



Article **Practical Approaches towards NO_x Emission Mitigation from Fluid Catalytic Cracking (FCC) Units**

Aleksei Vjunov *, Karl C. Kharas, Vasileios Komvokis, Amy Dundee and Bilge Yilmaz *D

BASF Corporation, 25 Middlesex/Essex Turnpike, Iselin, NJ 08830, USA; karl.kharas@basf.com (K.C.K.); vasileios.komvokis@basf.com (V.K.); amy.dundee@basf.com (A.D.)

* Correspondence: aleksei.vjunov@basf.com (A.V.); bilge.yilmaz@basf.com (B.Y.); Tel.: +1-732-205-7003 (A.V.); +1-732-205-5232 (B.Y.)

Abstract: There appears to be consensus among the general public that curtailing harmful emissions resulting from industrial, petrochemical and transportation sectors is a common good. However, there is also a need for balancing operating expenditures for applying the required technical solutions and implementing advanced emission mitigation technologies to meet desired sustainability goals. The emission of NO_x from Fluid Catalytic Cracking (FCC) units in refineries for petroleum processing is a major concern, especially for those units located in densely populated urban settings. In this work we strive to review options towards cost-efficient and pragmatic emissions mitigation using optimal amounts of precious metal while evaluating the potential benefits of typical promoter dopant packages. We demonstrate that at present catalyst development level the refinery is no longer forced to make a promoter selection based on preconceived notions regarding precious metal activity but can rather make decisions based on the best "total cost" financial impact to the operation without measurable loss of the CO/NO_x emission selectivity.

Keywords: Pd-based promoter; NO_x emission; environmental catalysis; refinery compliance; FCC

1. Instructions

As society develops awareness and concern regarding the extent that environmental pollution, in particular that of the atmosphere, has a negative impact on the quality of life, there is an ever-increasing demand for the (petro)chemical industry to take action and contribute to the overall goal of environmental protection [1]. In an earlier communication we presented our view of the pragmatic approach towards CO oxidation in a fluid catalytic cracking unit, both from a catalyst design as well as implementation cost perspective [2]. There are, however, further considerations refineries may need to account for when operating in highly regulated areas, where additional focus is dedicated to NO_x emissions [3].

For readers' reference, the schematic depiction of the FCC unit regenerator setup as well as the relevant catalyst movement steps under operating conditions are shown in Figure 1. Aside from CO₂, a greenhouse gas that is, unfortunately, emitted as part of the FCC process due to spent catalyst regeneration, the regenerator is also potentially a major source of CO emissions. These emissions are typically addressed by adding a CO promoter component, often Pt- or Pd-based, to the FCC catalyst formulation [4,5]. The specific promoter choice is often based on the FCC unit certification and existing emissions levels, as well as the financial commitment of the refiner towards environmental protection. Commonly, some 2–5 pounds of CO promoter per ton of FCC catalyst are necessary to maintain a reasonable (1–3 ppm) platinum group metal (PGM) concentration in the circulating catalyst inventory [6].



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Figure 1. The FCC unit regenerator as well as the associated catalyst logistic streams are schematically shown. Image reprinted from a prior publication [2].

The critical downside of using promoter catalysts is that typically the PGM used to successfully convert CO to CO_2 is also prolific at oxidizing nitrogen-containing compounds to NO_x under the oxygen-rich conditions of the FCC regenerator [7,8]. The NO_x emissions from the regenerator may originate from a multitude of reaction pathways. As an example, nitrogen species may originate from crude oil and then be deposited as part of coke-species on the spent catalyst surface [9]. The combustion of coke in this case would lead to a release of this nitrogen in the form of NO_x once the catalyst is treated in the oxidizing environment of the regenerator. Alternatively, NO_x can also originate from nitrates and nitrites that can be present in the crude oil feedstock and are decomposed in the regenerator to form nitrous oxides. Finally, while not too common, residual ammonia species that were not removed in the riser can be oxidized to NO_x in the regenerator and thus contribute to the overall FCC unit NO_x emission footprint [10,11].

Regardless, the key concern is that the generated NO_x emissions are not only corrosive to the refinery equipment but are also highly harmful to the environment and human health [12]. Sometimes a refinery exhaust stack system will include a selective noncatalytic reduction (SNCR) process or selective catalytic reduction (SCR) emission system that allows for NO_x conversion to N₂ by means of treatment with NH₃ while invoking the help of a catalyst [13,14]. While the general notion is that the SCR units can successfully take care of NO_x, there is still significant concern around the consistency and concentration of the NO_x emissions over time as well as the ability of the SCR unit to accurately control the NH₃ dosing to match the ammonia demand to the NO_x emissions at any given time during the SCR unit operation [15]. The reason this aspect deserves significant attention is that the failure to comply with the emissions regulations may force a refinery FCC unit shutdown or may result in hefty financial penalties from the regulating authorities [16].

With the above considerations in mind, refineries located in areas with stringent emissions regulations are therefore required to carefully select the promoter package used in the FCC unit to achieve the delicate balance between CO oxidation and possible NO_x generation. Moreover, the refiner is also interested in a linear or at least as linear as possible, emissions profile, to avoid any NO_x emissions spikes that could potentially disrupt the SCR operation and lead to a NO_x breakthrough at the stack.

In the past, there have been several extensive and fundamental studies into the NO_x formation and mitigation chemistry [17,18]. Certainly, there is a significant degree of understanding and a number of strategies, especially in mobile emissions catalysis, as to ways for NO_x mitigation [19]. In this work, however, we will review and discuss the poten-

tial pathways towards improved NO_x generation control as well as the practical aspects of a catalyst design implementation in a refinery FCC unit. We will review approaches that allow suitable CO/NO_x selectivity, i.e., desired CO oxidation at acceptable NO_x generation levels. Furthermore, the impact of different types of dopants on the promoter activity and selectivity will be discussed. We will also share some of the considerations the typical refiner needs to account for to maintain both an economically viable as well as environmentally sustainable unit operation.

