

Modeling of NO_x Emissions from the Laboratory Regeneration of Spent Fluid Catalytic Cracking Catalyst

Scott A. Stevenson,[†] Richard F. Socha,* and Mark F. Mathias[‡]

ExxonMobil Research and Engineering Company, Annandale, New Jersey 08801

We have collected data on the emissions of NO, HCN, and N₂ during the regeneration of spent fluid catalytic cracking catalyst in two different laboratory-scale units. We have developed a model that describes how coke nitrogen is converted into gas-phase nitrogen-containing species during catalyst regeneration. In this model, the combustion of coke causes the volatilization of nitrogen as HCN, which then can be oxidized to NO or hydrolyzed to NH₃. In the presence of coke, NO can be reduced to N₂; this reaction is accelerated by the presence of CO. Our model accurately describes the main elements of the collected emissions data.

Introduction

As stricter regulations have been imposed, refinery operators have sought ways to reduce NO_x emissions. Because they contribute a large fraction of total refinery NO_x emissions, emissions from the fluid catalytic cracking (FCC) regenerator have received considerable attention. Typically, an FCC regenerator will produce 50–500 ppm of NO_x, depending on its design and operating conditions;^{1–3} this can represent up to half of the total refinery NO_x emissions.⁴ A variety of approaches to reducing FCC regenerator NO_x emissions have been detailed in the patent literature, including catalyst modifications,^{5–7} modifications to the CO combustion promoter,^{8–12} changes in the regenerator design,^{13–16} optimal control of operating parameters, for example, temperature, coke on the catalyst, amount of flue gas O₂, and promoter level,^{17,18} addition of fuel,¹⁹ promotion of selective or nonselective catalytic reduction of NO by NH₃,^{20–24} conversion of NH₃ to nitrogen,²⁵ treatment of the feed,²⁶ or modification of the riser design. Some of these strategies, especially those involving design modifications, are only conceptual and have not been tested under refinery conditions, while others are based on limited data or experience and may not be applicable to other operating conditions or regenerator designs. Most are backed with little fundamental understanding of the mechanism of regenerator NO_x formation, and evaluating their applicability to a specific unit is problematic.

In recent years, some published studies have begun to address the underlying chemistry of NO_x formation in the FCC regenerator. The largest body of published work has come from a group at Grace Davison, a leading manufacturer of FCC catalyst. Their work, performed in both pilot-^{3,27,28} and laboratory²⁹-scale FCC units, showed that only 3–5% of the total nitrogen fed to the FCC unit was released as NO_x from the regenerator;^{3,27,28} this is in reasonable agreement with published reports of 2–8% for commercial units.¹ The Grace

researchers observed that approximately half of the feed nitrogen was released during the regeneration of the spent catalyst but that only 10–15% of this nitrogen was converted to NO; the remainder was emitted as N₂.^{3,27} Experiments in which the spent catalyst was regenerated with an O₂/argon mixture suggested that thermal NO_x, i.e., the conversion of atmospheric nitrogen to NO_x, did not play a significant role in regenerator NO_x formation.^{3,27} Although no data were presented, analogies to coal combustion were used to suggest that HCN and NH₃ were probably intermediates in the conversion of coke nitrogen to NO.^{2,3} They suggested that NO could be reduced to N₂ by either coke, CO, or NH₃, with metals such as Ni and V possibly playing an important role in the reduction of NO by CO.^{2,3,27,28} Decreasing excess O₂ was found to reduce NO_x.^{3,27} Increasing concentrations of Pt in the catalyst were found to increase NO_x emissions,^{2,3,27–29} in agreement with earlier reports.¹⁸

Very recent studies into the formation and reaction of nitrogen-containing species in FCC suggest that the nitrogen in FCC coke is contained in polycyclic aromatic compounds.³⁰ During regeneration, the pyrolysis of these compounds leads to the formation of HCN and NH₃, which can be converted to NO by oxidation; this oxidation is accelerated by the presence of Pt-based CO combustion promoters. It was proposed that N₂ could be formed either from the reduction of NO by CO or from the reaction of NO and NH₃.³¹

The goal of our work was to develop a basic understanding of the chemistry underlying NO_x formation in the FCC regenerator. In this paper, we summarize the results of some of our mechanistic studies, describe the development of a simple regenerator model, and compare the results of this model with emissions measurements made during the laboratory regeneration of spent catalyst.

Experimental Section

Two different catalyst regeneration experiments were carried out. In the first experiment, referred to as the batch-burn experiment, a quartz fixed fluid-bed reactor was charged with 10 g of a spent FCC catalyst, which was fluidized by a flow of 400 cm³/min of helium (20 °C, 1 atm). The catalyst temperature was raised to 700 °C under a helium flow; after the temperature stabi-

* To whom correspondence should be addressed. E-mail: richard.f.socha@exxonmobil.com.

[†] Current address: SABIC Americas, Inc., 1600 Industrial Boulevard, Sugar Land, TX 77478. E-mail: scott.stevenson@sabicusa.com.

[‡] Current address: General Motors—Fuel Cell Activities, 10 Carriage Street, Honeoye Falls, NY 14472.

lized, a gas mixture containing 1.65% O_2 with balance helium was introduced. The composition of the flue gas was monitored until the concentrations of the combustion gases fell to near zero, indicating that combustion was complete and that all coke had been removed from the catalyst; this required approximately 40 min. Under reaction conditions, the reactor pressure was approximately 6 psig (140 kPa) and the density of the fluidized catalyst was approximately 0.49 g/cm^3 .

In the second set of experiments, referred to as the continuous-burn experiments, a different quartz fixed fluid-bed reactor was used that allowed the continual addition of coked FCC catalyst and the simultaneous withdrawal of partially regenerated catalyst. Catalyst was added from a hopper by means of a pressurized screw feeder and a catalyst feed tube, which introduced the catalyst to the bottom of the fixed fluid bed. Catalyst was withdrawn by means of an open tube extending from the top of the catalyst bed through the bottom of the reactor into a collection vessel. The height of this tube defined the height of the fixed fluid bed, since catalyst pushed higher than this level would fall into the tube and out of the reactor; this maintained the total catalyst inventory at approximately 8.3 g. In these experiments, the reactor was maintained at a constant temperature of 700°C ; the reactor pressure was approximately 6 psig. A mixture of 2.79% O_2 in helium was fed to the bottom of the reactor at a rate of $400 \text{ cm}^3/\text{min}$ (20°C , 1 atm), while the catalyst feed rate was varied from 0.25 to 2.25 g/min . A constant catalyst feed rate was maintained until the flue gas concentrations became stable, indicating that steady state had been reached.

Flue gas concentrations were measured by a combination of methods. NO and NO_2 were measured continuously by a Beckman chemiluminescence NOx analyzer. CO and CO_2 were measured continuously by a Siemens nondispersive infrared analyzer. O_2 was measured continuously by a Custom Sensors electrochemical analyzer. During the batch-burn experiment, N_2 was measured at 2.5 min intervals using an MTI Micro-sensor gas chromatograph. Spot measurements of hydrogen cyanide and ammonia were made using Matheson–Kitagawa tubes, but NH_3 levels remained below the detection limit of the tubes.

