Development and Evaluation of Ir-Based Catalytic Additives for the Reduction of NO Emissions from the Regenerator of a Fluid Catalytic Cracking Unit

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A series of Ir-based additives were developed to reduce the NO emissions during the regeneration of spent fluid catalytic cracking (FCC) catalyst. Catalytic additives were prepared using different catalytic supports and varying the metal loading. The evaluation of the additives' performance was initially carried out in a laboratory fluidized-bed reactor at 700 °C using a 2% O_2 in N_2 feed. The amounts of NO and CO emitted during regeneration in the presence of Ir-based additives were compared with those obtained when a commercial, Pt-based, CO promoter (1% CP-3) was used. All Ir-based additives exhibited high NO reduction ability in the bench scale reactor (up to 55%). The highest deNOx efficiency was measured when the additive was supported on a commercial alumina or on a stoichiometric spinel. The CO oxidation ability of Ir-based additives was, in general, lower than that over CP-3. Higher Ir loadings (0.1−1%) on alumina enhanced the CO oxidation, but inhibited the NO reduction. Addition of Ce on alumina improved the CO oxidation ability and, at the same time, maintained the NO emissions at low levels. Introducing CO into the O_2/N_2 feed enhanced the NO reduction performance. The combination of Ir-based additives and CP-3 resulted in the lowest NO and CO emissions. Selected Ir-based additives were tested in a pilot plant scale FCC unit. The pilot plant scale results were in good agreement with the corresponding bench scale experiments. Use of Ir additives in the pilot plant experiments led to up to 72% reduction of the NO emissions from the regenerator.

1. Introduction

The flue gas stream at the exit of a fluid catalytic cracking (FCC) regenerator contains O_2, N_2, CO, CO_2, H_2O, SOx, and NOx. NOx emissions formed in the FCC regenerator make up to 50% of the total NOx emissions in a modern integrated refinery. NOx is formed by the oxidation of nitrogen-containing compounds in coke (fuel NOx).[1,2] Although some of the NO can be primary formed by the coke nitrogen, the majority of it comes through intermediates such as HCN and NH_3. The relative formation of these two compounds depends on the type and basicity of nitrogen compounds in the FCC feed (pyrolic, pyridinic, etc). Recent studies have fully validated the existence of HCN and NH_3 and propose a mechanistic pathway of NOx formation via these intermediates.[3−5] Typical NOx concentrations range between 50 and 500 ppm depending upon feed nitrogen levels and regenerator conditions.[6] Nitrogen oxides (NOx) are toxic gases related to many environmental problems; therefore, limitations on the NOx emissions from all refinery sources including FCC regenerators are expected to become stricter worldwide.[7] Use of catalytic additives is the most attractive among all up-to-date NOx control strategies, as it is simple, cost-effective, and applicable in existing FCC units (FCCUs). As Pt-based CO promoters[8] are used today in most refineries, catalyzing the CO oxidation but increasing NO emissions,[2] there is need to develop novel deNOx catalytic additives. These additives should either reduce

NO emissions in the presence of a conventional CO promoter or have the ability to simultaneously decrease NO and CO emissions. In addition, these additives should neither affect the cracking activity and selectivity of FCC catalyst nor lead to the formation of undesired pollutants. NOx reduction additives have been previously patented[9−16] or reported[17−22] by several groups. The synthesis of two NOx reduction additives (DeNOx and XNOx) has been recently patented by W. R. Grace.[15,16] The first one acts in the presence of a CO promoter,[15] while the latter additive acts both as a CO promoter and a deNOx additive.[7,16]

Tauster and Murrell[23] studied the NO reduction by CO over Ir catalysts showing that Ir is the only noble metal favoring the NO−CO over the CO−O_2 reaction in the presence of O_2. A 90% conversion of NO was measured in the presence of a 75% excess of oxidants (NO + O_2) over Ir/alumina catalysts containing either 0.1 or 0.001wt % Ir. The most dilute catalyst required higher temperature to achieve complete removal of CO. Adsorbed oxygen on Ir active sites was the predominant surface species, and its reaction with gaseous CO generated free surface sites. These sites were available for the chemisorption of NO and O_2, leading ultimately to N_2 formation. These results were confirmed by Taylor and Schlatter,[24] who studied the NO reduction by CO in the presence of O_2 over Ir/, Rh/, Pt/, and Pd/alumina catalysts. The highest effectiveness of Ir as compared to the other precious metals was attributed to its strong ability to adsorb and dissociate NO in the presence of excess O_2. Ogura et al.[25] studied several Ir catalysts supported on different carriers and showed that CO is a

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selective NO reductant under oxidizing conditions. Among these catalysts Ir on silicalite showed the highest activity, selectivity for this reaction, and tolerance in the presence of SO_2 and excess oxygen.[25] The NO reduction with CO or C_3H_6 over Ir catalysts was even promoted by the SO_2 presence.[25−27] The selective reduction of NO by CO was enhanced by SO_2 in the presence of O_2, whereas in the absence of O_2, NO reduction by CO was considerably inhibited by SO_2.[26] Similar behavior was noticed when other reductants (H_2, C_3H_6, $C_{10}H_{22}$, or acetone) were used, and this was attributed[27] to some sort of irreversible change in the structure of supported iridium in the presence of SO_2. An Ir/ZSM-5 catalyst was also very active for NO reduction by CO under lean conditions due to its high NO dissociation rate. The presence of steam in the feed gas had no effect on NO conversion, and the decrease of the Ir content enhanced NO reduction.[28,29]