2. Results and Discussion

2.1. Promoter Pd-Loading

There is a general tendency for refiners to assume that when emissions related promoters containing PGM are concerned, a higher loading (wt. % or ppm) of the precious metal will yield higher activity, e.g., for CO oxidation. And, in fact, oftentimes this is the case; however, the obvious question that a refiner will ask next is regarding the cost. That is, is it worth the increased operating expenses?

To address this concern, we have prepared a series of catalysts with identical support but varying concentration of Pd as shown in Figure 2. All samples discussed in this work are summarized in Table 1 in the experimental section. The 250–1000 ppm Pd range is quite typical for industrial applications [9], with higher concentrations generally less viable in the refining industry due to the prohibitively high costs. As an example, 1000 ppm Pd in a promoter would result in an ~900 \$/kg Pd metal surcharge (at 2800 \$/oz.t. Pd price on 1 July 2021) [20]. In this work we have chosen a ceria/alumina support as basis for all testing since the extent to which one can achieve lower NO_x emissions has been shown to depend on the ceria-content of CO promoters [2]. Among other possible explanations, we want to mention here the potential of ceria to reduce a portion of the NO_x emissions by trapping some of the NO₂ in the regenerator and storing it in the form of cerium nitrate which can then be decomposed in the FCC unit riser. Examples of successful implementation of this strategy are well known from prior reports of mobile emissions catalyst systems [21–23].



Figure 2. CO conversion (%) and NO_x generation emission (%) values for identical CO promoters varying only in Pd content are reported. The values are generated following the procedure described in Section 3.2.

Promoter	CeO ₂ (wt. %)	CuO (wt. %)	SrO (wt. %)	Pd (ppm)	Pt (ppm)	Total Surface Area (m²/g) ²	CO Conversion (%) ¹	NO _x Generation (%) ¹	CO/NO _x Ratio
Reference-1	10	0	0	250	0	87	47.0	80.6	0.58
Reference-2	10	0	0	500	0	87	53.7	80.9	0.67
Reference-3	10	0	0	1000	0	87	55.7	90.2	0.62
Catalyst A	10	0.6	0	0	0	88	23.5	35.3	0.67
Catalyst B	10	0.3	0	500	0	86	46.8	65.1	0.72
Catalyst C	10	0.6	0	500	0	88	49.8	67.5	0.74
Catalyst D	10	0	0.6	0	0	90	4.8	6.8	0.71
Catalyst E	10	0	0.6	500	0	90	47.7	67.5	0.71
Catalyst F	10	0	1.2	500	0	86	47.6	79.1	0.60
Catalyst G	10	0	0	0	300	87	72.5	107.6	0.67

Table 1. The sample composition as well as measured CO conversion, NO_x generation and CO/NO_x ratio values for the samples discussed in this contribution are reported.

¹ Test: 99% spent FCC catalyst + 1% fresh promoter, plug flow reactor operating at 1 L/min flow rate with a feed of 2 vol. % O₂ in N₂ at 700 °C. Values determined by comparing to a promoter-free base case experiment. The method used to calculate CO conversion and NO_x generation is reported in the next chapter. ² The same batch of alumina support was used for all samples allowing for comparable pore size distribution and structure for all catalysts. The typical total pore volume for this support is $0.2 \text{ cm}^3/g$.

From Figure 2, Reference-1 (250 ppm Pd) appears to be only slightly inferior to Reference-2 (500 ppm Pd) when the CO conversion efficiency is concerned. There is also minimal to no variability in NO_x emission, which one could consider surprising at first, yet there may be a plausible explanation to this observation. As reported previously [24,25], the effective PGM surface area available for the reaction does not necessarily scale proportionally with the total PGM content in the sample. That is, while in a 1 nm Pd particle ~50% of Pd atoms form the surface, the surface Pd atoms in at 20 nm particle account for only ~5% of the total Pd present in the particle. Therefore, it should not be surprising that the activity benefit observed from the higher Pd content in Reference-2 and Reference-3 (Figure 2) offers are minor benefit to the overall promoter performance. This is especially concerning from a practical utilization aspect since the Reference-2 and Reference-3, due to their Pd content, come at a two- and 4-fold premium in PGM cost, respectively, when compared to Reference-1.

Before we move on, we also need to emphasize that one of the key parameters which may be used to assess promoter efficiency is the CO/NO_x ratio, i.e., the NO_x generation penalty or cost for CO oxidation. Unsurprisingly, higher values would be more desirable, and even seemingly minor shifts in this ratio can significantly affect the refinery's decision regarding the type of promoter/catalyst to be used in the unit. The CO/NO_x ratios for the reference promoters are listed in Table 1 with the Reference-2 design exhibiting the best value at 0.67. With the above in mind, as well as considering the fact that in this contribution we aim to demonstrate options that the typical refinery faces, and also in order to stay within the reasonable PGM content limits that are typical for the industry, we will use Reference-2 in subsequent comparisons.

2.2. Impact of Dopant Package

Based on the findings in the previous section, further testing is performed using catalysts that contain 500 ppm Pd in all cases. The focus here is the impact of dopants which may or may not affect the CO and NO_x activity of the promoters. Figure 3 shows the results observed for several samples that were prepared and tested in this study.



Figure 3. CO conversion (%) and NO_x generation emission (%) values for 500 ppm Pd promoters with varying dopant packages are reported. The values are generated following the procedure described in Section 3.2.

