

Laboratory deactivation testing for the stability of FCC CO combustion promoters

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Abstract

Realistic lab deactivation facilitates the development of low NO_x, CO combustion promoters for fluid catalytic cracking (FCC) applications. Cyclic deactivation, which provides a close simulation of the FCC operation, can address many possibilities for the deactivation of CO combustion promoters. Here we present our results using a combination of cyclic deactivation and a coke combustion test to predict additive performance after deactivation. By using this newly developed method, CO combustion promoters with exceptional performance were identified. These novel materials feature CO reduction performance similar to that of Pt-based promoters while still offering significant NO_x reduction relative to Pt. Examples are also given using a more traditional hydrothermal deactivation approach.

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1. Introduction

NO_x emissions from the regenerator of an FCC unit (FCCU) make up 50% of the total NO_x emissions in a modern integrated refinery, which is about 2000 tonnes/year [1]. One contributor to such high NO_x emission is the wide application of conventional Pt-based CO combustion promoters. The function of CO combustion promoters is to enhance CO oxidation in the dense bed of FCCU regenerators where the catalyst can act as a heat sink, while reducing the exothermic CO oxidation in the dilute bed and, therefore, prevent the afterburn damage to the regenerator hardware. The significant increase in NO_x formation induced by Pt-based promoters is partly caused by the resulting lack of CO to reduce NO_x. In addition, it has been suggested that Pt promotes NO_x formation from N-containing intermediates [2]. Thus, it becomes environmentally attractive to develop non-Pt-based low NO_x CO combustion promoters

which provide sufficient CO oxidation while markedly reducing NO_x formation.

To develop such additives, realistic lab testing is important for the prediction of additive performance in commercial applications. The state-of-the-art lab evaluation approach is to investigate additive performance on CO_x, SO_x and NO_x simultaneously during catalyst regeneration (known as coke combustion test) [3–8]. Chin studied Zn- and Sb-based additives for NO_x reduction during lab simulated regeneration of a spent catalyst [3,4]. Yaluri et al. developed a lab-scale regenerator test unit for the evaluation of NO_x reduction additives and low NO_x CO combustion promoters [5]. The work of Efthimiadis et al. indicated that the coke combustion test using a bench-scale unit gave good prediction of additive performance in their pilot plant as well as commercial units [7]. This sophisticated method facilitates the fast screening in the lab of potential candidates for low NO_x, CO combustion promoters as well as SO_x and NO_x reduction additives.

The severe operating conditions of the FCC require successful emission control additives that have high resistance to deactivation. In a commercial unit, the emission control additives circulate along with FCC catalyst and go through oil cracking, stripping, and regeneration cycles. Thus, many factors can lead to additive deactivation. Deactivation mechanisms for environmental emission control additives include the pore collapse and

Abbreviations: FCC, fluid catalytic cracking; CD, cyclic deactivation; AATU, advanced additive testing unit

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surface area loss for the support as well as sintering and changes in metal oxidation state. A realistic additive deactivation protocol should also consider the interaction between FCC catalyst and additives as well as the interaction between additive and feed.

At present, only a few investigations have been reported on lab deactivation of emission control additives. Iliopoulou applied the NO + CO reaction to study the stability of Rh or Ru containing additives for NO_x reduction [9,10]. Yaluris studied the performance of CO combustion promoters after oxidation and reduction cycles [6]. Because of the complexity in the deactivation process, simple oxidation/reduction or flow experiments may not be sufficient to simulate additive deactivation in industrial FCC units. To this end, the deactivation of additives under simulated FCC conditions was investigated. Cyclic deactivation (CD), which deactivates FCC catalyst through cracking, stripping and regeneration cycles, provides a close simulation of the FCC operation and is one of the best deactivation approaches to address additive deactivation [11,12]. By combining CD with the coke combustion test, a more realistic rank of CO combustion promoters can be obtained. As a comparison, the results of a more traditional hydrothermal deactivation protocol are also discussed in this work.

