On the mechanism of the NO reduction by propylene over supported Pt catalysts

Dinyar K. Captain[a], Corina Mihut[a], James A. Dumesic[b] and Michael D. Amiridis[a,*]
[a] University of South Carolina, Department of Chemical Engineering, Columbia, SC 29208
[b] University of Wisconsin-Madison, Department of Chemical Engineering, Madison, WI 53076

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Different mechanisms have been proposed in the literature for the selective catalytic reduction of NO by hydrocarbons (and in particular by propane and propylene) over supported Pt catalysts. This manuscript reviews the available experimental evidence in support of a scheme involving the initial partial oxidation of the hydrocarbon and the subsequent formation of a surface cyanide or isocyanate intermediate. Furthermore, we present results of reaction kinetics analyses which indicate that such a reaction scheme can describe the available kinetic data at a quantitative level.

KEY WORDS: selective catalytic reduction; NO; propylene; platinum; mechanism.

1. Introduction

Emissions of nitrogen oxides are strictly regulated due to their role as acid rain precursors and contributors to the formation of city smog. The selective catalytic reduction (SCR) of nitrogen oxides by hydrocarbons has certain advantages over existing technologies used for NO_x abatement and has received considerable attention in the catalysis community since it was first introduced in 1991 [1–3]. Supported platinum-based catalysts used for this application are active at relatively low temperatures and are not significantly affected by the levels of water and sulfur dioxide present in the exhaust stream. Given the potential of these catalysts for further commercial development, significant research efforts have recently focused on their performance [4–19]. As a result of these efforts, several mechanistic schemes, often in conflict with each other, have been proposed, and the most important of these schemes are summarized below.

Burch and coworkers [9,20–21] have suggested that the first step in the reduction of NO_x by propylene is the reduction of surface Pt-O sites by the hydrocarbon. NO dissociation then follows on the reduced metal sites. The nitrogen atoms formed can combine to yield N_2 or (at lower temperatures) can also react with adsorbed nitric oxide molecules to yield N_2O. Support for such a scheme involving an NO decomposition step is rendered by the analysis of steady state and transient kinetic studies, conducted by this and other groups [9,19–22].

Alternatively, others and our own group [23,24] have proposed that the primary route for NO reduction proceeds via the reaction of NO with a partially oxidized hydrocarbon species. Although the exact nature of this species has not been identified, results of *in situ* spectroscopic studies indicate the presence of surface cyanide and isocyanate species on the catalyst under reaction conditions, demonstrating that a reaction between NO and an organic species may take place. Furthermore, these organic species selectively react with nitrogen oxides, which supports their proposed role as SCR reaction intermediates.

The objective of this paper is to review the available evidence, which, in our opinion, supports the proposed mechanism involving a cyanide or isocyanate intermediate. Furthermore, new kinetic analysis results are presented in this manuscript in support of such a mechanism.

2. Results and discussion

2.1. Activation of propylene

Activity *versus* temperature profiles for the reduction of NO and the oxidation of C_3H_6 over Pt/SiO_2 and Pt/Al_2O_3 catalysts are shown in figure 1. These results are typical of what has been observed in other kinetic studies over supported Pt catalysts [*e.g.*, 8,9]. The NO reduction curves have a bell-shaped profile and exhibit a maximum in NO reduction with temperature in the vicinity of 300 °C (285 °C for Pt/SiO_2 and 300 °C for Pt/Al_2O_3). At temperatures below that of the maximum NO reduction, the propylene oxidation and NO reduction curves closely match each other. Complete oxidation of C_3H_6 is achieved at approximately the same temperature at which NO reduction reaches its maximum. Above this

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* To whom correspondence should be addressed.
E-mail: amiridis@engr.sc.edu

