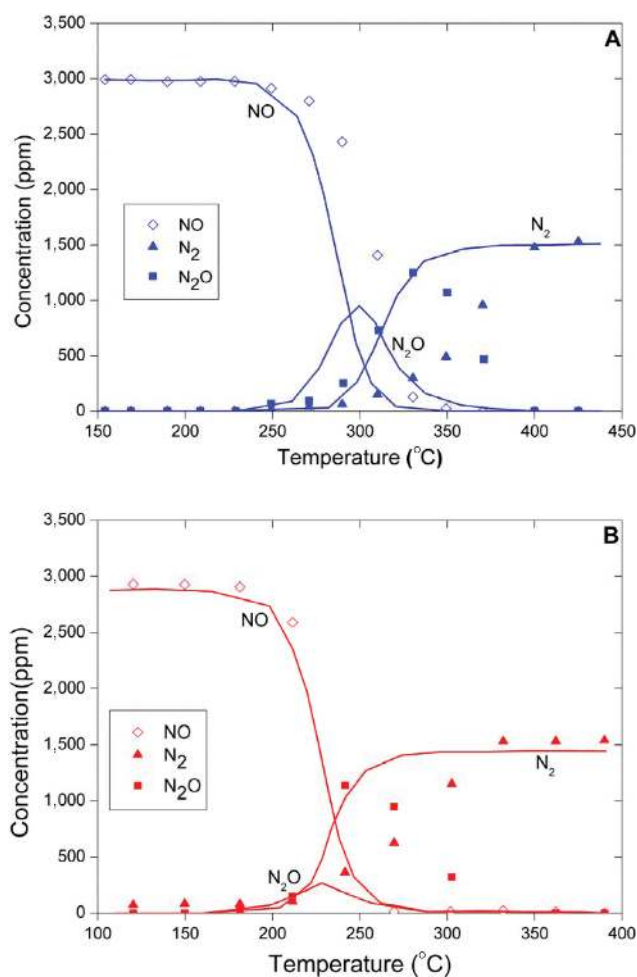


Figure 1 Effect of temperature on outlet gas concentrations for NO–CO reaction on Pt (A) and Rh (B) catalysts. Comparison between model (PSR) results and experimental results (symbols) [17]

parameters, in this work. The prediction of experiments [17] is shown in Figure 1. It will be observed that the outlet concentrations of NO and CO are well captured at all temperatures for both the catalysts.

Moreover, the selectivity to N_2O at lower temperatures and N_2 at higher temperatures is also predicted by the model. The N_2O concentration is expected to be lower in case of Rh catalysts, as compared with Pt; furthermore, Rh is more active at lower temperatures than Pt.

In this study, reactor simulations for the NO–CO reaction, at realistic inlet NO:CO ratios, were performed for Pt and Rh catalysts separately, using the corresponding microkinetic models. Next, the mixture condition was simulated at the same operating conditions by incorporating both the Pt and the Rh kinetic models simultaneously. Here, the assumption is that the Pt and Rh sites are present on separate silica particles, and are

non-interacting, maintaining their individual activities. Both the sites are available for the reaction simultaneously. The maximum reaction temperature in these studies is 500°C . It is reasonable to assume that this temperature is not high enough to cause migration of Pt and Rh crystallites from silica particles to form the alloy, and hence both the catalyst sites are separately available for chemisorption and subsequent chemical reaction.

Two important catalyst properties that affect the overall conversion activity are catalyst site density and internal surface area. The site density is a very important parameter and is derived from the lattice constant and crystal structure for both the metals. The value for site density is $\sim 2.07 \times 10^{-9}$ mol/cm² for monometallic Pt and Rh, and this is used in the simulations as a characteristic value. In case of the active metal surface area, a measured value of ~ 500 cm² was obtained based on our CO chemisorption analysis. However, this value was increased threefold in our simulations in order to obtain better agreement with experimental data on individual catalysts. For the binary mixture, the site density was taken as half this value for each of Pt and Rh, so that it sums up to the original one. Table 3 indicates some of the important parameters used in the CHEMKIN simulations.