No NH_3 or NO_2 was detected during either experiment. The absence of NO_2 is consistent with the fact that the equilibrium ratio of NO_2 to NO under these conditions is less than 0.02. Material balances for the batch-burn run were as follows: carbon, 88%; nitrogen, 78%; hydrogen, 74%. It is likely that some of this discrepancy is due to losses that occurred during the heating of the sample in helium before O_2 was introduced. Material balances were not obtained for the continuous-burn experiments.

The two similar samples of spent FCC catalyst used were obtained from a refinery FCC unit and consisted primarily of Y zeolite in a silica–alumina clay matrix. Elemental analysis of the sample used for the batch-burn experiment indicated that it contained approximately 0.69% carbon, 0.021% nitrogen, 0.031% hydrogen, 0.009% sulfur, and 0.8 ppm platinum. Elemental analysis of the sample used in the continuous-burn experiments indicated that it contained 0.73% carbon, 0.025% nitrogen, 0.030% hydrogen, 0.006% sulfur, 0.029% nickel, 0.048% iron, and 0.8 ppm platinum.

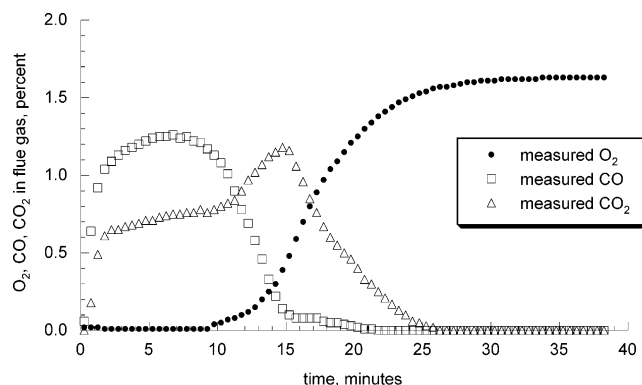


Figure 1. Flue gas concentrations as a function of time for batch-burn experiments.

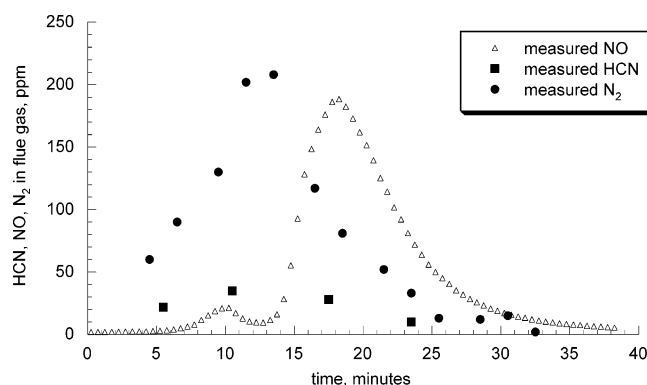


Figure 2. HCN, NO, and N_2 concentrations as a function of time for batch-burn experiments.

The results of some kinetic experiments are briefly described; these experiments and their results are not discussed in detail, but the results were useful in the formulation of our reaction model. In these experiments, known amounts of one or two reactant gases (e.g., HCN and O_2 or NO and CO) were passed over the FCC catalyst and the products were measured using Fourier transform infrared spectroscopy. In most of these experiments, the coke was removed from the catalyst by combustion prior to use. When the inlet concentrations and reaction conditions were varied, the kinetics, rate constants, and activation energies of the various reactions could be estimated.

Results of the Batch-Burn Experiment

Figure 1 shows the amounts of CO, CO_2 , and O_2 measured in the flue gas as a function of time for the batch-burn experiment. CO and CO_2 both increase sharply during the first 2 min as O_2 is introduced into the bed and then remain relatively constant until a total of about 10 min has elapsed. Up to this point, essentially no O_2 is observed in the flue gas. However, at 10 min, O_2 begins to break through; as soon as it does, the CO concentration falls sharply. At this point, the CO_2 concentration rises, reaching a maximum at approximately 15 min, and then falls steadily as the amount of carbon left on the catalyst approaches zero. By 26 min, the measured CO and CO_2 concentrations have fallen below the detection limit of 0.01%, although the flue gas O_2 concentration does not reach its inlet value until almost 34 min has elapsed.

Figure 2 shows the measured emissions of the nitrogen-containing species as a function of time. As mentioned above, no NH_3 was detected during this experi-

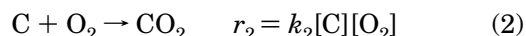
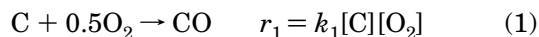
ment. Significant amounts of HCN and N₂ are observed from the onset of the run, but NO does not exceed 4 ppm until more than 6 min has passed. The HCN concentration reaches a maximum of 35 ppm at about 10.5 min; the N₂ concentration peaks shortly thereafter, reaching 208 ppm at 13.5 min. In contrast, the NO concentration remains low until 14 min, after which it rises rapidly and reaches a maximum of about 190 ppm at 18 min. After this time, all nitrogen-containing species decline gradually, with NO being the last to disappear; the NO concentration does not fall below 10 ppm until almost 34 min has elapsed.

Model Formulation

By combining our own experimental observations with literature information on combustion, we developed a simple model of catalyst regeneration that describes our observed emissions data, is useful in predicting and understanding NO_x emissions from actual FCC regenerators, and can be used to develop effective control strategies for commercial units.

General Approach. The catalyst was assumed to be perfectly mixed. The most important consequence of this assumption is that the catalyst carbon and nitrogen concentrations are not a function of position in the bed. Direct observation of the catalyst under reaction conditions suggested that this was a reasonable assumption. The gas moving through the bed was assumed to observe plug-flow behavior. The effects of mass transfer were assumed to be insignificant, and the catalyst bed was assumed to be isothermal. The temperature of the gas above the bed was allowed to rise according to the extent of homogeneous CO oxidation, using the calculated heat of combustion and the heat capacities of the gas components. Kinetic expressions for each of the reactions included in the model were converted to ordinary differential equations and solved simultaneously using standard numerical techniques. Rate constants for each of the kinetic equations were adjusted until the best fit to the data was achieved.

Carbon Reaction Network. Four reactions were used to model the formation of CO and CO₂: the combustion of carbon to CO, the combustion of carbon to CO₂, the oxidation of CO to CO₂ in the catalyst bed, and the homogeneous oxidation of CO to CO₂ in the gas phase above the bed. Coke combustion is reported to be first order in carbon concentration;³² it is reported to be first order in O₂ when combustion is diffusion-limited³² but may be somewhat less than first order in O₂ when diffusion is not rate-controlling.³³ We assumed that the oxidation of coke to both CO and CO₂ was first order in both carbon and O₂.



It has been observed that the ratio of CO to CO₂ formed from carbon combustion is a function of temperature only;^{33,34} from the correlation of Arthur,³³ this ratio would be expected to be 4.1 at 700 °C. However, we achieved better agreement between the model and the experimental data by using a ratio of 2.8.

The homogeneous oxidation of CO to CO₂ has been observed to be first order in CO concentration and half order in O₂.³⁵ The kinetics of heterogeneous CO oxidation are complex; a reaction order near 1 for O₂ and a

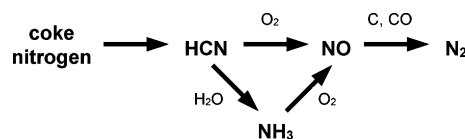
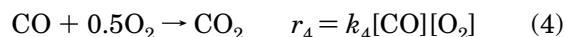
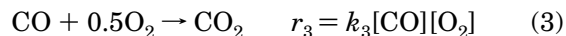


Figure 3. Proposed pathway for conversion of nitrogen-containing species.

negative reaction order in CO are typically observed over noble metals.^{36,37} However, these catalytic studies were conducted at temperatures of 500 °C and below; the actual kinetics under regenerator conditions are not known. Lacking better information, we have assumed that both the homogeneous and catalytic oxidations of CO are first order in both O₂ and CO.