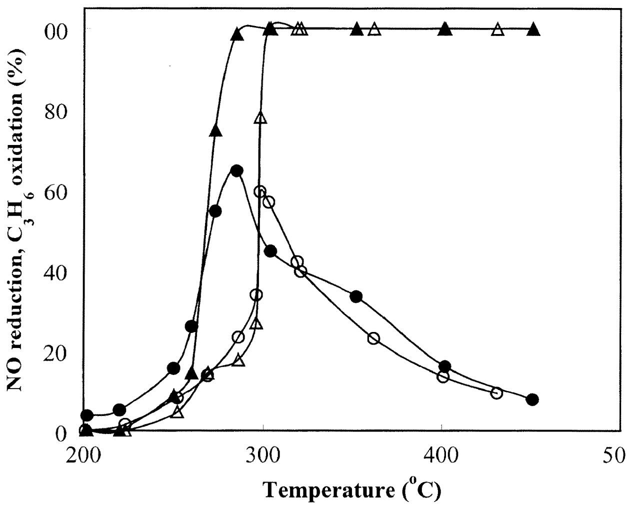

Figure 1. NO reduction and C_3H_6 oxidation as functions of temperature for 0.8% Pt/Al_2O_3 (NO: ○; C_3H_6: △) and 0.9% Pt/SiO_2 (NO: ●; C_3H_6: ▲) catalysts (1000 ppm NO, 1000 ppm C_3H_6, 1% O_2, balance He).

temperature, propylene oxidation remains at 100% conversion, while the NO reduction decreases with a further increase in the temperature. This behavior is characteristic of the presence of two competing reactions of C_3H_6 with NO and O_2, with the second reaction dominating at higher temperatures (and hence the process becoming non-selective for NO). Further evidence for the significance of this competition is found in the results of kinetic studies examining the effect of oxygen.

The activity profiles for the reduction of NO and the oxidation of C_3H_6 as functions of O_2 concentration over a Pt/SiO_2 catalyst are shown in figure 2. These results indicate that under conditions favoring complete oxidation of propylene (*i.e.*, oxygen levels above 2% at 267 °C or above 0.5% at 402 °C) the rate of NO reduction decreases with an increase in oxygen concentration. Once again, the competition between NO and O_2 is responsible for this effect. Similar results have been obtained regardless of the support used [4,5]. The results of figure 2, however, further demonstrate that under conditions where propylene oxidation is below 100% conversion, O_2 has a promoting effect on the rate of NO reduction. Furthermore, the results of studies conducted with a variety of SiO_2 Al_2O_3, and TiO_2 supported Pt catalysts, including catalysts with different dispersions as well as bimetallic Pt-Au catalysts prepared *via* different synthetic routes, indicate a strong correlation between the temperature of maximum NO reduction and the temperature at which 50% oxidation of C_3H_6 is reached in the absence of NO (figure 3). These results strongly suggest that over supported Pt catalysts the activation of propylene by oxygen is a kinetically significant step for the SCR reaction at temperatures below the temperature of maximum NO reduction.

The results of kinetic studies examining the effect of NO concentration [4,5] indicate that the reaction is approximately zero order in NO at temperatures below that of maximum NO reduction. In contrast, a first-order dependence on NO is observed at higher temperatures.