Table 3 The various parameters used in the reactor model for Pt and Rh catalysts

Parameter	Value
Diameter of the reactor (cm)	0.8
Length (cm)	1.0
Weight of the catalyst (mg)	200
Volume of reactor (cm ³)	0.8042
Flow rate (cm ³ /min)	850
Catalytic surface (cm ²)	1,500
NO in feed (ppm)	220
CO in feed (ppm)	1,800

4 Results

Figure 2 depicts the NO conversion obtained from experiments (symbols) and the mathematical simulations (in lines) for all the three cases – Pt alone, Rh alone, and a 50:50 physical mixture of Pt and Rh. It is observed that the microkinetic model simulations agree very well with the experimental results. It can be seen that physical mixture of Pt and Rh shows activity similar to that of single metal Rh though the mixture has half the amount of Rh as compared to the pure Rh catalyst.

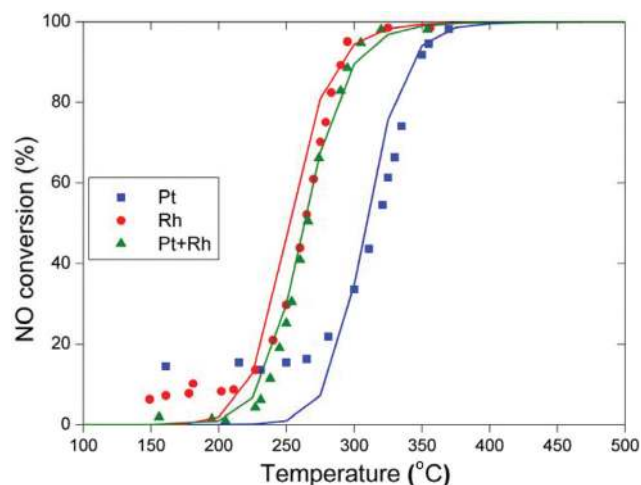


Figure 2 Activity of physical mixture, experimental (symbols) and simulations (lines)

Thus, it is demonstrated that the chosen model and inherent assumptions are acceptable for the purpose of simulating these laboratory-scale reactor experiments. Next, the model is used to make predictions related to the product distribution. In particular, the roles of individual metals in a mixture of Pt and Rh toward providing suitable product selectivity are identified in this study. In Figure 3, the outlet NO conversion is plotted versus reactor temperature for four cases – pure Pt, pure Rh, Pt + Rh mixture, and finally, the arithmetic average conversion for Pt and Rh. Here, the pure catalyst simulations are performed with site density value of 1.04×10^{-9} mol/cm² unlike in Figure 2, in order to compare situations wherein same amount of Pt and Rh is present.