This allows us to combine the heterogeneous and homogeneous rates in the catalyst bed. In the section of the reactor above the bed, however, only homogeneous oxidation is assumed to occur. The catalyst bed may safely be assumed to be isothermal; however, because of the low heat capacity of helium, homogeneous oxidation above the bed may result in a significant temperature rise, depending on the rate of heat transfer out of the gas to the reactor. To achieve a reasonable fit of the data, it was necessary to allow this homogeneous combustion to raise the temperature of the gas above the bed adiabatically. We believe that this effect is responsible for the sharp rise in the CO₂ concentration observed at approximately 10–12 min; at this point, CO oxidation above the bed causes a temperature rise large enough to significantly increase the total amount of homogeneous combustion. Before this time, the concentration of O₂ leaving the bed is too low to support enough CO combustion to result in a large temperature rise. After approximately 15 min, there is not enough CO leaving the bed to result in a large temperature rise; this is why the CO concentration declines more slowly after this time.

The combustion of the hydrogen in the coke to water was assumed to proceed at a rate proportional to the rate of carbon combustion. In agreement with the experimental data, the model assumed that all of the hydrogen was removed from the catalyst by the time that 80% of the carbon was removed.

Nitrogen Reaction Network. Although a network involving a large number of reactions can be envisioned, we propose that the formation and interconversion of the various nitrogen-containing species can be accounted for by only five reactions: the volatilization of coke nitrogen as HCN, the oxidation of HCN to NO, the hydrolysis of HCN to NH₃, the oxidation of NH₃ to NO, and the reduction of NO to N₂ by carbon. This network is shown schematically in Figure 3.

Most of the evidence for the volatilization of HCN as the initial step in the reaction pathway is indirect but comes from several sources. It has been shown that the heating of nitrogen-containing organic compounds (e.g., pyridine and benzonitrile) in the absence of air results in the release of HCN;^{38,39} in fact, essentially all of the nitrogen in these compounds is converted to HCN. The same study also found that pyrolysis of fuel oils under inert gas yields HCN. Studies of NO_x formation during coal combustion have also reached the conclusion that

HCN volatilization is the primary source of nitrogen release.^{40,41} Very recent studies have demonstrated the release of HCN during temperature-programmed desorption of coked FCC catalyst; NH₃ was suggested to form via hydrolysis of HCN or NCO species.³¹ In our own laboratory, we have observed that the heating of coked FCC catalyst to 700 °C and above in inert gas results in the release of HCN. In continuous regeneration studies similar to those presented below but in which the inlet O₂ concentration was varied at a constant catalyst flow rate, as the inlet O₂ concentration was decreased to 1% or less, the amount of NO fell to near zero, while the selectivity to HCN rose to more than two-thirds and the selectivity to N₂ fell to less than one-third. This observation is consistent with the requirement that, as conversion goes to zero, selectivity to all nonprimary products must also go to zero. Finally, the fact that most coke nitrogen is present in aromatic heterocyclic compounds suggests that HCN is the most likely initial product because it can be formed by the breaking of two carbon–carbon bonds, while formation of N₂, NO, or NH₃ would require a more complex rearrangement. Although we cannot rule out that some of the nitrogen released during coke combustion is in the form of other compounds, as suggested by Zhao and co-workers,³ we believe that the majority of it is released as HCN.

Our understanding of coke combustion is not sufficient to predict quantitatively the rate of HCN volatilization. We have, therefore, relied on an empirical correlation of the data to relate the nitrogen concentration in the coke at various times to the carbon concentration. Figure 4 shows that as carbon is initially removed from the catalyst little nitrogen is released; when 20% of the carbon is gone, only 4% of the nitrogen has been removed, while when 50% of the carbon has been burned, less than 20% of the nitrogen has been released. Even when 90% of the carbon has been removed, almost one-third of the original nitrogen remains on the catalyst. These data are consistent with other published data;^{3,27,30} Barth and co-workers³⁰ suggest that the aromatic, homocyclic portions of the nitrogen-containing coke compounds are preferentially oxidized, leaving progressively smaller nitrogen-containing species. We have fitted our data using the function

$$\frac{N}{N_0} = \frac{1.2635 \left(\frac{C}{C_0} \right)^{0.548}}{1 + 0.2635 \left(\frac{C}{C_0} \right)^{2.093}} \quad (5)$$

where N is the nitrogen concentration on the catalyst, N_0 is the initial nitrogen concentration on the catalyst, C is the carbon concentration on the catalyst, and C_0 is the initial carbon concentration on the catalyst. In our model, we have used eqs 1 and 2 to estimate the rate at which carbon is being removed from the catalyst and have then used eq 5 to calculate the rate of HCN release.

Once HCN is released from the coke, two things can happen to it: it can be oxidized to NO, or it can be hydrolyzed to NH₃. We have shown using kinetic studies performed in a fixed fluid-bed reactor that the hydrolysis of HCN does occur over FCC catalyst. We observed that the rate is first order in HCN concentration but zero order in water for water concentrations between 2 and 8%. However, the rate of HCN hydrolysis was found to

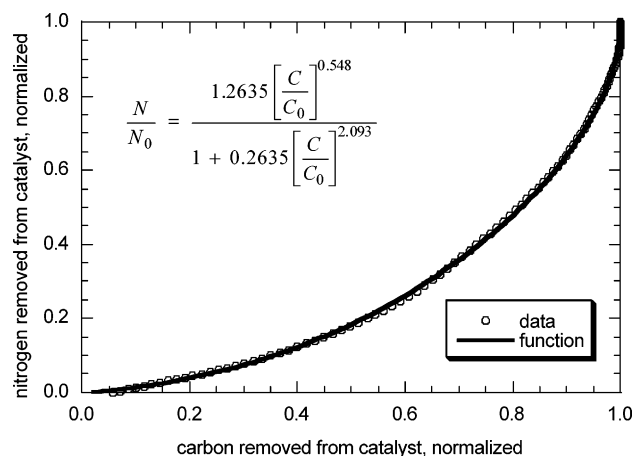


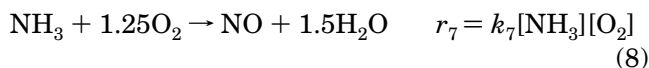
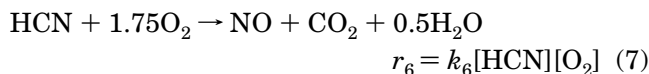
Figure 4. Relationship between nitrogen release and carbon combustion.

be more than an order of magnitude slower than the rate of HCN oxidation in the presence of 1% O₂, suggesting that significant amounts of NH₃ would be observed only if nearly all of the O₂ was consumed and if contact times between the gas and catalyst were relatively long. We have modeled HCN hydrolysis using the equation



In our modeling, we have not adjusted the value of k_5 but have used a value in the range of those estimated from our kinetic studies.