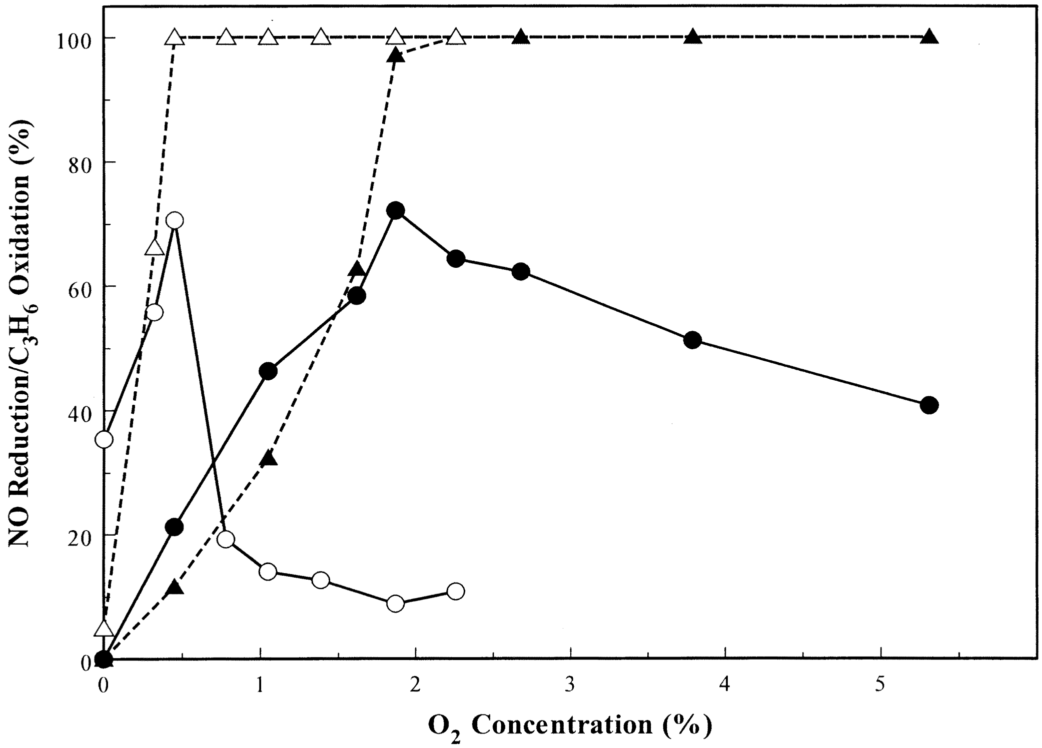

Figure 2. Effect of O_2 concentration on NO reduction (●, ○) and C_3H_6 oxidation (▲, △) over a 0.9 wt% Pt/SiO_2 catalyst at 267 °C (closed symbols) and at 402 °C (open symbols) (1000 ppm NO, 1000 ppm C_3H_6).

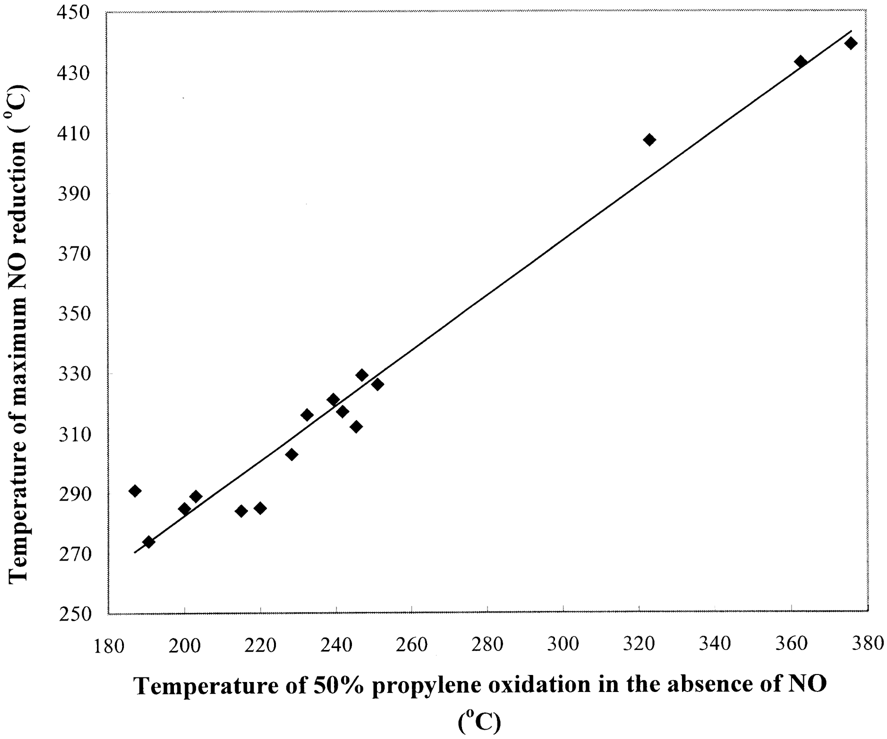

Figure 3. Temperature of maximum NO reduction *versus* temperature of 50% C_3H_6 oxidation for different Pt and Pt–Au catalysts.

The zero-order dependence in the low-temperature range suggests that either the catalyst surface is saturated with N-containing species (a possibility clearly ruled out based on the results of the *in situ* FTIR studies [23,24]) or that the N-containing species are not participating in the kinetically significant step under these conditions. Consequently, these kinetic results appear to offer further support to the assumption that propylene activation by molecular oxygen is the rate-determining step under these conditions. A different situation prevails at higher temperatures or higher concentrations, as indicated by the first-order dependence on NO and the negative effect of O_2. These results suggest that under these conditions propylene activation is now fast, and a different step (that involves NO or another N-containing species) has become limiting.