The benchmark promoter in this series is the dopant-free Reference-2 catalyst that demonstrates a 53.7% CO conversion efficiency at an 80.9% NO_x generation level, which yields value of 0.67 CO/NO_x. The addition of just 0.3% CuO, Catalyst B in Figure 3, leads to a decrease of CO conversion to 46.8% while generating only 65.1% NO_x in the process, i.e., we observe a 0.72 CO/NO_x yield. Interestingly, while the nominal yield of CO/NO_x has gone up from 0.67 observed for the undoped Reference-2 sample, the overall activity with regards to absolute emission value has dropped significantly. This observation suggests that CuO acts as a poison for the Pd that was deposited on the support surface. We note, however, that this observation is not totally surprising as copper affinity to PGM is well known [26,27] and has been earlier shown to be generally detrimental to Pd performance in mobile emissions catalysts [21]. Cu can alloy with Pd, possibly forming Pd-core Cu-shell structures as have been reported previously [28]. The encapsulation of Pd, i.e., deactivation of the surface, would also explain the drop in NO_x generation observed for Catalyst B.

Following the logic of the observation above, it would be reasonable to expect that further addition of CuO would lead to an even stronger degree of Pd encapsulation and deactivation. However, this is not the case. When doping 500 ppm Pd with 0.6% CuO (Catalyst C), the promoter appears to gain some CO activity (49.8%) and develops additional NO_x (67.5%). As a result, a CO/NO_x ratio of 0.74 is observed, which appears to be an improvement, in fact to be the best sample discussed in this set so far. The results suggest that CuO may be a CO promoter that just happens to partially deactivate Pd, at least to a certain degree.

To further explore the behavior of CuO as a catalyst under chosen reaction conditions, a Pd-free 0.6% CuO Catalyst A is tested (Figure 3). With a CO conversion level of 23.5% at a NO_x generation of 35.3% the catalyst exhibits a CO/NO_x of 0.67, which, coincidentally, is same as the Cu-free Reference-2 catalyst. This observation suggests that the PGM-free catalyst exhibits the same selectivity for CO as the Pd-design yet achieves only ~44% of the total activity of the PGM option (Reference-2). The importance of this observation is that beyond the simple "highest conversion catalyst" choice one now needs to also address concerns of a more practical nature to determine the "best" solution for the application in each specific case.

In most cases, the refinery will first need to consider whether the performance of a promoter, present typically at a 0.5–1 wt. % loading in the FCC catalyst blend, is sufficient to meet the set emissions targets. In this case, one would expect CuO-based, or similar in nature, catalysts to dominate the CO promoter field. Alternatively, the refinery could choose to accept a blend with a much higher promoter loading, yet that could come at the expense of the FCC activity [29]. Furthermore, the addition of higher promoter amounts tends to effectively serve as a cracking catalyst dilutant and, therefore, may result

in reduction of the unit conversion as well as gasoline and LPG yields, a compromise most refiners would not be willing to accept. Furthermore, increasing the dosing of the CuO-based promoter, e.g., such as Catalyst A, would lead to significant CuO-levels in the equilibrium catalyst (ECat) that is periodically extracted from the FCC unit. Blending of Catalyst A and Reference-2 to achieve reduced Cu levels is described in detail in the Supporting Information section (Figure S1).

The equilibrium catalyst, also referred to as purchased equilibrium catalyst (ECat or PCat), is not necessarily a refinery waste stream. On the contrary, this material is a commodity that the refinery can often sell to another refinery that operates under different constraints or has a very limited operating budget, in which case the purchase of the relatively cheap PCat may be a financially viable option to maintain business. In fact, under the COVID-19 economic conditions, when the demand for transportation fuels dropped to historically low levels [30], a significant number of refineries were forced to switch to elevated levels of PCat purchasing from certain large and complex FCC units globally to be able to sustain operations. One of the main concerns around using CuO in FCC units is the strong tendency to dehydrogenate hydrocarbons, which in turn leads to significant amounts of H₂ and coke as well as has a detrimental effect on gasoline and LCO yields [31,32]. For those reasons, the general notion in the refining community is to avoid adding metals such as Cu, Ni or Co to the FCC units. Certainly, this makes the CuO-containing CO promoters less attractive and becomes a concern for potential buyers of PCat.

A further concern is that the increase of CuO concentration in PCat can trigger several environmental health and safety (EH&S) concerns around the handling and disposition of spent catalyst, with Cu known to be a potential hazard for aquatic species when exposed to marine environments or landfilled in significant concentrations [33,34].

With the limitations for CuO-based promoter use as described above, a more common approach for a refinery is to choose a PGM-based promoter, often using Pt or Pd as the key catalytic species. This in turn brings us back to the results described above where the Pd-based CuO-free system (Reference-2) offers a CO/NO_x selectivity of 0.67 at an overall CO conversion level of ~53.7%. That is, the catalyst has the necessary activity density such that when it is added to the FCC blend at a maximum level of 1 wt. %, the desired emissions targets can be met without diluting the cracking catalyst.