Once formed during regeneration, either HCN or NH₃ can be oxidized to NO. We have carried out measurements of HCN and NH₃ oxidation and have found that both reactions proceed rapidly over coke-free FCC catalyst; the rates of HCN and NH₃ oxidation are approximately equal at 700 °C. Only NO is formed because NO₂ is thermodynamically unstable under these conditions and would be rapidly converted to NO. Kinetic measurements suggested that the rate of HCN oxidation is Langmuir–Hinshelwood first order in HCN concentration and Langmuir–Hinshelwood half order in O₂ concentration. We observed the presence of water to inhibit the rate of HCN oxidation slightly. Both the oxide and metal components of the FCC catalyst were observed to contribute to the oxidation rates. In our model, to reduce the number of adjustable parameters, we have simplified these kinetics and described both HCN and NH₃ oxidation as first order in HCN or NH₃ and first order in O₂, i.e.,



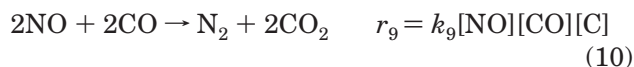
The modeling results were not found to be significantly affected by the kinetic form used for these equations. In the model, the rate constant for HCN oxidation was varied to give the best fit to the data while the rate constant for NH₃ oxidation was assumed to be the same as the rate constant for HCN oxidation.

The overall selectivity of coke nitrogen conversion to N₂ during FCC catalyst regeneration is generally observed to be high for laboratory, pilot, and commercial

units; selectivities of 90–98% are typically observed in commercial operations.^{1,3,27,28} In laboratory measurements, where conditions can be more widely varied, we have observed coke nitrogen to N₂ selectivities of between 25 and 90%. Clearly, there is a reaction or series of reactions that converts nitrogen-containing species to N₂ under regenerator conditions; as discussed below, we believe that the primary reactions responsible for this high N₂ selectivity are the reduction of NO to N₂ by carbon and CO.

It is known in the literature that various types of carbon, including activated carbon,^{42–44} raw coal,^{42,45} coal char,^{42,46} petroleum coke,⁴² graphite,⁴⁷ activated cane sugar charcoal,⁴⁸ and peat,⁴⁵ can reduce NO to N₂. The reduction of NO by FCC coke has been claimed in the patent literature and has been observed by Peters and co-workers.²⁸ We have demonstrated a similar reduction of NO by coked FCC catalyst; we have found that this reaction is first order in both NO concentration and in carbon concentration and is somewhat inhibited by the presence of water. We have also found that the rate of this reaction is greatly accelerated by the presence of percent levels of CO; the rate of NO reduction was found to be approximately 7 times faster in the presence of 1% CO than in its absence. A similar enhancement in the rate of NO reduction over graphite and activated carbon has been previously reported.^{49,50} The reduction of NO by CO has also been proposed by Peters and co-workers;^{3,27,28} they suggest that this reduction is catalyzed by noble metals and metal oxides in the catalyst. However, our experiments indicate that this reduction occurs almost entirely on the FCC coke, where the CO enhances the rate of NO reduction by efficiently removing surface O₂ from the active sites.

On the basis of these observations, we have represented the rate of NO reduction by coked FCC catalyst according to the equations



The overall rate of NO reduction was adjusted by varying k_8 ; k_9 was adjusted such that the ratio of the two rates was in the range of the ratios observed in our kinetic studies.

No other N₂ formation mechanism seems likely to play an important role in the FCC regenerator. A direct conversion of coke nitrogen to N₂, while thermodynamically favorable, is not supported by the studies discussed above and seems unlikely given the low concentration of nitrogen in the coke. The reduction of NO by NH₃, while known to occur at this temperature, is not important because of the more rapid oxidation of NH₃ to NO; additionally, our data indicate that at no point in the catalyst bed are significant quantities of NH₃ and NO present simultaneously. Extensive studies in our laboratory have demonstrated that the reduction of NO by CO in the absence of coke does not occur to any significant degree under these conditions, regardless of the metals content of the catalyst. Finally, because we have used helium rather than nitrogen as the inert gas in our experiments, none of the NO can come from the thermal fixation of N₂; we agree with the Grace group^{3,27,28} that the temperature in an FCC regenerator is too low for significant amounts of NO_x to be formed by this mechanism.

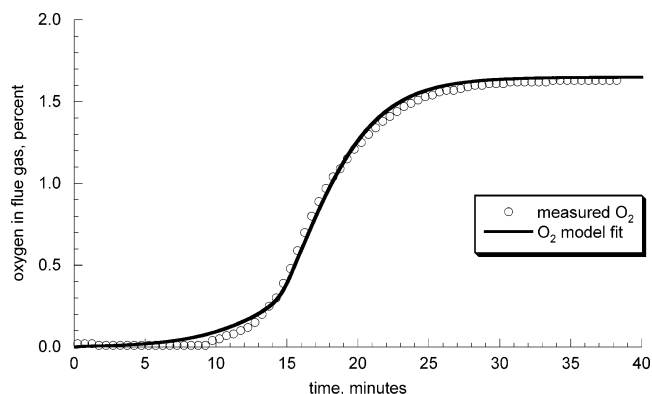


Figure 5. Flue gas O₂ concentration as a function of time for batch-burn experiments.

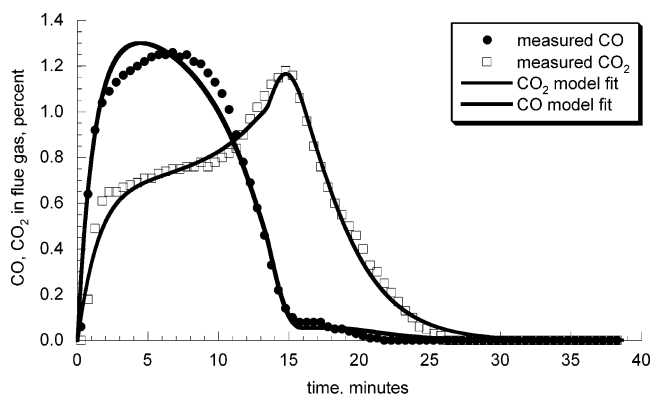


Figure 6. Flue gas CO and CO₂ concentrations as a function of time for batch-burn experiments.

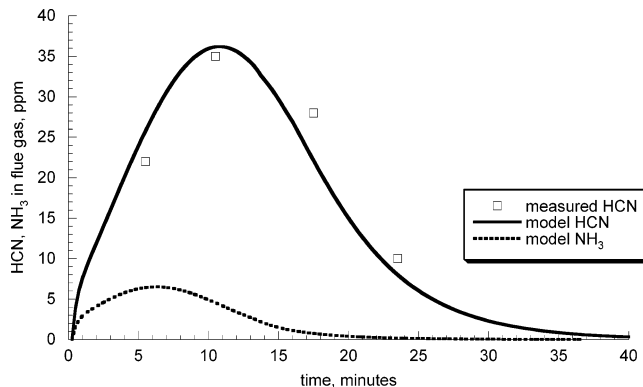


Figure 7. Flue gas HCN and NH₃ concentrations as a function of time for batch-burn experiments.

Modeling Results: Batch-Burn Experiment

The results of our kinetic modeling of the batch-burn data are shown in Figures 5–9. The data were modeled using HiQ software. The differential equations were approximated using a Runge–Kutta–Fehlberg method, and the parameters were optimized using a least-squares approach.