Different Ir-based catalysts have been recently prepared and tested for the SCR of NO under oxidizing conditions using various hydrocarbons as reductants.[30−36] Compared with other noble metals, Ir/alumina catalysts are active at higher temperatures (typically between 400 and 600 °C), while formation of N_2O is low.[30,31] Ir supported on a variety of carriers[30−36] has been studied (TiO_2, $BaSO_4$, ZrO_2, Al_2O_3, SiO_2, and H-USY or H-ZSM-5 zeolites) using mostly propylene as the reductant. The selection of the support for Ir-based catalysts takes into account the following two parameters. First, the reductant should not be oxidized over the support, and second, the support interaction with Ir should not lead to higher Ir dispersion.[31,37] Bimetallic Ir/In/H-ZSM-5 also presented a high catalytic activity and selectivity for SCR of NO by methane. The NO was initially oxidized to NO_2, and NO_2 was consequently reduced to N_2. The role of Ir was not only to promote NO oxidation but also to enhance NO_2 chemisorption.[38,39] Finally, several mechanical mixtures of Ir black or IrO_2 with various materials such as silica xerogel, alumina, and H-ZSM-5 were tested for the SCR of NO by propene. Independently of the solid mixture, the unsupported Ir showed outstanding deNOx activity as compared to its supported counterparts.[34,37]

Nakatsuji[31] studied a series of Ir catalysts supported on alumina, TiO_2, H-USY zeolite, SiO_2, and $BaSO_4$. He concluded that the prerequisite for achieving high activities in NOx reduction is the formation of relatively large Ir metal particles formed on inert supports, rather than the formation of an Ir metal state on the catalyst.[31] The effect of the size of the Ir particles on deNOx activity was always discussed and is related[23,24] to the interaction of CO with NO and O_2.

Activation of Ir catalysts was achieved by high-temperature pretreatments[28,30,31] or by in situ activation during catalytic tests.[33] In the latter case the feed gas composition was extremely important. Both in situ activation and high-temperature pretreatment led to crystallite growth and the development of a certain $Ir:IrO_2$ ratio.[37]

The limited use of Ir in commercial products can be attributed to several factors: the scarcity of Ir, problems with Ir loss due to the formation of volatile Ir chlorides, oxychlorides, and IrO_2 and IrO_3 oxides, and its underestimated catalytic potential due to lack of studies as compared with the other noble metals.[31,40]

Given that CO is the dominant reducing medium in the FCC regenerator and Ir preferentially catalyzes NO reduction by CO with respect to CO oxidation, Ir-based catalysts could be promising additives for the reduction of the NO emissions from the flue gases of an FCC regenerator. The conditions prevailing in the regenerator (high-temperature environment, presence of SO_2 and H_2O) are expected to favor the activity of Ir-based catalysts. The above remarks led us to the development of a series of Ir-based additives for the reduction of the NO emissions during the regeneration of spent FCC catalyst. The parameters that were investigated included the type of catalytic support and the Ir loading on the additive. Experiments in the presence of 1 wt % CP-3 (a Pt-based conventional CO promoter) were used as the base case for the bench scale evaluation of the additives' performance following a testing protocol developed in our previous work.[41] Following the promising catalytic performance of Ir-based materials, selected samples were prepared in larger amounts for bench scale and pilot plant scale experiments. The Ir-based additives were evaluated in a pilot plant unit, and their performance was compared to that of state of the art commercial products (DeNOx, XNOx).

2. Experimental Section

2.1. Materials. Spent (coked) catalyst and three FCC catalytic additives (CP-3, DeNOx, and XNOx) were supplied by Grace GmbH. CP-3 is a Pt-based commercial CO promoter, while DeNOx and XNOx are catalytic additives that reduce the NO emissions. For the evaluation of the additives in the pilot plant unit, the OMV Schwechat refinery supplied commercial unpromoted FCC catalyst and feed gas oil.

A series of Ir-based catalytic additives were prepared using the dry impregnation technique. $IrCl_3 \cdot 4H_2O$ 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 3 h under airflow. The catalytic support was either a commercial γ-alumina (CPBase) or a commercial kaolin, both 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 Ir were deposited sequentially. Ce was initially impregnated, using $Ce(NO_3)_3 \cdot 6H_2O$ as the precursor salt, the sample was calcined at 500 °C for 3 h, and Ir impregnation followed. Finally, two types of stoichiometric $MgO \cdot Al_2O_3$ spinels were synthesized via coprecipitation with NH_3 from the corresponding nitric salts ($Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$) and used as catalytic supports. The precipitated samples were—after overnight drying at 120 °C—calcined under airflow at 750 °C for 6 h and 1000 °C for 5 h, respectively, resulting in two different spinel samples (spinel 1 and spinel 2). All catalytic supports used during this work are summarized in Table 1. The specific surface area of the supports was determined by nitrogen adsorption (BET method), using an Autosorb-1 Quantachrome flow apparatus, and is also included in Table 1.