The cost of the catalyst support in the example studied here would be essentially the same in all cases as we have purposefully used the same ceria/alumina support throughout the study. Hence, the differentiation of the cost is predominantly driven by the cost of the PGM and/or dopants, if these are present. To keep the overall analysis transparent, we need to make an assumption that the fixed cost of PGM and/or CuO deposition on the support is identical and will thus not affect the overall financial estimates. That is, we focus here on the cost of raw materials while omitting the large-scale manufacturing concerns to simplify the discussion. We also use a Pd metal spot value of 2800 \$/oz.t. (reasonable average value for the late Q2 2021) [20] and a Cu-nitrate solution (28%) value of 3 kg. With the constraints in mind, Reference-2 with the CO/NO_x selectivity of 0.67 costs ~450 \$/kg in Pd for a promoter achieving a total CO conversion of ~53.7%. The refinery may choose to go for a higher CO/NO_x selectivity, e.g., 0.74 achieved by Catalyst C (500 ppm Pd + 0.6% CuO), which would still cost ~450 \$/kg because of the negligible (<0.1 /kg) cost impact from addition of the CuO in this case. Therefore, at first glance, it would seem the shift in selectivity is essentially free, however, as discussed earlier, CuO has some tendency to poison Pd, i.e. the shift in selectivity also leads to a decrease of the overall CO conversion efficiency from ~53.7 to ~49.8%. While seemingly minor, this ~7.2% relative decrease of activity must be considered. If the refinery is operating well below the CO emission limit while being close to the maximum allowed NO_x emission, the refinery may choose to pay the premium and accept the less-than-perfect Pd utilization. On the contrary, if the refinery is somewhat concerned about NO_x , but aims to comply with the CO emissions regulation, the unit would be forced to use a more selective catalyst but increase

the dosing. For example, to match the CO activity of the CuO-free catalyst, one would need to dose 7–8% more of the Pd/CuO promoter, which in turn further increases cost to ~480–490 \$/kg, a roughly 30 - 40 \$/kg premium for the improved CO/NO_x selectivity. Considering the promoter consumption across a network of refineries on an annual basis, especially in light of recent margin pressure, a decision to purchase premium promoters with better selectivity as opposed to a "good-enough" promoter, becomes quite costly.

In addition to addressing the NO_x emissions in the regenerator through a careful choice of a promoter catalyst, one can also choose to trap and store NO_x using a NO_x adsorber, which can then be regenerated in the riser, where NO_x would be reduced to N_2 and NH₃, both of which can be removed at the top of the riser column. The concept of trapping NO_x is well established in the field of mobile emissions control, where elements such as Sr and Ba are used to selectively trap NO₂, e.g. in diesel motor emissions control systems [35–37]. The adsorber functions in a stoichiometric way and, ideally, should not introduce any adverse performance effects to the overall promoter system. To explore the potential of the trapping concept, we have decided to invoke Sr (Catalyst D, E & F) and compare it's impacts on the promoter activity with the Pd-only (Reference-2) system. Sr was chosen over Ba due to its molecular weight (87.62 g/mol for Sr compared to 137.33 g/mol for Ba), which means that at the same nominal wt. % in the promoter formulation we can achieve a significantly higher number of Sr-sites, and consequently an ~32% higher potential nitrate capacity (SrO vs. BaO) as both elements can bind two NO₂ molecules [38]. The CO conversion % as well as NO_x generation % values for the compared samples are reported in the Figure 4.



Figure 4. CO conversion (%) and NO_x generation emission (%) values for select promoters with varying dopant packages are reported. The values are generated following the procedure described in Section 3.2.

Since Sr is known to have no redox activity [38,39], it is a reasonable assumption that the addition of Sr does not lead to an increase in the CO oxidation activity. It is also not likely that the addition of a relatively small (0.6 wt. %) amount of SrO dopant could markedly block CeO₂ (or rather the mixture of Ce₂O₃ and CeO₂) that is part of the catalyst support, from delivering some "background" CO oxidation activity. This is exemplified in Figure 4 where Catalyst D (PGM-free SrO/CeO₂-based design) shows a 4.79% CO conversion efficiency and a 6.82% NO_x generation. CO/NO_x ratio in this case is 0.71, however, we do not deem it to be significant since the overall activity is extremely low. The unanswered question, nonetheless, is whether the addition of Sr has any benefit. That is, whether Sr can capture NO_x, but the amount generated on the ceria support is overwhelming the trap or whether the trap cannot effectively function due to the high operating conditions of the regenerator. This concern gains importance since the traditional NO_x trap operating window in mobile emissions applications, e.g. for Fuel Cut NO_x Trap (FCNT) applications, is between ~300 and 500 $^{\circ}$ C with temperature above ~650–700 $^{\circ}$ C used for the trap regeneration [40].

To explore this concern further we have prepared the promoter Catalyst E with 500 ppm Pd and 0.6 wt. % SrO on the same particle, see Figure 4. Interestingly, there is no benefit in NO_x emission reduction, but there appears to be a reduction in the CO oxidation activity. Whether this observation suggests that Sr affect the Pd/support interaction and limits the PGM ability to make CO₂ remains unclear at this time. To further probe the concept, we have also prepared Catalyst F (500 ppm Pd with 1.2% SrO), which seems to maintain the CO activity same as Catalyst E, but now allows a slight decrease in NO_x generation. While conceptually possible, we suggest that further increase of SrO content becomes impractical for refineries for reasons like those discussed for CuO earlier. SrO is certainly less of an EH&S concern when it comes to catalyst handling, however, there is still the potential for Sr-mobility. Specifically, there is the concern of Sr forming carbonate deposits around valves and fittings in an FCC unit, which while not highly likely, is something refiners would consider, especially when the Sr levels are increasing above ~1–2 wt. % in the promoter catalyst.

2.3. Pt vs. Pd Comparison

Let us now turn to the obvious question the reader may have after the Pd-based catalyst analysis: how does a Pd-based promoter compare to a Pt-based promoter? In the past it was common to argue that NO_x-sensitive FCC units ought to use a Pd promoter and all other units can use Pt-based catalysts. While there may have been a performance-related rationale in the past, when emissions standards were less stringent and the promoter catalyst designs were very simple, e.g. PGM/Al₂O₃. Furthermore, Pd used to be more affordable in the past compared to Pt [19,20]. This trend reversed in 2015 with the decrease in consumer preference for diesel-powered light-duty vehicles, which led to a decline in the global Pt prices [41]. Today, in 2021, with Pd price is more than double that of Pt, the number of refineries willing to utilize Pd-based promoters is declining. To address the question at hand, we have compared Reference-2 with a Pt-based promoter (Catalyst G) using the design and sample synthesis methods reported in a previous publication [2]. Because the support material is ceria-alumina in both cases, we can specifically probe the impact of the PGM on the observed performance. The comparison is reported in Figure 5.



