NO Reduction Studies in the FCC Process. Evaluation of NO Reduction Additives for FCCU in Bench- and Pilot Plant-Scale Reactors

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During FCC catalyst regeneration, part of the nitrogen in coke forms NO_x, which makes up a significant part of the total NO_x refinery emissions. The addition of a small percentage (≤ 1 wt %) of catalytic additive(s) in the FCC inventory can reduce the NO_x emissions from the flue gases of the FCC regenerator. In this paper, experimental techniques are considered for evaluating, in laboratory reactors, the performance of two commercially available NO_x removal additives. It has been shown that in an FCC regenerator the gas residence time and the concentration of CO in the flue gases are key parameters in controlling NO_x emissions. For example, pilot plant experiments showed that the addition of a CO oxidation promoter (CP-3) in the catalytic inventory decreases the CO emissions significantly and increases the NO_x emissions about 4 times. Replacement of the active CO oxidation promoter (CP-3) with an additive (XNO_x) with moderate CO oxidation activity reduced the NO_x emissions by 78%. Comparison of regeneration results performed in bench-scale reactors with those measured in our FCC pilot plant unit showed that it is possible to evaluate NO_x reduction additives in bench-scale experiments. The proposed protocol for this evaluation is to mix spent FCC catalyst with the NO_x reduction additive and to load this mixture in a fluidized bed reactor. The above mixture is then regenerated at 700 °C by 2% O_2 diluted in N_2.
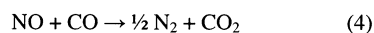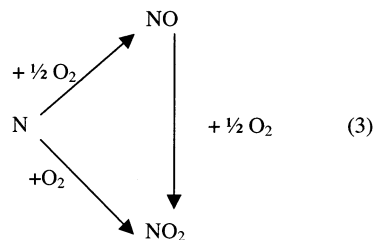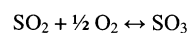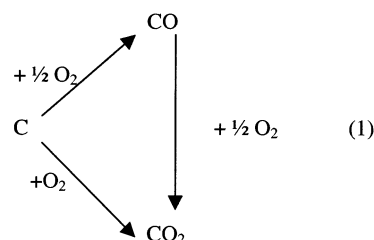
1. Introduction

Nitrogen oxide (NO_x) emissions from the regenerator of a fluid catalytic cracking (FCC) unit make up to 50% of the total NO_x emissions in a modern integrated refinery. Other NO_x sources in a refinery are the process furnaces and the utility boilers. The NO_x emissions in an FCC regenerator originate from the nitrogen containing species deposited on the catalyst during the cracking cycle. Depending on FCC operation conditions, about 5 wt % of the gas oil feed forms coke. It has been reported[1] that about 40% of the nitrogen contained in the FCC feed is deposited with the coke on the cracking catalyst.

During catalyst regeneration, coke containing C, H, N, and S is burned off the catalyst and its activity is restored. In a simplistic way, the reaction scheme (1)−(4) can represent the coke burning reactions.[2]

It has been mentioned[3] that CO and CO_2 are concurrently formed during coke combustion. Subsequent CO oxidation (afterburning) occurs in the dilute phase of a regenerator[2] with the result of a significant temperature rise. It is believed that the presence of significant amounts of CO in the dense bed of the regenerator results in low NO_x concentrations, because reaction 4 takes place.

The high dilute phase temperatures and their negative effect on cyclone life led Mobil researchers in the 1970s to patent the use of Pt promoters,[4] that is, compounds which accelerate the oxidation of CO (CO + $^1/_2O_2 \rightarrow CO_2$) as soon as it is formed in the dense bed.

$$C \nearrow^{+ \frac{1}{2} O_2} CO \quad ; \quad CO \xrightarrow{+ \frac{1}{2} O_2} CO_2 \qquad (1)$$

$$C \searrow_{+ O_2} CO_2$$

$$S + O_2 \rightarrow SO_2 \qquad (2)$$

$$SO_2 + \tfrac{1}{2} O_2 \leftrightarrow SO_3$$

$$N \nearrow^{+ \frac{1}{2} O_2} NO \quad ; \quad NO \xrightarrow{+ \frac{1}{2} O_2} NO_2 \qquad (3)$$

$$N \searrow_{+ O_2} NO_2$$

$$NO + CO \rightarrow \tfrac{1}{2} N_2 + CO_2 \qquad (4)$$

Thus, the heat release from the CO oxidation is taking place inside the regenerator dense bed, where the catalyst serves as a heat sink. The net result is that the dilute phase temperature is significantly reduced. The introduction of CO promoters, however, brought a significant change in the extent of chemical reactions 1−4. In particular, reaction 4 can no longer take place to the extent of a nonpromoted regenerator operation with the net result of a significant increase in NO_x emissions.[1,5−8]

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The chemistry of NO_x production in the FCC regenerator is not today sufficiently understood, although it is known today that the NO_x consists mainly of NO. It is believed[1,6] that, although some of the NO_x can be primarily formed by the coke nitrogen, the majority of it comes through intermediates such as HCN and NH_3. The relative formation of these two compounds depends on the type and basicity of nitrogen compounds in the FCC feed (pyrrolic, pyridinic, etc). This basicity is directly related with the FCC catalyst properties, since the coke production is the main driver for the NO_x formation in the regenerator. Results from a current European (GROWTH) research project have fully validated the existence of HCN and NH_3 intermediates from the coke nitrogen. Moreover, in this project the pathways leading to the formation of NO were proposed:[9]
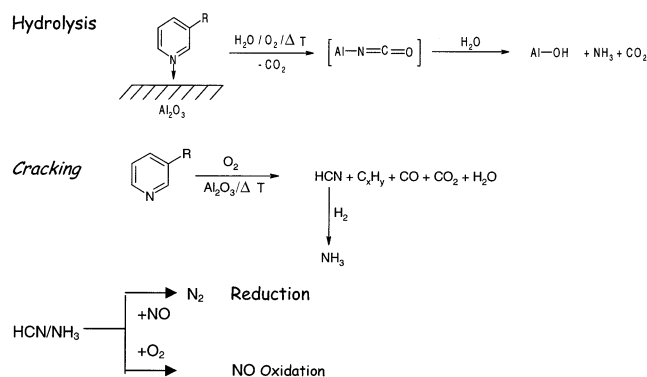
It has recently been realized that NO_x emissions significantly contribute to acid rain formation, photochemical air pollution, the greenhouse effect and the depletion of the ozone layer. These emissions are also related with humans' health problems such as pneumonia, bronchitis and susceptibility to virus infections. The above implications led countries to impose severe limitations on the NO_x emissions from all refinery sources including FCC regenerators. Hence, there is a need to search for NO_x control technologies from the FCC unit, without adversely affecting the yield of valuable products such as gasoline and light olefins. Three different schemes can be evaluated for reducing NO_x emissions: feed pretreatment, flue gas treatment, and in situ NO_x reduction.