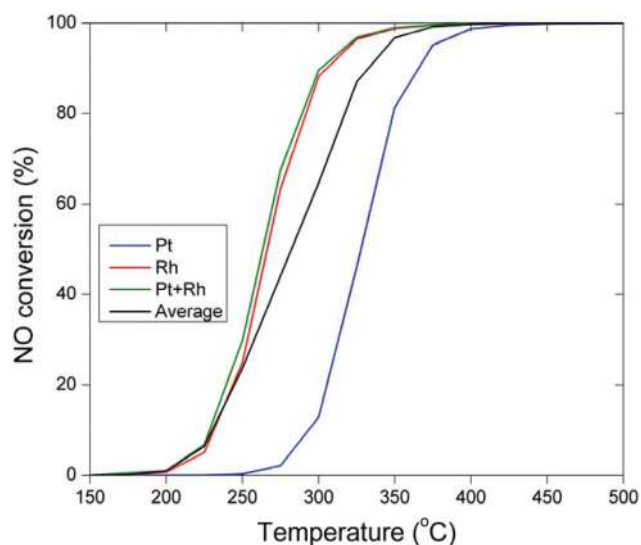


Figure 3 Mixture behavior compared with additive activity

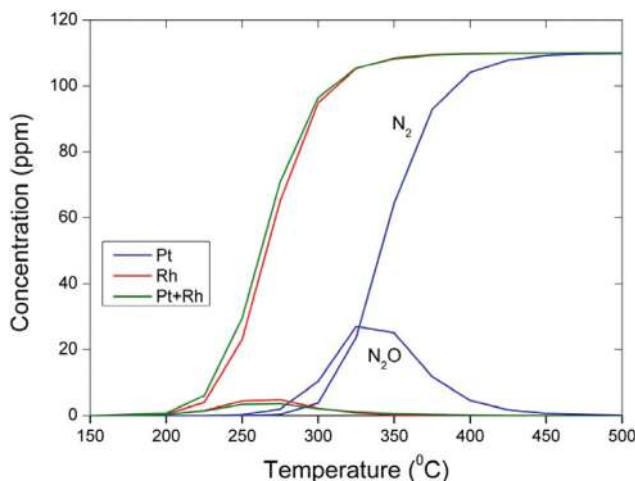


Figure 4 N₂ and N₂O formation for mixture and single metal cases

It is clear that the actual conversion obtained for the mixture is larger than the average, demonstrating the synergy in this system. Figure 4 shows the predicted concentrations of N₂ and N₂O as a function of reactor temperatures, for the same inlet conditions as mentioned above. It is seen clearly that of the three cases considered – Pt alone, Rh alone, and a 50:50 mixture of Pt and Rh catalysts, the product distribution in case of the mixture is very similar to that in the case when Rh alone is used as a catalyst. In other words, the addition of Rh to the Pt has resulted in improving the reactor performance in terms of selectivity to the desired product (N₂), significantly; in addition to providing reactant conversion at much lower temperatures. The mixture catalyst is overall cheaper than the pure Rh, thus we are able to obtain good conversions and selectivities at a much lower cost due to the mixing. In the next section, we examine the reasons behind this synergistic behavior.

5 Discussion and analysis of results

The dominant surface species (most abundant reactive intermediates, MARIs) based on the CHEMKIN simulations are CO_S, NO_S, and N_S for these conditions. These are plotted in Figure 5 for the various cases. Here, surface coverages labeled Pt in mixture and Rh in mixture represent the species coverages on Pt and Rh sites, for the mixture. The ones labeled Pt and Rh are for the single catalyst cases.

These results throw up many interesting facts: as far as the coverages of CO_S and N_S are concerned, the