A series of Ir-based additives on different supports were initially prepared according to the previous procedure, all of them having a 1 wt % Ir loading. Following that, a series of Ir/CPBase alumina catalytic additives were synthesized by varying the Ir loading from 0.1% to 1%. Development of Ir-based additives for reduction of NOx emissions from the regenerator of an FCC unit was an innovation of Prof. Burch and his research group, of the Queens University of Belfast (QUB). This

Table 1. List of Supports Used for the Development of Ir-Based Catalytic Additives

catalytic support	preparation technique	calcination conditions	metal loading	precursor salt	SA (m^2/g)
CPBase alumina	supplied by Grace				181
kaolin					23.71
Ce1CPBase	dry impregnation	500 °C/3 h/air	10% Ce	Ce(NO$_3$)$_3$·6H$_2$O	145.1
Ce2CPBase			20% Ce		132.6
spinel 1	coprecipitation with ammonia	750 °C/6 h/air		Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O	114.7
spinel 2		1000 °C/5 h/air			20.38

Table 2. List of Ir-Based Catalytic Additives (Synthesized in the Laboratory and Scaled-Up Materials)

additive	preparation technique	metal loading	precursor salt
Ir(0.1%)/CPBase	dry impregnation	0.1% Ir	IrCl$_3$·4H$_2$O
Ir(0.5%)/CPBase		0.5% Ir	
Ir(1%)/CPBase		1% Ir	
Ir(1%)/Ce1CPBase		1% Ir, 10% Ce	IrCl$_3$·4H$_2$O, Ce(NO$_3$)$_3$·6H$_2$O
Ir(1%)/Ce2CPBase		1% Ir, 20% Ce	
Ir(1%)/kaolin		1% Ir	IrCl$_3$·4H$_2$O
Ir(1%)/spinel 1		1% Ir	
Ir(1%)/spinel 2		1% Ir	
500IrCPBase	scaled up by Grace	0.05% Ir	
1000IrCPBase		0.1% Ir	
5000IrCPBase		0.5% Ir	
1000IrKaolin		0.1% Ir	

work won the Institute of Chemical Engineers Award for Innovation in Applied Catalysis 2003 and is the subject of a relevant patent. A series of Ir catalysts were also prepared in large quantities by Grace GmbH according to the recipe from QUB. All the Ir-based catalytic additives prepared and tested during this work are summarized in Table 2. Additives Ir(0.1%)CPBase and 1000IrCPBase have the same Ir loading (0.1 wt %) but are named differently to underline that the former was prepared in our laboratory, while the latter was a scaled-up catalyst prepared in large quantities by Grace.

For a more accurate measurement of the actual metal loading of each Ir additive synthesized in our laboratory, we tried to apply the ICP/AES technique (using a Plasma 400 (Perkin-Elmer) spectrometer, equipped with a Cetac6000AT+ ultrasonic nebulizer). Samples of the catalysts were immersed into hot concentrated nitric acid to convert the metal into a soluble nitrate salt, unsuccessfully. Digestion with other acids, e.g., sulfuric acid, hydrochloric acid, and all possible combinations of them, extensive heating, and continuous stirring were applied. Unfortunately, all our efforts were unsuccessful, implying that the Ir phase formed after calcination at 700 °C is extremely difficult to dissolve.

Difficulties in measuring Ir loading by applying the ICP technique are also reported in the literature.[31] Chemical attacks were used to dissolve the Ir-based catalytic samples. Prior to these attacks the samples were reduced with H$_2$, as Ir^0 is easier to dissolve than the oxides. When the sample was calcined at 700 °C under oxidative conditions, complete dissolution was observed only after the HCl + HF attack in a bomb at 120 °C overnight. This was never achieved for catalysts calcined at higher temperatures.[31] Since metallic Ir^0 is much more soluble than the corresponding salts, we submitted our catalytic materials to a reduction pretreatment. Unfortunately, dissolution of the Ir phase was still not possible. Measurement of metal loading with other techniques (e.g., XRF) was not feasible due to lack of the necessary large quantities of catalytic samples.

2.2. Bench Scale Unit. All regeneration experiments were carried out in a bench scale reaction unit using a protocol that sufficiently simulates the regenerator of an FCC unit operating in a full-burn mode.[41] A detailed description of the bench scale unit can be found in our previous work.[41] All experiments were carried out in a fluidized-bed reactor using a 2% O$_2$ in N$_2$ or 1% CO−1% O$_2$ in N$_2$ feed. The total flow rate was 1000 cm^3/min, and the reactor loading was 10 g. Mechanical mixtures of spent catalyst with candidate additives were loaded into the reactor, and regeneration took place at 700 °C.

2.3. FCC Pilot Plant Unit. To evaluate the additives' performance under more realistic conditions, the most promising materials were tested in the CPERI FCC pilot plant unit. The pilot plant unit operates in full circulating mode with continuous regeneration. It consists of a vertical reactor (riser), a fluid-bed regenerator, the stripper, and the lift line. A full description of the unit is given elsewhere.[42] The composition of the regenerator flue gases was measured on-line using an analyzer (Horriba, PG-250), which can measure the following flue gases: O$_2$, CO$_2$, CO, NO, NOx, SO$_2$.