Feed pretreatment is based on the fact that the NO_x emissions from an FCC unit are directly related to the feed basic nitrogen content.[1,6] Hence, nitrogen removal from the feed will have a direct impact on NO_x emissions. However, hydrotreatment is an expensive method and it does not have a significant impact on the reduction of N-containing species deposited on coke during the cracking cycle. *Flue gas treatment* with either NH_3 or hydrocarbon injection[10,11] is feasible. However, this approach requires high capital and operating costs. *In situ methods* offer the most convenient way because they lead to a reduction of NO_x emission with additives and without significant modifications in the regenerator design or the unit operating conditions. Additives with the ability to reduce NO_x emissions have been reported by previous researchers, and they are based on a variety of metal compounds. Examples include the following:

(1) Chin and co-workers[12-15] used antimony trioxide, zinc oxide, lanthanum titanate, and bismuth trioxide.

(2) Diekman and Labrador[16] used spinel/perovskite containing at least one transition metal and a spinel containing at least one group IIA element and at least one IIIA element, while a compound of copper or zinc was added as stabilization component.

Recently, FCC catalyst manufacturers have started to commercialize additives for the reduction of NO_x emissions from FCCU. Patents granted to W.R. Grace[17,18] disclose two additives with the commercial names $DENO_x$ and XNO_x. $DENO_x$ is a NO reduction additive for FCCUs[17] that can be used simultaneously with a CO promoter. Finally, XNO_x is an additive that acts as both CO promoter and NO reduction additive.[18] According to the Grace patents, $DENO_x$ and XNO_x are supported on an acidic carrier of high surface area such as silica–alumina. An alkali metal and a metal oxide having oxygen storage capacity, such as ceria, are deposited initially. A metal or a mixture of metals is then impregnated on the previous substrate. Cu and Ag control the NO emissions in $DENO_x$, and Pd promotes CO oxidation and minimizes NO formation in XNO_x.

Results for the effectiveness of these additives (DE-NO_x, XNO_x) have been reported in the literature from both pilot plant and commercial units.[19-21] However, the reaction mechanism that leads to lower NO emissions when these additives are mixed in the FCC inventory is not clearly understood. The simplest explanation was that these additives promote the direct reaction of NO and CO (reaction 4). However, recent experiments in Grace have shown that the effect of these additives is more pronounced not on NO but on the N intermediates that lead to NO formation. Thus, Yaluris et al.[22] have proposed a reaction mechanism where these additives (and especially XNO_x) act on the HCN and NH_3 intermediates that are formed from the coke nitrogen. A non-platinum combustion promoter (such as XNO_x) catalyzes the reaction of these intermediate species to N_2. The Pt-based promoter favors the oxidation of these species to NO.

The correct evaluation of the candidate NO reduction additive is a very important issue both for the refineries and those that synthesize NO reduction additives. Methods are needed to evaluate in bench-scale reactors and under realistic conditions the performance of candidate NO reduction additives. W.R. Grace has developed the regenerator test unit (RTU), which simulates in the laboratory the performance of the FCC regenerator.[22] This unit is a continuous fluid bed reactor, where spent catalyst is fed and regenerated catalyst is always withdrawn. However, the RTU is an expensive unit and it requires high amounts of coked catalyst.

The scope of this work is to simulate the performance of the FCC regenerator with a bench-scale reactor (fixed or fluidized bed). In these experiments pure spent catalyst or spent catalyst mixed with additive(s) was used. The bench-scale results were compared with the results measured in an FCC pilot plant operating in our laboratory. It has previously been reported[23] that this pilot plant sufficiently simulates the performance of an industrial-scale FCC unit. The validation of the bench-scale experiments with the pilot plant-scale ones was used to develop a testing protocol for NO reduction additives in bench-scale reactors.

2. Experimental Section

2.1. Materials. Spent (coked) unpromoted FCC catalyst was supplied by Grace GmbH for the bench-scale regeneration studies. This catalyst was collected from the Davison Circulating riser (DCR) and had a carbon

Table 1. Properties of the Feedstocks Used in the FCC Pilot Plant Studies

|	high nitrogen feed	low nitrogen feed
API	23.57	24.73
sulfur, wt %	2.249	0.2455
total nitrogen, wt %	0.1622	0.108
refractive index (70 °C)	1.483 76	1.483 54
MeABP, °C	463	462

content of 1.41 wt % (1.18×10^{-3} gmol/g). The nitrogen content was 266 ppm wt (1.66×10^{-5} gmol/g), and the sulfur content was 107 ppm wt (3.34×10^{-6} gmol/g). These measurements were performed with elemental analyzers.

For the FCC pilot plant studies a commercial unpromoted catalyst was used. This catalyst was also supplied by Grace (total surface area SA = 195.4 m²/g, zeolite SA = 110.3 m²/g, UCS = 24.25 Å, Ni = 563 ppm, V = 1173 ppm). Finally, Grace GmbH supplied us with three FCC commercial additives: CP-3, DENO$_x$, and XNO$_x$. CP-3 is a commercial platinum (Pt) CO promoter, an additive that enhances the CO oxidation. Two types of feedstocks, with a high and a low nitrogen and sulfur content, were used in the FCC unit. The properties of these feeds are given in Table 1.

2.2. Bench-Scale Reactors. The reaction unit used for the bench-scale studies consists of the feed gas system, a fixed and a fluidized bed reactor, two three-zone furnaces controlled by PID controllers, one for each type of reactor, and the gas analysis system. The fixed and fluidized bed reactors are connected in series and can be bypassed by the feed. The i.d. of the former reactor is 1.7 cm, and that of the latter one is 3.2 cm. In the fixed-bed experiments, the flow rate of the inlet gas was 500 mL/min and the reactor loading was 2 g. In the fluidized bed experiments the flow rate of the inlet gas was 1000 mL/min and the reactor loading was 10 g. Mechanical mixtures of spent catalyst with commercial additives were loaded in the reactors to evaluate the performance of each additive.