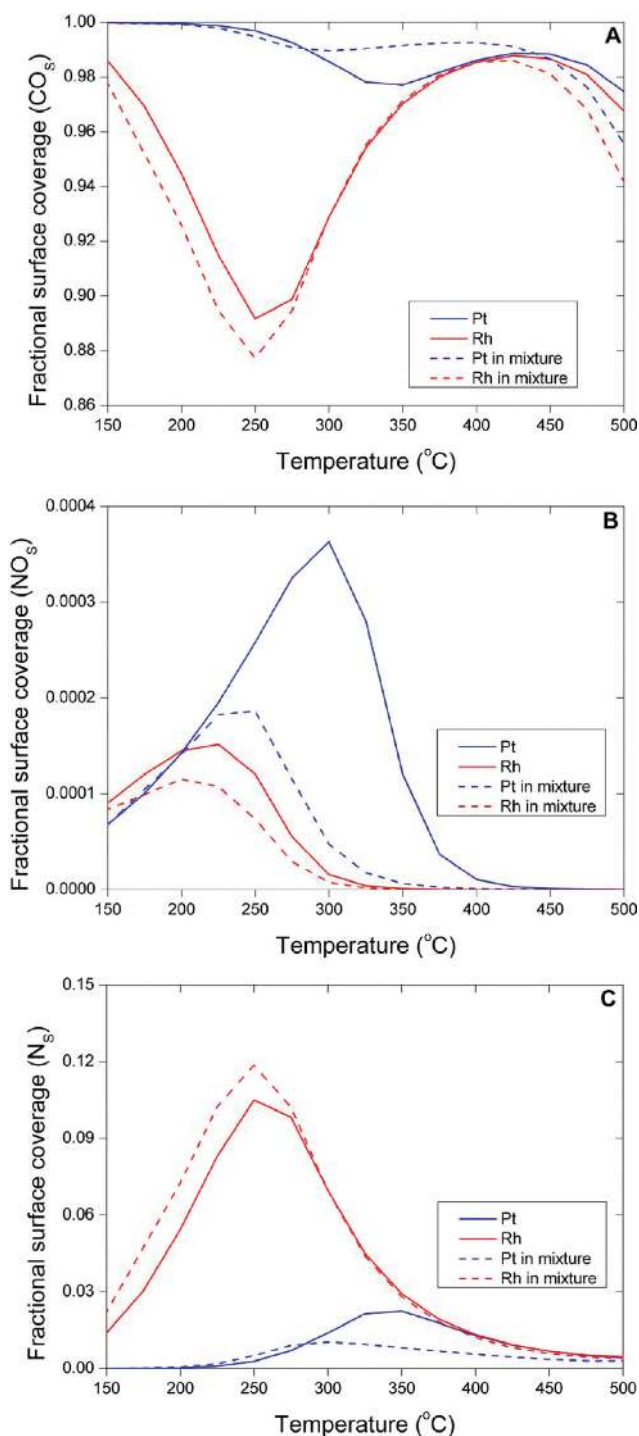


Figure 5 Fractional surface coverages of MARIs

individual catalysts more or less retain their original behavior in the mixture. In particular, CO tends to adsorb more strongly on Pt than Rh (due to a higher sticking coefficient); N_s concentrations are routinely higher on Rh (due to the higher rate of dissociation of NO_s). Rh catalysts have demonstrated lower tendency for N_2O

formation as compared to Pt, because Rh catalysts favor the adsorption and subsequent dissociation of NO.

Figure 5B demonstrates that as far as NO_s concentrations are concerned, there is evidently large difference in behavior of Pt sites in the mixture versus the sites in pure Pt catalysts. The NO_s concentration on Pt sites in the mixture is in fact, closer to the behavior of Rh catalysts. Clearly, this is the reason why the mixture exhibits behavior close to pure Rh catalysts despite the presence of a significant amount of Pt in it.

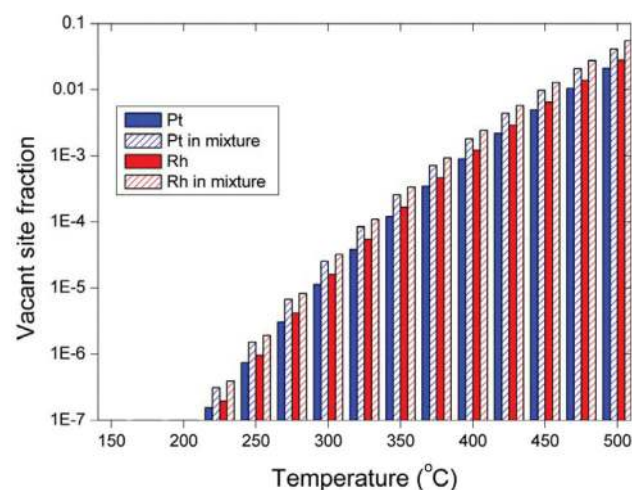


Figure 6 Vacant site fraction on metal catalysts

Figure 6 is a plot of the vacant site fraction on the Rh and Pt components in both cases. It is observed that the mixture routinely has more free Rh and Pt sites available than the pure catalysts. Vacant catalyst sites might be an important rate determining entity. Authors [18] studied the $\text{NO} + \text{CO}$ reaction on Pt/SiO_2 at atmospheric pressure using a pulse technique. They found that the reaction is limited by the availability of reduced Pt dissociation sites. This is likely to be the case in our simulations as well – due to the differences in adsorption capability of CO and NO on Rh and Pt sites, several advantageous situations arise, leading to better conversion, and for this system, better selectivity as well: As Pt tends to adsorb CO better, the “poisoning” of the Rh catalyst by CO at low temperatures is reduced; allowing for NO adsorption and subsequent reaction on Rh. Due to the NO dissociation occurring at higher rates, the rate of the $\text{NO}_s + \text{N}_s$ recombination reaction, leading to N_2O , is reduced, yielding better selectivity to N_2 . Thus, the overall behavior of the mixture catalyst is better than that of the individual catalysts, with the added attraction of lower costs.

For a given catalyst, the dissociation rate can be increased by either reducing the activation energy or increasing the vacant site fraction and that is done by simultaneous presence of Pt which preferentially adsorbs CO leaving more number of vacant sites on Rh for NO to dissociate.

