REACTION MECHANISM FOR THE FORMATION OF NITROGEN OXIDES (NO\textsubscript{x}) DURING COKE OXIDATION IN FLUIDIZED CATALYTIC CRACKING UNITS

Sree Vidya Chaparala,\textsuperscript{1} Abhijeet Raj,\textsuperscript{1} and Suk Ho Chung\textsuperscript{2}
\textsuperscript{1}Department of Chemical Engineering, The Petroleum Institute, Abu Dhabi, United Arab Emirates
\textsuperscript{2}Clean Combustion Research Centre, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia

Fluidized catalytic cracking (FCC) units in refineries process heavy feedstock obtained from crude oil distillation. While cracking feed, catalysts get deactivated due to coke deposition. During catalyst regeneration by burning coke in air, nitrogen oxides (NO\textsubscript{x}) are formed. The increase in nitrogen content in feed over time has resulted in increased NO\textsubscript{x} emissions. To predict NO\textsubscript{x} concentration in flue gas, a reliable model for FCC regenerators is needed that requires comprehensive understanding and accurate kinetics for NO\textsubscript{x} formation. Based on the nitrogen-containing functional groups on coke, model molecules are selected to study reactions between coke-bound nitrogen and O\textsubscript{2} to form NO and NO\textsubscript{2} using density functional theory. The reaction kinetics for the proposed pathways are evaluated using transition state theory. It is observed that the addition of O\textsubscript{2} on coke is favored only when the free radical is present on the carbon atom instead of nitrogen atom. Thus, NO\textsubscript{x} formation during coke oxidation does not result from the direct attack by O\textsubscript{2} on N atoms of coke, but from the transfer of an O atom to N from a neighboring site. The low activation energies required for NO formation indicate that it is more likely to form than NO\textsubscript{2} during coke oxidation. The favorable pathways for NO\textsubscript{x} formation that can be used in FCC models are identified.

Keywords: Coke oxidation; Density functional theory; NO\textsubscript{x}; Reaction kinetics

INTRODUCTION

The increasing demand for transportation fuels is primarily being met by gasoline and diesel, which constitute the light products of distillation and fluidized catalytic cracking (FCC) units (Cheng et al., 1998; Gupta et al., 2007; Jiménez-Garcia et al., 2011; Sadeghbeigi, 2012). The FCC units process heavy feedstock from crude oil distillation units (Gupta et al., 2007; Sadeghbeigi, 2012). While cracking feed, the catalysts get covered with coke, a carbonaceous material containing aromatic hydrocarbons with nitrogen and oxygen containing functional groups (Barth et al., 2004; Stevenson et al., 2005).

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Address correspondence to Abhijeet Raj, Department of Chemical Engineering, The Petroleum Institute, P.O. Box 2533, Abu Dhabi, United Arab Emirates. E-mail: abgupta@pi.ac.ae
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The catalysts are reactivated in a regenerator by oxidizing coke. Over time, with an increasing amount of nitrogen-containing compounds in heavy oil (Cheng et al., 1998; Gupta et al., 2007), the nitrogen-content of coke has also increased, which has resulted in increased emission of nitrogen oxides (NO\textsubscript{x}) from FCC regenerators where nitrogen in coke oxidizes to form NO\textsubscript{x}.

The concentration of NO\textsubscript{x} in the flue gas exiting FCC can vary between 50 and 500 ppm (Babich et al., 2005; Dishman et al., 1998; Iliopoulou et al., 2004; Stevenson et al., 2005) depending upon operating conditions. However, even at such concentrations, these reactive compounds can harm the environment and human health. Two common nitrogen oxides, nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}), are responsible for acid rain, smog, and ozone layer depletion (Otterstedt et al., 1986; Rana et al., 2007). A continuous exposure to NO can damage lungs and hemoglobin (Rana et al., 2007). Therefore, technologies to reduce their emissions are required. To develop such technologies, it is important to understand the pathways through which they form.

In this direction, several researchers have conducted experimental as well as theoretical studies to measure NO\textsubscript{x} emissions and to understand their formation pathways during the oxidation of structurally similar carbonaceous materials, such as coke, char, and soot (Kim et al., 2011; Molina et al., 2000; Montoya et al., 2002b; Sørum et al., 2001; Stanczyk, 1999; Thomas, 1997; Zhang et al., 2012; Zhao et al., 1997). In Babich et al. (2005), coke from the nitrogen-containing compounds in heavy FCC feed, such as pyridine, pyrrole, and aniline, were produced through their pyrolysis in the presence of catalysts. During coke oxidation at temperatures in the range of 650–750°C (close to FCC regenerator temperature of about 715°C), it was found that, along with CO and CO\textsubscript{2}, NO was also formed, and some NO molecules reacted further with coke and CO to form N\textsubscript{2}O. In Dishman et al. (1998), commercial catalysts were coked in a fluidized bed using vacuum heavy gas oil doped with pyridine, indole, carbazole, quinoline, and hydroxypyridines. The study showed that most of the emitted NO\textsubscript{x} contained NO, while some of them were reduced to N\textsubscript{2}. In some earlier studies (Glarborg et al., 2003; Molina et al., 2000; Pershing and Wendt, 1979), a simple mechanism for NO formation during the oxidation of carbon-bound nitrogen (CN) was proposed, that is, \((CN) + O_{2} \rightarrow (CNO) \rightarrow NO + (C^\ast)\).