 $^{\circ}$ Reference-2 normalized to match the CO activity of Catalyst G assumil linear CO/NO_x response in the studied promoter loading range

Figure 5. CO conversion (%) and NO_x generation emission (%) values for select Pt- and Pd-based promoters are reported. The values are generated following the procedure described in Section 3.2.

Catalyst G exhibits strong CO conversion at 72.5% while generating 107.6% NO_x emission, which yields a CO/NO_x ratio of 0.67. Incidentally, and quite surprisingly, this is exactly the CO/NO_x ratio observed for the Pd-based Reference-2. For readers convenience, we have also included a linear extrapolation of the performance of Reference-2 (reported as Reference-2* is Figure 5) performance at an elevated usage in the unit assuming the goal

of the experiment were to match CO activity of the Pd-based design to that of Catalyst G. Not surprisingly, the NO_x is almost identical to what is observed for the Pt-based catalyst G since the CO/NO_x ratio in this assumption remains unchanged. Considering the PGM cost of Reference-2 is ~450 \$/kg, increasing the dosage by ~26% to match the CO activity to Catalyst G (300 ppm Pt design), the PGM cost of Reference-2* is estimated at ~567 \$/kg. Note that Catalyst G, a Pt-based CO promoter, has a PGM cost of only ~107 \$/kg at current Pt (1135 \$/oz t. in July 2021) value [20], making Catalyst G very attractive from a cost to operate perspective.

What the observation also suggests is that because the CO/NO_x ratios of the two promoters, Catalyst G and Reference-2, are identical, one can now choose the suitable PGM based on refinery environmental regulatory (e.g., EPA in the US) consent decrees or PGM price, rather than NO_x performance. In other words, the former notion of having to use a Pd-based promoter for FCC units that are NO_x constrained is not necessarily true at present. This in turn is excellent for the refineries, who can now maximize the cost savings by choosing the product based on current market PGM-price. That is, in Q2 2021 Pt-based promoters are strongly preferred, however, in the future, should Pd once again be lower priced than Pt, the Pd-based promoters can once again become financially attractive. Moreover, it appears there is flexibility in the choice of PGM, after all, the two catalysts compared here are supported on the exact same kind of ceria-alumina support.

3. Experimental

3.1. Material Synthesis

A series of reference and experimental catalysts was prepared-the full list is provided in Table 1. In all cases, γ -Al₂O₃ microspheres with a typical D₅₀ of 80 µm and a total surface area (TSA) of 90 m²/g were used as the alumina support. Commercially available cerium nitrate, copper nitrate and strontium nitrate, industrial grade in all cases, were used as precursors to form the doping package for the alumina support. An aqueous solution of Pd-nitrate, with a typical Pd-content of 20 wt. %, and Pt-nitrate, with a typical Pt content of 10 wt. % was used as PGM source. Both dopants as well as PGM were deposited via incipient wetness impregnation to afford even metal distribution on the support.

Reference catalysts 1–3 were prepared by impregnating the alumina support with the aqueous palladium nitrate solution such that the desired final metal concentration is achieved. The reference catalysts included in this study (reported in Table 1) are Pd/Al_2O_3 with 250–1000 ppm precious metal loading, as earlier reported as industry standard and reference point in the past [9]. Experimental Catalysts A–G were prepared by first impregnating the alumina support with cerium-nitrate such that the desired final CeO_2 concentration is achieved. The support is then calcined at 550 °C for 2 h. For Catalyst A, the ceria-alumina support was further impregnated with Cu-nitrate at incipient wetness and the material was then calcined at 550 °C for 2 h. Catalyst B is prepared like catalyst A but using half the amount of Cu-nitrate to achieve the desired CuO-concentration. The material is then calcined at 550 °C for 2 h. Subsequently, the desired amount of the Pd nitrate solution is impregnated onto the CeO₂/CuO/Al₂O₃ support. Catalyst C is prepared by impregnating Catalyst A with the desired amount of the Pd nitrate solution such that the final Pd concentration target is met. Catalyst D is prepared by impregnating the ceria/alumina support with strontium nitrate followed by a calcination at 550 °C for 2 h. Catalyst E is prepared by impregnating Catalyst D with the desired amount of the Pd nitrate solution such that the final Pd concentration target is met. Catalyst F is prepared by impregnating the ceria/alumina support with strontium nitrate followed by a calcination at 550 $^{\circ}$ C for 2 h. Subsequently, the material is impregnated with the desired amount of the Pd nitrate solution such that the final Pd concentration target is met. Catalyst G is prepared by impregnating the ceria/alumina support with the desired amount of the Pt nitrate solution. For all catalysts, upon PGM deposition, samples were calcined at 550 °C for 2 h.

values are essentially equivalent to those reported in Table 1, with a typical uncertainty of ~0.1 wt. % for base and first transition row metals and ~15 ppm for Pd and Pt. As there is no indication that the reported levels of experimental uncertainty in the chemical composition analysis could significantly affect the observations or conclusions presented in this work, these values were rounded up when reported in Table 1.

3.2. Catalyst Ageing and Testing

All catalyst testing work was performed as the Chemical Process & Energy Resources Institute (CPERI) located in Thessaloniki, Greece. The testing was in accord with the industry standard protocol of CPERI; detailed description of this test protocol was previously reported [42].

The protocol for the evaluation includes mixing spent FCC catalyst with the additive (1 wt. %) and loading this mixture in a fluidized bed reactor. The above mixture is then regenerated at 700 °C by 2 vol. % O_2 diluted in N_2 . The NO_x and CO emissions were measured during the regeneration procedure. The reduction in CO emissions resulted in increased NO_x emissions.

