

Ag-Based Catalytic Additives for the Simultaneous Reduction of NO and CO Emissions from the Regenerator of a FCC Unit

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Spent FCC catalyst was regenerated in a fluidized-bed reactor at 700 °C using a 2% O₂ in N₂ feed. The NO and CO emissions during regeneration were measured when Ag-based additives were used and compared with those when a commercial Pt-based CO promoter (1% CP-3) was added. All Ag/alumina additives exhibited high NO reduction ability (up to 70%), with the highest deNO_x efficiency achieved with moderate Ag loading (3%). A different trend was measured for the CO emissions: the higher the Ag loading (1–5%) on alumina, the higher was the CO oxidation. However, higher CO emissions were always measured when Ag-based additives were used as compared to those when CP-3 was used. The Ag-based additives exhibited stability problems, as disaggregation of Ag particles from the alumina support was observed. When the support was promoted with 10% Ce, stable Ag-based additives were synthesized and the CO oxidation ability was enhanced. When we increased the metal loading (up to 10% Ag) and/or the Ce percentage (up to 20%) on the catalytic support, the CO oxidation over Ag/Ce-based additives was further enhanced and the NO reduction was maintained to adequately high levels (≥36%). The NO and CO emissions were simultaneously reduced to the desired level, when we increased the amount of the most promising additive (Ag(5%)/Ce(20%)CPBase) in the reactor or when we used this additive in combination with small amounts of CP-3. The performance of Ag/Ce-based additives was linked with formation of different crystal phases on the additive. The presence of the Ag₂O crystal phase on the most promising additive resulted in the reduction of the NO and CO emissions. When the Ag loading increased, metallic silver was formed that enhanced the CO oxidation.

Introduction

Limitations on the nitrogen oxides (NO_x) emissions from all refinery sources including FCC regenerators are becoming more and more stringent worldwide. 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, while the NO_x (mainly NO) concentration in flue gases varies between 50 and 500 ppm.¹ The origin of NO_x emissions in an FCC regenerator is burning off the nitrogen-containing species in coke deposited on the catalyst during the cracking cycle (fuel NO_x).² Among candidate NO_x control technologies, use of catalytic additives is the most attractive one, as it is simple, cost-effective, and applicable in existing FCC units without significant modifications in the regenerator design or the unit operating conditions. The function of these additives in the FCC inventory is to reduce the NO emissions without adversely affecting the cracking activity and selectivity of FCC catalyst and without the formation of undesired pollutants. CO promoters catalyze the CO oxidation³ and are used in most refineries. Therefore, NO_x reduction additives should either operate in the presence of a conventional CO promoter or have the ability to simultaneously reduce NO and CO emissions. NO_x reduction additives have been previously patented^{4–9} or reported^{10–12} by several groups. The synthesis of two NO_x reduction additives (DeNO_x and XNO_x) has been

patented by Grace.^{13,14} The former additive is a NO_x reduction additive for FCCU¹³ that can be used simultaneously with a CO promoter, while the latter one is an additive that acts both as CO promoter and NO_x reduction additive.¹⁴ According to the first patent¹³ Cu and/or Ag is the active site that reduces the NO emissions in the DeNO_x additive.

The activity of Ag-based catalysts for the selective catalytic reduction (SCR) of NO_x by a reductant in the presence of excess O₂ has been studied previously. Ag was supported on various materials, while various reductants including hydrocarbons or oxygenates were tested (refs 15–35 and 38 and references herein). Ag-based catalysts are promising for commercial applications, as they are active and durable in the presence of water and sulfur dioxide,^{15–21} especially at high reaction temperatures.^{21–23} Even a promotional effect of SO₂ on the deNO_x activity of Ag/alumina catalysts has been reported.^{15,24} The selectivity to N₂ formation over Ag-based catalysts is high, and this renders these materials more attractive as compared to catalysts based on noble metals.²⁵

The preparation method of Ag-based catalysts affects their catalytic performance. When lactic silver was used as the precursor salt, Ag metal distributed homogeneously on the alumina support.^{15,24} Ag/alumina catalysts were also synthesized from inverse microemulsions²⁶ or from boehmite needles,¹⁶ which were formed by a hydrolysis of aluminum triisopropoxide. Use of boehmite needles as a precursor of the alumina support proved to be very useful for the formation of catalytically active sites for NO_x reduction.¹⁶ Several other prepara-

