

PROCESS OF REMOVING NO_x FROM FLUE GAS

5 CROSS-REFERENCE TO RELATED APPLICATION

This application claims the priority benefit of U.S. Provisional Patent Application No. 61/602,331 filed on February 23, 2012.

FIELD OF THE INVENTION

10 The invention relates to a process of reducing the amount of nitrogen oxides discharged to atmosphere from a fluid catalytic cracking unit or any combustion process.

BACKGROUND OF THE INVENTION

15 The fluid catalytic cracking (FCC) process is a major source of SO_x and NO_x gas emissions in petroleum refining. In the FCC process, heavy hydrocarbon fractions are cracked to produce lighter, valuable products (gasoline, distillate, and C₂-C₄ olefins and saturated hydrocarbons). The cracking process takes place in the riser section of a FCC unit, where the hydrocarbon
20 fractions are contacted with a FCC catalyst and other additive particles at elevated temperature. As the endothermic cracking reactions occur, coke (containing carbon, sulfur and nitrogen, among other components) is deposited onto the FCC catalyst and any additive particles. These particles are carried from the FCC unit's reactor to the catalyst regenerator, and the coke is burned off
25 to form carbon monoxide, carbon dioxide, and a wide-range of gaseous sulphur and nitrogen species, e.g., SO₂, SO₃, COS, H₂S, N₂, NO, N₂O, NO₂, NH₃, and HCN.

The exact composition of these gases in the flue gas depends upon the detailed reaction conditions in the regenerator. For example, under full-burn
30 conditions (excess oxygen used in combustion of coke) the main species are SO₂, SO₃, N₂ and NO. Under partial-burn conditions (sub-stoichiometric oxygen levels) much higher levels of the "reduced" S and N species (COS, H₂S, NH₃, HCN) may also be present. Most partial-burn FCC units will have a CO-boiler (COB) downstream to convert the CO to CO₂ in order to control CO emissions

and recover the energy for steam production. Most of the reduced S and N species in the flue gas are converted to more highly oxidized forms in the CO-boiler. So COS and H₂S are converted to SO₂ and SO₃; and NH₃ and HCN are converted to N₂, NO, N₂O, and NO₂. Therefore, in both full-burn and partial-burn operations, the flue gas contaminants are predominantly sulfur oxide gases (e.g., SO₂ and SO₃ which are often collectively referred to as "SO_x" gases) and nitrogen oxide gases (e.g., NO, N₂O, NO₂ which are often collectively referred to as "NO_x" gases). Other species are only present at much lower concentrations. Unless captured or removed, the hydrogen cyanide would be emitted to the atmosphere along with other flue gases.

Various processes have been taught to remove or reduce the amount of these gases discharged to atmosphere from a FCC unit. One method to remove NO_x gases has been to use ammonia as a reductant to reduce the NO_x to from nitrogen. See, for example, U.S. Pat. No. 4,778,665 which teaches the reduction of NO_x with ammonia in the presence of a crystalline zeolite catalyst. U.S. Pat. No. 4,778,665 teaches that at an appropriate point downstream of the ammonia injection, after reduction of the NO_x, the particles are recovered by a cyclone separator or by an electrostatic precipitator, and the flue gas then is discharged.

It is desirable to attain still further improvements in the reduction of NO_x gas in the effluent from an FCC unit.

SUMMARY OF THE INVENTION

The invention includes a process for reducing the amount of nitrogen oxides (NO_x) discharged to atmosphere from a fluid catalytic cracking (FCC) unit. A NO_x-containing flue gas is discharged from the regenerator of the FCC unit and is then passed to a collecting means for collecting and supporting catalyst particles. The process comprises adding a catalyst to the NO_x-containing flue gas prior to the collecting means and precipitating the catalyst in the collecting means to form a catalyst bed in the collecting means. Ammonia or an ammonia precursor is added to the flue gas prior to the collecting means and/or added to the flue gas within the collecting means. NO_x in the flue gas is reacted with the ammonia or ammonia precursor at a temperature ranging from 200°C to 800°C in the presence of the catalyst bed to reduce the amount of NO_x in the flue gas, and

the flue gas containing a reduced amount of NO_x is discharged to atmosphere. The catalyst is one or more supported transition or lanthanide metal catalysts. The process can also be utilized to remove NO_x from any combustion process.