The fits shown were obtained by independently varying six of the nine kinetic constants described above; to simplify the fitting, k_5 was held constant at a value consistent with our kinetic studies, k_7 was set equal to k_6 , and k_9 was set such that the ratio of r_8 to r_9 was the same as that observed in our kinetic studies. Figure 5 shows that model predictions of the flue gas O₂ concentration are in good agreement with the experimental observations, although the model predicts O₂ breakthrough to occur somewhat earlier than was actually

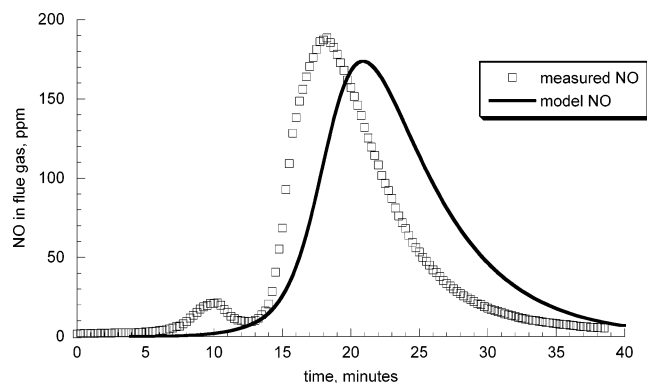


Figure 8. Flue gas NO concentration as a function of time for batch-burn experiments.

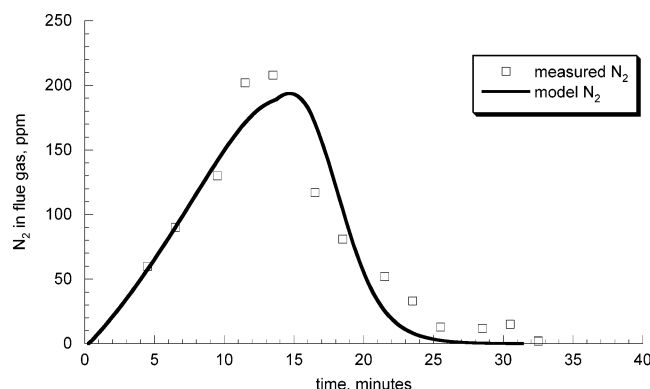


Figure 9. Flue gas N₂ concentration as a function of time for batch-burn experiments.

observed. Figure 6 compares the CO and CO₂ concentrations predicted by the model with the data. The model correctly predicts the initial rise of CO and CO₂, the steep fall of CO and the rise of CO₂ that begins at approximately 10 min, and the plateau and slow decrease of CO as the remainder of the carbon on the catalyst is removed. One small but important deviation between the model and the data is that the observed CO₂ flue gas concentration falls to zero at approximately 26 min, indicating that the removal of coke from the catalyst is complete at this point. In contrast, the model predicts that the CO₂ concentration does not fall below 0.01% (the detection limit of the CO₂ nondispersive infrared analyzer) until almost 5 min later. Although the disagreement in this region is small, not exceeding 500 ppm CO + CO₂, it has significant consequences for N₂ and NO emissions, since a large amount of the coke nitrogen is released during removal of the last fraction of the carbon. To fit the actual shape of the CO₂ data would have required that the rate constants for coke combustion, k_1 and k_2 , increase as the amount of coke remaining on the catalyst nears zero. It is possible that carbon combustion is at least partially limited by the rate of O₂ diffusion when the coke concentration is high and that an increase in the diffusion rate as the combustion nears completion gives rise to an apparent increase in the combustion rate constants.

Figure 7 shows a comparison between observed and predicted HCN emissions. The agreement between the model and the data is excellent, especially considering the measurement error of the Matheson–Kitagawa tubes. In our model, only two factors have a significant effect on flue gas HCN concentrations: the rate of coke combustion and the rate of HCN oxidation. The ability

Table 1. Comparison of Observed Selectivities (%) with Model Predictions

species	observed	model
HCN	7.8	8.1
NH ₃	0.0	1.0
NO	23.7	25.9
N ₂	68.5	65.0

of the model to accurately fit the data suggests that the actual emissions are controlled primarily by these two factors.

Figure 7 also shows the concentration of flue gas NH₃ predicted by the model using the rate of HCN hydrolysis predicted from our kinetic experiments. The model predicts that the maximum concentration of NH₃ is less than 7 ppm; concentrations in this range would have been difficult to detect with the Matheson–Kitagawa tubes used. Because the rate of NH₃ oxidation is much larger than the rate of HCN hydrolysis, any NH₃ that is formed is quickly removed by oxidation if excess O₂ is available, as is the case after 12–14 min. Before this time, the amount of NH₃ is controlled by the rate of hydrolysis; in our laboratory reactor, the short contact time leads to low amounts of NH₃. In commercial units, where gas/solid contact times are typically much longer, we would expect that in the absence of excess O₂ much of the HCN is converted to NH₃. In any case, it is very unlikely that any HCN is emitted to the atmosphere from commercial FCC regenerators, since if these units are operated with low excess O₂ (so-called partial burn mode), they are almost invariably operated in conjunction with a CO boiler; the high temperatures achieved in this boiler will convert all of the reduced nitrogen species to NO and N₂.

Figure 8 shows the model predictions for NO emissions as a function of time. In general, the shape of the NO emissions curve obtained from the model is similar to that observed in the actual experiment. However, the entire model curve is shifted in time by approximately 3 min relative to what was actually measured. We believe that this is largely a consequence of the fact that the model does not precisely match the carbon burning data for times of 22 min and later, as discussed above. Because the model releases the carbon, and hence the coke nitrogen, more slowly than is actually observed, the NO peak is shifted by several minutes, since the nitrogen released during this time period is converted almost entirely to NO. If the coke release was modified, for example, by increasing k_1 and k_2 as the amount of coke remaining on the catalyst nears zero, as discussed above, the NO peak would shift forward in time and more closely approximate the observed emissions. Additionally, the model fails to capture the small NO peak observed from 8 to 12 min. This peak may be due to poor mixing in a small region of the bed, or it may be due to homogeneous conversion of some HCN and NH₃ to NO in the volume above the bed. No artifact like this was observed in the continuous experiments.

Figure 9 shows a comparison of the observed N₂ concentrations with the model predictions for N₂. In general, the agreement is good, although the model predicts the amount of N₂ formed to decrease more rapidly than is actually observed; this may reflect regions of the catalyst bed that are not perfectly mixed. The model does correctly predict that N₂ is the predominant nitrogen-containing flue gas species except near the end of the experiment, where the CO concentration is low and the O₂ concentration is high.

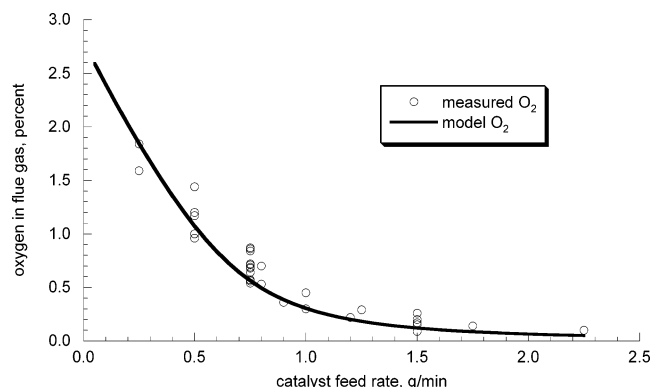


Figure 10. Flue gas O_2 concentration as a function of the catalyst feed rate for continuous-burn experiments.