3. Results and Discussion

3.1. Bench Scale Studies. In our previous work[21,41] we presented regeneration experiments of either unpromoted spent FCC catalyst or a mechanical mixture of the same unpromoted spent FCC catalyst with a commercial Pt-based CO promoter (CP-3). Regeneration took place at 700 °C using a fluidized-bed reactor and a 2% O$_2$ in N$_2$ feed.[41] The presence of a conventional CO promoter (CP-3) in the catalytic inventory decreased the CO emissions by approximately 1 order of magnitude, but almost tripled the NO emissions.[21,41] In this work the experimental data are presented as the overall CO and NO emissions measured during the regeneration experiment. 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 moles per gram of spent catalyst in the reactor. Given that we developed additives qualified for use in FCCUs operating in the full burn mode, which contain a CO promoter in their

Table 3. Effect of the Catalytic Support on the Total CO and NO Emissions (mol/g of Spent Catalyst) and the Percentage of CO Oxidized (Positive Sign) and NO Reduced (Positive Sign) during Regeneration of Spent Catalyst in the Presence of 1% Ir-Based Catalysts[a]

additive	total emissions		% conversion	
	CO	NO	CO	NO
none	31.5×10^{-5}	2.62×10^{-6}		
1% CP3	3.25×10^{-5}	8.93×10^{-6}	base case	
Ir(1%)/CPBase	2.94×10^{-5}	5.92×10^{-6}	9.64	33.73
Ir(1%)/Ce1CPBase	2.5×10^{-5}	5.79×10^{-6}	23.08	35.11
Ir(1%)/Ce2CPBase	1.84×10^{-5}	6.11×10^{-6}	43.35	31.62
Ir(1%)/kaolin	5.54×10^{-5}	6.55×10^{-6}	−70.46	26.7
Ir(1%)/spinel 1	22.7×10^{-5}	4.02×10^{-6}	−598.46	55.0
Ir(1%)/spinel 2	2.57×10^{-5}	7.19×10^{-6}	21.06	19.45

[a] Bench scale regeneration experiments at 700 °C with 2% O_2 in N_2 as the feed.

Table 4. Effect of Ir Loading on the Total CO and NO Emissions (mol/g of Spent Catalyst) and Percentage of CO Oxidized (Positive Sign) and NO Reduced (Positive Sign) during Regeneration of Spent Catalyst in the Presence of 1% Ir-Based Catalysts[a]

additive	total emissions		% conversion	
	CO	NO	CO	NO
none	31.5×10^{-5}	2.62×10^{-6}		
1% CP3	3.25×10^{-5}	8.93×10^{-6}	base case	
Ir(0.1%)/CPBase	16.0×10^{-5}	5.1×10^{-6}	−392.62	42.9
Ir(0.5%)/CPBase	7.9×10^{-5}	5.7×10^{-6}	−144.92	36.17
Ir(1%)/CPBase	2.94×10^{-5}	5.92×10^{-6}	9.64	33.73

[a] Bench scale regeneration experiments at 700 °C with 2% O_2 in N_2 as the feed.

inventory, we considered as the 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 reduction or CO oxidation 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.[21,22,41]

3.1.1. Effect of the Catalytic Support. We initially examined the effect of the catalytic support on the deNOx performance of Ir-based catalytic additives. In all samples the Ir loading was 1 wt %, while the carriers used for the catalysts' preparation are listed in Table 1. It is suggested in the literature that the surface chloride ions play an important role by accelerating the growing rate and consequently the size of the iridium particles.[43] This suggestion combined with the fact that larger Ir particles are related to enhanced NO reduction activity[23,24,32] made us consider that utilization of IrCl$_3$· 4H$_2$O as a precursor salt would be rather beneficial for the ability of catalytic additives to reduce nitrogen oxides.

Mechanical mixtures of 1% additive−99% spent catalyst were loaded into the fluid-bed reactor and regenerated at 700 °C using the 2% O_2 in N_2 feed. The overall NO and CO emissions (mol/g of spent catalyst) during regeneration of pure spent catalyst or spent catalyst mixed with catalytic additives (CP-3 or Ir-based materials) are given in Table 3. For comparison reasons we included in this table the corresponding overall NO and CO emissions during the regeneration of pure spent FCC catalyst (absence of any additive).[41] The percentage of NO and CO that is reduced and oxidized, respectively, as compared to the base case is also summarized in Table 3.

All Ir-based catalytic additives were efficient for NO reduction (19−55% reduction as compared with the base case). Use of CPBase alumina as a support resulted in the simultaneous reduction of both pollutants (∼34% and ∼10% reduction of NO and CO emissions, respectively). Therefore, Ir(1%)/CPBase alumina is more efficient than CP-3 for CO oxidation, while at the same time it reduces the NO emissions significantly. Promoting CPBase alumina with 10% Ce enhanced the performance of the additive, mainly improving its ability to oxidize CO (oxidation activity increased from ∼10% to ∼23%). A further increase of the Ce loading on the catalytic support led to even higher enhancement of the CO oxidation activity (to ∼43%), but also to a small inhibition of the NO reduction ability. When we used

CPBase alumina promoted with 10% Ce (Ce1CPBase) as a deNOx additive, we observed ca. 54% reduction in the NO emissions and high CO emissions. This was attributed to the NO adsorption and the subsequent formation of nitrates. When we impregnated Ir on the above support, we observed combined activity for NO reduction and CO oxidation. We are currently investigating whether the role of Ce in this sample is to directly participate in the NO reduction or to modify the structure and morphology of the Ir active site.