To improve our mechanistic understanding on NO\textsubscript{x} formation, it was important to find the distribution of nitrogen-containing functional groups on coke. In this direction, experiments on the surface analysis of coke and char were conducted (Arenillas et al., 2010; Burchill and Welch, 1989; Kambara et al., 1993; Kelemen et al., 1994; Pels et al., 1995; Stanczyk, 1999; Wójtowicz et al., 1995). In Glarborg et al. (2003), X-ray photoelectron spectroscopy (XPS) studies showed the presence of nitrogen complexes in heterocyclic ring moieties and in side chains. Most commonly, pyridinic (\(-C=N–C\)=), anilinic (\(>C–NH_2\)), pyrrolic (\(=C–NH–C\)=), and nitroso (\(>C–NO\)) groups were found on the surface, while some N atoms were present in the basal plane. In Barth et al. (2004), through the characterization of coked catalysts using infrared spectroscopy, magic angle spinning-nuclear magnetic resonance, and matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy, it was shown that carbazole, imidazole, and porphyrin derivatives were also present on them. Moreover, the X-ray absorption near edge structure studies in Mitra-Kirtley et al. (1993), Kirtley et al. (1993), and Mullins et al. (1993) revealed that pyrrolic and pyridinic groups are also abundant in coal. Based on these findings, a representation of coke surface with various nitrogen-containing functional groups are presented in Figure 1.
This information on nitrogen functionalities on coke provides a way to study, in detail, the mechanisms through which they react with O\textsubscript{2} to form NO\textsubscript{x}. Some molecular modeling studies have been carried out on mechanism development (Montoya et al., 2002b; Zhang et al., 2012). In Montoya et al. (2002b), the evolution of NO using density functional theory (DFT) was studied using a model molecule having pyridine-N-oxide (\(>\text{N–O}\)) group on it. The mechanism for NO desorption was found to be similar to CO desorption during coke oxidation, but the desorption rate constant for CO was higher than that for NO. However, such a result cannot be generalized since other N-complexes were not studied. In Zhang et al. (2012), a reaction mechanism for the interaction between char and O\textsubscript{2} to form NO was developed using DFT. A polycyclic aromatic hydrocarbon (PAH) model, rich in zigzag sites with a pyridinic group, was selected, but this model molecule had consecutive radicals on N and three C atoms. This makes the model molecule less realistic since the concentration of radicals is significantly less than that of H atoms (Raj et al., 2012), and, thus, finding consecutive radicals on coke will be difficult. Moreover, it has been shown in Raj et al. (2012) that the presence of H atoms near radicals can significantly affect the energetics of the reactions during soot oxidation by O\textsubscript{2}, and, thus, the effect of H atoms near radicals should not be ignored while studying NO\textsubscript{x} formation. Moreover, the study was focused on a pyridinic group on zig-zag sites only, while other types of sites are also present on coke. Thus, studies are required to understand the role of H atoms near radicals on reaction energetics, and the pathways for NO\textsubscript{x} formation from different sites containing N functional groups on coke.

This article presents a detailed reaction mechanism for the interaction between coke-bound nitrogen complexes and O\textsubscript{2} during FCC catalyst regeneration to determine the favorable pathways for NO\textsubscript{x} formation. The reaction energetics have been studied using density functional theory, and the reaction kinetics have been evaluated using transition state theory. The effect of the presence of radical on the N atom and on the C atom of the model molecules on NO\textsubscript{x} formation has been investigated. Various pathways for the formation of NO and NO\textsubscript{2} have been obtained, and through the comparisons of reaction energies and activation energies for different pathways, the probable routes for their formation have been determined.
COMPUTATIONAL DETAILS

The chemical species and transition states involved in the reactions have been optimized using DFT with the Becke three-parameter exchange and Lee, Yang, and Parr correlation (B3LYP) functional and 6-311++G(d,p) basis set. The molecular structures were optimized with different spin multiplicities to identify the multiplicity with a minimum energy, reasonable geometry, and low spin contamination. All of the optimizations were performed using Gaussian 09 software (Gaussian et al., 2009).

An inaccuracy in the quantum calculations can arise due to spin contamination in open shell systems thereby affecting the energy, geometry, and calculated spin density of the molecules (Young, 2001). The eigenvalue of the spin operator $\hat{S}^2$, $\langle \hat{S}^2 \rangle$ gives a measure of the amount of spin contamination introduced by a given level of theory. It is seen in the literature that DFT introduces a negligible amount of spin contamination (Raj, 2010; Raj et al., 2012), which is also concluded in this work. The higher levels of theory, such as coupled-clusters singles, doubles, and perturbative triples (CCSD(T)), can provide more accurate results than DFT. However, they can only be used for small molecules in a reasonable computational time. DFT is considered to be a standard choice for large molecules, such as aromatic hydrocarbons, as it is computationally less expensive and yields reliable results (Coelho et al., 2012; Liu et al., 2014; Montoya et al., 2002a, 2002b; Raj et al., 2011, 2012, 2013, 2014). The unrestricted wavefunctions were selected for calculations.

The rate constants, $k$, for the reactions involved in the proposed processes were evaluated using transition state theory. The expression for $k$ is given below:

$$k = \kappa(T) \frac{k_B T}{h} \frac{Q^\dagger}{N_R} \frac{e^{E_a/k_B T}}{\prod Q_i}$$

Here, $\kappa$ is tunneling correction factor, $T$ is the temperature, $k_B$ is Boltzmann’s constant, $h$ is Planck’s constant, $Q^\dagger$ is the total partition function of the transition state, $Q_i$ is the total partition function of reactant $i$, $N_R$ is the total number of reactants, and $E_a$ is the activation energy. The total partition function is evaluated as the product of the translational partition function $Q_t$, rotational partition function $Q_r$, vibrational partition function $Q_v$, and electronic partition function $Q_e$, where $Q_e$ is approximated as the electronic (spin) multiplicity of the molecular structure, which is equivalent to the degeneracy of the ground state. The expressions for the other partition functions are given below:

$$Q_t = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2}$$

$$Q_r = \left( \frac{8\pi^{7/3} k_B T}{h^2} \right)^{3/2} (I_a I_b I_c)^{1/2}$$

$$Q_v = \prod_{j=1}^\eta \frac{e^{-h v_j/2k_B T}}{1 - e^{-h v_j/k_B T}}$$

Here, $m$ is the molecular mass, $I_a, I_b,$ and $I_c$ are the moments of inertia along the principal axes, $v_j$ is a non-negative vibrational frequency, and $\eta$ is the total number of non-negative vibrational frequencies.
The partition functions for the transition states and reactants were calculated at temperatures, $T$, in between 300 K and 3000 K using the vibrational frequencies, moments of inertia, mass and electronic multiplicity, all of which are given by the quantum calculations. A linear least-square fitting algorithm was used to fit the modified Arrhenius expression $k(T) = AT^n e^{(E/R T)}$ to the data points of the rate constants in order to obtain the kinetic parameters of the frequency factor $A$, the temperature exponent $n$, and the activation energy $E$. To assess the role of quantum tunneling, in the literature, there are four efficient methods to evaluate the tunneling correction factor, $\kappa$ (also called transmission constant): Wigner correction, Eckart correction, zero-curvature tunneling correction, and small curvature tunneling correction. At temperatures above 500 K, the corrections from all of the methods converge to similar values (Bell and Truong, 1994; Gonzalez-Lafont et al., 1991). In this article, the Wigner method was employed to obtain $\kappa(T)$, which is expressed as:

$$\kappa(T) = 1 - \frac{1}{24} \left( \frac{\hbar \bar{\nu}^*}{k_B T} \right)^2$$

where $\bar{\nu}^*$ is the imaginary frequency of the transition state.