2. Experimental

2.1. Materials

A commercial spent (coked) catalyst (henceforth referred to as Spent Cat) was obtained from a commercial FCC unit. This coked catalyst contained 0.91 wt.% carbon, 470 ppm sulfur, and 220 ppm nitrogen. Several Pt-based commercial CO combustion promoters, referred to as Pt375 to Pt900, were evaluated by the coke combustion test using the Spent Cat. The numbers here indicate the ppm concentration of Pt on the promoters. These promoters came from different vendors and little information was available on their supports.

Table 1

Properties of pre-steamed FCC catalyst (PST FCC Base)

Properties	
RE (wt.%)	2.37
SiO ₂ (wt.%)	40.3
Al ₂ O ₃ (wt.%)	54.5
BET surface area (m ² /g)	137
Micro pore volume (ml/g)	0.0186
Matrix surface area (m ² /g)	97

Two commercial CO combustion promoters, Pt550 and a non-Pt-based Eliminox (Albemarle Grade), were extensively studied for their performance after deactivation. An FCC catalyst was pre-steamed at 788 °C for 20 h in a fixed-fluidized bed reactor under 100% steam before being used in the cyclic deactivation study. The properties of this pre-steamed catalyst (PST FCC Base) are listed in Table 1. A Kuwait vacuum gas oil was used in the cyclic deactivation process. This feedstock has a sulfur content of 3.1 wt.%, total nitrogen concentration of 1027 ppm, and basic nitrogen concentration of 301 ppm. Several developmental samples were also evaluated for their performance before and after cyclic deactivation. These samples are referred to as additives 1–4.

2.2. Catalytic testing

CO combustion promoters were evaluated in the Albemarle advanced additive testing unit (AATU) during the simulated regeneration of a coked catalyst. The reaction unit has a gas feeding system, a fixed-fluidized bed reactor and a gas analysis system (Fig. 1). A multi-gas, FT-IR-based analyzer (MKS 2030) was chosen as the primary gas analyzer. The gases that can be measured include CO_x, SO_x, NO_x (NO, N₂O, NO₂) and HCN as well as some hydrocarbons typically observed during coke combustion. O₂ analysis is conducted using a paramagnetic oxygen analyzer (Oxygen Analyzer Model 100P,

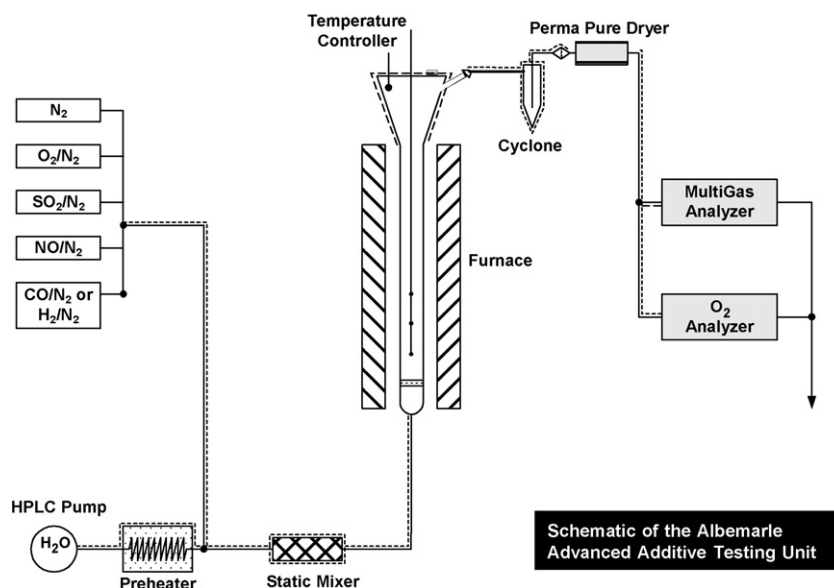


Fig. 1. Schematic of the Albemarle advanced additive testing unit (AATU).