2.2. N-containing intermediates

Analysis of FTIR spectra of Pt/SiO_2 and Pt/Al_2O_3 catalysts collected *in situ* under reaction conditions at 250 °C suggests the presence of cyanide and isocyanate species on the catalyst surfaces under these conditions [23,24]. Additionally, there is strong evidence for the presence of significant amounts of surface carboxylate species associated primarily with the support. These species, however, are not reactive towards NO and/or O_2 and are probably spectators in the SCR process. Finally, there is evidence in the *in situ* spectra of the formation of the N_2O product, either in the gas phase or very weakly adsorbed on the catalyst. Only the formation of the cyanide species was observed in the case of the Pt/SiO_2 catalyst [23,24]. Furthermore, this species is weakly held onto the surface of the catalyst, and the corresponding peak disappeared within a short period after removal of the reacting gas mixture from the IR cell and flushing of the sample with He. The formation of both surface cyanide and isocyanate species was observed with the Pt/Al_2O_3 catalyst [23,24]. In this case, however, the intensity of the cyanide peak remains constant upon removal of the reacting gas mixture from the cell and flushing with He, O_2, and NO, suggesting that the cyanide species is held strongly on the Pt/Al_2O_3 surface and does not participate in further reactions. In contrast, the isocyanate peak is held weakly on the catalyst surface. These results suggest a potential role for the support. In fact, previous studies of the three-way catalysts have indicated that surface cyanide and isocyanate species may migrate from the metal sites on which they are formed to the support, where they are stabilized [25,26].

To investigate the origin of these C–N-containing species (*i.e.*, CN species in the case of Pt/SiO_2 and NCO species in the case of Pt/Al_2O_3) additional transient studies were conducted with NO flowed over catalysts that had been pre-exposed to propylene-containing mixtures. The formation of both of these species was significantly enhanced when oxygen was present during the catalyst exposure to propylene, indicating that a propylene activation step precedes their formation. This result is consistent with the kinetic results demonstrating the promoting role of oxygen under similar conditions. Similar results were also obtained when a hydrocarbon-saturated surface was exposed to a short pulse of oxygen, indicating that this activation process involves a surface hydrocarbon derivative. It is important to note that when a longer pulse of oxygen was used, no cyanide or isocyanate species were formed. This behavior is consistent with the dual role of oxygen discussed in the previous paragraphs. Under an extended oxygen pulse, the formed activated hydrocarbon intermediate reacts further with O_2, resulting in the formation of CO_2 and H_2O.

Further *in situ* FTIR reactivity studies involving isotopically labeled ^{15}NO were conducted over the Pt/SiO_2 catalyst. The results of these studies indicate that the surface cyanide species in this case reacts with O_2, NO, and NO_2. This reaction with the nitrogen oxides is faster, indicating a selectivity toward these species. Transient reactor studies conducted in parallel with the FTIR experiments indicate that only N_2 and CO_2 are formed during the reaction of O_2 with the surface cyanide. In contrast, both N_2 and N_2O are formed during the reaction of the same species with NO and NO_2. The rates of formation of N_2 and N_2O are almost identical, regardless of whether NO or NO_2 was used as the reactant. Similar results were also obtained with a Pt/Al_2O_3 catalyst, when, in this case, the surface isocyanate species is considered as a reaction intermediate [23].

The presence of cyanide or isocyanate species on the surface of supported-Pt catalysts and their involvement in the selective catalytic reduction of NO by hydrocarbons has also been reported by others. Bamwenda *et al.* [27,28], for example, have proposed a mechanism for the reduction of NO by hydrocarbons over Pt catalysts that involves partial oxidation of the hydrocarbon, followed by reaction with adsorbed nitrogen oxides toward adsorbed cyanides (–CN) and isocyanates (–NCO). Misono and coworkers [29,30] have also observed the presence of an isocyanate species on the catalyst surface, during the reduction of NO by hydrocarbons over a Pt/SiO_2 catalyst.