**RESULTS AND DISCUSSION**

This section presents the detailed mechanisms for the reactions between nitrogen-containing functional groups on coke and $O_2$ to determine the pathways for the formation of NO and NO$_2$ during coke oxidation. As shown in Figure 1, several nitrogen functionalities can be present on the coke or char surface. For this study, model molecules with pyridinic and anilinic functional groups have been selected for DFT calculations, while the results for the other functional groups will be presented in a forthcoming publication to keep the length of this article reasonable. The reaction mechanism can vary depending upon the type of sites present near a functional group. Figure 2 presents the structures of some sites that are commonly found on aromatic hydrocarbons. In carbonaceous materials, zig-zag and free-edge sites are present in high concentrations (Raj et al., 2009). Therefore, we have considered these sites near the nitrogen functional groups on the model molecules. For $O_2$ addition on coke, a free radical is required that can be created through the desorption of H atom or through the abstraction of H atom by $O_2$, OH, and other gas phase species. This has already been studied (Raj et al., 2012), and, therefore, the H-abstraction reactions from coke surface have not been studied here. Only one free radical for $O_2$ addition is assumed on the model molecule because on carbonaceous materials, such as soot and coke, the fraction of radicals as compared to H atoms is only about $10^{-2}$–$10^{-4}$ (Raj et al., 2012), and, thus, it is unlikely to have two or more adjacent radicals on them. Moreover, the free radical can be present on the C atom as well on the N atom. The variation in the reaction pathways with the change in the radical position on coke surface has also been considered. In the forthcoming sections, the chemical species will be represented by CS, and the transition states will be represented by TS.
Figure 2 Different reactive sites present on an aromatic structure. A free-edge site is formed by two C atoms, a zig-zag site by three C atoms, an armchair site by four C atoms, and a bay site by five C atoms (Raj, 2010).

Figure 3 Pathway 1. A potential energy diagram at 0 K for the oxidation of a model molecule having a pyridinic group on a free-edge site and a radical on C atom. Routes a and b for CS4 are shown.

Pyridinic Group: Pathway 1

Figure 3 shows the potential energy diagram for oxidation by O\(_2\) of a model molecule, CS1, with pyridinic group on a free edge site and a radical on C atom that is adjacent to N atom. The chemisorption of O\(_2\) on the radical on CS1 to form a peroxy group in CS2 is barrierless, where a reaction energy of 173.4 kJ/mol is released. A small activation energy of 20.5 kJ/mol is required to form CS3 where N atom and O radical come close to each other. The next step involves the attack by the O radical in CS3 on the N atom, where the primary O atom detaches from the secondary O to form pyridine-N-oxide and ketone groups in CS4. This reaction requires overcoming a high activation energy of 180.6 kJ/mol. The resultant species, CS4, is more stable than CS3 by 186.6 kJ/mol. Any intermediate species with N–O–O ring was not found with B3LYP level of theory. Hereafter, there are four possible routes that CS4 may follow for its decomposition, as detailed below as routes a–d.

- Route a: Shown by solid lines in Figure 3, this route involves the attack by O radical on the C atom of the ketone group to form a seven-membered ring in CS5. Thereafter,
molecular rearrangement takes place to convert the seven membered ring to a five-membered ring in CS6 and NO molecule, which requires crossing an activation energy of 181.1 kJ/mol.

- **Route b**: This route, shown by dotted lines in Figure 3, involves the formation of a C–O bond between the O radical and the embedded C atom adjacent to N in CS4 to give rise to a three-member ring in CS7. Such a structure was found to be unstable in the previous route. To break the three-member ring in CS7 to form a seven-member ring in CS8, an activation energy of only 14.8 kJ/mol is required. The species CS8 appears similar to CS5, but has higher energy than CS5 by 49.8 kJ/mol. Similar to CS5 in the previous route, CS8 undergoes conversion of a seven-member ring to a five-membered ring in CS6 through the loss of NO molecule, but a much higher activation energy of 296.4 kJ/mol is involved in this reaction as compared to CS5 → CS6. The reason for this high difference in activation energies for CS5 → CS6 and CS8 → CS6 could be the structures of CS5 and CS8. While CS5 is planar, CS8 is non-planar. Moreover, the C–O bond that breaks to assist the release of NO is stronger in CS8 than in CS5 (C–O bond length in CS8 is 1.39 Å, while it is 1.41 Å in CS5). Thus, the species CS8, being less stable and non-planar, is more likely to form CS7 instead of releasing NO to form CS6.

- **Route c**: Shown by solid lines in Figure 4, this route involves the desorption of NO from CS4 to form CS6, and involves an activation energy of 279.3 kJ/mol to be overcome. Out of routes a, b, and c, route c involves the least overall activation energy, and should be a preferred route for NO desorption.

- **Route d**: The dotted lines in Figure 4 present this route that involves the formation of NO$_2$. Through the breakage of a C–N bond in CS4 and the formation of O–O bond, a four-member N–O–O ring is formed in CS9 after overcoming a very high activation energy of 620.7 kJ/mol. The C–O bond in CS9 breaks to form N–O–O chain in CS10 after crossing an activation energy of 62.5 kJ/mol. The O radical in CS10 then attacks the N atom to form a three-member N–O–O ring in CS11 after crossing an activation

![Figure 4](https://example.com/figure4.png)

**Figure 4** Pathway 1. A potential energy diagram at 0 K for routes c and d for the decomposition of CS4.
energy of 164.2 kJ/mol. The desorption of NO₂ can then take place from CS11, but it requires overcoming a potential energy of 257.2 kJ/mol. By comparing the overall activation energies for the four routes, it is clear that NO formation (through routes a, b, or c) is more favorable than NO₂ formation.