5 DETAILED DESCRIPTION OF THE INVENTION

The invention includes a process for reducing the amount of nitrogen oxides (NO_x) discharged to atmosphere from a fluid catalytic cracking unit. The FCC unit comprises a regenerator and a collecting means for collecting and supporting catalyst particles, wherein a NO_x -containing flue gas is discharged
10 from the regenerator and is then passed to the collecting means.

A typical FCC unit comprises a riser/reaction section in which FCC catalyst particles contact and vaporize a hydrocarbon feedstock entering the bottom of the riser of the FCC unit. The vaporized hydrocarbon carries the FCC catalyst up the riser into the reactor section. Cracked hydrocarbon product exits the top of
15 the reactor and FCC catalyst particles are retained in a bed of particles in the lower part of the reactor. During cracking of the hydrocarbon, coke is deposited on the FCC catalyst.

The coked FCC catalyst is then passed to the regenerator of the FCC unit. As used in this application, the term "regenerator" also includes the combination
20 of a regenerator and a CO boiler, particularly when the regenerator itself is run under partial burn conditions. In the regenerator, coke on the FCC catalyst is burned off in a fluidized bed in the presence of oxygen and a fluidization gas which are typically supplied by entering the bottom of the regenerator. The regenerated FCC catalyst is withdrawn from the fluidized bed and returned to the
25 riser for reuse in the cracking process.

Since the coke generally contains some nitrogen compounds, when the coke is burned in the regenerator nitrogen oxides (i.e., NO , NO_2 , etc., collectively known as NO_x) are formed. Unless some means is provided to control the release of the NO_x from the regenerator, they will be exhausted to atmosphere
30 along with the other combustion gases in the flue gas. The flue gas from the regenerator of an FCC unit will typically contain between about 25 to 2000 ppm of nitrogen oxides.

The NO_x -containing flue gas (typically also containing some oxygen along with the other combustion gases) exiting the regenerator will typically carry

entrained catalyst fines. A collecting means for collecting the catalyst fines (e.g., an electrostatic precipitator) is usually included in a FCC unit in order to collect catalyst fines so that they are not released to the atmosphere.

In the process of the invention, the NO_x-containing flue gas is discharged from the regenerator and is then passed to the collecting means. A catalyst is added to the flue gas prior to entering the collecting means. The catalyst is one or more supported transition or lanthanide metal catalysts. Although not critical for the invention, the mean particle size of the catalyst particles useful in the invention are preferably from 1 μm to 200 μm, more preferably from 10 μm to 100 μm.

The supported transition or lanthanide metal catalyst comprises one or more transition or lanthanide metals and one or more supports. The transition metal includes any Group 3-12 transition metal. The transition or lanthanide metal is preferably vanadium, tungsten, iron, platinum, copper, ceria, or mixtures thereof.

The support is preferably an inorganic oxide and most commonly includes the oxides of Groups 2, 3, 4, 5, 13 and 14 elements. Useful inorganic oxide supports preferably have specific surface areas in the range 10 to 700 m²/g, pore volumes in the range 0.1 to 4 mL/g, and pore diameters from about 10 to 1000 Angstroms (1 to 100 nm). The inorganic oxide support is preferably magnesia, alumina, silica, titania, zirconia, ceria, niobia, tantalum oxides, molybdenum oxides, tungsten oxides, or mixed oxides or composite oxides of any two or more thereof, e.g. magnesia-alumina, silica-alumina, or titania-silica.