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Table 1. List of Ag-Based Catalytic Additives Synthesized Using the Dry Impregnation Technique^a

additive	metal loading (%)		precursor salt
	nominal	measured by ICP	
Ag/CPBase	1% Ag	0.8 ± 0.05% Ag	AgNO ₃
	3% Ag	2.3 ± 0.1% Ag	
	5% Ag	4.1 ± 0.2% Ag	
Ag/Ce1CPBase	5% Ag, 10% Ce	4.0 ± 0.2% Ag, 8.7 ± 0.2% Ce	AgNO ₃ , Ce(NO ₃) ₃ ·6H ₂ O
	10% Ag, 10% Ce	8.5 ± 0.5% Ag, 8.2 ± 0.5% Ce	
Ag/Ce2CPBase	5% Ag, 20% Ce	4.1 ± 0.2% Ag, 17.1 ± 0.9% Ce	
	10% Ag, 20% Ce	7.2 ± 0.3% Ag, 16.3 ± 0.9% Ce	

^a Calcination conditions: 700 °C for 6 h under air flow.

tion techniques have been applied for the synthesis of Ag/alumina catalysts resulting in very active materials for the SCR of NO_x. These included multiple impregnations,²⁷ a single-step co-gelation process,¹⁷ a polyol process, usually applied for synthesis of monodisperse metal powders,²⁸ coprecipitation,²⁹ and sol–gel methods.^{29–31} The sol–gel catalysts were the most active ones. They were thermally stable and exhibited enhanced resistance to the presence of water vapor and SO₂.²⁹ Finally, ZSM-5-supported silver catalysts were prepared by an ion-exchange procedure carried out in the dark.^{32,33} Li and Flytzani-Stephanopoulos^{32, 33} also reported a synergistic effect between Ce and Ag over a cerium-promoted Ag-ZSM-5 catalyst. Incorporation of Ce into Ag-ZSM-5 enhanced its activity and selectivity for the selective catalytic reduction of NO_x by methane. The role of Ce was to catalyze NO oxidation to NO₂ (reduction of NO₂ takes place on Ag sites), to suppress the combustion of the reductant, and to stabilize Ag in the Ag⁺ state. Ag was also better dispersed in the presence of Ce, as interaction of Ce and Ag inhibited the formation of large metallic silver particles.^{32,33} A Ce-promoted support could also act as a sink for sulfur-containing species present during reaction, thus permitting an improved sulfur resistance.³⁴ A similar synergism between Cu/Ce was also reported when the NO reduction activity by CO was measured in the presence of O₂, H₂O, and SO₂ under conditions similar to those found in the dense phase bed of an FCC regenerator.¹² Among three catalysts, CuMgAlO, CeMgAlO, and CuCeMgAlO prepared by coprecipitation, the CuCe-cat exhibited an enhanced performance. This was attributed to a synergistic effect between copper and cerium ions, which results in the formation of large amounts of Cu⁺ ions and oxygen vacancies in the sample.¹² Ag-based catalysts receive special attention in a recent review on SCR of NO_x with hydrocarbons, where the reaction mechanism on silver-based formulations is extensively discussed.³⁵ It is suggested that different Ag loadings result in different catalytic phases that are related to different reaction pathways.³⁵

The scope of this work was to develop a series of Ag-based additives for the simultaneous reduction of the NO and CO emissions during regeneration of spent FCC catalyst. Experiments in the presence of 1% CP-3 (a Pt-based conventional CO promoter) was used as the base case for the evaluation of the additives' performance. The parameters that were investigated included the type of catalytic support, the metal loading on the additive, and the amount of Ag-based additive used during regeneration. The evaluation of additives performance followed a testing protocol developed in our previous work.³⁶ Ag-based additives were evaluated in the absence or the presence of CP-3. Differences in the catalytic performance of the additives were associated with differences in the physicochemical properties of the samples.