California Analytical Instruments). The reactor can handle sample sizes in the 10–200 g range allowing evaluation of emission control additives at a wide range of concentrations.

Spent Cat was used as the coke source for evaluation of CO combustion promoters in the coke combustion test. In a typical test, 0.5 g of the CO combustion promoter was blended with 49.5 g of Spent Cat and the blend was pretreated in a fixed-fluidized bed reactor under N₂ (1000 sccm) at 700 °C for 1 h. After the pretreatment, 2% O₂ in N₂ was introduced into the reactor at a flow rate of 1000 sccm. The emission gases were monitored by the FT-IR multi-gas analyzer. Reaction temperature was maintained at 700 °C during the coke combustion process. The temperature and O₂ concentration were selected as being representative of full-burn regenerator operation.

CO, SO₂ reduction and NO increase were calculated according to the difference in the total gases released with or without additives (base case) as follows (Eqs. (1)–(3)):

$$\text{CO reduction} = 1 - \frac{\text{Total CO}_{(\text{additive blends})}}{\text{Total CO}_{(\text{base case})}} \quad (1)$$

$$\text{SO}_2 \text{ reduction} = 1 - \frac{\text{Total SO}_{2(\text{additive blends})}}{\text{Total SO}_{2(\text{base case})}} \quad (2)$$

$$\text{NO increase} = \frac{\text{Total NO}_{(\text{additive blends})}}{\text{Total NO}_{(\text{base case})}} - 1 \quad (3)$$

2.3. Additive deactivation

2.3.1. Hydrothermal deactivation

Eliminox and Pt500 were deactivated under 100% steam at different temperatures in a fixed bed reactor. The deactivated promoters were then blended with the Spent Cat at 1 wt.% level and tested in the AATU using a coke combustion test as described in Section 2.2.

2.3.2. Cyclic deactivation

The detailed CD method has been described elsewhere [7,8]. This method has been shown to properly simulate the effects of contaminant metals on FCC materials. Deactivation of the CO combustion promoter was conducted by CD of a blend of additive and the PST FCC base catalyst (Table 1) using the high sulfur Kuwait VGO. No additional metal was added to the feed. The additive level in the blend was 5 wt.%. The deactivation went through cracking, stripping, regeneration cycles and finished after a catalyst regeneration step. This last regeneration step removes deposited coke on the deactivated additive/catalyst blend, negating any impact on the coke combustion test itself from the deactivation process. The number of CD cycles can be adjusted to reflect different deactivation severities. During the regeneration cycles, the partial pressure of steam applied was low in order to better simulate the commercial FCCU operation.

After deactivation, 10 g of the additive/FCC catalyst blend was mixed with 49.5 g of Spent Cat, to keep the overall additive amount 0.5 g. Variation of additive levels can be obtained by changing the amount of the additive/FCC catalyst blend being

mixed with the Spent Cat. The mixture was then evaluated by the coke combustion test.

3. Results and discussion

3.1. Performance of fresh CO combustion promoters

During coke combustion, gases are generated in the order as shown in Fig. 2. CO is detected at the beginning of the coke combustion. For the N-containing compounds, HCN is detected first, followed by N₂O. NO is detected last, when most of the CO is exhausted. These observations are consistent with those observed by other research groups [7].