Between the two types of stoichiometric spinel supports tested, we observed that only a certain type of spinel (spinel 2) reduced both the NO and CO emissions. This sample was supported on the spinel that was calcined at 1000 °C for 5 h. These preparation conditions led to a material of high crystallinity and low surface area.[21] Specifically, the Ir(1%)/spinel 2 additive reduced the NO and CO emissions by 19% and 21%, respectively. On the other hand, the Ir(1%)/spinel 1 additive exhibited limited activity for CO oxidation and reduced the NO emissions by 55%. Obviously, NO reduction over the last sample is linked with the high CO concentration in the reactor. Finally, when we used kaolin as a support (Ir-(1%)/kaolin), we observed insufficient CO oxidation activity. Besides that, this additive exhibited lower NO reduction activity than the Ir(1%)/CPBase alumina.

3.1.2. Effect of Ir Loading. Iridium is costly, and this is a disadvantage for its use in industrial applications. However, catalysts of low Ir loading are equally or more effective than Ir catalysts with higher metal loadings.[23,24,28] For instance, over Ir/ZSM-5 catalysts a high content of Ir facilitates the oxidation of CO by O_2, while a lower Ir content enhances the oxidation of CO by NO, suggesting that the NO/CO/O_2 reaction over Ir/ZSM-5 is structure sensitive.[29] The scope of this work was to minimize the Ir content and, at the same time, to achieve adequate NO reduction. On the basis of the results presented in the previous section, we chose CPBase alumina as the optimum catalytic support, and we prepared two additional Ir/CPBase alumina catalytic additives with 0.5% and 0.1% Ir. These additives were examined using the standard evaluation procedure, while the corresponding results (total amounts of NO and CO and percentage of reduction of NO and CO emissions) are presented in Table 4. Decreasing the Ir loading from 1% to 0.5% and finally to 0.1% resulted in the enhancement of NO reduction (from 34% to 36% and 43%, respectively) and the inhibition of CO oxidation ability. This result agrees with a previous work,[28] where it was reported that during the selective catalytic reduction studies of NO by CO or C_3H_8 over a series of Ir/ZSM-5 monoliths with varying metal loading, a low Ir content enhances NO reduction, while a high Ir

Table 5. Effect of the Feed Used on the Total CO and NO Emissions (gmol/g of Spent Catalyst) and on the Percentage of CO Oxidized (Positive Sign) and NO Reduced (Positive Sign) as a Result of the Presence of 1% Catalytic Additive(s) (Ir Scaled-Up Catalysts, DeNOx, XNOx)

	2%O_2 in N_2 feed				1%CO−1%O_2 in N_2 feed			
	total emissions		% conversion		total emissions		% conversion	
additive(s)	CO	NO	CO	NO	CO	NO	CO	NO
none	31.5×10^{-5}	2.62×10^{-6}			95.2×10^{-5}	1.35×10^{-6}		
1% CP3	3.25×10^{-5}	8.93×10^{-6}	base case		18.4×10^{-5}	6.57×10^{-6}	base case	
500IrCPBase	7.7×10^{-5}	5.8×10^{-6}	−136.89	35.0	23.7×10^{-5}	3.08×10^{-6}	−28.89	53.14
1000IrCPBase	4.54×10^{-5}	6.65×10^{-6}	−39.71	25.6	16.1×10^{-5}	3.39×10^{-6}	12.74	48.18
5000IrCPBase	2.28×10^{-5}	7.03×10^{-6}	29.9	21.3	9.35×10^{-5}	3.51×10^{-6}	49.17	46.54
1000IrKa olin	9.16×10^{-5}	6.41×10^{-6}	−181.71	28.2	29.9×10^{-5}	3.57×10^{-6}	−62.55	45.64
1% DeNOx + 1% CP-3	3.62×10^{-5}	7.96×10^{-6}	−11.29	10.83	14.4×10^{-5}	5.1×10^{-6}	21.52	22.44
XNOx	3.28×10^{-5}	5.87×10^{-6}	−0.83	34.29	32.6×10^{-5}	3.85×10^{-6}	−76.93	41.38

content promotes the oxidation of the reductant. Similar results were obtained when a series of Rh-based additives were evaluated for the simultaneous reduction of NO and CO emissions from the FCC regenerator.[21] Increasing Rh loading enhanced the additives' ability for CO oxidation but in this case had no effect on DeNOx performance. Rh additives were rather more efficient than Ir additives as they exhibited a combined performance for CO oxidation and NO reduction.[21] However, the extremely high price of Rh was a serious drawback that motivated us to additionally study other catalytic additives such as the Ir-based catalysts of the present work.

3.1.3. Evaluation of Scaled-Up Ir-Based Materials. The promising performance of the Ir-based catalytic additives motivated us to scale up the preparation procedure. As a result, Grace GmbH prepared according to a recipe supplied from QUB about 3 kg of these samples (Table 2). For these samples unpromoted CPBase alumina and kaolin were used as catalytic supports. The Ir loading on CPBase alumina was 0.05%, 0.1%, and 0.5% (500, 1000, and 5000 ppm Ir), while the Ir loading on kaolin was 0.1% (1000 ppm Ir). The evaluation studies of these catalytic additives took place in the bench scale unit by applying the aforementioned testing protocol.[41] Thus, mechanical mixtures of 1% candidate Ir-based additive with 99% spent catalyst were loaded into the fluidized-bed reactor and regenerated at 700 °C using the 2% O_2/N_2 feed. The corresponding total amounts of NO and CO emissions (mol/g of spent catalyst) are summarized in Table 5. For comparison reasons we also included in this table the corresponding overall NO and CO emissions during the regeneration of pure spent FCC catalyst (absence of any additive), as well as the NO and CO emissions when commercial additives (DeNOx and XNOx) developed by Grace were used.[34] The percentage of NO reduction and CO oxidation as compared to the base case are also given in Table 5.