Pyridinic Group: Pathway 2

In this section, the pathways for NOₓ formation are explored during the oxidation of a model molecule with pyridinic group on a free-edge site, but with a radical on the N atom instead of C atom to assess the effect of radical position on NOₓ mechanism. To maintain the resonance structure of the base hydrocarbon structure containing N radical, a new model molecule was selected, which is shown as CS13 in Figure 5. The reaction between CS13 and O₂ begins with the addition of O₂ on the radical after overcoming an activation energy of 127.7 kJ/mol to form CS14. The reaction is endothermic with a reaction energy of 115.5 kJ/mol. Note that the addition of O₂ on the C radical in the previous section was highly exothermic. The pathway, hereafter, can follow three routes, as discussed below as routes a–c.

- Route a: Shown by solid lines in Figure 5, this route involves the addition of the O radical in CS14 to the C atom on the free-edge site to form CS15 with a four-member ring. An activation energy of 152.2 kJ/mol is required for this reaction. The species CS15 is unstable possibly due to weak and stretched O–O bond in it. The O–O bond length in CS14 is 1.50071 Å, while it is 3.34750 Å in CS15. To form CS16 from CS15, an activation energy of only 21 kJ/mol is required to be overcome. From CS16, NO is then released after overcoming an activation energy of 321.9 kJ/mol.
Route b: This route is shown by dotted lines in Figure 5, and involves the migration of the O atom from the dangling NOO chain in CS14 to the C atoms at the free-edge site to form an epoxy group in CS18. The activation energy for this reaction is 123.9 kJ/mol. The six-member ring containing pyridine-N-oxide group in CS18 is converted to a five-membered ring and NO chain in CS19 after overcoming an activation energy of 328.8 kJ/mol. The resultant species CS19 is unstable, and it releases NO to form CS20.

Route c: This route, shown by dash-dotted lines in Figure 5, involves the desorption of NO_2 during CS1 oxidation. The O radical in CS14 attacks the N atom to form a three-member N-O-O ring in CS21, but this requires a high activation energy of 348.1 kJ/mol and a positive reaction energy of 327.5 kJ/mol. The species CS21, being unstable, releases NO_2 for which only a small activation energy of 6.8 kJ/mol is required to be overcome.

Based on the overall activation energies of 267.7 kJ/mol (corresponding to TS14) for route a, 323.2 kJ/mol (corresponding to TS18) for route b, and 463.6 kJ/mol (corresponding to TS20) for route c, it is clear that NO formation (through routes a and b) is energetically more favorable than NO_2 formation (through route c).

Pyridinic Group: Pathway 3

Figure 6 presents the potential energy diagram for the oxidation by O_2 of a model molecule, CS23, that contains zig-zag sites on the either sides of the pyridinic group with radical only on one of the C atoms. The reaction begins with the chemisorption of O_2 on the radical to form peroxy group in CS24. This addition reaction is barrierless where a reaction energy of 186.3 kJ/mol is released. This value is similar to the reaction energy for CS1 + O_2 → CS2. A bond rotation in CS24 to bring the O radical close to the N atom in CS25 requires a small activation energy of 17.1 kJ/mol. The O radical of the peroxy chain then attacks the N atom to form a five-membered ring in metastable species, CS26. The

![Figure 6](image-url)
formation of CS26 requires overcoming an activation energy of 151.1 kJ/mol. In Zhang et al. (2012), the chemisorption of O2 on a zig-zag site with pyridinic group and containing four consecutive radicals on 3 C atoms and one N atom was studied. In their work, a structure similar to CS26 was found to be relatively stable with energy of 271 kJ/mol below the reactants, model molecule + O2 (though the spin multiplicities used for structure optimization were not mentioned). In this work, CS26 is only 30.4 kJ/mol below the reactants with doublet spin multiplicity. The species CS26 can, thereafter, follow two routes (discussed below as routes a and b).

- **Route a:** The route shown by solid lines in Figure 5 involves CS27 formation from CS6 through the breakage of weak O–O bond in the metastable species, CS26. This reaction is barrierless, and leads to the formation of a highly stable species, CS27. It can be inferred that the addition of O2 on CS23 would most preferably lead to the formation of CS27 having two O atoms separately bonded to the N atom and a nearby C atom, and involving an overall reaction energy of 294.4 kJ/mol for CS23 + O2 → CS27. Thereafter, NO desorption takes place from CS27 to form CS28 after overcoming an activation energy of 301.5 kJ/mol. This reaction was endothermic with a reaction energy of 120.9 kJ/mol.

- **Route b:** The route, shown by dotted lines in Figure 5, involves CS29 formation from CS26 through C–O bond breakage, where a high activation energy of 190.6 kJ/mol is required to be overcome. This endothermic reaction has a reaction energy of 186.5 kJ/mol. The species, CS29, with high energy has low stability with an activation energy of only 4 kJ/mol for the reverse reaction. The radical present on the O atom of the peroxy group can attack the N atom to form a three-membered N–O–O ring in CS30, but a very high activation energy of 364.9 kJ/mol is required for this reaction. From CS30, NO2 desorption to form CS31 involves an activation energy of 42.4 kJ/mol. On comparison of the overall activation energies of 7.1 kJ/mol (corresponding to TS3) for NO formation and 521.1 kJ/mol (corresponding to TS6) for NO2 formation, it is clear that NO desorption from this model molecule is more favorable than NO2.