The coke combustion test was carried out on a series of commercial Pt-based CO combustion promoters, with Pt levels ranging from 375 to 900 ppm. The results (Fig. 3) clearly show that, as expected, CO reduction capability increases with the Pt level of the additive, regardless of the manufacturer. NO_x formation increases about 3.5 times compared to the base case (an FCC spent catalyst with no additive) when Pt-based additives are present. This high NO_x emission changes only slightly with variations in Pt load, indicating substantial NO_x reduction cannot be achieved when Pt-based promoters are utilized. A considerable decrease in NO_x formation is observed when non-Pt-based CO combustion promoters are used. Fig. 3

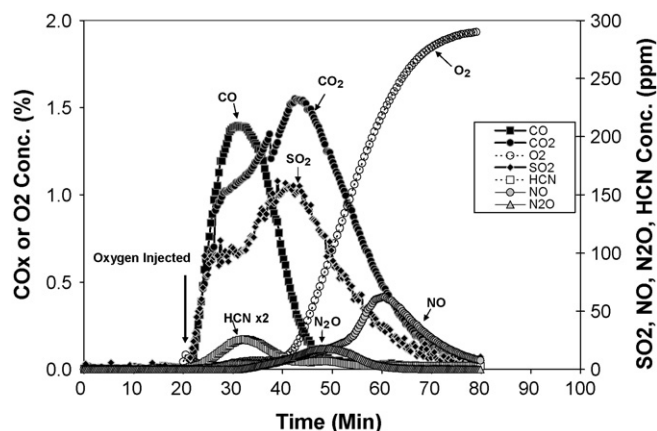


Fig. 2. Gases released during coke combustion of a spent catalyst.

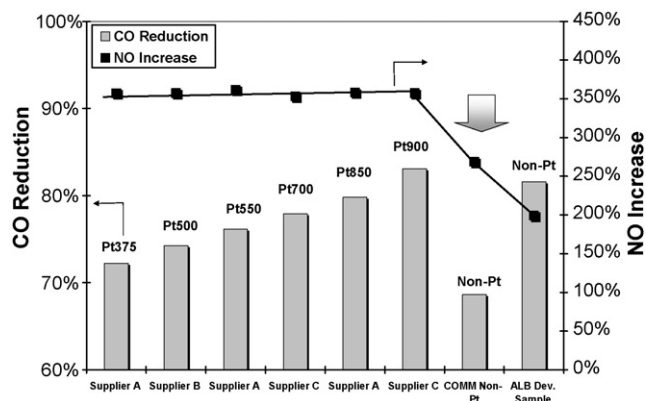


Fig. 3. Coke combustion test results for several commercial CO combustion promoters and an Albemarle development sample.

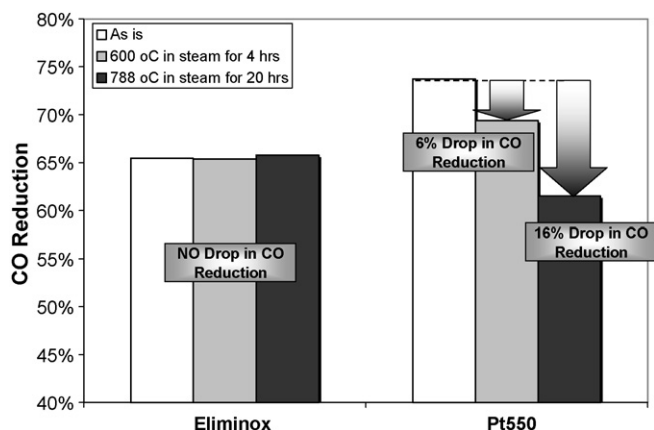


Fig. 4. Performance of Eliminox and Pt550 after hydrothermal deactivation.

demonstrates this effect for a commercially available material and a novel Albemarle-developed non-Pt promoter.

3.2. Performance of deactivated CO combustion promoters

Successful commercial FCC additives require superior resistance to deactivation. To evaluate the deactivation effect on additive performance, hydrothermal deactivation and cyclic deactivation were evaluated.

3.2.1. Hydrothermal deactivation

Hydrothermal deactivation is widely used to deactivate FCC catalyst and additives because of its simplicity. For additives, this deactivation method can lead to change of metal dispersion, as well as changes in surface area and morphology for the additive support. Hydrothermal deactivation was conducted on commercial samples of Eliminox and Pt500 at 600 °C for 4 h and 788 °C for 20 h under 100% steam. The performance of the deactivated additives was compared to that of the fresh additives (Fig. 4). No decrease in CO reduction capability was observed for Eliminox after hydrothermal deactivation; however, 16% drop in CO activity was observed for Pt500 after deactivation at 788 °C for 20 h.