2.3. Reaction mechanism and kinetic analysis

Based on the above results we have proposed the following general reaction scheme for the selective catalytic reduction of NO by propylene over Pt/SiO_2 catalysts:

$$C_3H_6 + {}^* \Rightarrow C_xH_y^* \qquad (1)$$

$$C_xH_y^* + O_2 \Rightarrow I_1^* \qquad (2)$$

$$I_1^* + NO \Rightarrow CN^* \qquad (3)$$

$$C_xH_y^* + NO \Rightarrow CN^* \qquad (3')$$

$$I_1^* + O_2 \Rightarrow CO_2 + H_2O \qquad (4)$$

$$CN^* + NO/NO_2 \Rightarrow N_2 + N_2O + CO_2 \qquad (5)$$

$$CN^* + O_2 \Rightarrow N_2 + CO_2. \qquad (6)$$

Over Pt/Al_2O_3 catalysts, the reaction proceeds *via* an isocyanate intermediate, and steps (3), (5), and (6) are replaced by the following steps:

$$I_1^* + NO + O_2 \Rightarrow NCO^* \qquad (3a)$$

$$NCO^* + NO/NO_2 \Rightarrow N_2 + N_2O + CO_2 \qquad (5a)$$

$$NCO^* + O_2 \Rightarrow N_2 + CO_2. \qquad (6a)$$

The feasibility of the above reaction scheme was tested by conducting analyses of reaction kinetics data using a simplified kinetic model. In particular, we assumed that the most abundant surface species on the catalyst were adsorbed oxygen atoms and CN species. The surface chemistry of the above reaction scheme was then written in terms of the following six lumped reactions:

$$C_3H_6 + 3NO + O^* + 2^* \Rightarrow 3CN^* + 3H_2O + \tfrac{1}{2}O_2 \qquad (I)$$

$$C_3H_6 + 3NO + 3^* \Rightarrow 3CN^* + 3H_2O \qquad (II)$$

$$C_3H_6 + 9O^* \Rightarrow 3CO_2 + 3H_2O + 9^* \qquad (III)$$

$$CN^* + 3NO \Rightarrow N_2 + N_2O + CO_2 +^* \qquad (IV)$$

$$2CN^* + 4O^* \Rightarrow N_2 + 2CO_2 + 6^* \qquad (V)$$

$$O_2 + 2^* \Rightarrow 2O^* \qquad (VI)$$

where step (I) represents the combined effects of steps (1), (2), and (3); step (II) represents the combined effects of steps (1), (2), and (3′); step (III) represents the combined effects of steps (1), (2), and (4); step (IV) represents step (5); step (V) represents step (6); and step (VI) represents the adsorption of oxygen on the surface. The rate expressions for these six lumped reactions were assumed to be given by:

$$R_I = k_1 P_{C_3H_6} P_{NO} \theta_O \theta^*$$

$$R_{II} = k_2 P_{C_3H_6} P_{NO} \theta^*$$

$$R_{III} = k_3 P_{C_3H_6} \theta_O$$

$$R_{IV} = k_4 P_{NO} \theta_{CN}$$

$$R_V = k_5 \theta_{CN} \theta_O$$

$$R_{VI} = k_6 P_{O_2} \theta^*$$

The kinetic model was then constructed by solving algebraic steady-state equations for adsorbed oxygen and CN species (*i.e.*, θ_O and θ_{CN}), an algebraic site balance for all surface species in terms of the fraction of the surface that is unoccupied (θ^*), and differential mass-balance equations for the pressures of propylene, nitric oxide, and oxygen *versus* axial distance along a plug-flow reactor. The values of the rate constants were then adjusted to fit the reaction kinetics data collected at 267 and 402 °C. Values of fitted parameters, along with 95% confidence limits, were determined using the Athena Visual Workbench [31]. This software employs a general regression analysis of the reaction kinetics data, with the reactor treated as a plug-flow reactor.

The kinetic model was parameterized in terms of six rate constants and six activation energies, using the

Table 1
Values of kinetic parameters. All rate constants have units of $\mathrm{Torr}^{-1}\,\mathrm{sec}^{-1}$, and all rates are in TOF units (*i.e.*, molecules per site per sec).