**Pyridinic Group: Pathway 4**

Figure 7 presents the potential energy diagram for the interaction between O2 and the N radical present on the model molecule, CS32, with pyridinic group on zig-zag sites. The reaction begins with O2 addition to the N radical on CS32 to form N–O–O chain in CS33. This is an endothermic reaction with a reaction energy of 129.8 kJ/mol, and an activation energy of 131 kJ/mol. A reason for the endothermicity on the reaction involving O2 addition on N radical could be the resonance stabilization of the radical present on N atom. Consequently, the free radical on N atom is not entirely available for reactions, which makes O2 addition on it unfavorable. In our previous study as well (Raj et al., 2011), it was observed that NO addition on N radical is highly unfavorable, while a high reaction energy is released when NO is added to C radicals. In Zhang et al. (2012), the addition of O2 on N radical with multiple C radicals neighboring it was studied, where the addition was found to be exothermic with reaction energy of 119 kJ/mol (as opposed to endothermicity for such a reaction found in this work where there was no C radical neighboring N radical).
The species, CS33, thus formed can follow two routes, with one leading to NO desorption and the other leading to NO$_2$ desorption, as discussed below.

- **Route a**: In the route shown by solid lines, an activation energy of 100.4 kJ/mol is required to be overcome to form N–O–O–C ring in CS34 through the attack by O radical in CS33 to a nearby C atom (while in Zhang et al. (2012), for such a reaction, only 35.8 kJ/mol of activation energy was required as the presence of nearby C radical assisted in N–O–O–C ring formation). The O–O bond is significantly stretched from 1.48 Å in CS33 to 3.75 Å in CS34 in this reaction, which weakens the bond. The breakage of the O–O bond in CS34 takes place almost barrierlessly to form an epoxy group in CS35. Thereafter, NO is released through the formation of a five membered ring in CS36. This desorption step requires crossing a high activation energy of 358 kJ/mol, and the reaction is endothermic with a reaction energy of 169.3 kJ/mol. For a similar reaction involving NO desorption in Zhang et al. (2012), an activation energy of 419.3 kJ/mol was reported, which is higher than the value observed in this work, indicating that the presence of H atom on C atoms supports NO desorption. Interestingly, in Zhang et al. (2012), due to the presence of a radical site on a nearby C atom, an alternate route involving migration of NO chain to a nearby C atom to form a nitroso group was also suggested, which involved lower activation energy of 359.7 kJ/mol. Such a route could not be found in this work as the molecule resulting from the migration of NO to a nearby C atom was not stable due to an existing H atom on it. Moreover, if consecutive C radicals are present, O radicals can undergo migration reaction to nearby C atoms (Zhang et al., 2012), which is not allowed if H atoms are present on C atoms.
Route b: In the route shown by dotted lines, the O radical in CS33 attacks the N atom to form a 3-member N–O–O ring in CS37 after crossing an activation energy of 404.8 kJ/mol. The species CS37 is a metastable species with a reverse activation energy of only 3 kJ/mol. It can undergo molecular rearrangement to form a five-member ring in CS38 that requires an activation energy of 51.6 kJ/mol. The species CS38 can then release NO2 through an exothermic reaction by crossing a small activation energy of 11.8 kJ/mol. In this pathway, as well, the overall activation energy for the formation of NO2 was higher than that for the formation of NO.

While the reactions involved in the oxidation of model molecules, CS1 and CS13, with a pyridinic group on a free-edge site have some similarities with the reactions for the model molecules, CS23 and CS32, with a pyridinic group on a zig-zag site, the energetics (and therefore, the rate constants) of the elementary reactions are different, which indicate their dependence on the types of sites present near a functional group.

Anilinic Group: Pathway 1

Figure 8 presents the potential energy diagram for the oxidation by O2 of a model molecule, CS40 with an anilinic group on a zig-zag site, and a radical on the surface C atom adjacent to NH2 group. Similar to previous pathways involving a radical on a C atom, O2 addition on CS40 to form CS41 is barrierless and exothermic where a reaction energy of 179.1 kJ/mol is released. Thereafter, one of the two H atoms from the anilinic group migrates to the O radical to form a hydroxyl group with a radical on N atom in CS42 after crossing a small activation energy of 12.9 kJ/mol. The loss of OH molecule then takes place to form a singlet species, CS43, with a five-member ring. Since the loss of OH is highly favored in this pathway, NO2 formation could not be studied. For further reactions, there are two routes that the species CS43 may follow.

Route a: Shown by solid lines in Figure 8, this route involves the breakage of C–N bond in CS43 to form a diradical species, CS44, where an activation energy of 360.3 kJ/mol
is involved. The H atom present in the ONH chain of CS44 migrates to the C radical to form CS45, which is followed by the loss of NO from CS45 to form CS46.

- **Route b:** This route, represented by dashed lines in Figure 8, involves the breakage of C–O bond in CS43 after crossing an activation energy of 393.1 kJ/mol to form a diradical species, CS47. The H atom present in the ONH group of CS47 then migrates to the radical on the C atom to form a stable singlet species, CS48, with nitroso group on it. Thereafter, NO is released to form CS49. This barrierless and endothermic reaction involves a reaction energy of 212.9 kJ/mol. A similar reaction involving the loss of NO from a nitroso group was studied in Zhang et al. (2012), and an activation energy of 214.8 kJ/mol and a reaction energy of 215.9 kJ/mol were found, which compares very well with the reaction energy of 212.9 kJ/mol found in this work. This indicates that the loss of NO from nitroso group is not affected by the presence of radicals on nearby C atoms.

Since the overall activation energy for route a is lower than that for route b, NO formation through route a will be preferred.

### Anilinic Group: Pathway 2

Figure 9 presents the potential energy diagram for the interaction between O$_2$ and a model molecule, CS50, having an anilinic group on zig-zag site with a radical on N atom.

![Figure 9](image_url)

**Figure 9** Pathway 2. A potential energy diagram at 0 K for the oxidation of a model molecule (CS50) having an anilinic group on zig-zag site and a radical on N atom.
The addition of $O_2$ on the $N$ atom of CS50 to form CS51 was endothermic with an activation energy of 85.5 kJ/mol and a reaction energy of 75.2 kJ/mol. Compared to the addition of $O_2$ on pyridinic-$N$ radicals in Figures 5 and 7, lower activation and reaction energies for this endothermic reaction were obtained, indicating that the addition of $O_2$ is more favorable on anilinic-$N$ radicals than pyridinic-$N$ radicals. The species CS52 can follow two routes, one leading to NO formation, and the other leading to NO$_2$ formation, as detailed below.