The support is preferably a hydrotalcite, a clay, or a zeolite. Suitable clays include halloysites, rectorites, hectorites, montmorillinites, synthetic montmorillinites, sepiolites, activated sepiolites, and kaolins. Suitable zeolites may be any natural or a synthetic zeolite, including molecular sieves, and is preferably composed of aluminum, silicon, and/or phosphorus. The zeolites typically have a three-dimensional arrangement of SiO₄, AlO₄, and/or PO₄ that are joined by the sharing of oxygen atoms. The zeolite frameworks are typically anionic, which are counterbalanced by charge compensating cations, typically alkali and alkaline earth elements (e.g., Na, K, Mg, Ca, Sr, and Ba) and also protons. Other metals (e.g., Fe, Ti, and Ga) may be incorporated into the

framework of the zeolite to produce a metal-incorporated zeolite, e.g., titanium silicalite. The zeolite is preferably a beta zeolite, a faujasite (such as an X-zeolite or a Y-zeolite, including NaY and USY), an L-zeolite, a ZSM zeolite (e.g., ZSM-5, ZSM-48), an SSZ-zeolite (e.g., SSZ-13, SSZ-41, SSZ-33), a mordenite, a
5 chabazite, an offretite, an erionite, a clinoptilolite, a silicalite, an aluminum phosphate zeolite (including metalloaluminophosphates such as SAPO-34), a mesoporous zeolite (e.g., MCM-41, MCM-49, SBA-15), a metal-incorporated zeolite, or mixtures thereof; more preferably, the zeolites are beta zeolite, ZSM-5 zeolite, or SSZ-33, or Y-zeolite. The zeolite is most preferably beta zeolite or
10 ZSM-5 zeolite.

The hydrotalcite may be a hydrotalcite or hydrotalcite-like material (HTL). The hydrotalcite or HTL may be collapsed, dehydrated and or dehydroxylated. Non-limiting examples and methods for making various types of HTL are described in U.S. Patent No. 6,028,023; U.S. Patent No. 6,479,421; U.S. Patent
15 No. 6,929,736; and U.S. Patent No. 7,112,313; which are incorporated by reference herein in their entirety. Other non-limiting examples and methods for making various types of HTL are described in U.S. Patent No. 4,866,019; U.S. Patent No. 4,964,581; and U.S. Patent No. 4,952,382; which are incorporated by reference herein in their entirety. Preferably, the hydrotalcite is a magnesia-
20 alumina hydrotalcite.

Alumina is also a preferred support. The alumina is a solid material that contains a major proportion of aluminum oxide. Amorphous (i.e., non-crystalline) aluminum oxides are particularly preferred for use. In general, suitable aluminas are further characterized by having a relatively large surface area in relation to
25 their mass, preferably the average specific surface area is from 1 m²/g to 1000 m²/g, and most preferably from about 50 m²/g to 500 m²/g. "Specific surface area" is used normally in the art and expresses the relationship of surface area to mass. Preferred aluminas include α -alumina, γ -alumina, and activated aluminas. Activated aluminas are partially hydroxylated aluminum oxide whose chemical
30 compositions can be represented by the formula $\text{Al}_2\text{O}_{(3-x)}(\text{OH})_{2x}$, where x ranges from about 0 to 0.8. Activated aluminas are particularly preferred.

Preferably, the amount of transition or lanthanide metal present in the supported transition or lanthanide metal catalyst will be in the range of from 0.01

to 30 weight percent. When the transition metal is a noble metal such as palladium, platinum, gold, silver, iridium, rhenium, ruthenium, and osmium, the amount of transition metal is more preferably from 0.01 to 10 weight percent, most preferably 0.02 to 5 weight percent. For lanthanide metals and transition
5 metals other than the noble metals, the amount of transition metal present in the supported transition or lanthanide metal catalyst is more preferably 2.5 to 25 weight percent. The manner in which the transition or lanthanide metal is incorporated onto the support is not considered to be particularly critical. For example, a transition or lanthanide metal compound (e.g., copper nitrate) may be
10 supported on a hydrotalcite by impregnation, adsorption, incipient wetness, ion-exchange, precipitation, or the like.