Samples from the exit gas stream were analyzed to identify the gas products during regeneration. The nitrogen oxides (NO and NO$_2$) were measured in a chemiluminescent NO$_x$ analyzer (Thermo Environmental, model 42H) while CO and CO$_2$ were measured with a dual channel NDIR analyzer (Rosemount, model NGA 2000). The SO$_2$ concentration was measured in an NDUV analyzer (Anarad, model AR3000). The N$_2$O concentration was measured in a NDIR analyzer (Horiba, model VIA-510). Gas mixtures of standard composition were used to calibrate the gas analysis system. The NO$_2$ and N$_2$O concentrations were practically zero in all experiments of this study. The experimental results are presented either as the raw data expressed as the concentration of CO, CO$_2$, NO, SO$_2$ or O$_2$ versus the regeneration time or as the overall amount of the emitted gases. The overall emissions were calculated from the integration of the raw data using the trapezoidal rule. In the presentation of experimental data, we calculate the NO and CO conversion, defined as the percentage of NO reduced and CO oxidized to CO$_2$ in a given experiment as compared to those in the base case experiment.

2.3. FCC Pilot Plant Unit. The CPERI FCC pilot plant operates in full circulating mode with continuous regeneration. It consists of a vertical reactor (riser), a fluid bed regenerator, the stripper, and the lift line. A full description of the unit is given elsewhere.[23] The
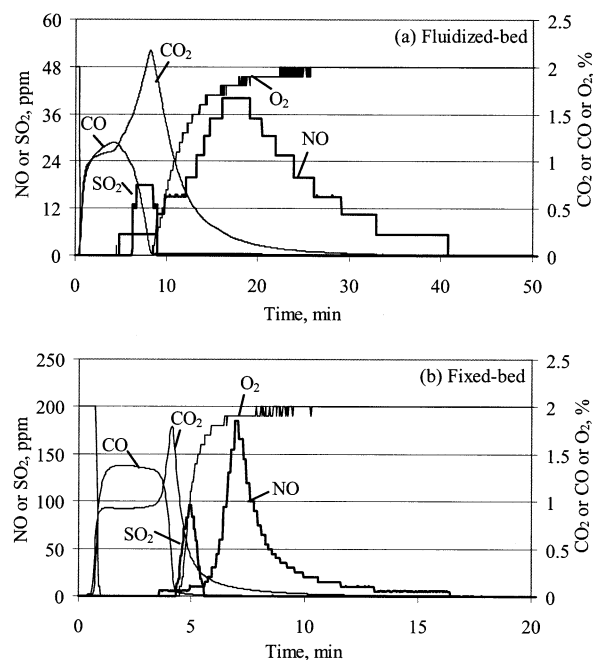
Figure 1. Typical emissions data during regeneration of spent FCC catalyst in a fluidized- (a) and fixed- (b) bed bench-scale reactor.

reactions take place in the riser, and the separation (stripping) of gases from the solid catalyst occurs in the stripper vessel. The solids flow through a second slide valve and through the spent catalyst lift line return to the reactor bottom following regeneration. The fluid bed regenerator reactor is used to burn the carbon that covers the catalyst surface as a byproduct of the cracking process. The fluidization gas (air) is introduced from the base of the regenerator, and its flow rate is controlled by a mass flow controller. The spent catalyst enters the top of the fluid bed countercurrent to the air flow. The regenerator exit stream passes through cyclones that remove any entrained solids. The remaining products are cooled by a heat exchanger, and subsequently their total flow is measured by a wet test meter and analyzed by GC. Flue gas concentrations were also measured on-line using an analyzer (Horriba, PG-250), which can measure the following flue gases: O$_2$, CO$_2$, CO, NO, NO$_x$, and SO$_2$. The gas sample for this analyzer comes directly from the regenerator exit.

3. Results and Discussion

3.1. Bench-Scale Reactors. The regeneration of pure FCC spent catalyst (without any additive) was studied using two bench-scale reactors: either a fixed or a fluidized bed. During regeneration, NO was formed from the N-containing species of the spent catalyst. The following standard experimental conditions were used for both reactors: regeneration temperature, 700 °C; feed composition, 2 vol % O$_2$ in N$_2$. These conditions were selected as representative for a full-burn regenerator operation. The experimental results at the above standard conditions are presented in Figure 1. The shapes of the concentration versus time curves in the fluidized and fixed bed reactors were, in general, similar. The experimental curves were broader in the fluidized bed reactor because of the flow patterns. CO was detected at the beginning of the experiment, and NO was formed after most of the CO was released. In the CO-rich part of the experiment, no NO was detected
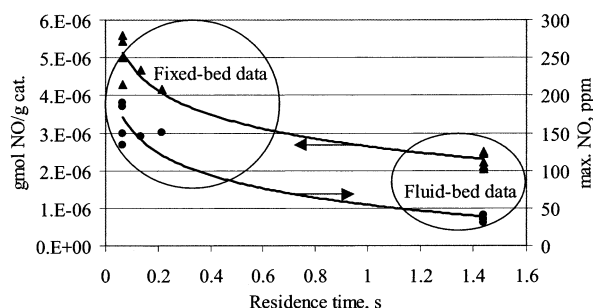
Figure 2. Effect of gas residence time on NO formed during spent catalyst regeneration in bench-scale reactors.

and the O_2 concentration was zero. This implies that at the beginning of the experiment some of the coke nitrogen was converted to N_2 either by direct formation of N_2 inside the FCC catalyst or as a result of the reduction of nitrogen-containing species to N_2. Only when the CO concentration diminished was the coke nitrogen converted to NO. Dishman et al.[4] measured the combustion gases during regeneration and observed similar behavior. Carbon on coke is burned initially, followed by nitrogen on coke. As the amount of carbon on coke decreased, the nitrogen was enriched in spent catalyst (increased nitrogen concentration in coke) and thus nitrogen was removed last. TPO experiments in the literature also showed the same behavior.[24]

The integration of the curves in Figure 1 shows that more CO and NO were formed in the fixed bed experiment than that in the fluidized bed. This difference motivated us to examine the effect of residence time on the experimental results. In Figure 2 we present the NO emissions as a function of the residence time of the feed gas in the reactor at the same reaction temperature (700 °C). We varied the flow rate in the fixed bed experiments to change the residence time, and we included in the same figure the fluidized bed data. The gmol of NO per g of spent catalyst and the maximum NO concentration measured at the reactor exit followed two parallel curves. The NO emissions decreased when the residence time increased. The same trend was observed for the CO emissions, though the slope was significantly lower. We attribute this difference to the higher CO oxidation rates as compared to the NO reduction rates. These results imply that the extent of the NO reduction by CO depends on the residence time of the gases.