Step	k_i (T_{ave})	E_i (kJ/mol)
I	52 ± 37	0^*
II	0.73 ± 0.22	0^*
III	37 ± 11	190^{**}
IV	0.0047 ± 0.002	25 ± 19
V	6.8 ± 3.6	170 ± 19
VI	4.0 ± 2.1	0^*

* Process assumed to be non-activated.
** Insensitive parameter.

following relation:

$$k_i(T) = k_i(T_{ave}) \exp[-E_i(1/RT - 1/RT_{ave})]$$

where $k_i(T)$ is the rate constant for reaction i at temperature T, T_{ave} is the average temperature of the data set (*i.e.*, 607 K), $k_i(T_{ave})$ is the value of the rate constant at temperature T_{ave}, and E_i is the activation energy. Table 1 gives the values of $k_i(T_{ave})$ and E_i for the six reactions of the kinetic model.

Simulation results were compared to the experimental data collected at different temperatures and NO and O_2 concentrations. The mathematical model developed based on the proposed reaction scheme can accurately predict the complex kinetic behavior of the SCR system. In particular, it predicts the change in the kinetic dependencies on NO from zero to first order at temperatures below and above the temperature of maximum NO conversion. Furthermore, it can successfully simulate the maximum in NO conversion observed with oxygen concentration at different temperatures (figure 4). These results suggest that the proposed reaction scheme captures the fundamental surface chemistry taking place during the hydrocarbon-SCR process.

3. Conclusions

Combined results of experimental reaction kinetics and *in situ* FTIR spectroscopic studies suggest that the selective catalytic reduction of NO by propylene over supported Pt catalysts proceeds via the formation of C–N-containing intermediates. In particular, surface cyanide and isocyanate species were identified as these intermediates in the cases of Pt/SiO_2 and Pt/Al_2O_3 catalysts, respectively. The formation of these intermediates is the result of a surface reaction between a hydrocarbon derivative activated by oxygen and NO. Once they are formed, these species can selectively reduce nitrogen oxides to N_2 and N_2O. Oxygen also reacts with the C–N-containing intermediates, but this reaction is not detrimental to the SCR process, since it yields nitrogen. Reaction kinetics analyses based on the proposed mechanism can simulate the kinetic behavior of the SCR system. These results further validate the proposed mechanistic scheme and demonstrate that such a mechanism captures the fundamental surface chemistry taking place during the hydrocarbon–SCR process.

Acknowledgments

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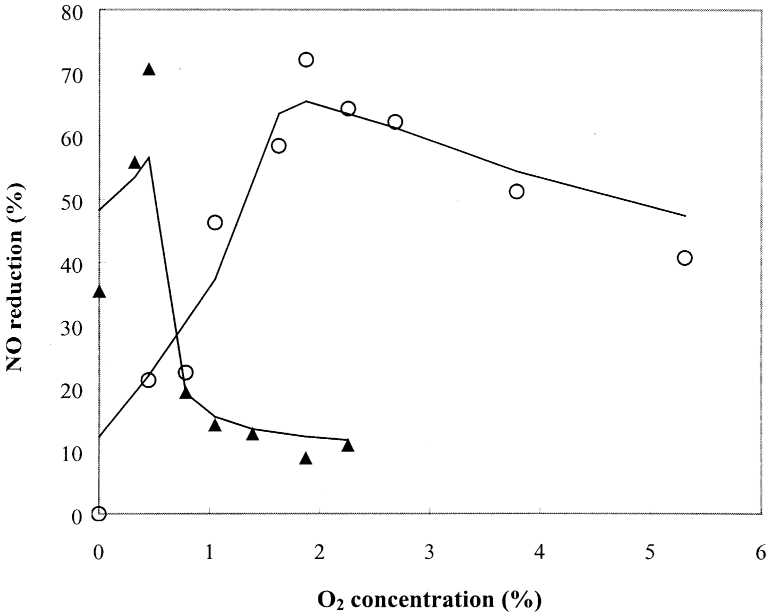

Figure 4. Effect of O_2 concentration on NO reduction over a 0.9 wt% Pt/SiO_2 catalyst (○, ▲: experimental measurements at 267 °C and 402 °C respectively; ——: model predictions) (1000 ppm NO, 1000 ppm C_3H_6, balance He).

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