Preferred supported transition or lanthanide metal catalysts include a supported platinum catalyst. The supported platinum catalyst preferably comprises platinum and an inorganic oxide; and more preferably comprises
15 platinum on alumina. Preferred supported transition or lanthanide metal catalysts also comprise (a) vanadium, tungsten, copper, iron, cerium, or mixtures thereof, and (b) a hydrotalcite, a clay, or a zeolite; and more preferably comprises copper and a hydrotalcite. Because the flue gas may contain sulfur oxides, it may be preferable to use catalysts that are also capable of removing SO_x in the flue gas
20 or that are resistant to sulfur poisoning.

After the addition of the catalyst to the NO_x -containing flue gas, the catalyst is then collected in the collecting means to form a catalyst bed in the collecting means. Suitable collecting means include an electrostatic precipitator, a filter, a pebble bed, a third stage separator, and the like. Suitable filters include
25 a bag filter and a sintered metal filter. Preferred collecting means include an electrostatic precipitator, a bag filter and a sintered metal filter. In the case of an electrostatic precipitator (ESP), the catalyst collects on plates contained in the ESP and forms a catalyst bed within the ESP. The plates also serve as a support for the catalyst to aid in contacting the NO_x -containing flue gas with the catalyst.

30 Another preferred collecting means includes a combination of a fast fluidized bed and a cyclone. The fast fluidized bed may be a wide point in the flue gas exit line that will contain a dilute number of catalyst particles that act as the fluidized bed. The fast fluidized bed allows particles entrained in the flue gas stream exiting the FCC regenerator to pass through the vessel without increasing

pressure drop. The cyclone acts to prevent catalyst from exiting the FCC unit and being emitted to atmosphere, while allowing fines to exit the process. The catalyst particles trapped by the cyclone can be added back into the fast fluidized bed.

5 Preferably, an additional contact unit is added prior to or after the collecting means in order to ensure good contact between the additive and flue gas.

Ammonia or an ammonia precursor is added to the flue gas. Suitable ammonia precursors include urea, ammonium carbonate, ammonium carbamate, ammonium hydrogen carbonate, and ammonium formate. The ammonia or
10 ammonia precursor can be introduced to the flue gas prior to entering the collecting means and/or within the collecting means. Preferably, the ammonia or ammonia precursor is introduced into the flue gas at a point prior to the collecting means to allow good mixing of the ammonia or ammonia precursor in the flue gas
15 to occur. Preferably, the ammonia and the catalyst are added at the same location to the flue gas.

The amount of ammonia or ammonia precursor present in the flue gas is not considered critical, but preferably the molar ratio of ammonia to NO_x ($\text{NO} + \text{NO}_2$) is in the range of 0.05 to 1.5, more preferably 0.6 to 1, so that preferably 5
20 to 100 percent and more preferably at least 60 percent, reduction of NO_x can be achieved.

Although the presence of oxygen is believed to be necessary for the reduction of nitrogen oxides in accordance with the invention, sufficient free oxygen generally remains mixed with the combustion gases leaving the
25 regenerator for the process to occur. Additional oxygen can be added if insufficient oxygen is present, as for example where the regenerator is operated in an oxygen lean mode.

The NO_x in the flue gas is reacted with the ammonia or ammonia precursor in the presence of the catalyst bed in the collecting means to reduce
30 the amount of NO_x in the flue gas. Preferably, the reaction occurs at a temperature ranging from 200°C to 800°C, more preferably from 200°C to 500°C. The ammonia reduction of NO_x results in the production of N_2 . Thus, a flue gas

having a reduced amount of NO_x is produced and it is then discharged to atmosphere.

It may be preferable to cool the flue gas prior to the collecting means. Any suitable cooling means may be utilized, including heat exchangers. The addition
5 of the ammonia or ammonia precursor, along with possible diluent gases, may cool the flue gas prior to the collecting means. Preferably, the gases are cooled prior to the point of introducing the ammonia or ammonia precursor to minimize spontaneous combustion of the ammonia or ammonia precursor.