We examined the effect of the feed O_2 concentration (in the range 0−5 vol %) during regeneration of pure spent catalyst in a fluidized bed reactor. Negligible amounts of CO_2, CO, NO, and SO_2 were detected when a pure N_2 feed (0% O_2) was used in the regeneration. Increase in the O_2 concentration enhanced the oxidation reactions as the maximum concentration of gases formed during regeneration (CO_2, CO, NO, and SO_2) increased with the O_2 concentration. The integrated (overall) amount of NO and SO_2 did not vary with the O_2 concentration, while low O_2 concentrations favored the CO formation.

3.1.1. Effect of CO Promoter (CP-3) on NO Emissions. We mixed the unpromoted FCC catalyst of the previous studies with a commercial CO promoter (CP-3) in order to study the effect of this additive on the NO and CO emissions. In all cases, the concentration of CP-3 in the reactor inventory was 1%. The experimental results for both reactors are presented in Figure 3. Addition of CP-3 broadened the NO concentration
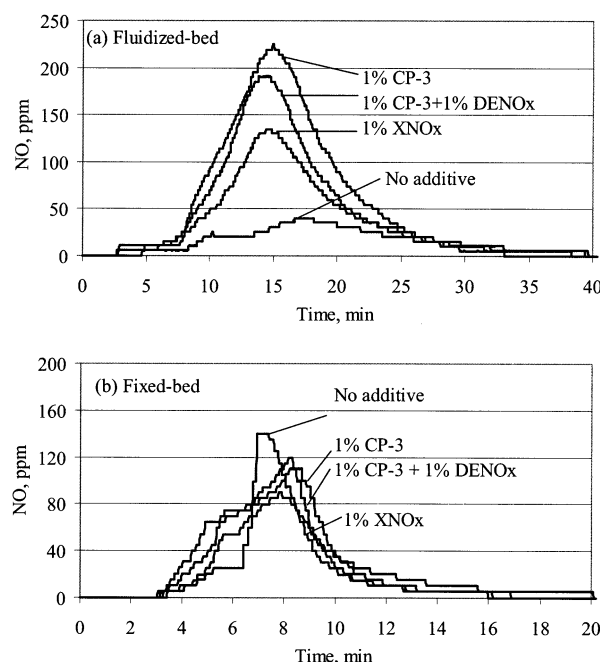

Figure 3. Performance of CP-3, DENO$_x$, and XNO$_x$ additives in bench-scale reactors.

versus time curve as compared to the case of the additive-free experiment (no additive curve) in the fixed bed configuration. We also summarize the total NO, CO, and CO_2 emissions data (gmol/g of spent catalyst) in Table 2. The presence of CP-3 in the fluidized bed reactor tripled the NO emissions, while the CO emissions decreased by 1 order of magnitude. In the fixed bed experiments the addition of CP-3 reduced the CO emissions by 1 order of magnitude and increased the NO emissions by almost 25%. All commercial FCC plants operating in a full-burn mode use CO promoter in their inventory. This motivated us to use as base case experiment the one where spent catalyst was mixed with 1% CP-3.

3.1.2. Effect of DENO$_x$ on NO Emissions. For the evaluation of DENO$_x$, we employed mechanical mixtures of the CO promoter (CP-3) and the DENO$_x$ additive. When spent catalyst mixed with 1% of each of the above additives was regenerated, the NO emissions were hardly decreased as compared to the base case (1% CP-3 only) (Table 2, Figure 3). This reduction was 11% for the fluidized bed experiment and 10% for the fixed bed experiment (Table 4). On the other hand, the CO emissions were about the same as those in the base case experiment where only CP-3 additive was used (Table 2).

3.1.3. Effect of XNO$_x$ on NO Emissions. We replaced CP-3 with XNO$_x$ and regenerated this blend of 1% XNO$_x$−99% pure spent catalyst with 2% O_2 in N_2 at 700 °C. The raw experimental data are shown in Figure 3, while the integrated NO, CO, and CO_2 emissions are given in Table 2. Lower NO emissions were measured in both the fixed and the fluidized bed experiments as compared to the CO promoter-containing experiments. This reduction (Table 4) was 31% for the former and 34% for the latter type of reactor. Moreover, for the fluidized bed, the CO emissions were low and comparable to those in the presence of the CO promoter (Table 2).

3.1.4. Effect of CO Presence in the Reactor Feed. The CO concentration in a countercurrent regenerator

Table 2. Total (Integrated) CO$_2$, CO, and NO Emissions during Regeneration of a Mixture of Spent Catalyst and Additive(s) at 700 °C with 2% O$_2$ in N$_2$ as the Feed

	fluidized bed reactor			fixed bed reactor		
additive(s)	10^{-4}CO$_2$ gmol/g	10^{-4}CO gmol/g	10^{-6}NO gmol/g	10^{-4}CO$_2$ gmol/g	10^{-4}CO gmol/g	10^{-6}NO gmol/g
none	7.57	3.15	2.62	6.5	3.5	4.46
1% CP-3	11.2	0.325	8.93	11.0	0.28	5.53
1% DENO$_x$ + 1% CP-3	12.2	0.36	7.96	10.9	0.33	4.95
1% XNO$_x$	11.1	0.33	5.87	9.57	0.75	3.82

Table 3. Total (Integrated) CO$_2$, CO, and NO Emissions during Regeneration of a Mixture of Spent Catalyst and Additive(s) at 700 °C with 1% O$_2$ and 1% CO in N$_2$ as the Feed

	fluidized bed reactor			fixed bed reactor		
additive(s)	10^{-3}CO$_2$ gmol/g	10^{-4}CO gmol/g	10^{-6}NO gmol/g	10^{-2}CO$_2$ gmol/g	10^{-4}CO gmol/g	10^{-6}NO gmol/g
none	6.67	9.52	1.35	1.27	21.8	4.12
1% CP-3	9.03	1.84	6.57	1.48	1.9	5.61
1% DENO$_x$ + 1% CP-3	10.7	1.44	5.1	1.46	1.27	4.21
1% XNO$_x$	10.2	3.26	3.85	1.46	5.73	4.09

Table 4. Percentage of CO Oxidized (Positive Sign) and NO Reduced (Positive Sign) as a Result of the DENO$_x$ or XNO$_x$ Use as Compared to the Base Case Experiment (1% CP-3)[a]

|	fluidized bed reactor		fixed bed reactor	
additive(s)	CO	NO	CO	NO
1% CP-3	base	base	base	base
1% DENO$_x$ + 1% CP-3	−11%	+11%	−19%	+10%
1% XNO$_x$	0%	+34%	−168%	+31%

[a] Bench-scale regeneration experiments at 700 °C with 2% O$_2$ in N$_2$ as the feed.