The experimental data in Table 5 show that the scaled-up additives are more efficient for NO reduction and less efficient for CO oxidation. In agreement with our experimental results presented in the previous section, kaolin was less efficient than CPBase alumina. The variation of the Ir loading in Ir/CPBase alumina additives showed that the lower the Ir loading the higher the NO reduction and the lower the CO oxidation. Comparison of the experimental data in Tables 3 and 5 between samples prepared in the laboratory and those prepared on a larger scale by Grace GmbH shows differences in the NO and CO emissions, though the variation in the Ir loading exhibits the same trend for both series of samples.

The performance of additives developed in this work was compared with that of state of the art commercial products (DeNOx and XNOx). The experimental data in Table 5 show that all Ir-based additives exhibit higher NO reduction activity than the DeNOx commercial additive. Among all Ir-based additives examined in this work, 500IrCPBase is the most promising, because it combines the highest NO reduction and the lowest Ir loading. This sample reduces the NO emissions to significantly low levels, comparable to those emitted when the commercial XNOx additive is used. The CO emissions when 500IrCPBase is used are higher than those when XNOx is used, though significantly lower than those in the absence of a CO promoter.

3.1.4. Effect of CO Presence in the Feed. During evaluation of Ir-based catalytic additives, we noticed that the higher the deNOx activity the lower the CO oxidation ability. Exposure of Ir-based catalysts to a CO-containing gas stream increased the deNOx activity and stabilized the catalyst, irrespectively of the oxidizing or reducing pretreatment procedure.[30,31,33] In commercial regenerators the O_2 concentration is high in the dense phase and drops to low concentrations in the dilute phase of the regenerator, while the opposite trend is observed for the CO concentration.[44] Therefore, to simulate the reaction conditions in the dilute phase of the regenerator, we repeated the regeneration experiments in the presence of Ir scaled-up materials using a 1% O_2−1% CO in N_2 feed. This feed contains 100% excess O_2 if complete oxidation of the inlet CO is considered. Experimental results are presented in Table 5. The percentage of NO and CO conversion is calculated with respect to the base case (presence of 1% CP-3, when the feed was 1% O_2−1% CO in N_2).

Use of the CO/O_2/N_2 feed instead of the O_2/N_2 feed substantially enhanced the deNOx performance of all scaled-up Ir catalysts. This was noticed independently of the catalytic support and the Ir loading. The CO addition in the feed resulted in such an enhancement of the catalytic performance that all Ir scaled-up additives (including 1000IrKaolin) were more efficient for NO reduction than the XNOx commercial catalytic additive. At this point it should be noted that in any case of using Ir-based additives N_2O was not detected.

3.1.5. Compatibility of Ir-Based Materials with a CO Promoter. Use of Ir-based additives resulted in a significant decrease of NO emitted during regeneration, though this was not always the case for the CO emissions. High CO emissions were measured, when the metal loading in the additive was low. We examined the synergy between a commercial CO promoter (CP-3) and an Ir-based additive using mechanical mixtures of the two additives. The role of the former additive would be
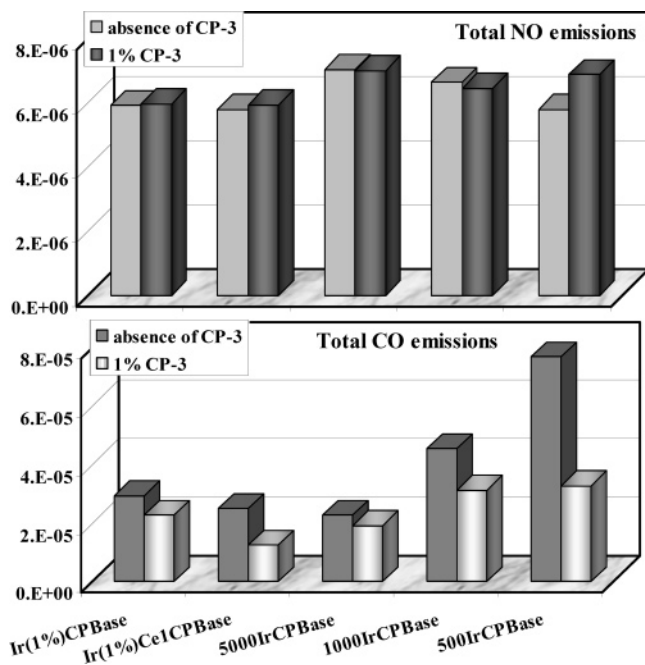
Figure 1. Comparison of NO and CO emissions during the regeneration of spent FCC catalyst after the addition of an Ir-based additive in the presence or the absence of 1% CP-3.
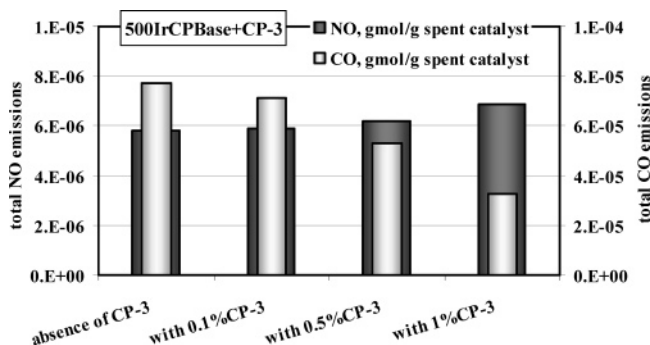