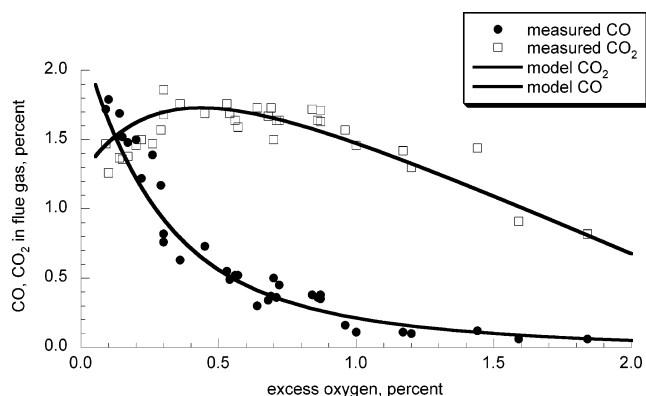


Figure 11. Flue gas CO and CO_2 concentrations as a function of excess O_2 for continuous-burn experiments.

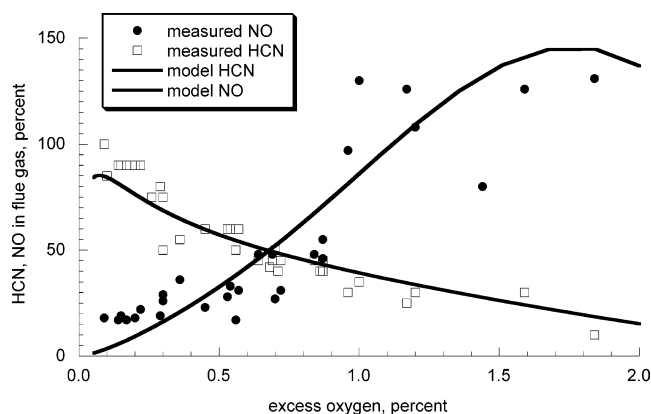


Figure 12. Flue gas HCN and NO concentrations as a function of excess O_2 for continuous-burn experiments.

Table 1 compares the total observed selectivities of coke nitrogen conversion to HCN, NH_3 , NO, and N_2 with those calculated from the model.

Modeling Results: Continuous-Burn Experiments

To further test the validity of our model, we attempted to use it to describe the data collected in our continuous-burn experiments; these data are shown in Figures 10–12. Figures 10 and 11 show that flue gas O_2 , CO, and CO_2 concentrations vary with the catalyst feed rate as might be expected. When the rate of catalyst addition is low, most of the coke is removed from the catalyst and excess O_2 is high; consequently, low concentrations of flue gas CO are observed. As the catalyst feed rate is increased, however, the amount of carbon fed to the

reactor increases accordingly; this results in a sharp decrease in excess O_2 and an increase in the CO/ CO_2 ratio.

To model these data, we have used the same values of k_1 , k_2 , k_3 , and k_4 that were found to give the best fit to the batch-burn data. The only change made to the carbon-burning portion of the model was that the rate of temperature rise above the catalyst bed due to homogeneous CO oxidation was decreased by a factor of 3.5; this change is most likely due to a much higher level of catalyst fines in the continuous-burn experiments. The agreement between the model and the data, as shown in Figures 10 and 11, is excellent for CO, CO_2 , and O_2 , especially considering that the values of k_1 , k_2 , k_3 , and k_4 were not adjusted to improve the fit.

Unfortunately, using the values estimated for k_5 , k_6 , k_7 , k_8 , and k_9 from modeling of the batch-burn data did not produce equally satisfying results for the continuous-burn data. To obtain an acceptable fit of the model to the data, it was necessary to decrease k_6 , k_7 , k_8 , and k_9 by factors ranging from 2.0 to 2.4 (see Table 2); k_5 was decreased by a like amount for the sake of consistency. This gave good agreement between the model and the data for both HCN and NO, as can be seen in Figure 12. The model does slightly underpredict NO emissions at high catalyst feed rates (i.e., when excess O_2 is low), where the observed NO concentrations do not tend to zero as quickly as predicted; this is most likely due to imperfect mixing of the catalyst under these conditions. The model also predicts that most of the coke nitrogen is converted to N_2 except at very low catalyst feed rates, where the excess O_2 is high; N_2 selectivities range from 30 to 84% across the range of feed rates studied. The model predicts that NH_3 concentrations will not exceed 8 ppm under any of the conditions studied, in agreement with the fact that no significant amounts of NH_3 were observed using Matheson–Kitagawa tubes. The low levels of water and the relatively short contact time in our laboratory-scale reactor appear to preclude the formation of large amounts of NH_3 ; however, in a larger-scale unit, it is possible that HCN hydrolysis occurs to a much larger degree. We believe, however, that the general trends in the emissions of nitrogen-containing species seen in Figure 12 are consistent with the reaction pathway presented in Figure 3. When little excess O_2 is present, the oxidation of HCN and NH_3 is slow relative to NO reduction because the O_2 concentration is low and concentrations of coke and CO are high. Under these conditions, NO emissions will be low relative to the emissions of reduced nitrogen species. In contrast, when significant excess O_2 is present, the oxidation of HCN and NH_3 is fast relative to the reduction of NO because the O_2 concentration is higher and the concentration of the reductants, coke and CO, has been significantly reduced. Under these conditions, NO emissions will be higher than those of HCN and NH_3 .

It is not clear why the values of k_6 , k_7 , k_8 , and k_9 required to produce a good fit with the data were slightly smaller in the case of the continuous-burn data. One possible explanation is that the water concentrations were significantly higher in the continuous-burn experiments because the catalyst was not dried prior to use. In our kinetic experiments, we observed water to inhibit the rates of HCN oxidation and NO reduction by CO and to have little effect on the rate of NH_3 oxidation. It

Table 2. Comparison of Experimentally Estimated Values of Rate Constants with Those Used in Modeling

constant ^a	reaction	units	batch-burn model	continuous-burn model	kinetic experiments
k_1	CO formation	cm ³ /g _C /min	7.2×10^4	7.2×10^4	
k_2	CO ₂ formation	cm ³ /g _C /min	2.5×10^4	2.5×10^4	
k_3	homogeneous CO oxidation	cm ³ /mol/min	6.3×10^7	6.3×10^7	
k_4	catalytic CO oxidation	cm ⁶ /mol/g _{cat} /min	2.3×10^8	2.3×10^8	
k_5	HCN hydrolysis	cm ³ /g _{cat} /min	45	22	40–95
k_6	HCN oxidation	cm ⁶ /mol/g _{cat} /min	6.8×10^9	3.4×10^9	$(1.6–2.0) \times 10^{10}$
k_7	NH ₃ oxidation	cm ⁶ /mol/g _{cat} /min	6.8×10^9	3.4×10^9	$(2.2–13.4) \times 10^9$
k_8	NO reduction	cm ³ /g _C /min	2.1×10^5	8.6×10^4	$(1.4–4.4) \times 10^4$
k_9/k_8	CO-assisted NO reduction	cm ³ /mol	3.3×10^7	3.3×10^7	$(1.1–4.6) \times 10^7$

^a k_6 and k_8 were adjusted to provide the best fit, k_5 and the ratio k_9/k_8 were held constant, and k_7 was set equal to k_6 .

is also possible that the actual temperature was slightly lower in the case of the continuous-burn data.