Table 5. Percentage of CO Oxidized (Positive Sign) and NO Reduced (Positive Sign) as a Result of the DENO$_x$ or XNO$_x$ Use as Compared to the Base Case Experiment (1% CP-3)[a]

	fluidized bed reactor		fixed bed reactor	
additive(s)	CO	NO	CO	NO
1% CP-3	base	base	base	base
1% DENO$_x$ + 1% CP-3	+22%	+22%	+33%	+25%
1% XNO$_x$	−77%	+41%	−201%	+27%

[a] Bench scale regeneration experiments at 700 °C with 1% O$_2$ and 1 % CO in N$_2$ as the feed.

operating in the full-burn mode is high near the air grid (dense phase) and drops to low values in the dilute phase of the regenerator.[25] Therefore, CO should be added in the feed of bench-scale experiments to simulate the performance of NO reduction additives in the dense phase of the regenerator. On the basis of this remark, the bench-scale studies described in the previous sections were repeated using a feed consisting of 1% CO + 1% O$_2$. We used this feed in order to have always 0.5% O$_2$ excess in the feed gas stream even if all inlet CO is converted to CO$_2$. In other experiments where the inlet O$_2$ was in deficiency with respect to the inlet CO, incomplete regeneration of coke was observed. In Table 3 we compare the overall (integrated) amount of NO, CO, and CO$_2$ from the two reactors when 1% CO + 1% O$_2$ was used as the feed. In Table 5 we list the relative performance of the additives in the two reactors in the presence of CO in the feed. The addition of DENO$_x$ and CP-3 decreased considerably the NO as compared to the case of the experiment where only CP-3 was used. Thus, the presence of CO enhanced the NO reduction capacity of DENO$_x$ as compared to the case of experiments where the feed was 2% O$_2$ in N$_2$. Comparison of the experimental data listed in Tables 2−5 showed that XNO$_x$ is more efficient for the NO reduction than DENO$_x$ for both feeds.
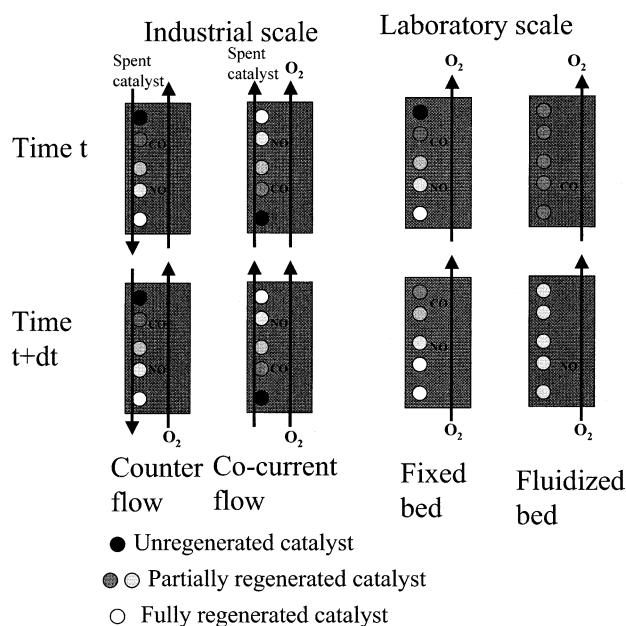
Figure 4. Comparison of flow patterns of bench-scale and commercial reactors.

The previous results showed that both the feed composition and the type of reactor could affect the performance of NO reduction additives in bench-scale reactors. Both DENO$_x$ and XNO$_x$ catalyze the NO reduction by CO; however, the latter NO reduction additive is efficient even when the feed does not contain CO (Figure 3). Research is currently carried out to elucidate the reaction mechanism of NO reduction over both additives.

3.1.5. Effect of Reactor Configuration. Our experimental data showed that the type of reactor affects the performance of NO reduction additives. The most important difference between commercial FCC regenerators and bench-scale reactors is that the former operate in a continuous mode, where carbon on catalyst and CO are perpetual, while laboratory reactors operate in the batch mode. In Figure 4 we depict the flow patterns of bench-scale and commercial reactors. In commercial regenerators the spent catalyst and oxygen can follow counter- or cocurrent flow, depending on the type of the FCCU. In the initial stages of regeneration, CO is primarily formed followed by NO. However, diffusion of NO in the regenerator (typical residence time of gases ∼ 10 s) leads to reaction of NO with spent catalyst and CO. On the other hand, regeneration in a

Table 6. FCC Pilot Plant Base Case Operating Conditions

	high nitrogen feed	low nitrogen feed
riser temp, °C	526	526
regenerator temp, °C	700	700
catalyst-to-oil ratio (C/O)	11	8.5
HCs partial press., psia	10	10
coke on spent catal (wt %)	0.507	0.38
coke on regen catal (wt %)	0.035	0.03
conversion, wt %	65	67
gasoline yield, wt %	45.2	49
coke yield, wt %	5.2	3.2
dry gas yield, wt %	2.6	1.8
LPG yield, wt %	12.0	13.0

fixed bed reactor gives rise to a regeneration front in the bed that moves from the feed entrance (less coke on the catalyst) to the reactor exit (more coke on the catalyst). NO formed primarily from the spent catalyst located close to the feed entrance can be reduced to N_2 by coke or CO formed in the upper part of the reactor. The fixed bed arrangement (PFR reactor) seems to simulate better the countercurrent flow case in Figure 4. Finally, all particles in the fluidized bed (CSTR reactor) exhibit the same regeneration extent. This implies that, at the earlier stages of the experiment, CO is primarily formed, while NO is emitted when the regeneration has proceeded. It is obvious that neither type of bench-scale reactor simulates perfectly the operation of the FCC regenerator.

The protocol for the evaluation of NO reduction additives in bench-scale reactors should determine the configuration of the bench-scale reactor and the composition of the feed gas stream. We decided to experimentally determine the aforementioned protocol by comparing our bench-scale results with experimental results from our pilot plant-scale FCCU.

3.2. FCC Pilot Plant NO$_x$ Studies. All the experiments in the FCC pilot plant were performed at constant operating conditions using equilibrium unpromoted catalyst. The operating conditions of the tests are described in Table 6. In all these studies, constant excess oxygen was used (2 vol %), since the excess oxygen influences strongly the NO reaction mechanisms in the regenerator and, thus, the NO concentration in the flue gases.[1,4] The conversion and the coke yield were kept constant in order to always have the same nitrogen content in the spent catalyst of the regenerator and to have the same coke content in the recirculated catalyst (Table 6).