- **Route a:** Similar to the previous pathway, this route, shown by solid lines in Figure 9, involves H migration from the anilinic-$N$ to the O radical after overcoming an activation energy of 101.5 kJ/mol to form $N-O-O-H$ chain in CS52. The desorption of OH from CS52 involves a small activation energy of 29.6 kJ/mol to form CS48 (a species that was also present in the previous pathway), from where NO removal takes place.

- **Route b:** This route is represented by dashed lines in Figure 9. The O radical in CS51 can attack the N atom to form NOO ring with the simultaneous removal of an H atom. This reaction, however, requires overcoming a high activation energy of 419.9 kJ/mol. The resulting species, CS53 is very unstable, and it barrierlessly releases NO$_2$ to form CS49.

### Reaction Rate Constants

Table 1 provides the high pressure limit rate constants for the elementary reactions involved in the formation of NO and NO$_2$ during the oxidation of model molecules representing coke, as discussed in the previous sections. For the barrierless reactions ($CS1 + O_2 \rightarrow CS2$, $CS32 + O_2 \rightarrow CS33$, $CS40 + O_2 \rightarrow CS41$, $CS26 \rightarrow CS27$, and $CS48 \rightarrow CS49 + NO$), variational transition state theory was used to determine their rate constants through partial geometry optimizations at different bond lengths with an interval of 0.1 Å (da Silva and Bozzelli, 2008; Raj et al., 2012). Due to convergence issues with B3LYP/6-311++G(d,p) in partial geometry optimization for the first four reactions out of five mentioned above, O3LYP/6-31G(d) level of theory, similar to da Silva and Bozzelli (2008), was used in this work.

Figure 10 provides a comparison of the rate constants for the addition of $O_2$ on the radicals of the model molecules. It was seen in the previous six sections that $O_2$ addition to the C radicals (on CS1, CS23, and CS40) was exothermic and barrierless, while its addition to the N radicals (on CS13, CS32, and CS50) was endothermic and had positive activation energies. As a result, the rate constants for $O_2$ addition on the C radicals were significantly higher than the rates for its addition on the N radicals. Moreover, while the rates for $O_2$ addition on molecules with C radicals were very similar, the rates differed within two orders of magnitude in the cases of molecules with N radicals. The addition of $O_2$ on N radical was most favored for the anilinic case. From this figure, as well as from the energetics involved in the pathways for model molecules with N radicals, it can be concluded that NO$_x$ formation during coke oxidation may not result from the direct attack of $O_2$ on N atoms, but from the transfer of an O atom to the N atom from a neighboring site.

Figure 11 provides a comparison of the rate constants for the desorption of NO from different model molecules. In this figure, the rate constants of CS4, CS16, CS18, CS27, CS35, and Montoya et al. (2002b) correspond to the removal of NO from pyridine-N-oxide groups, and the rate constant for CS48 refers to NO removal from a nitroso group.
| No. | Reactions                              | A          | n    | E      |
|-----|----------------------------------------|------------|------|--------|
| 1   | CS1 + O \textsubscript{2} → CS2         | 5.38 × 10\textsuperscript{9} | 0.748 | −7.8   |
| −1  | CS2 → CS1 + O \textsubscript{2}         | 4.85 × 10\textsuperscript{11} | 0.598 | 27,149.0 |
| 2   | CS2 → CS3                               | 9.06 × 10\textsuperscript{9} | 0.746 | 3601.1 |
| −2  | CS3 → CS2                               | 1.27 × 10\textsuperscript{9} | 0.939 | 1630.1 |
| 3   | CS3 → CS4                               | 8.0 × 10\textsuperscript{9} | 0.929 | 41,746.3 |
| −3  | CS4 → CS3                               | 1.42 × 10\textsuperscript{9} | 1.261 | 84,160.7 |
| −4  | CS5 → CS4                               | 8.15 × 10\textsuperscript{9} | 0.998 | 51,605.1 |
| 5   | CS5 → CS6 + NO                          | 9.06 × 10\textsuperscript{9} | 0.556 | 27,260.3 |
| −5  | CS6 + NO → CS5                          | 4.85 × 10\textsuperscript{9} | 0.693 | 51,154.8 |
| 6   | CS4 → CS5                               | 8.0 × 10\textsuperscript{9} | 1.048 | 52,981.3 |
| −6  | CS7 → CS4                               | 4.22 × 10\textsuperscript{9} | 0.963 | 1692.8 |
| −7  | CS8 → CS7                               | 9.16 × 10\textsuperscript{9} | 0.805 | 14,529.7 |
| 8   | CS8 → CS6 + NO                          | 7.92 × 10\textsuperscript{9} | 0.501 | 67,099.2 |
| −8  | CS6 + NO → CS8                          | 9.59 × 10\textsuperscript{9} | −0.064 | 90,026.4 |
| 9   | CS4 → CS6 + NO                          | 6.56 × 10\textsuperscript{9} | 1.257 | 48,668.5 |
| −9  | CS6 + NO → CS4                          | 3.57 × 10\textsuperscript{9} | 0.920 | 48,668.5 |
| 10  | CS4 → CS9                               | 8.49 × 10\textsuperscript{9} | 0.855 | 14,4950 |
| −10 | CS9 → CS4                               | 9.34 × 10\textsuperscript{9} | 0.777 | 42,749.5 |
| 11  | CS9 → CS10                              | 6.79 × 10\textsuperscript{9} | 0.948 | 12,997.6 |
| −11 | CS10 → CS9                              | 7.58 × 10\textsuperscript{9} | 0.630 | 32,111.3 |
| 12  | CS10 → CS11                             | 7.43 × 10\textsuperscript{9} | 0.809 | 37,056.7 |
| −12 | CS11 → CS10                             | 3.92 × 10\textsuperscript{9} | 0.838 | −868.8 |
| 13  | CS11 → CS12 + NO                        | 6.55 × 10\textsuperscript{9} | 0.025 | 56,520.2 |
| −13 | CS12 + NO \textsubscript{2} → CS11      | 1.71 × 10\textsuperscript{9} | −0.571 | 72,090.0 |
| 14  | CS13 + O \textsubscript{2} → CS14       | 7.06 × 10\textsuperscript{9} | 0.380 | 34,230.8 |
| −14 | CS14 → CS13 + O \textsubscript{2}       | 3.60 × 10\textsuperscript{9} | 1.316 | 568.2 |
| 15  | CS14 → CS15                             | 2.77 × 10\textsuperscript{9} | 0.910 | 34,187.8 |
| −15 | CS15 → CS14                             | 4.62 × 10\textsuperscript{9} | 1.358 | 7455.6 |
| 16  | CS15 → CS16                             | 9.71 × 10\textsuperscript{9} | 1.219 | 2416.7 |
| −16 | CS16 → CS15                             | 8.23 × 10\textsuperscript{9} | 1.027 | 74,111.5 |
| 17  | CS16 → CS17 + NO                        | 8.15 × 10\textsuperscript{11} | 0.696 | 73,992.8 |
| −17 | CS17 + NO → CS16                        | 9.06 × 10\textsuperscript{11} | 0.013 | 61,454.2 |
| 18  | CS14 → CS18                             | 9.50 × 10\textsuperscript{9} | 0.908 | 27,910.5 |
| −18 | CS18 → CS14                             | 3.67 × 10\textsuperscript{9} | 1.569 | 55,755.9 |
| 19  | CS18 → CS19                             | 8.15 × 10\textsuperscript{11} | 0.541 | 76,140.9 |
| −19 | CS19 → CS18                             | 9.06 × 10\textsuperscript{11} | 0.091 | 29,444.5 |
| 20  | CS19 → CS20 + NO                        | 1.87 × 10\textsuperscript{9} | 1.007 | −956.3 |
| −20 | CS20 + NO → CS19                        | 4.90 × 10\textsuperscript{9} | 0.563 | 17,556.6 |
| 21  | CS14 → CS21                             | 2.76 × 10\textsuperscript{9} | 1.318 | 78,921.1 |
| −21 | CS21 → CS14                             | 6.80 × 10\textsuperscript{9} | 1.085 | 2318.9 |
| 22  | CS21 → CS22 + NO                        | 6.55 × 10\textsuperscript{9} | 1.054 | −362.0 |
| −22 | CS22 + NO \textsubscript{2} → CS21      | 1.63 × 10\textsuperscript{9} | 0.563 | 10,827.8 |
| 23  | CS23 + O \textsubscript{2} → CS24       | 5.60 × 10\textsuperscript{9} | 0.734 | −160.8 |
| −23 | CS24 → CS23 + O \textsubscript{2}       | 2.92 × 10\textsuperscript{11} | 0.679 | 31,107.0 |
| 24  | CS24 → CS25                             | 1.19 × 10\textsuperscript{9} | 0.982 | 2415.9 |
| −24 | CS25 → CS24                             | 4.98 × 10\textsuperscript{9} | 0.768 | −851.4 |
| 25  | CS25 → CS26                             | 9.60 × 10\textsuperscript{9} | 1.430 | 36,191.8 |
| −25 | CS26 → CS25                             | 3.40 × 10\textsuperscript{9} | 1.753 | 2488.7 |
| 26  | CS26 → CS27                             | 1.43 × 10\textsuperscript{11} | 0.192 | −2148.4 |