Experimental Section

Materials. Spent (coked) catalyst and CP-3, a Pt-based commercial CO promoter, were supplied by Grace GmbH. Spent catalyst was regenerated in a bench-scale unit that simulates the regenerator of a fluid catalytic cracking unit.³⁶ A series of Ag-based catalytic additives were prepared using the dry impregnation technique. AgNO₃ was used as the precursor salt. After the impregnation, all catalysts were dried at 120 °C for 2 h and then calcined at 700 °C for 6 h under air flow. The catalytic support used was CPBase, a commercial γ -alumina, supplied by Grace GmbH. CPBase-alumina was used either unpromoted or promoted with 10% Ce (Ce1CPBase) or 20% Ce (Ce2CPBase). When Ce was added in the catalyst, Ce and Ag were deposited sequentially. Ce was initially impregnated, using Ce(NO₃)₃·6H₂O as the precursor salt, the sample was calcined at 500 °C for 3 h, and Ag impregnation followed. A series of Ag/CPBase-alumina catalytic additives was initially prepared according to the previous procedure. The Ag loading ranged from 1 to 5%. A series of Ag/Ce1CPBase-alumina or Ag/Ce2CPBase-alumina additives was prepared varying the Ag loading on the additive from 5 to 10%. All catalytic additives prepared and tested during this work are summarized in Table 1.

Experimental Setup. All regeneration experiments were carried out in a bench-scale reaction unit using a protocol that sufficiently simulates the regenerator of a fluid catalytic cracking unit operating in a full-burn mode.³⁶ Detailed description of this unit can be found in our previous work.³⁶ All experiments were carried out in a fluidized-bed reactor (i.d. 3.2 cm), and the total flow rate was 1000 cm³/min. Superficial gas velocity (at 700 °C) in the bubbling fluidized bed is calculated to be ~6.5 cm/s (with u_{mf} ~0.3–1 cm/s).³⁷ This is a value very similar to that of the CPERI pilot plant FCC unit (~6 cm/s) that, as validated in our previous work,³⁶ simulates adequately the operation of commercial units in full burn. A 2% O₂ in N₂ feed was used in all cases, while the reactor loading was 10 g. Mechanical mixtures of spent catalyst with candidate additives were loaded in the reactor and regeneration took place at 700 °C.

ICP/AES analysis was carried out in a Plasma 400 (Perkin-Elmer) spectrometer, equipped with Cetac-6000AT+ ultrasonic nebulizer. The crystalline structure of the supports was studied taking X-ray diffraction patterns in a Siemens D500 diffractometer, using Cu(K α) radiation. Scanning electron microscope (SEM) pictures were taken using a JEOL 6300 instrument

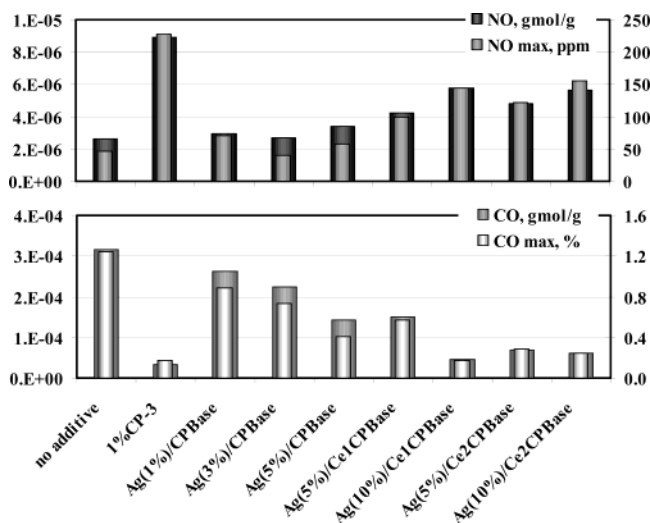


Figure 1. Overall amount and maximum concentrations of NO and CO emitted during regeneration of spent FCC catalyst in the absence or presence of 1% additive (CP-3 or Ag-based materials).

equipped with an X-ray microanalyzer (Oxford ISIS 2000). The SEM magnification ability was from 10 to 300,000. Elemental microanalysis and mapping of surfaces was achieved using the X-ray energy dispersive spectroscopy system.