In Figure 5 we present the NO and CO concentrations at the regenerator exit with the high sulfur and nitrogen feed and the unpromoted base equilibrium catalyst (E-cat). The NO concentration was about 75 ppm, while the corresponding average CO concentration was 275 ppm. The regenerator of our FCC pilot plant is relatively small and well mixed, and thus, CO combustion is effective even without CO promoter. However, for a pilot plant operation, this concentration of CO is relatively high, and this is the reason that we measure this low NO concentration in the flue gases. Taking into account the NO concentration, the flue gas flow rate, and the nitrogen in the feed, it is estimated that about 4% of the feed nitrogen is finally converted to NO. This result is in agreement with other nitrogen balance studies around the FCCU.[1,6,24] These literature studies showed that about 40% of the feed nitrogen appears in the coke on the catalyst. However, only 10−30% of the coke nitrogen appears as NO in the flue gases.
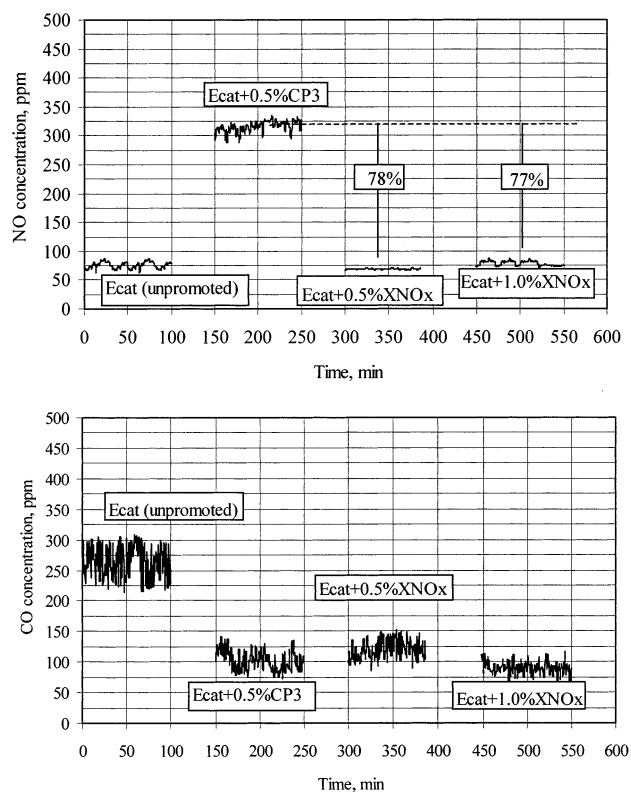

Figure 5. Comparison of the performance of CP-3 and XNO$_x$ additives in the CPERI FCC pilot plant (high nitrogen and sulfur feed).

3.2.1. Effect of CO Promoter (CP-3) on NO Emissions. With the addition of 0.5% CP-3 (Pt−CO promoter) in the unpromoted FCC inventory, the CO concentration was considerably decreased to about 100 ppm while the NO concentration increased to about 320 ppm (Figure 5). As is fully validated today from commercial operations, the presence of CP-3 in the inventory increased considerably the NO concentration in the flue gases as compared to the experiment where unpromoted catalyst was used. These results were in agreement with our bench-scale studies (Tables 2 and 3 and Figure 3). The performance of our FCC pilot unit with the CO promoter is in agreement with other pilot plant studies and with commercial data from FCCUs operating in full combustion mode (in the presence of a Pt−CO promoter).[19−22] It seems that the very high oxidative activity of a CO platinum promoter (like CP-3) depletes the CO and other reductants present in the FCC regenerator and favors the oxidation of coke(N) and/or nitrogen containing reaction intermediates (like HCN or NH_3) to NO. For a partial combustion FCCU the presence of large amounts of CO and coke on catalyst can substantially reduce the NO emissions. In this case, most of the NO is reduced to nitrogen. However, the majority of the commercial units are now operating in a full combustion mode using a Pt−CO promoter and consequently emit high NO concentrations (in comparison to partial burning units). Up to now the refineries could not sacrifice CO conversion for the sake of NO$_x$ reduction. For this reason, in the following studies, the FCC pilot plant operation in the presence of CP-3 is considered as the base case. The reduction achieved with each additive is estimated in relation to the flue gas emissions from the inventory with the CP-3.

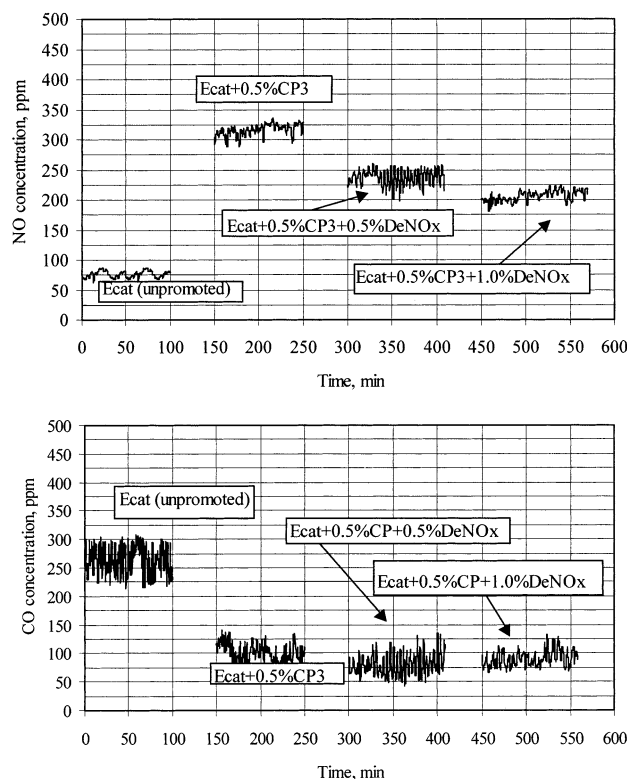**3.2.2. Effect of XNO$_x$ on NO Emissions.** The first approach used in this study for the reduction of NO$_x$

Figure 6. Comparison of the performance of CP-3 and DENO$_x$ additives in the CPERI FCC pilot plant (high nitrogen and sulfur feed).

Figure 7. DENO$_x$ performance when a low sulfur and nitrogen feed was used.