Table 2 summarizes the values of the kinetic constants used to fit both data sets and compares these to estimates made from our kinetic measurements of the individual reactions. The values used in the modeling for k_5 , k_7 , and the ratio k_9/k_8 are within the ranges estimated by the kinetic measurements (k_5 and the ratio k_9/k_8 were fixed within these ranges and were not varied). However, the values of k_6 needed to get good agreement between the model and the data are 2.5–5 times smaller than those estimated from the kinetic measurements. This suggests that the rate of HCN oxidation is somewhat slower during the actual regeneration of the FCC catalyst than would be expected from the rate data obtained by passing HCN and O₂ over a coke-free FCC catalyst. It is possible that the difference is due to the state of the catalyst; coke or adsorbed gas species present on the catalyst during regeneration may slow the rate significantly relative to the rate obtained over a clean catalyst in the presence of only HCN and O₂. Table 2 also shows that the values of k_8 used in the modeling are 2–5 times larger than the highest values estimated from the kinetic measurements; because k_9 was set as a ratio to k_8 , it is also larger than expected from the kinetic data. This indicates that the rate of NO reduction is significantly faster during catalyst regeneration than would be predicted from the data obtained by passing NO, with and without CO, over coked catalyst. One possible explanation for this discrepancy is that during combustion both NO and CO are formed at the surface of the catalyst particles; if reduction of NO and/or oxidation of CO are fast relative to diffusion, their local concentrations may be higher than the concentrations in the bulk of the gas phase and the rate of NO reduction would be higher than expected based on the bulk concentrations. It is also possible that the coke combustion process creates additional active sites for NO reduction, so that the activity for NO reduction is higher in the presence of O₂ than in its absence. Further work is necessary to determine the cause of these differences between the kinetic data and the model predictions.

Summary and Conclusions

The simple model that we have proposed for the combustion of FCC coke effectively describes the nitrogen emissions observed during both the batch- and continuous-burn experiments. We believe that the same reaction pathway used to model the formation of nitrogen-containing species during the combustion of FCC coke in the laboratory can also be used to explain some of the trends in emissions of these same species in commercial FCC regenerators.

For example, NO emissions from commercial units increase as excess O₂ increases.^{2,3,27} Our model suggests that this is because when excess O₂ is high, the amount of carbon on the catalyst and the concentration of CO are low and the rate of NO reduction becomes slower. Our model predicts that the highest selectivity of coke nitrogen to N₂ will be found where the oxidation of HCN and NH₃ is roughly balanced with the reduction of NO to N₂.

NO emissions from commercial units are also observed to rise when large amounts of Pt-containing CO oxidation promoter are added.^{2,8,18,27,29} Our model explains this behavior in terms of lower CO concentrations and hence slower rates of NO reduction. Similarly, any change to the effectiveness of the CO combustion promoter, e.g., by steaming it,⁹ by poisoning it,¹⁸ or by replacing Pt with a metal with a lower ability to oxidize CO,¹⁰ will also reduce NOx by increasing the amount of CO available to reduce NOx. As a practical strategy, however, such procedures are not terribly useful because the same result could be achieved by simply adding less promoter.

Acknowledgment

We thank Dave Shihabi, Gary Green, Minas Apelian, Allen Hansen, Amos Avidan, and Sanjay Sharma for their suggestions, comments, and contributions during the course of this work.

Literature Cited

- (1) Avidan, A. A.; Beech, J. H.; Schipper, P. H.; Miller, R. B.; Johnson, T. E. Comparison of the Performance of Single and Two-Stage Fluid Bed Regenerators. NPRA Annual Meeting, San Antonio, TX, 1996.
- (2) Cheng, W.-C.; Kim, G.; Peters, A. W.; Zhao, X.; Rajagopalan, K. Environmental Fluid Catalytic Cracking Technology. *Catal. Rev.-Sci. Eng.* **1998**, 40 (1 & 2), 39–79.
- (3) Zhao, X.; Peters, A. W.; Weatherbee, G. W. Nitrogen Chemistry and NOx Control in a Fluid Catalytic Cracking Regenerator. *Ind. Eng. Chem. Res.* **1997**, 36 (11), 4535–4542.
- (4) Mathias, M. F.; Stevenson, S. A.; Socha, R. F. The NOx Formation Mechanism in an FCC Regenerator. AIChE Annual Meeting, Los Angeles, 1997.
- (5) Bhattacharyya, A.; Foral, M. J.; Reagan, W. J. Process for Removing Sulfur Oxides or Nitrogen Oxides from a Gaseous Mixture in an FCC Process. U.S. Patent 5,750,020, May 12, 1998.
- (6) Dieckmann, G. H.; Labrador, E. Q. FCC NOx Reduction Using a Perovskite-type Additive. U.S. Patent 5,565,181, Oct 15, 1996.
- (7) Yaluris, G.; Rudesill, J. A. Nitrogen oxide emission reduction from petroleum cracking units using compositions containing exhaust gas catalysts and oxygen storage components. U.S. Patent 6,660,683, Dec 9, 2003.
- (8) Blanton, W. A. NOx Control in Platinum-promoted Complete Combustion Cracking Catalyst Regeneration. U.S. Patent 4,290,878, Sept 22, 1981.
- (9) Chessmore, D. O.; Rudy, C. E., Jr. NOx Control in Cracking Catalyst Regeneration. U.S. Patent 4,199,435, Apr 22, 1980.