Results and Discussion

Regeneration Studies. In our previous work, we presented regeneration experiments of either pure spent FCC catalyst or a mechanical mixture of the same unpromoted spent FCC catalyst with a commercial Pt-based CO promoter (CP-3) at 700 °C in a fluidized-bed reactor using a 2% O₂ in N₂ feed.³⁶ The presence of a conventional CO promoter (CP-3) in the catalytic inventory decreased the CO emissions by ~1 order of magnitude but almost tripled the NO emissions.³⁶ In this work, we present either the overall CO and NO emissions during the experiment or the maximum concentrations measured during regeneration. The overall CO and NO emissions are calculated from the integration of the raw data (NO and CO concentration vs regeneration time) using the trapezoidal rule and are expressed as gram moles per gram of spent catalyst in the reactor. Given that we evaluate the performance of additives for FCCUs operating in the full-burn mode, in other words, adding CO promoter in their inventory, we considered as base case the CO and NO emissions during the experiment where the reactor was loaded with 99% spent catalyst and 1% CP-3. The percentage of the NO or CO reduction was calculated by comparing the total amounts of NO or CO emitted in the presence of each additive with the corresponding emissions emitted in the presence of 1% CP-3, respectively.³⁶

A series of Ag/CPBase-alumina additives with different Ag loadings was initially tested loading the reactor with mechanical mixtures of 1% of these additives with pure spent FCC catalyst. The Ag loading on the additive was 1, 3, and 5%, and regeneration took place at 700 °C using a 2% O₂ in N₂ feed. In Figure 1 and Table 2, we present the total amounts of CO and NO emitted during regeneration in the presence of these Ag/CPBase additives. In Figure 1, we also present the maximum concentrations of NO and CO during the experiment. For comparison reasons we included in Figure 1 and

Table 2. Total CO and NO Emissions during Regeneration of Spent Catalyst in the Absence or in the Presence of 1% Catalytic Additive^a

additive	total emissions (g mol/g of spent catalyst)	
	NO ($\times 10^{-6}$)	CO ($\times 10^{-5}$)
none	2.62	31.50
CP-3	8.93	3.25
Ag(1%)/CPBase	2.92	26.32
Ag(3%)/CPBase	2.71	22.30
Ag(5%)/CPBase	3.39	14.39
Ag(5%)/Ce(10%)CPBase	4.21	15.10
Ag(10%)/Ce(10%)CPBase	5.74	4.54
Ag(5%)/Ce(20%)CPBase	4.81	6.82
Ag(10%)/Ce(20%)CPBase	5.63	6.06

^a Regeneration at 700 °C with 2% O₂ in N₂.

Table 3. Percentage of CO Oxidized (Positive Sign) and NO Reduced (Positive Sign) as a Result of the Presence of 1% Ag-Based Additives As Compared to the Base Case Experiment (1% CP-3)^a

additive	NO (%)	CO (%)
CP-3	base	base
Ag(1%)/CPBase	67.32	-709.85*
Ag(3%)/CPBase	69.65	-586.15*
Ag(5%)/CPBase	62.07	-342.77*
Ag(5%)/Ce(10%)CPBase	52.85	-363.17*
Ag(10%)/Ce(10%)CPBase	35.69	-39.55*
Ag(5%)/Ce(20%)CPBase	46.17	-109.94*
Ag(10%)/Ce(20%)CPBase	36.93	-86.34*

^a Regeneration at 700 °C with 2% O₂ in N₂.

Table 2 experimental results from experiments where no additive or 1% CP-3 (base case) was used. In Table 3 we present the NO and CO conversion as a result of the additives' presence in the reactor as compared to the base case. The negative values in the CO conversion are the result of the higher CO emissions in the presence of the Ag additives as compared to the base case. All Ag/CPBase additives are effective for NO reduction. An increase in the Ag loading from 1 to 3% slightly increased the NO conversion from ~67 to ~70%, while a further increase of Ag loading to 5% decreased the NO conversion to ~62%. These results imply that in agreement with the literature^{20,26,38} intermediate Ag loading (3%) on the additive led to the maximum reduction of NO emissions. The CO oxidation ability of the additives was strongly enhanced when the Ag loading increased, though higher CO emissions were always measured as compared with those in the presence of CP-3 (base case). The NO emissions when Ag/CPBase additives were used were approximately the same as those in the additive-free experiments. However, these additives oxidize CO to a lesser extent as compared to the CP-3-containing experiments. During storage of Ag/CPBase catalytic additives, we additionally observed that they exhibited stability problems with time. This was evidenced by a color change from white to gray and a disaggregation of the silver phase from the alumina support. This was attributed to the modification of the silver phase.