Figure 8. Effect of DENO$_x$ concentration on NO removal (FCC pilot plant data).

from a FCCU regenerator was with the use of a non-platinum CO promoter that does not increase the NO$_x$ concentration in the regenerator and achieves the same oxidation to CO. As was described in the Introduction, there are now such commercial additives.[18-22] As in the bench-scale studies, one of these additives, the Grace XNO$_x$, was tested in the FCC pilot plant unit. Thus, instead of CP-3, the same concentration (0.5 wt %) of the XNO$_x$ additive was added in the unit. We run the unit at exactly the same conditions as those with the presence of CP-3, and the experimental results are shown in Figure 5. Compared with the base case (CP-3) shown in Figure 5, the amount of NO$_x$ in the flue gases was reduced about 78% while at the same time the CO concentration remained at about the same level as compared to the case with the Pt−CO promoter. It is clear that XNO$_x$ acts both as a CO promoter and as a catalyst for the reaction of NO or NO intermediates (NH$_3$, HCN) to N$_2$. These experimental results are in agreement with results presented in the literature from both pilot and commercial tests. It seems that from about 10 commercial tests[21] the achieved NO$_x$ reduction with the presence of XNO$_x$ was between 50 and 80%. Similar results were also reported by Grace from studies performed in both RTU and DCR (Davison Circulation Riser).[19,20,22]

3.2.3. Effect of DENO$_x$ on NO Emissions. The second approach for the FCCU regenerator NO$_x$ control is the reduction of NO$_x$ in the presence of a conventional platinum (Pt) CO promoter. The performance of such an additive (the Grace DENO$_x$ additive) was tested in the FCC pilot plant. Thus, in the catalyst inventory with the CO promoter (CP-3), the DENO$_x$ additive was added. The results are depicted in Figure 6 for both NO and CO emissions. It seems that the DENO$_x$ additive can reduce the NO about 27−35% (depending on the addi-
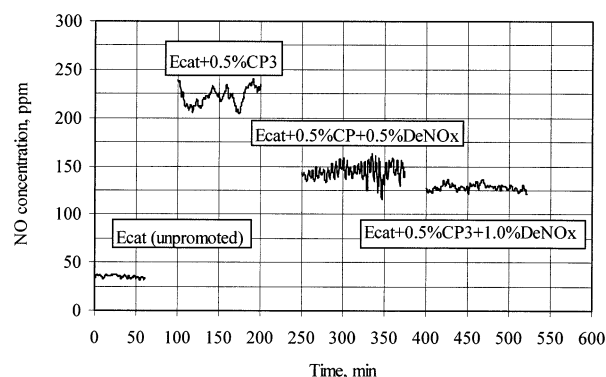
tive concentration in the FCC inventory). No effect of this additive on CO concentration was observed. The already very low CO concentration (100 ppm) was also retained in the presence of DENO$_x$. This type of additive reduces the NO$_x$ independent of CO promotion. The present result is also quite similar with results presented in the literature with this additive from both pilot plant and commercial units.[19-22]
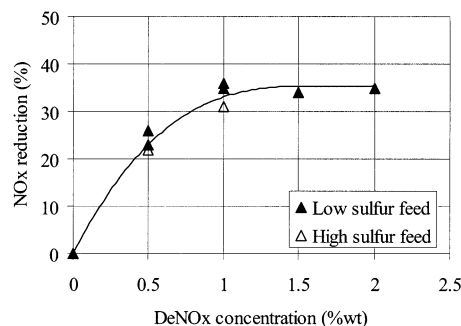
3.2.4. Effect of Type of Feedstock and Additive Concentration on NO Reduction. The work described above for both XNO$_x$ and DENO$_x$ was repeated with the low nitrogen and sulfur feed (Table 1) in order to investigate if different levels of NO$_x$ (and SO$_x$) in the regenerator can influence the additives' ability for NO$_x$ reduction. The results with the DENO$_x$ additive are given in Figure 7. The reduction achieved with the DENO$_x$ additive with this feed is almost similar with that obtained by the high S&N feed (Figure 6). It is clear that the type of feedstock has no effect on the performance of both additives. Similar results were also concluded for the performance of the XNO$_x$ additive.

The effect of additive concentration (in the FCC pilot plant catalyst inventory) was also studied in this work. The experimental results with 1 wt % concentration of these additives are shown in Figures 5−7. For the DENO$_x$, additive two more concentrations (1.5 and 2 wt %) were also tested. The effect of a higher XNO$_x$ concentration is depicted in Figure 5 for the two additives. It seems that the addition of 1 wt % additive has no effect on NO reduction (in relation to 0.5 wt %); however, it slightly decreases the CO concentration. Figures 8 and 9 summarize the concentration effects of both additives. It seems that the optimum XNO$_x$ concentration is about 0.5−0.7% while for DENO$_x$ it is about 1%. All the above experimental results are in accordance with commercial trials performed by Grace
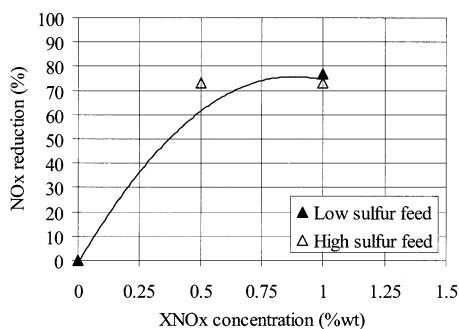
Figure 9. Effect of XNO_x concentration on NO removal (FCC pilot plant data).
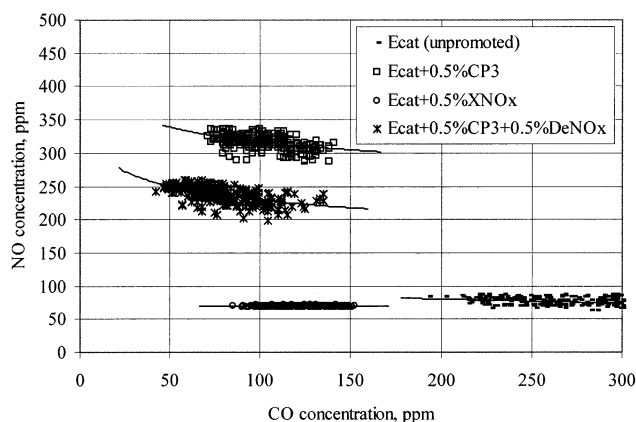

Figure 10. Effect of CO concentration on NO emissions in FCCU regenerator (FCC pilot plant data).

in refineries.[21] It must also be noted that the above additives have no effect on the FCC products in the riser (Table 6).