Simulations were also performed for the same input conditions but for different Pt:Rh mixtures. Figure 7A shows overall activity toward the NO + CO reaction. Figure 7B shows the N₂ selectivity trend with increasing Rh

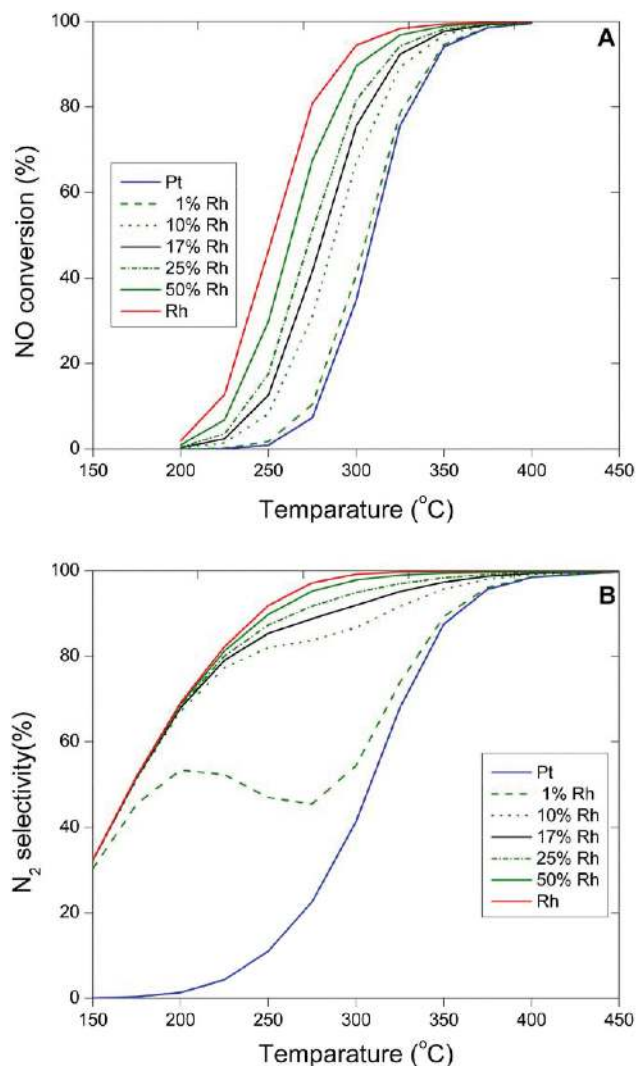


Figure 7 Physical mixture activity and selectivity for various Pt:Rh ratios

Table 4 Effect of Rh addition to NO reduction activity of Pt at 300 °C

% Rh in mixture with Pt	NO conversion (%)	N ₂ selectivity (%)
0	34.9	41.4
10	67.2	86.7
17	75.6	92.0
50	89.6	97.8
100	94.4	99.1

site density in the Pt + Rh mixture. The synergistic effect of Pt addition to Rh is observed in terms of enhanced N₂ selectivity. For Pt, addition of Rh enhances both NO conversion and N₂ selectivity significantly as shown in Table 4. The results in Table 4 demonstrate that even a small percentage of Rh will have significant impact in terms of both conversion and selectivity of the TWC.

The composition of a typical TWC catalyst is Pt and Rh in a ratio of around 5:1. This ratio corresponds to 17% of Rh in the Pt + Rh mixture. From Figure 7A, it can be seen that the line for 17% Rh represents the average conversion for monometallic Pt and Rh.

6 Conclusions

In this article, the effect of the simultaneous presence of Pt and Rh metals in automotive catalytic converters is examined using a well-characterized situation of laboratory-scale experiments for the NO–CO reaction. It is shown using both packed bed reactor experiments and microkinetic simulations that the Pt–Rh mixtures demonstrate several attractive behaviors. This has potential benefit in automotive catalysis, as it results in the formation of significantly lower amounts of N₂O, an undesirable side-product and greenhouse gas; at a lower cost than if pure Pt/Rh catalysts were used. The microkinetic model simulations also illustrate the details of the surface phenomena that lead to this synergistic effect. In addition to the NO–CO interaction, several other important reactions occur in a TWC. Currently, efforts are on in the group to extend this analysis to other systems as well.

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