We have previously mentioned that the preparation of Ag-based catalysts (preparation procedure, precursor salt, and catalytic support) critically affects their catalytic performance. The several positive effects of Ce presence on the catalytic performance of Ag-based materials were previously underlined and motivated us to add Ce in our catalytic formulations. We incorporated Ce in our Ag/CPBase catalyst, aiming at the enhancement of catalyst stability and at the improvement of its activity. We synthesized Ag(5%)/Ce(10%)CPBase, and

we observed no disaggregation of Ag from the alumina support with time. This behavior was in agreement with the work of Li and Flytzani-Stephanopoulos, where the Ce presence hindered catalyst color gradation from white to gray.³³ Moreover, CO oxidation over Ag(5%)/Ce(10%)CPBase was maintained, while its NO reduction ability decreased as compared to the Ag(5%)/CPBase (Table 2). Following that, we increased the cerium or silver loading from 10 to 20% and from 5 to 10%, respectively. The four Ag/Ce additives are listed in Table 1. Mechanical mixtures of 1% of these additives with pure spent FCC catalyst were loaded in the fluid-bed reactor and regeneration took place with 2% O₂ in N₂. The overall NO and CO emissions and the percentage of NO and CO conversion due to the presence of additives in the reactor are summarized in Tables 2 and 3. The overall and the maximum NO and CO emissions during regeneration in the presence of Ag/Ce additives are also presented in Figure 1. Promoting CPBase-alumina with higher Ce loadings (20%) or increasing the Ag loading up to 10% led to the enhancement of the CO oxidation and the inhibition of the NO reduction ability of the additives. When Ag was impregnated on the Ce1CPBase support, NO reduction ability decreased from 53 to 36% and CO oxidation increased from -363 to -40% (Table 3). As a result, this catalytic formulation is moderately efficient for NO reduction and adequately efficient for CO oxidation. Simultaneous reduction of the NO and CO emissions was observed over Ag(5%)/Ce-(20%)CPBase, where the NO conversion reached 46%. The higher the Ag or Ce loading the higher was the CO oxidation. On the other hand, when Ce was added in the support, the higher the Ag loading the lower was the NO conversion. The effect of Ag loading on the extent of the SCR of NO_x has been studied in previous works.^{20,21,26,33,38–41} According to the literature, catalysts with low Ag loading contained silver in the +1 oxidation state, while catalysts of higher Ag loading contained Ag⁰ particles.^{31,35,38} The Ag interaction with the alumina support enhances the Ag stabilization in a certain oxidization state. On the contrary, higher Ag loadings resulted in lower deNO_x activity. This was attributed to the enhancement of the hydrocarbon (reductant) oxidation at the expense of its reaction with NO. In some SCR studies, higher Ag loadings led to low selectivity for N₂ formation, as significant amounts of N₂O were formed during NO_x reduction.^{42,43} No N₂O formation was detected during the regeneration experiments of this study, even when the highest Ag loading (10% Ag) was used. This was attributed to N₂O decomposition at the regeneration temperature of this work that was significantly higher than those used in SCR studies.

All previous regeneration experiments were performed mixing 1% of each one of the candidate Ag-based additives with 99% spent catalyst. This percentage was selected because if a lower one was used we could face mixing problems in the preparation of the reactor loading. In commercial applications, the addition of the additives in the inventory is continuous and a lower or a higher percentage of the additive in the inventory can be used. We studied the effect of the additive's percentage in our reactor using three concentrations of the additive: 1, 3, and 5%. In these experiments, the additive was Ag(5%)/Ce2CPBase. The overall NO and CO emissions due to the presence of additive are presented in Figure 2 and Table 4. An increase of the additive concentration from 1 to 3% and to 5% resulted