In Figure 10 we present the NO concentration versus CO concentration from various runs performed in the FCC pilot plant with all additives. The CO concentration was affected in the unit by changing the excess oxygen. It is concluded that there is a direct effect of CO presence in the FCCU regenerator with the NO. For a constant catalyst/additive ratio, when the CO concentration is increased, the NO concentration decreases. However, below a certain value of CO concentration, the NO concentration increases almost exponentially. All pilot plant tests showed that the CO concentration is the most crucial parameter for testing the performance of NO_x reduction additives. Consequently, it is very important to compare the NO_x reduction achieved by various catalysts/additives by comparing the NO data only at the same CO concentration.

3.3. Proposed Protocol for Bench-Scale Evaluation of NO Reduction Additives. In the presentation of our pilot plant-scale results, we mentioned that these data are, qualitatively, in agreement with the experimental results in our bench scale studies. However, in the latter type of experiments, we used two reactors and two feeds. Testing the NO reduction ability of a candidate additive under different regeneration conditions is beneficial in research works but not practical in routine works. Therefore, the question remains what is the testing protocol that we should follow in a bench-scale reactor that best simulates the behavior of an additive mixed in the inventory of a commercial FCCU. The criteria that we set for the choice of these reaction conditions follow:

(I) Use of an NO reduction additive should result in a qualitatively similar change in both the NO and the

Table 7. Percentage of CO Oxidized (Positive Sign) and NO Reduced (Positive Sign) as a Result of the $DENO_x$ or XNO_x Use as Compared to the Base Case Experiment (CP-3)[a]

	FCC pilot plant reactor	
additive(s)	CO	NO
0.5% CP-3	base	base
$DENO_x$ + 0.5% CP-3	$\pm 10\%^b$	$30-35\%^b$
XNO_x	$\pm 20\%^b$	$73-77\%^b$

[a] Pilot plant regeneration experiments at 700 °C with 2% O_2 in N_2 as the feed. [b] For the various XNO_x and $DENO_x$ concentrations tested.

CO emissions in the bench- and the pilot plant-scale experiments.

(II) Under the same regeneration conditions, use of two (or more) NO reduction additives should result in changes in the NO and CO emissions of the same trend.

When the above two criteria are met, we can estimate the effect of an NO reduction additive in both NO and CO emissions and we can evaluate the performance of different additives from bench-scale tests.

The comparison of the bench-scale data (presented in Tables 4 and 5) with the pilot plant-scale ones (Figures 5–7) is summarized in Table 7. For the pilot plant results of this table, we give a range of NO reductions because of the fact that various additive concentrations were used. The comparison of the bench-scale and pilot-scale data led us to conclude that an FCCU operating in full burn mode is best simulated by a fluidized bed reactor fed by 2% O_2 in N_2. This type of reactor (fluidized bed) and the above reaction conditions (2% O_2 in N_2) were selected for the following reasonse:

(a) In the presence of the CP-3 in the unpromoted fluid catalyst bed (fed by 2% O_2 in N_2), the observed increase of NO was about 240% (Table 2), which is on the same order as that from the FCC pilot plant (330%, Figure 5). The corresponding increase in the fixed bed reactor was only 23% (Table 2).

(b) When the fixed bed reactor with 2% O_2 in N_2 as the feed was used, we measured very high amounts of CO at the reactor exit when XNO_x was added (168% more than the CP-3 case, Table 4). The corresponding increase of CO with the fluid bed reactor (2% O_2) was only 1% (Table 4). It is clear that the fluid bed data are very close to the pilot data where the XNO_x shows similar CO concentration with the CP-3 ($\pm 20\%$) with the various XNO_x concentrations tested. Moreover, the relative activity of XNO_x and $DENO_x$ for NO reduction in the fluid bed (2% O_2 in N_2 as the feed) was similar to that observed from the FCC pilot plant. We attribute the inefficiency of the fixed bed reactor to simulate the pilot plant data to the significantly lower residence time in this reactor as compared to the fluidized bed reactor (Figure 2).

(c) When the CO-containing feed was used in the fluidized bed reactor, the NO reduction followed the same trend as that in the pilot plant experiment, when $DENO_x$ and XNO_x were added, but in the presence of XNO_x, the CO emissions were relatively high.

4. Conclusions

Pure spent FCC catalyst was regenerated in bench-scale reactors (fixed and fluidized bed). The addition of a commercial CO promoter (CP-3) reduced the CO emissions by an order of magnitude and increased the NO emissions significantly in both fixed and fluid bench-

scale reactors. The efficiency of two commercial NO reduction additives (XNO_x and $DENO_x$) was also tested. Replacement of CP-3 by XNO_x resulted in low CO and NO emissions. When CP-3 and $DENO_x$ were mixed with spent catalyst, we measured lower reduction of the NO emissions as compared to the case of the XNO_x containing experiments. In all experiments, where CP-3 was mixed with $DENO_x$, the CO emissions were low.

The efficiency of the above additives was validated in pilot plant-scale experiments. Addition of the CO promoter (CP-3) decreased the CO and increased the NO emissions significantly. Following the addition of $DENO_x$ or the replacement of CP-3 with XNO_x in the FCC inventory, the CO concentration was as low as that in the experiment where only CP-3 was present and the NO concentration was significantly lower as compared to that for the experiment containing only CO promoter. The pilot plant results showed that the CO presence in the FCC regenerator is a crucial parameter for the performance of NO reduction additives. The evaluation of these additives must only be performed at a constant CO level basis. The pilot plant-scale experiments were in good agreement with results from commercial tests. The FCC pilot study also showed that the type of feedstocks has no influence on the behavior of the two additives. Moreover, the optimum concentration of the XNO_x and $DENO_x$ in the FCC pilot plant inventory was found to be 0.5% and 1%, respectively.

Comparison of regeneration results performed in the bench-scale reactors with those measured in our pilot plant FCCU showed that it is possible to evaluate NO reduction additives in bench-scale experiments. The proposed protocol for the evaluation of NO reduction additives is to mix spent FCC catalyst with the NO reduction additive and to load the mechanical mixture in a fluidized bed reactor. The above mixture is then regenerated at 700 °C by 2% O_2 diluted in N_2, when the operation of an FCCU that operates in the full-burn mode is simulated. Use of a fixed bed reactor leads to high CO emissions at the reactor exit. When CO is present in the feed of the fluidized bed reactor, the CO emissions are relatively high when XNO_x is used, while the opposite is measured in the pilot plant-scale results.

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