The effect of catalyst mixtures on NO_x and CO emissions during regeneration of FCC catalyst was tested using a fluidized-bed reactor. A three-zone radiant heater furnace is used to heat up the reactor to the desired temperature, achieved via standard temperature controllers. Reaction temperature is measured by a thermocouple placed inside the catalytic bed. The bench-scale unit is equipped with a gas feed system, capable to supply the following gas components: O₂ and N₂. The volume flow rates of individual components, at the laboratory temperature, are monitored by mass flow controllers. The analysis section of the unit involves a FT-IR gas analyzer from MKS Instruments (MKS-MG2030). For the purposes of this study the signals from the NO_x and CO were recorded and stored in the PC every 5 s. Integration of the gas concentration vs. time curves provided the cumulative amounts of gases produced or consumed.

All of the additives were evaluated in respect to their ability to affect NO_x and curtail CO emissions during the regeneration of the spent FCC catalyst. The pure spent catalyst was used for the base case tests, while for the evaluation studies mixtures of 1 wt. % of the additive and 99 wt. % of the spent catalyst were loaded on the reactor. All catalytic materials were sieved at $63-106 \mu m$. The reaction conditions for this protocol are summarized in Table 2. Pure spent catalyst was tested as a base case and each experiment was carried out more than once for repeatability reasons. All results showed great repeatability, for the chosen reactor setup and under the specific experimental conditions reported in this study, an average variation of $\pm 5\%$ was determined. For readers' reference, this variation is also reported as error bars in the Figures presented in this report. The NO_x generation and CO conversion, defined as follows from integrated amounts (gmol/gr of spent catalyst), is also calculated in relation to the base case. All catalysts were tested after a simulated steam-ageing, which is used to simulate the regenerator portion of the FCC operation cycle and has been demonstrated sufficient to discern trends and draw reasonable conclusions for promoter catalyst previously [2]. The chosen procedure is a 12 h ageing with a T_{max} = 787 °C using a closed, fluidized steam reactor that using 90% H₂O-steam/10% N₂ mixture.

Reactor Type	Fluid Bed				
Reactor loading	10 gr				
Catalyst mixture	99 wt. % spent FCC catalyst + 1 wt. % CO promoter				
Inlet gas flow rate	1 L/min				
Inlet gas composition	2 vol. % O ₂ in N ₂				
Reactor bed temperature	700 °C				

Table 2. The CO promoter testing parameters are reported.

The CO conversion (% decrease) values were calculated using the formula reported in Equation (1) below, where the "Base Case" refers to the CO emissions as measured for the non-promoted base system, i.e., the spent FCC catalyst without any additional environmental additives. In this "Base Case" the spent FCC catalyst is diluted with 1 wt. % inert microsphere phase to allow for correct catalyst amount for subsequent comparisons (inert replaced with active ingredients). The "Promoter" refers to the CO emissions observed when the spent FCC catalyst is promoted with the respective additive at a 1 wt. % doping level. In this way, the measured results can directly be related to the additive performance.

$$CO (\% \text{ decrease}) = 100 \times \frac{CO_{\text{Base Case}} - CO_{\text{Promoter}}}{CO_{\text{Base Case}}}$$
(1)

The NO_x generation (% increase) values were calculated using the formula reported in Equation (2) below, where the "Base Case" refers to the NO_x emissions as measured for the non-promoted base system, i.e., the spent FCC catalyst without any additional environmental additives. Similar to the approach described above, in the "Base Case" the spent FCC catalyst is diluted with 1 wt. % inert microsphere phase to allow for correct catalyst amount for subsequent comparisons (inert replaced with active ingredients). The "Promoter" refers to the NO_x emissions observed when the spent FCC catalyst is promoted with the respective additive at a 1 wt. % doping level. In this way, the measured results can directly be related to the additive performance. Note that the general trend for CO promoters to oxidize CO to CO₂ and N-species to NO_x, in the context of Equation (2), results in positive values for NO_x generation, as it describes the additional NO_x forming as a result of promoter addition to the FCC catalyst.

$$NO_{x} (\% \text{ increase}) = 100 \times \frac{NO_{xPromoter} - NO_{xBase Case}}{NO_{xBase Case}}$$
(2)

4. Conclusions

In this work we have considered the conceptual approaches toward NO_x mitigation from a refinery FCC unit and have found that the key consideration when choosing a catalyst is not only based on the absolute activity values, but also on the CO/NO_x selectivity as well as the overall promoter cost to the refinery. There are clear benefits of using dopants, e.g. Cu and Sr, however their practical application is limited due to a number of operational, economic as well as EH&S concerns. With the current generation of promoter catalysts as well as the existing emissions regulations in mind, it is now viable to use Pt-based promoters instead of Pd-based ones, that were preferred in the past when the Pt/Pd cost spread was significantly in favor of Pd.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/catal11101146/s1, Figure S1: The CO conversion and NO_x generation emission values observed for selected catalysts are reported. The values are generated following the procedure described in Section 2.2. Table S1: The estimated sample cost as well as measured CO conversion, NO_x generation and CO/NO_x ratio values for the samples discussed in this contribution are reported.

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Abbreviations

Platinum group metal (PGM), oxygen storage component (OSC), fluid catalytic cracking (FCC).