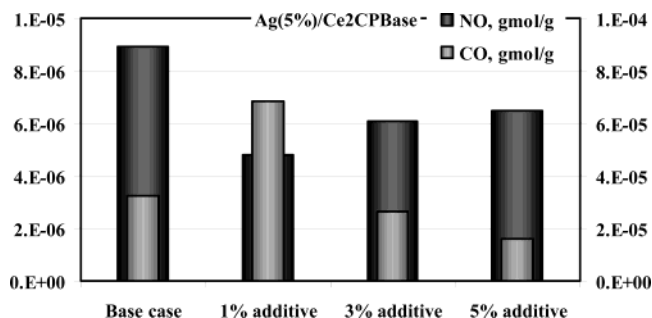


Figure 2. Effect of the percentage of Ag(5%)/Ce(20%)CPBase in the reactor mixed with spent catalyst on the simultaneous reduction of CO and NO emissions during regeneration as compared to the base case (1% CP-3).

Table 4. Effect of the Percentage of Ag(5%)/Ce(20%)CPBase in the Reactor^a

additive	total emissions (g mol/g of spent catalyst)	
	NO ($\times 10^{-6}$)	CO ($\times 10^{-5}$)
1% CP-3	8.93	3.25
1% Ag(5%)/Ce(20%)CPBase	4.81	6.82
3% Ag(5%)/Ce(20%)CPBase	6.09	2.65
5% Ag(5%)/Ce(20%)CPBase	6.46	1.61

^a Regeneration at 700 °C with 2% O₂ in N₂.

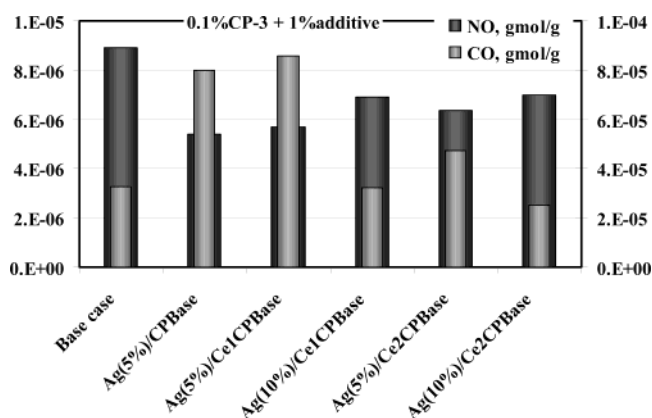


Figure 3. Effect of the coexistence of 0.1% CP-3 and 1% Ag-based additives (supported on unpromoted or Ce-promoted CPBase-alumina) on the overall CO and NO emissions during regeneration. Base case: regeneration in the presence of only 1% CP-3.

in lower NO conversions (46, 32, and 28%, respectively). However, CO oxidation was significantly enhanced as the percentage of the additive in the reactor increased, reaching lower CO emissions than in the presence of CP-3. When the intermediate concentration of the additive (3 wt % Ag(5%)/Ce2CPBase) was used, adequately low NO and CO emissions were measured.

The simultaneous reduction of NO and CO emissions can be managed either using one additive that acts as both an NO_x reduction additive and a CO promoter or using two distinct additives for the NO reduction and the CO oxidation. In the previous sections of this work, we considered the former case. Following that, the latter case was examined using mechanical mixtures of additives synthesized in this work and a conventional CO promoter (CP-3). We added small amounts (0.1%) of CP-3, as the Ag-based additives already exhibit some CO oxidation activity. In this series of experiments, the reactor was loaded with mechanical mixtures of 1% Ag-based additive, 0.1% CP-3, and 98.9% spent catalyst. The feed in the regeneration experiments was 2% O₂ in N₂. The experimental results are presented in Figure 3