(Continued)
| No. | Reactions                  | A         | n  | E     |
|-----|---------------------------|-----------|----|-------|
| −26 | CS27 → CS26               | 4.33 × 10^7 | 0.893 | 50,270.0 |
| 27  | CS27 + NO → CS28          | 8.15 × 10^11 | 0.395 | 70,372.8 |
| −27 | CS28 + NO → CS27          | 9.06 × 10^11 | −0.343 | 47,268.5 |
| 28  | CS26 → CS29               | 5.06 × 10^9  | 1.060 | 43,390.7 |
| −28 | CS29 → CS26               | 6.99 × 10^9  | 0.757 | −458.7 |
| 29  | CS29 → CS30               | 8.91 × 10^9  | 1.153 | 83,959.2 |
| −29 | CS30 → CS29               | 9.59 × 10^9  | 1.051 | 23,145.9 |
| 30  | CS30 → CS31 + NO_2        | 8.15 × 10^9  | 1.261 | 7232.6  |
| −30 | CS31 + NO_2 → CS30        | 9.06 × 10^9  | 0.416 | 97,935.9 |
| 31  | CS32 + O_2 → CS32         | 1.27 × 10^11 | 0.122 | 35,905.1 |
| −31 | CS32 → CS31 + O_2         | 9.13 × 10^11 | 0.409 | 1146.3  |
| 32  | CS33 → CS34               | 1.58 × 10^11 | 0.466 | 24,618.7 |
| −32 | CS34 → CS33               | 9.71 × 10^9  | 0.298 | 4451.8  |
| 33  | CS34 → CS35               | 6.32 × 10^9  | 0.906 | −1400.9 |
| −33 | CS35 → CS34               | 9.75 × 10^9  | 1.136 | 50,561  |
| 34  | CS35 → CS36 + NO          | 2.78 × 10^9  | 1.276 | 82,024.4 |
| −34 | CS36 + NO → CS35          | 5.47 × 10^9  | 0.421 | 47,613.1 |
| 35  | CS33 → CS37               | 2.78 × 10^11 | 0.906 | 95,620.9 |
| −35 | CS37 → CS33               | 5.47 × 10^11 | 0.219 | 86.3    |
| 36  | CS37 → CS38               | 1.58 × 10^9  | 0.842 | 10,367.5 |
| −36 | CS38 → CS37               | 9.71 × 10^9  | 0.899 | 26,332.4 |
| 37  | CS38 → CS39 + NO_2        | 9.57 × 10^9  | 1.057 | 594,608 |
| −37 | CS39 + NO_2 → CS38        | 4.85 × 10^9  | 0.426 | 106,960 |
| 38  | CS40 + O_2 → CS41         | 6.44 × 10^9  | 1.522 | −1822.5 |
| −38 | CS41 → CS40 + O_2         | 3.31 × 10^11 | 0.688 | 30,262.0 |
| 39  | CS41 → CS42               | 8.15 × 10^9  | 0.657 | −83,946 |
| −39 | CS42 → CS41               | 9.06 × 10^9  | 0.455 | −2807.5 |
| 40  | CS42 → CS43 + OH          | 6.32 × 10^9  | 0.907 | 7818.4  |
| −40 | CS43 + OH → CS42          | 9.75 × 10^9  | 1.298 | −1538.3 |
| 41  | CS43 → CS44               | 5.47 × 10^9  | 1.426 | 81,506.2 |
| −41 | CS44 → CS45               | 9.58 × 10^9  | 0.684 | 11,890.1 |
| 42  | CS44 → CS46               | 9.65 × 10^9  | 0.951 | 13,936.7 |
| −42 | CS45 → CS44               | 1.58 × 10^9  | 1.384 | 37,025.6 |
| 43  | CS45 → CS46 + NO          | 9.71 × 10^9  | 1.414 | 13,850  |
| −43 | CS46 + NO → CS45          | 9.57 × 10^9  | 0.754 | 7822.8  |
| 44  | CS43 → CS47               | 4.85 × 10^9  | 1.317 | 91,511.1 |
| −44 | CS47 → CS43               | 8.00 × 10^9  | 0.637 | 40,224.1 |
| 45  | CS47 → CS48               | 1.42 × 10^9  | 1.033 | 3291.2  |
| −45 | CS48 → CS47               | 4.22 × 10^9  | 1.145 | 46,939.4 |
| 46  | CS48 → CS49 + NO          | 2.98 × 10^11 | 0.873 | 38,112.0 |
| −46 | CS49 + NO → CS48          | 4.01 × 10^9  | 0.905 | 477.5   |
| 47  | CS50 + O_2 → CS51         | 9.16 × 10^9  | 0.324 | 23,793  |
| −47 | CS51 → CS50 + O_2         | 7.92 × 10^9  | 0.749 | 464.3   |
| 48  | CS51 → CS52               | 9.59 × 10^9  | 0.801 | 19,938.2 |
| −48 | CS52 → CS51               | 6.56 × 10^9  | 0.899 | 28,300.9 |
| 49  | CS52 → CS48 + OH          | 8.15 × 10^9  | 1.012 | 4747.6  |
| −49 | CS48 + OH → CS52          | 9.06 × 10^9  | 0.759 | 6456.8  |
| 50  | CS51 → CS53               | 6.32 × 10^11 | 0.354 | 95,193.4 |
| −50 | CS53 → CS51               | 9.75 × 10^10 | 0.807 | 4549.7  |
For CS18 → CS20, the rate constant for CS18 → CS19 is provided, since after the formation of CS19, NO desorbs almost barrierlessly. Clearly, the removal of NO from a nitroso group is significantly faster than the pyridine-N-oxide groups. Moreover, the rate constants for the loss of NO from pyridine-N-oxide groups also differed within about two orders of magnitude, which indicates that the difference in molecular arrangement around a functional group can significantly affect the rate of a reaction involving it.