References

- 1. Petroleum Sector (NAICS 324), US EPA. Available online: https://www.epa.gov/regulatory-information-sector/petroleum-sector-naics-324 (accessed on 21 September 2021).
- Vjunov, A.; Kharas, K.C.; Komvokis, V.; Dundee, A.; Zhang, C.C.; Yilmaz, B. Pragmatic Approach toward Catalytic CO Emission Mitigation in Fluid Catalytic Cracking (FCC) Units. *Catalysts* 2021, 11, 707. [CrossRef]
- 3. Air Emissions—Protecting Air Quality, Chevron Sustainability Roadmap. Available online: https://www.chevron.com/ sustainability/environment/air-emissions (accessed on 21 September 2021).
- 4. Lin, J.; Wang, X.; Zhang, T. Recent progress in CO oxidation over Pt-group-metal catalysts at low temperatures. *Chin. J. Catal.* **2016**, *37*, 1805–1813. [CrossRef]
- 5. van Spronsen, M.A.; Frenken, J.W.M.; Groot, I.M.N. Surface science under reaction conditions: CO oxidation on Pt and Pd model catalysts. *Chem. Soc. Rev.* 2017, *46*, 4347–4374. [CrossRef] [PubMed]
- 6. BASF USP™ CO Promoter, Ultra Stable Promoter (USP) BASF Catalysts. Available online: https://catalysts.basf.com/products/ ultra-stable-promoter-ups (accessed on 21 September 2021).
- 7. Iliopoulou, E.F.; Efthimiadis, E.A.; Vasalos, I.A.; Barth, J.-O.; Lercher, J.A. Effect of Rh-based additives on NO and CO formed during regeneration of spent FCC catalyst. *Appl. Catal. B* **2004**, *47*, 165–175. [CrossRef]
- Dishman, K.L.; Doolin, P.K.; Tullock, L.D. NO_x Emissions in Fluid Catalytic Cracking Catalyst Regeneration. *Ind. Eng. Chem. Res.* 1998, 37, 4631–4636. [CrossRef]
- 9. Chester, A.W. Chapter 6-CO combustion promoters: Past and present. Stud. Surf. Sci. Cat. 2007, 166, 67-77. [CrossRef]
- 10. Stockwell, D.M. Chapter 6—CO combustion promoters: Past and present. *Stud. Surf. Sci. Cat.* 2007, *166*, 79–102.
- 11. Cheng, W.-C.; Kim, G.; Peters, A.W.; Zhao, X.; Rajagolapan, K.; Ziebarth, M.S.; Pereira, C.J. Environmental Fluid Catalytic Cracking Technology. *Catal. Rev.* **1998**, 40, 39–79. [CrossRef]
- 12. Gary, J.H.; Handwerk, G.E. Petroleum Refining: Technology and Economics, 4th ed.; CRC Press: Boca Raton, FL, USA, 2001; ISBN 0824704827.
- 13. Sadeghbeigi, R. *Fluid Catalytic Cracking Handbook*, 3rd ed.; Chapter 14; Butterworth-Heinemann: Oxford, UK, 2012; ISBN 9780123869654.
- 14. Babich, I.V.; Seshan, K.; Lefferts, L. Nature of nitrogen specie in coke and their role in NO_x formation during FCC catalyst regeneration. *Appl. Catal. B Environ.* **2005**, *59*, 205–211. [CrossRef]
- Ye, X.; Schmidt, J.E.; Wang, R.-P.; van Ravenhorst, I.K.; Oord, R.; Chen, T.; de Groot, F.; Meirer, F.; Weckhuysen, B.M. Deactivation of Cu-Exchanged Automotive-Emission NH₃-SCR Catalysts Elucidated with Nanoscale Resolution Using Scanning Transmission X-ray Microscopy. *Angew. Chem. Int. Ed.* 2020, 59, 15610–15617. [CrossRef]
- 16. US EPA, Civil Cases and Settlements by Statute. Available online: https://cfpub.epa.gov/enforcement/cases/index.cfm? templatePage=12&ID=1&sortby=TYPE_OF_ORDER (accessed on 21 September 2021).
- 17. Zhao, X.; Peters, A.W.; Weatherbee, G.W. Nitrogen Chemistry and NO_x Control in a Fluid Catalytic Cracking Regenerator. *Ind. Eng. Chem. Res.* **1997**, *36*, 4535–4542. [CrossRef]
- Barth, J.-O.; Jentys, A.; Lercher, J.A. Elementary Reactions and Intermediate Species Formed during the Oxidative Regeneration of Spent Fluid Catalytic Cracking Catalysts. *Ind. Eng. Chem. Res.* 2004, 43, 3097–3104. [CrossRef]
- 19. Heck, R.M.; Farrauto, R.J.; Gulati, S.T. *Catalytic Air Pollution Control*; John Wiley & Sons: Hoboken, NJ, USA, 2009; ISBN 9781118397749. [CrossRef]