To correlate the change in performance with the change in additive properties, BET surface area (SA) and pore size distribution were analyzed for the fresh and deactivated Pt550 and Eliminox materials. Little difference was observed in SA loss for the two promoters after steam deactivation (Table 2). Pore size distribution indicates that for Pt550, small pores (diameter < 10 nm) collapse after steam deactivation at 600 °C for 4 h, while larger pores are generated after the more severe deactivation at 788 °C for 20 h (Fig. 5(a)). Loss in small pores

(diameter ~ 10 nm) is relatively less for Eliminox after hydrothermal deactivation (Fig. 5(b)). The Eliminox support appears to be more resistant to hydrothermal deactivation which leads to less metal encapsulation due to pore collapse. Consequently, hydrothermal deactivation has less influence on Eliminox compared to Pt550.

Hydrothermal deactivation at 788 °C for 20 h under 100% steam is a typical deactivation protocol for the deactivation of FCC catalysts. However, under this condition the CO reduction for the deactivated Pt550 is inferior to that of deactivated Eliminox; this is not in-line with our commercial experience. Therefore, this deactivation condition may be too severe for emission control additives. Furthermore, the effect of oil cracking on additive performance cannot be addressed by hydrothermal deactivation procedures. Thus, a more realistic, milder deactivation is needed to simulate the commercial performance of these additives.

3.2.2. Cyclic deactivation

Cyclic deactivation (CD) [6], which involves cracking, stripping and regeneration cycles, is widely accepted as a better representative to the FCC process. Using this method, most of the deactivation mechanisms in FCC can be addressed.

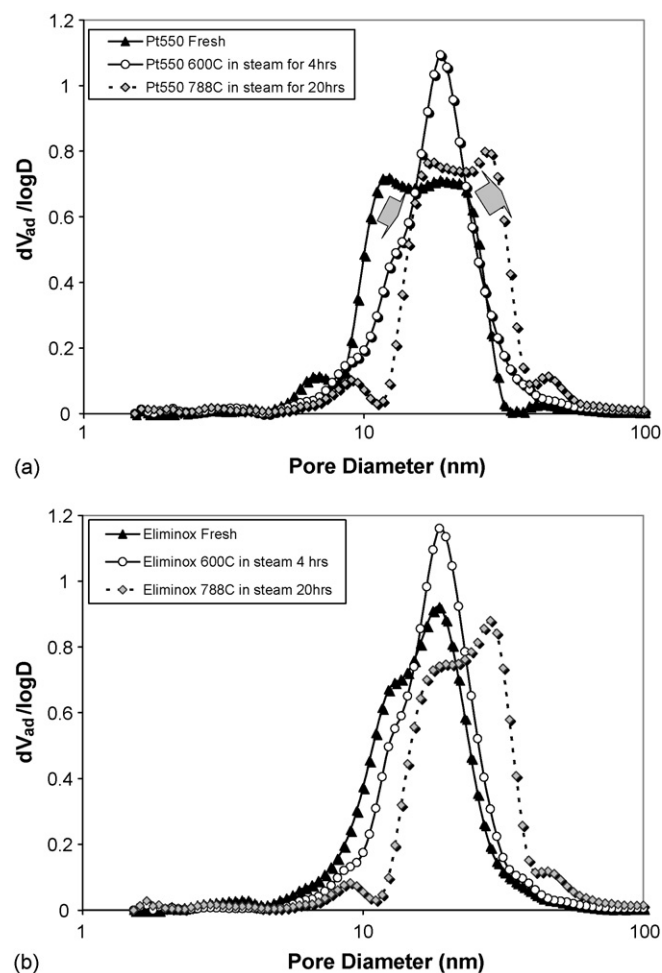


Fig. 5. Pore size distribution for (a) fresh and steam deactivated Pt550, and (b) fresh and steam deactivated Eliminox.