Figure 2. Effect of the CP-3 concentration on NO and CO emissions during the regeneration of spent FCC catalyst, when 1% 500IrCPBase is added into the reactor.

the reduction of the CO emissions and that of the latter one the reduction of the NO emissions. Mechanical mixtures of 1% Ir-based additive−1% CP-3−98% spent FCC catalyst were initially loaded into the fluid-bed reactor and regenerated at 700 °C using the 2% O_2 in N_2 feed. The experimental results are presented in Figure 1. The presence of CP-3 in the reactor inhibits the deNOx ability of Ir-based additives of low metal loading. For instance, use of both 500IrCPBase and CP-3 reduced the NO emissions by 23%, while use of 500IrCPBase reduced these emissions by 35%. The CO emissions in the experiments of Figure 1 were lower than those of the base case experiment (presence of only 1% CP-3). The latter was attributed to the CO oxidation ability of Ir-based additives.

We then loaded our reactor with a constant amount of 500IrCPBase (1%) and varied the percentage of CP-3 (0.1%, 0.5%, and 1%). The NO and CO emissions during regeneration are presented in Figure 2. Increasing the concentration of CP-3 (from 0 to 0.1%, 0.5%, and 1%) resulted in a progressive decrease in the CO emissions, and at the same time in an increase of the NO emissions (NO reduction decreased from ∼35% (in the absence of CP-3) to 34%, 31%, and 23%, respectively). As a result, the required amount of Ir-based additive and that of
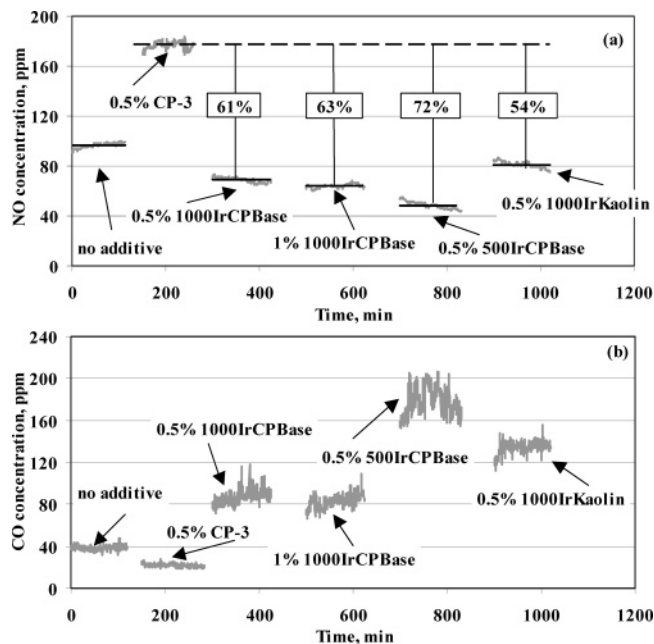

Figure 3. NO (a) and CO (b) emissions from the CPERI pilot plant scale FCCU when no additive or Ir-based additives prepared by Grace GmbH are used.

CP-3 depend on the desired extent of the reduction for the NO and CO emissions.

3.2. Pilot Plant Studies. In our previous work[41] we validated the operation of the CPERI pilot plant FCC unit that simulates adequately the operation of commercial units operating in full burn. A detailed description of the pilot plant unit is given elsewhere.[42] Additives developed in this work were tested in the pilot plant FCC unit using the operating conditions that were followed for the evaluation of the commercial additives developed by Grace (DENOx and XNOx).[41] However, in the present work the pilot plant studies were carried out using an OMV commercial unpromoted catalyst and an OMV feed. The initial additive loading in the inventory was 0.5 wt %. All additives were evaluated using the same excess O_2 in the flue gases to exclude the O_2 effect on the performance of the additives. The operation of the riser in the FCCU was not affected by the addition of any additive used in this work.

In the pilot plant tests we initially used Ir-based additives that were prepared by Grace (500IrCPBase, 1000IrCPBase, and 1000IrKaolin). The experimental results for NO and CO emissions are depicted in parts a and b, respectively, of Figure 3. It is clear that use of all new additives results in a significant reduction of the NO emissions that ranges from 54% up to 72% depending on the additive. The percentage of NO reduction was calculated with respect to the corresponding NO emissions of the base case experiment (presence of 0.5% CP3 for the pilot plant tests) that is also presented in Figure 3. In agreement with the experimental results from the bench scale unit, 500IrCPBase is the best additive for NO reduction, while the worst one is the 1000IrKaolin additive. The situation is different for the CO oxidation ability of Ir-based materials (Figure 3b). Increasing the Ir concentration enhanced CO oxidation, but inhibited NO reduction. The effect of the additive loading in the FCC inventory was also examined by increasing the concentration of 1000IrCPBase from 0.5% to 1%. This resulted in only a slight increase of NO reduction (from 61% to 63%) and it did not modify CO oxidation.
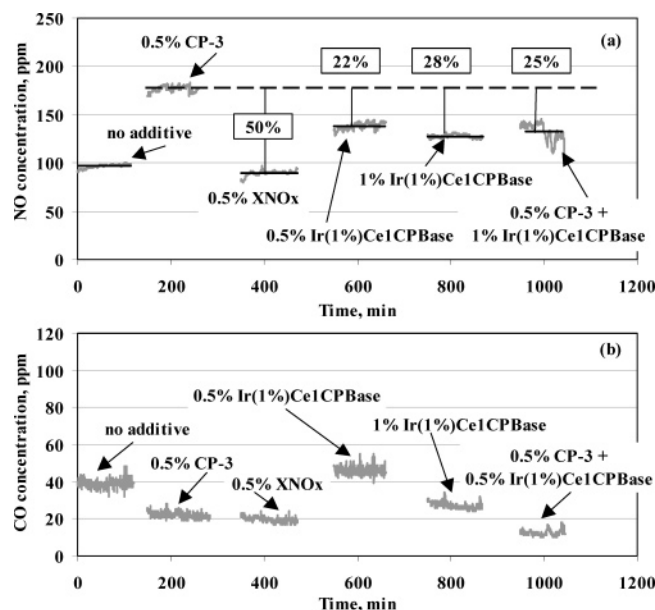
Figure 4. NO (a) and CO (b) emissions from the CPERI pilot plant scale FCCU when no additive or Ir-based additives prepared by CPERI are used.