Table 5. Total CO and NO Emissions during Regeneration of Mechanical Mixtures of 1% Ag-Based Additives-0.1% CP-3-98.9% Spent Catalyst Percentage of CO Oxidized (Positive Sign) and NO Reduced (Positive Sign) as Compared to the Base Case

additives	total emissions (g mol/g of spent catalyst)		% conversion	
	NO ($\times 10^{-6}$)	CO ($\times 10^{-5}$)	NO	CO
Ag(5%)/CPBase+CP-3	5.41	7.98	39.42	-145.54
Ag(5%)/Ce(10%)CPBase+CP-3	5.67	8.56	36.51	-163.38
Ag(10%)/Ce(10%)CPBase+CP-3	6.90	3.23	22.69	0.65
Ag(5%)/Ce(20%)CPBase+CP-3	6.35	4.72	28.89	-45.23
Ag(10%)/Ce(20%)CPBase+CP-3	6.97	2.52	21.94	22.55

^a Regeneration at 700 °C using 2% O₂ in N₂.

and Table 5. Comparison of the regeneration data in the absence (Tables 2 and 3) and the presence of CP-3 (Table 5) showed that the presence of small CP-3 concentrations in the reactor affected negatively the NO reduction over all additives. This was attributed mainly to the high oxidation efficiency of CP-3. As a result, CO is oxidized to CO₂ over the above additive, and thus, NO reduction by CO is inhibited. However, the additives' deNO_x performance is still substantial, while the CO emissions are comparable or even lower than those in the base case experiment.

Characterization Studies. We measured the actual Ag loading on the catalysts applying the ICP technique. The metal was converted to a soluble nitrate salt by immersing the catalyst into hot concentrated nitric acid. The ICP results are summarized in Table 1. In all cases, the measured Ag loading was lower than the nominal Ag loading. We attribute the difference between nominal and actual Ag loading to the following reason. Due to the high calcination temperature, part of the silver in the catalytic additives is bound to alumina so strongly that hot nitric acid cannot dissolve it.²⁹ According to the literature,^{40,44} this may enhance the catalytic performance. The calcination procedure induces an interaction between Ag particles and Al₂O₃, which stabilizes the silver compounds formed.^{18,38} The enhancement caused by high calcination temperatures may also be related to the formation of silver aluminate phases.^{17,43,44} When an XRD-detectable silver aluminate phase is generated by hydrothermal treatment at 800 °C, the performance of Ag-based catalysts is significantly improved.¹⁹

The catalytic performance of different Ag/Ce-based catalysts changed with the percentage of Ag and Ce in the sample. This motivated us to investigate the structure (type of Ag active phase) in four catalytic additives synthesized in this work. It has been reported that metallic silver particles prevail when high loadings are used, whereas silver oxide species are observed when lower loadings are used or the samples are calcined at high temperature.^{33,35,40,41} The metal loading may affect the oxidation state.^{26,30,35,38} Moreover, the reaction pathway for N₂ formation changes with the oxidation state of Ag.³⁵ A decomposition-type mechanism was proposed over metallic silver particles, whereas NO₂ formation and its subsequent reduction was proposed for the NO reduction over the Ag⁺ phase.^{35,42}

In Figure 4, we compare the XRD spectra of the four additives. Labels are used to indicate the crystalline structures that exist in each sample. Samples with different Ag or Ce loading exhibit different crystal phases. In all samples, the existence of γ -alumina and CeO₂ is evidenced. Peaks assigned to CeO₂ are more

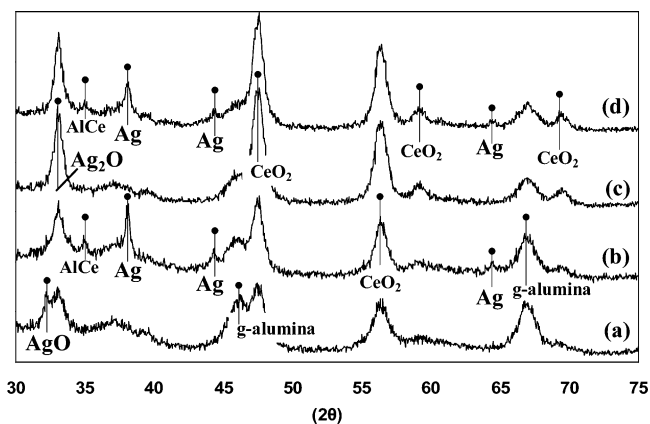


Figure 4. XRD patterns: (a) Ag(5%)/Ce(10%)CPBase-alumina, (b) Ag(10%)/Ce(10%)CPBase-alumina, (c) Ag(5%)/Ce(20%)CPBase-alumina, and (d) Ag(10%)/Ce(20%)CPBase-alumina catalytic additives. Identification of crystal phases formed.