Table 2
SA BET before and after hydrothermal deactivation

Additive	SA BET (m ² /g)		
	As Is	600 °C, 4 h ^a	788 °C, 20 h ^a
Eliminox	110	97	79
Pt550	106	93	79

^a Hydrothermal deactivation condition.

Table 3
Effect of FCC catalyst on the gas emission of the Spent Cat

Change in gas emission	%
CO reduction	–1
NO increase	–11
SO ₂ reduction	–13

The pre-steamed catalyst (PST FCC base) is introduced to crack the FCC feed during the deactivation process, as cyclic deactivation of the additives by themselves does not properly simulate a cracking environment. A 50 cycle procedure was chosen as the default for cyclic additive deactivation. The 50 CD cycles correspond to, roughly, a 1-day deactivation, selected because typical deactivation half-life for emission control additives can vary from a few hours to a few days. As the coke remaining on the deactivated FCC base/additive blend is negligible, the coke source for the coke combustion test is still the spent catalyst. Therefore, the amount and the type of coke continue to be constant for the performance evaluation. Compared to the coke combustion test for the fresh additives, an extra 9.5 g of cyclically deactivated FCC catalyst is present in the system. Traditional FCC catalysts should not have a large influence on the coke combustion of an external coke source, as confirmed by the results from a coke combustion test of the cyclically deactivated PST FCC base by itself (Table 3). Thus,

PST FCC base can be regarded as an inert carrier to the deactivation of CO combustion promoters.

Cyclic deactivation was conducted on several novel Albemarle developed low NO_x CO combustion promoters, additives 1–4. Pt550 and Eliminox were also evaluated as the benchmarks. Comparing the coke combustion test results for both the fresh and cyclically deactivated additives, it was found that the rank in CO reduction changed significantly after deactivation. Before deactivation, all four development samples provided similar or better CO reduction compared to Pt550 (Fig. 6(a)). In addition, the NO_x formation for these four additives was much lower than that of the Eliminox (Fig. 6(b)). After cyclic deactivation, additives 3 and 4 showed markedly reduced CO reduction, while additives 1 and 2 continued to provide better CO reduction compared to Pt550 and lower NO_x formation compared to Eliminox (Fig. 6(c) and (d)).

The change in additive performance after deactivation can be used to derive possible deactivation mechanisms at work. For example, depending on their support (and strength of the metal–support interaction), some additives will deactivate faster than others. It has also been observed that some additives with low metal loading, when tested fresh, exhibited similar activity in CO reduction compared to others with higher metal loading. However, after deactivation, their efficiency in CO reduction decreases. The good performance for the fresh low