Table 6. Evaluation of the New Ir-Based Additives in the CPERI Pilot Plant FCC Unit, Comparison with XNOx Commercial Additive

	% conversion	
additive	NO	CO
CP3	base	base
1000IrCPBase	61%	−240%
500IrCPBase	72%	−580%
1000IrKaolin	54%	−460%
XNOx	50%	0%
Ir(1%)/Ce1CPBase (or 10000IrCe1CPBase)	22%	−130

To enhance the CO oxidation ability of the Ir-based additives (500IrCPBase and 1000IrCPBase), we added small amounts of the XNOx commercial additive in the inventory and compared the NO and CO emissions between the two series of experiments. Following the addition of XNOx, the NO reduction ability of the 500IrCPBase additive was preserved, while the CO emissions were approximately as equally low as those of the base case experiment (presence of 0.5% CP-3). A similar behavior was noted when we used the 1000IrCP-Base additive in combination with XNOx.

In general, the novel Ir-based additives prepared by Grace GmbH reduced the NO emissions significantly. These emissions were sometimes lower than those in the experiment where no additive is used (regeneration of pure spent FCC catalyst). However, use of the Ir-based additives led to higher CO emissions as compared with the regeneration experiments in the presence of a CO promoter. The percentage of conversion of NO and CO emissions due to the presence of Ir-based additives in the inventory is summarized in Table 6, where for comparison reasons we have also included the corresponding data when the XNOx commercial additive developed by Grace was used.

The Ir(1%)/Ce1CPBase additive that was prepared in our laboratory was used in the pilot plant tests, as well. The effect of the additive's presence on NO and CO emissions is depicted in parts a and b, respectively, of Figure 4, while for comparison reasons we have also included in this figure the NO and CO emissions when XNOx was used. We initially added into the reactor 0.5

wt % Ir(1%)/Ce1CPBase and measured 22% NO reduction as compared to the base case (0.5% CP-3). In addition to that, the CO emissions are higher as compared with those in the presence of CP-3, but the difference is much more limited than in the case of the Ir scaled-up catalysts. We increased the concentration of Ir(1%)/Ce1CPBase additive in the inventory from 0.5% to 1% and measured 28% reduction in the NO emissions and CO emissions comparable to those in the presence of CP-3. Finally, we used a mechanical mixture of 0.5% Ir(1%)/Ce1CPBase and 0.5% CP-3 in the inventory and measured 25% reduction in the NO emissions and very low CO emissions. This implies that CO was oxidized over both the Ir additive and the CO promoter. Comparison between the performance of samples prepared in our laboratory and those prepared by Grace GmbH showed that lower NO and CO emissions were measured when the latter additives were used, in agreement with the results from the bench scale unit. We attribute the above difference to the type of support and/or to the different Ir loading of each sample.

4. Conclusions

We have synthesized and evaluated the performance of Ir-based additives for NO reduction in an FCC regenerator. In addition to the laboratory-made samples, materials prepared by Grace GmbH were tested in our facilities. The supports for the above samples were CPBase alumina, two types of stoichiometric spinels, and kaolin. The most promising carrier was CPBase alumina. Addition of Ce on CPBase alumina enhanced CO oxidation and did not affect NO reduction. Samples with different Ir loadings were synthesized. When we increased the Ir loading in the additive, we observed higher NO emissions and lower CO emissions. In our bench scale experiments we used O_2/N_2 and $O_2/CO/N_2$ feeds. The latter feed resulted in lower NO emissions during regeneration. Comparison between the performances of Ir-based additives showed that CPBase loaded with 1000 or 500 ppm Ir prepared by Grace GmbH exhibit the optimum combined activity (decrease of both NO and CO emissions). Other samples reduced the NO emissions to a greater extent but produced high CO emissions during regeneration. The latter problem can be solved with the addition of a small amount of a commercial CO promoter. Regeneration tests were carried out in the CPERI pilot plant FCC to validate the bench scale results. In general, the pilot plant tests were in agreement with the bench scale results. The novel Ir-based additives reduced the NO emissions up to 72%, while the commercial NO reduction additive (XNOx) reached 50% reduction of the NO emissions. However, more CO was emitted when the Ir-based additives were used. To overcome this problem, we added XNOx in the inventory and measured low CO emissions, as well.

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