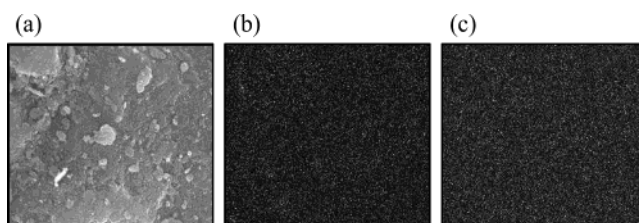


Figure 5. SEM micrographs of the Ag(5%)/Ce(20%)CPBase-alumina catalytic additive. Mapping of Ag (b) and Ce (c) on the catalytic surface.

intense in the samples of high (20%) Ce loading. In these samples, the peaks at $(2\theta) \sim 46$ and 67 (assigned to γ -alumina) are less intense, implying that either alumina is covered by CeO₂ or a mixed phase is formed. The peak at $(2\theta) \sim 35$ that is assigned to a AlCe phase supports the latter possibility. The AlCe phase may inhibit NO reduction. Formation of different Ag crystal phases is also noticed over the additives. In the XRD spectra of the Ag(5%)/Ce(20%)CPBase additive, we detected that Ag exists in the form of Ag₂O. According to the literature,³⁸ bulk Ag₂O decomposes to metallic Ag rapidly at 250 °C in air. We attribute the stabilization of the oxidized Ag phase over this sample to its interaction with alumina. The ability of this additive to simultaneously reduce the NO and CO emissions was linked to the existence of this crystal phase^{45,46} as Ag₂O can be either reduced to Ag⁰ or oxidized to AgO from the flue gases emitted during regeneration. Over the other samples that were characterized, we detected AgO, metallic Ag, or both. Metallic silver was detected over the two additives with the highest Ag loading (10%) in the form of a three peaks at $(2\theta) \sim 38$, 44 , and 64 .^{29,41,44} These two additives exhibited the best performance for CO oxidation in agreement with previous studies, where metallic silver was very active for the oxidation of the reductant.^{21,26,27,38,39}

SEM micrographs of Ag/CeCPBase catalytic additives were taken. In Figure 5a, we present some of these micrographs. No Ag particulates were detected over all materials under study. We also performed a mapping both for Ag (Figure 5b) and Ce (Figure 5c). Both Ag and Ce phases were finely dispersed on the catalyst surface. High Ag dispersion was measured over alumina support, and the dispersion was linked to the high activity for the NO reduction.³⁸

Conclusions

Regeneration studies of spent FCC catalyst were performed in a fluidized-bed reactor of a bench-scale unit using a protocol that simulates the operation of the regenerator of a FCC unit. The presence of a commercial CO promoter (CP-3) was used as the base case for the evaluation of a series of Ag-based additives. Initially, a series of Ag/alumina catalysts was tested as candidate materials for the simultaneous CO oxidation and NO reduction. All Ag/alumina additives were efficient for NO reduction, but high CO emissions were measured. These additives also exhibited stability problems. When 10% Ce was added to the support, stable Ag/Ce-based additives were synthesized with improved CO oxidation ability. An increase of the Ce content to 20% or the Ag loading to 10% enhanced the CO oxidation, while the NO reduction decreased. The Ag(5%)/Ce(20%)CPBase-alumina was the most promising additive. When the percentage of this additive in the reactor increased or when it was used along with small amounts of CP-3, the NO emissions were lower and the CO emissions were equally low or even lower than those in the base case experiment (presence of 1%CP-3). XRD characterization of the Ag/Ce-based additives showed that variation in the Ag or Ce loading affects the type of crystal phases formed on the catalytic surface. Additives that reduce both the NO and CO emissions contain Ag in the form of Ag₂O. Ag-based additives with high Ag loading are very active for the CO oxidation but are moderately active for the NO reduction. This was attributed to the presence of metallic silver. SEM pictures showed high dispersion of both Ag and Ce on the catalytic surface.

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