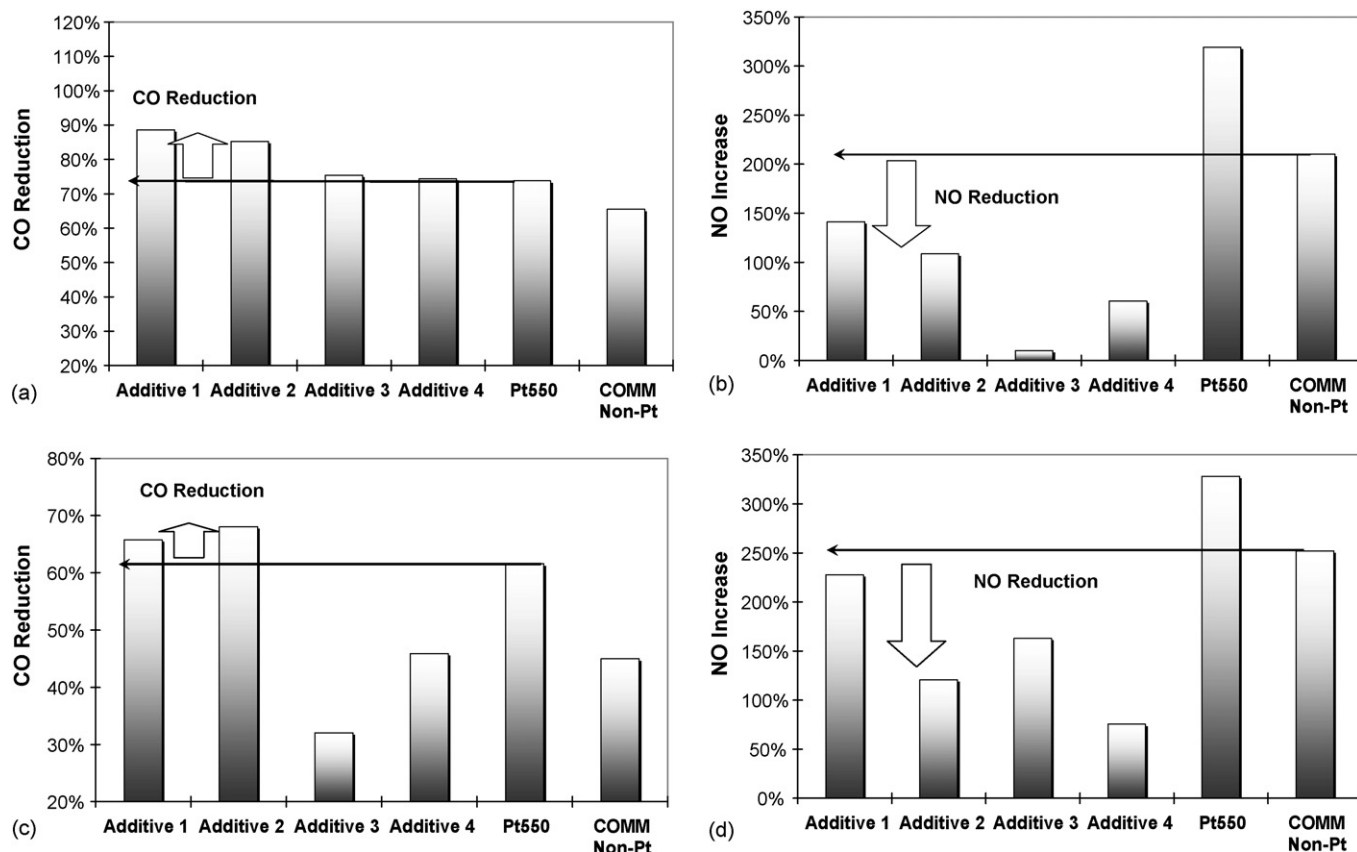


Fig. 6. (a) CO reduction for fresh lab-developed CO combustion promoters; (b) NO emission for fresh lab-developed CO combustion promoters; (c) CO reduction for lab-developed CO combustion promoters after cyclic deactivation; (d) NO emission for lab-developed CO combustion promoters after cyclic deactivation.

metal containing additives may result from initial better metal dispersion for these additives. However, after deactivation, metal sintering seems to lead to a quick decrease in their CO reduction ability. Thus, the expected ranking in performance is observed, with the high metal content additives featuring superior CO reduction ability than the lower metal materials.

4. Conclusion

Cyclic deactivation provides a close simulation of the FCC operation and can address many possibilities for the deactivation of CO combustion promoters. Results show that by combining cyclic deactivation with the coke combustion test, the performance ranking of commercial as well as developmental additives is significantly affected. Using this deactivation and testing protocols, CO combustion promoters with exceptional performance have been identified. These novel materials feature CO reduction performance similar to the Pt-based promoters while minimizing the attendant NO_x increase relative to Pt. This method can also be a powerful tool for the development of SO_x and NO_x reduction additives for FCC commercial operations.

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