In the mechanisms discussed above, the pathways for both NO as well as NO₂ were presented. Figure 12 provides a comparison of the rate constants for the initiation reactions of different routes. In all of the cases studied here, the routes leading to NO₂ removal from coke (CS4 → CS9, CS14 → CS21, CS26 → CS29, CS33 → CS37, and CS51 → CS53) had significantly lower rates than the routes leading to NO formation. This is in line with the experimental observation where the concentration of NO₂ in the exhaust gas from FCC regenerator is lower than that of NO (Babich et al., 2005; Dishman et al., 1998; Zhao et al., 1997). In this figure, the differences of several orders of magnitude in rate constants for NO and NO₂ routes also indicate that there may be other routes for the formation of NO₂, such as the reactions of NO with O₂, CO, or CO₂ in the gas phase.

Along with pyridinic and anilinic groups, there are other nitrogen-containing functional groups that can be present on coke, as shown in Figure 1. Thus, NOₓ formation from them is also required to be studied in the future to develop a suitable NOₓ model for a given FCC regenerator based on the functional groups dominating the surface of its coke.
CONCLUSION

The mechanisms for the formation of NO and NO\textsubscript{2} during coke oxidation in FCC regenerators have been studied using density functional theory. The energetics of the elementary reactions involved in the mechanisms have been evaluated using B3LYP/6-311++G(d,p). NO\textsubscript{x} formation from two types of nitrogen-containing functional groups (pyridinic and anilinic) were studied using model molecules with free-edge and zig-zag sites. To determine whether the formation of NO\textsubscript{x} is more favorable through the direct attack of O\textsubscript{2} on the N atom, or through the transfer of O atom from a neighboring site to the N atom, some model molecules with a free radical on C atom and the others with a free radical on N atom were chosen. It was found that the addition of O\textsubscript{2} on the C radicals was exothermic and barrierless, while the addition of O\textsubscript{2} on the N radicals was endothermic and had positive activation energies. The overall activation energies required for the formation of NO from those model molecules with radical on N atom were significantly higher than those model molecules with radical on C atom. Moreover, the rate constants of O\textsubscript{2} addition on N radicals were significantly lower than the rate constants for its additional C radicals. These indicate that NO\textsubscript{x} formation results mainly through the transfer of an O atom from a neighboring site to the N atom, and not through the direct addition of O\textsubscript{2} on N atoms on coke. The energetics involved in the formation of NO\textsubscript{2} for all of the model molecules studied in this work were comparatively higher than those for

Figure 11  Rate constants for the desorption of NO from different model molecules. The rate for this reaction, calculated by Montoya et al. (2002b), is also provided.

![Figure 11](image-url)
the formation of NO. By comparing the rate constants for the initiation reactions of the routes leading to NO and NO2 formation, it was clear that NO formation will be preferred over NO2 at all of the temperatures. This may indicate that other reactions

**Figure 12** Rate constants for the initiation reactions of different routes of CS4, CS14, CS26, CS33, and CS51. The rates for the routes involving NO formation were consistently higher for all of these species than that for the route of NO2 formation.
(such as the interactions of NO with O₂, CO, or CO₂) may also be contributing to NO₂ formation in FCC regenerators.

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SUPPLEMENTAL MATERIAL

The energies, coordinates, vibrational frequencies, moments of inertia, and spin multiplicity for all of the chemical species and transition states are provided in the Supplementary Material, which can be accessed on the publisher’s website (10.1080/00102202.2015.1059328).

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