- 20. APMEX Precious Metals Trading. Available online: https://www.apmex.com/platinum-price (accessed on 21 September 2021).
- 21. Campbell, L.E.; Danzinger, R.; Guth, E.D.; Padron, S. Process for the Reaction and Absorption of Gaseous Air Pollutants, Apparatus Therefor and Method of Making the Same. U.S. Patent 5,451,558, 19 September 1995.
- 22. Theis, J.; Lambert, C. The Effects of CO, C₂H₄, and H₂O on the NO_x Storage Performance of Low Temperature NO_x Adsorbers for Diesel Applications. *SAE Int. J. Engines* **2017**, *10*, 1627–1637. [CrossRef]
- Ferré, G.; Aouine, M.; Bosselet, F.; Burel, L.; Cadete Santos Aires, F.J.; Geantet, C.; Ntais, S.; Maurer, F.; Casapu, M.; Grunwaldt, J.-D.; et al. Exploiting the dynamic properties of Pt on ceria for low-temperature CO oxidation. *Catal. Sci. Technol.* 2020, 10, 3904–3917. [CrossRef]
- 24. Soliman, N.K. Factors affecting CO oxidation reaction over nanosized materials: A review. J. Mat. Res. Tech. 2019, 8, 2395–2407. [CrossRef]
- Fox, E.B.; Velu, S.; Engelhard, M.H.; Chin, Y.-H.; Miller, J.T.; Kropf, J.; Song, C. Characterization of CeO₂-supported Cu–Pd bimetallic catalyst for the oxygen-assisted water–gas shift reaction. *J. Catal.* 2008, 260, 358–370. [CrossRef]
- Koryabkina, N.A.; Phatak, A.A.; Ruettinger, W.F.; Farrauto, R.J.; Ribeiro, F.H. Determination of kinetic parameters for the water–gas shift reaction on copper catalysts under realistic conditions for fuel cell applications. *J. Catal.* 2003, 217, 233–239. [CrossRef]
- Rej, S.; Wang, H.-J.; Huang, M.-X.; Hsu, S.-C.; Tan, C.-S.; Lin, F.-C.; Huang, J.-S.; Huang, M.H. Facet-dependent optical properties of Pd–Cu₂O core–shell nanocubes and octahedra. *Nanoscale* 2015, 7, 11135–11141. [CrossRef]
- 28. Alabdullah, M.A.; Rodriguez Gomez, A.; Vittenet, J.; Bendjeriou-Sedjerari, A.; Xu, W.; Abba, I.A.; Gascon, J. A Viewpoint on the Refinery of the Future: Catalyst and Process Challenges. *ACS Catal.* **2020**, *10*, 8131–8140. [CrossRef]
- 29. US Bureau of Labor Statistics. From the barrel to the pump: The impact of the COVID-19 pandemic on prices for petroleum products, From the Barrel to the Pump: The Impact of the COVID-19 Pandemic on Prices for Petroleum Products. Available online: https://www.bls.gov/opub/mlr/2020/article/from-the-barrel-to-the-pump.htm (accessed on 21 September 2021).
- 30. US Energy Information Administration. COVID-19 Mitigation Efforts Result in the Lowest U.S. Petroleum Consumption in Decades, COVID-19 Mitigation Efforts Result in the Lowest U.S. Petroleum Consumption in Decades. Available online: https://www.eia.gov/todayinenergy/detail.php?id=43455 (accessed on 21 September 2021).
- 31. Mills, G.A. Aging of Cracking Catalysts. Ind. Eng. Chem. 1950, 42, 182–187. [CrossRef]
- 32. Venuto, P.B.; Habib, T. Catalyst-Feedstock-Engineering Interactions in Fluid Catalytic Cracking. Catal. *Rev. Sci. Eng.* **1978**, *18*, 1–150. [CrossRef]
- Kleldsen, P.; Barlaz, M.A.; Rooker, A.P.; Baun, A.; Ledin, A.; Christensen, T.H. Present and Long-Term Composition of MSW Landfill Leachate: A Review. *Critic. Rev. Environ. Sci. Technol.* 2002, 32, 297–336. [CrossRef]
- Kiaune, L.; Singhasemanon, N. Pesticidal Copper(I) Oxide: Environmental Fate and Aquatic Toxicity. *Rev. Environ. Contam. Toxicol.* 2011, 213, 1–26. [CrossRef]
- 35. Wittka, T.; Holderbaum, B.; Dittmann, P.; Pischinger, S. Experimental Investigation of Combined LNT + SCR Diesel Exhaust Aftertreatment. *Emiss. Contr. Sci. Technol.* 2015, 1, 167–182. [CrossRef]
- Onrubia-Calvo, J.A.; Pereda-Ayo, B.; Caravca, A.; De-La-Torre, U.; Vernoux, P.; Gonzalez-Velasco, J.R. Tailoring perovskite surface composition to design efficient lean NO_x trap Pd–La_{1-x}A_xCoO₃/Al₂O₃-type catalysts (with A = Sr or Ba). *Appl. Catal. B Environ.* 2020, 266, 118628. [CrossRef]
- 37. Zhang, Y.; Liu, D.; Meng, M.; Jiang, Z.; Zhang, S. A Highly Active and Stable Non-Platinic Lean NO_x Trap Catalyst MnO_x-K₂CO₃/K₂Ti₈O₁₇ with Ultra-Low NO_x to N₂O Selectivity. *Ind. Eng. Chem. Res.* **2014**, *53*, 8416–8425. [CrossRef]
- Cotton, F.A.; Wilkinson, G.; Gaus, P.L. Basic Inorganic Chemistry, 3rd ed.; John Wiley & Sons: Hoboken, NJ, USA, 1995; ISBN 9780471505327. [CrossRef]
- 39. Luther, G.W., III. Inorganic Chemistry for Geochemistry and Environmental Sciences: Fundamentals and Applications; John Wiley & Sons: Hoboken, NJ, USA, 2016; ISBN 978-1-118-85137-1. [CrossRef]
- 40. Choi, M.; Song, J.; Lee, E.; Ma, S.; Lee, S.; Seo, J.; Yoo, S.; Lee, J. *The Development of a NO_x Reduction System during the Fuel Cut Period for Gasoline Vehicles*; SAE Technical Paper 2019-01-1292; SAE International: Washington, DC, USA, 2019. [CrossRef]
- 41. Hachenberg, B.; Kiesel, F.; Schiereck, D. Dieselgate and its expected consequences on the European auto ABS market. *Econom. Lett.* **2018**, *171*, 180–182. [CrossRef]
- Efthimiadis, E.A.; Iliopoulou, E.F.; Lappas, A.A.; Iatridis, D.K.; Vasalos, I.A. NO Reduction Studies in the FCC Process. Evaluation of NO Reduciton Additives for FCCU in Bench- and Pilot Plant-Scale Reactors. *Ind. Eng. Chem. Res.* 2002, 41, 5401–5409. [CrossRef]