- (10) Meguerian, G. H.; Lorntson, J. M.; Vasalos, I. A. Catalytic Cracking with Reduced Emission of Noxious Gas. U.S. Patent 4,300,997, Nov 17, 1981.
- (11) Iliopoulou, E. F.; Efthimiadis, E. A.; Vasalos, I. A.; Barth, J. O.; Lercher, J. A. Effect of Rh-based additives on NO and CO formed during regeneration of spent FCC catalyst. *Appl. Catal., B* **2004**, 47 (3), 165–175.
- (12) Efthimiadis, E. A.; Iliopoulou, E. F.; Lappas, A. A.; Iatridis, D. K.; Vasalos, I. A. NO Reduction Studies in the FCC Process. Evaluation of NO Reduction Additives for FCCU in Bench- and Pilot Plant-Scale Reactors. *Ind. Eng. Chem. Res.* **2002**, 41 (22), 5401–5409.
- (13) Myers, D. N.; Tretyak, M.; Pittman, R. M.; Niewiedzial, S. FCC spent catalyst distributor. U.S. Patent 6,809,054, Oct 26, 2004.
- (14) Hall, R. N.; Carlson, F. B.; Thomson, W. J. Process for Combusting Carbonaceous Solids Containing Nitrogen. U.S. Patent 4,413,573, Nov 8, 1983.
- (15) Scott, J. W. Three-stage Catalyst Regeneration. U.S. Patent 4,325,833, Apr 20, 1982.
- (16) Scott, J. W. Method for Removing Coke from Particulate Catalyst. U.S. Patent 4,313,848, Feb 2, 1982.
- (17) Altrichter, D. M. Process of the Reduction of NO_x in an FCC Regeneration System by Select Control of CO Oxidation Promoter in the Regeneration Zone. U.S. Patent 5,021,144, June 4, 1991.
- (18) Luckenbach, E. C. Method of Reducing Oxides of Nitrogen Concentration in Regeneration Zone Flue Gas. U.S. Patent 4,235,704, Nov 25, 1980.
- (19) Blanton, W. A. Adding Fuel in Catalyst Regeneration. U.S. Patent 4,309,309, Jan 5, 1982.
- (20) Blanton, W. A.; Dimpfl, W. L. Process of Controlling NO_x in FCC Flue Gas in Which an SO₂ Oxidation Promoter Is Used. U.S. Patent 4,521,389, June 4, 1985.
- (21) Dimpfl, W. L.; Blanton, W. A. Simultaneous Sulfur Oxide and Nitrogen Oxide Control in FCC Units Using Cracking Catalyst Fines with Ammonia Injection. U.S. Patent 4,434,147, Feb 28, 1984.
- (22) Nishio, K.; Kawasaki, R.; Sugitani, T. Method for Denitration of Waste Gases from Petroleum Cracking Catalyst Regeneration. Jpn. Patent 63,156,524, 1988.
- (23) Sugitani, T. Removal of Nitrogen Oxides from Waste Gas. Jpn. Patent 62,273,040, 1987.
- (24) Barth, J. O.; Jentys, A.; Iliopoulou, E. F.; Vasalos, I. A.; Lercher, J. A. Novel derivatives of MCM-36 as catalysts for the reduction of nitrogen oxides from FCC regenerator flue gas streams. *J. Catal.* **2004**, 227 (1), 117–129.
- (25) Samish, N. C.; Gwyn, J. E. Process for the Reduction of Ammonia in Regeneration Zone Off-gas by Select Recycle of Certain-sized Ammonia Decomposition Catalysts. U.S. Patent 4,755,282, July 5, 1988.
- (26) Occeili, M. L. Process for Cracking Nitrogen-containing Feeds. U.S. Patent 4,731,174, Mar 15, 1988.
- (27) Peters, A. W.; Weatherbee, G. D.; Zhao, X. Origins of NO_x in the FCCU Regenerator. *Fuel Reformulation* **1995** (May/June), 45–50.
- (28) Peters, A. W.; Suárez, W.; Koranne, M.; Pereira, C.; Weatherbee, G. D.; Zhao, X.; Davey, S.; Lakhanpal, B. Control and Origin of NO_x in the FCCU Regenerator. The Performance of XNO_x-2, A Commercial NO_x Reduction Catalyst. *Prepr. Symp., Am. Chem. Soc., Div. Fuel Chem.* **1996**, 41 (3), 896–900.
- (29) Yaluri, G.; Zhao, X.; Peters, A. W. FCCU Regenerator Lab-Scale Simulator for Testing New Catalytic Additives for Reduction of Emissions from the FCC Regenerator. *Prepr. Symp., Am. Chem. Soc., Div. Fuel Chem.* **1996**, 41 (3), 901–905.
- (30) Barth, J. O.; Jentys, A.; Lercher, J. A. On the Nature of Nitrogen-Containing Carbonaceous Deposits on Coked Fluid Catalytic Cracking Catalysts. *Ind. Eng. Chem. Res.* **2004**, 43 (10), 2368–2375.
- (31) Barth, J. O.; Jentys, A.; Lercher, J. A. Elementary Reactions and Intermediate Species Formed during the Oxidative Regeneration of Spent Fluid Catalytic Cracking Catalysts. *Ind. Eng. Chem. Res.* **2004**, 43, 3097–3104.
- (32) Weisz, P. B.; Goodwin, R. D. Combustion of Carbonaceous Deposits within Porous Catalyst Particles I. Diffusion-controlled Kinetics. *J. Catal.* **1963**, 2 (5), 397–404.
- (33) Arthur, J. R. Reactions Between Carbon and Oxygen. *Trans. Faraday Soc.* **1951**, 47, 164–178.
- (34) Weisz, P. B.; Goodwin, R. B. Combustion of Carbonaceous Deposits within Porous Catalyst Particles. *J. Catal.* **1966**, 6, 227–236.
- (35) Howard, J. B.; Williams, G. C.; Fine, D. H. Kinetics of Carbon Monoxide Oxidation in Postflame Gases. *Proc. Int. Combust. Symp.* **1973**.
- (36) Cant, N. W.; Hicks, P. C.; Lennon, B. S. Steady-state Oxidation of Carbon Monoxide over Supported Noble Metals with Particular Reference to Platinum. *J. Catal.* **1978**, 54, 372–383.
- (37) Shishu, R. C.; Kowalczyk, L. S. The Oxidation of Carbon Monoxide on Supported Platinum. *Platinum Met. Rev.* **1974**, 18, 58–64.
- (38) Axworthy, A. E.; Schneider, G. R.; Shuman, M. D.; Dayan, V. H. *Chemistry of Fuel Nitrogen Conversion to Nitrogen Oxides in Combustion*; NTIS Report EPA-600/2-76-039; NTIS: Springfield, VA, 1976.
- (39) Houser, T. J.; Hull, M.; Alway, R. M.; Biftu, T. Kinetics of Formation of HCN during Pyridine Pyrolysis. *Int. J. Chem. Kinet.* **1980**, 12, 569–574.
- (40) Bergsma, F. Abatement of NO_x from Coal Combustion. Chemical Background and Present State of Technical Development. *Ind. Eng. Chem. Process Des. Dev.* **1985**, 24, 1.
- (41) Mitchell, J. W.; Tarbell, J. M. A Kinetic Model of Nitric Oxide Formation During Pulverized Coal Combustion. *AIChE J.* **1982**, 28, 302.
- (42) Furusawa, T.; Tsunoda, M.; Sudo, S.; Kunii, D. NO_x Reduction in Fluidized Bed Combustion of Carbonaceous Materials. *Prepr. Symp., Am. Chem. Soc., Div. Fuel Chem.* **1982**, 27, 262–273.
- (43) Furusawa, T.; Kunii, D.; Oguma, A.; Yamada, N. Rate of Reduction of Nitric Oxide by Char. *Ind. Eng. Chem.* **1980**, 20, 239–244.
- (44) Bedjai, G.; Orbach, H. K.; Riesenfeld, F. C. Reaction of Nitric Oxide with Activated Carbon and Hydrogen. *Ind. Eng. Chem.* **1958**, 50, 1165–1168.
- (45) Hampartsoumian, E.; Gibbs, B. M. NO Formation and Reduction in Fluidized Bed Combustors. *J. Inst. Energy* **1984**, 57, 402–410.
- (46) Beer, J. M.; Sarofim, A. F.; Chan, L. K.; Sprouse, A. M. NO Reduction by Char in Fluidized Combustion. *Proc. Int. Conf. Fluid. Bed Combust.* **1977**, 5, 577–592.
- (47) Edwards, H. W. Interaction of Nitric Oxide with Graphite. *AIChE Symp. Ser.* **1978**, 126, 91–101.
- (48) Smith, R. N.; Swineheart, J.; Lesnini, D. The Oxidation of Carbon by Nitric Oxide. *J. Phys. Chem.* **1959**, 63, 544–547.
- (49) Chan, L. K.; Sarofim, A. F.; Beér, J. M. Kinetics of the NO–Carbon Reaction at Fluidized Bed Combustor Conditions. *Combust. Flame* **1983**, 52, 37–45.
- (50) Furusawa, T.; Tsunoda, M.; Kunii, D. Nitric Oxide Reduction by Hydrogen and Carbon Monoxide over Char Surfaces. *ACS Symp. Ser.* **1982**, 296, 347–357.

Received for review November 15, 2004

Revised manuscript received January 13, 2005

Accepted February 2, 2005

IE048898E