The process of the invention may also be used to reduce NO_x emissions
10 from any combustion process that produces NO_x . Thus, the invention also includes a process for reducing the amount of nitrogen oxides discharged to atmosphere from a combustion process. The combustion process comprises a combustion unit and a collecting means for collecting and supporting catalyst particles. The flue gas containing NO_x that is discharged from the combustion
15 unit is passed to the collecting means. The process comprises adding a catalyst to the flue gas prior to entering the collecting means, and then precipitating the catalyst in the collecting means to form a catalyst bed in the collecting means. Ammonia or an ammonia precursor is added to the flue gas prior to entering the collecting means, to the flue gas within the collecting means, or both. The NO_x in
20 the flue gas is reacted with the ammonia or ammonia precursor at a temperature ranging from 200°C to 800°C in the presence of the catalyst bed to reduce the amount of NO_x in the flue gas, and the flue gas containing a reduced amount of NO_x is discharged to atmosphere.

All of these process steps are the same as described above. The catalyst
25 is one or more supported transition or lanthanide metal catalysts, as described above. The combustion unit is preferably a coal combustion unit, a fuel oil combustion unit, a wood product combustion unit, a fluid catalytic cracking unit, a fired heater, an ethylene heater, a hydrogen heater, or the like.

30 The following examples merely illustrate the invention. Those skilled in the art will recognize many variations that are within the spirit of the invention and scope of the claims.

EXAMPLE 1: PREPARATION OF CATALYSTS

Catalyst 1A: CuO on hydrotalcite-like material

Transition or lanthanide metals can be added to hydrotalcite-like materials as follows: A copper nitrate solution (1082 g, containing 16.76 wt.% solid) is added to a slurry of a MgO and Al₂O₃ mixture (6771 g, Mg/Al molar ratio 3/1). The mixture is stirred for 1 hour at room temperature, and the resulting mixture is then spray dried and calcined at 500°C. Catalyst 1A contains approximately 26 wt.% Al₂O₃, 55 wt.% MgO, and 19 wt.% CuO.

Catalyst 1B: Pt/Al₂O₃

Pt is added to Al₂O₃ as follows: An aqueous Pt(NH₃)₂Cl₂ solution (containing 0.137 g Pt(NH₃)₂Cl₂ (containing 54.8 wt.% solid) in 19.8 g H₂O) is sprayed onto Al₂O₃ (116 g). The resulting material is then dried at 120°C and calcined at 500°C. Catalyst 1B contains approximately 0.06 wt.% Pt.

Catalyst 1C: Fe₂O₃ and CeO₂ on hydrotalcite-like material

Catalyst 1C can be prepared according to the procedure of Catalyst 1A except that iron nitrate and cerium nitrate are used in place of the copper nitrate solution. Catalyst 1A contains approximately 21 wt.% Al₂O₃, 53 wt.% MgO, 10 wt.% Fe₂O₃, and 16 wt.% CeO₂.

Catalyst 1D: Pd/Al₂O₃

Catalyst 1D is prepared according to the procedure of Catalyst 1B except that Pd(NH₃)₂Cl₂ is used in place of the Pt(NH₃)₂Cl₂ solution. Catalyst 1D contains approximately 0.06 wt.% Pt.

Catalyst 1E: V₂O₅/TiO₂

Catalyst 1E is a commercial selective catalytic reduction catalyst containing approximately 85 wt.% TiO₂, 2.5 wt.% V₂O₅, and 9 wt.% SiO₂.

The physical properties of the catalysts are listed in Table 1.

EXAMPLE 2: NO REDUCTION TESTS

Except for Catalyst 1E, all the samples were calcined at 732°C for one hour before testing. The catalysts of Example 1 are tested in a fix bed quartz reactor. A gas mixture (260 cc/min) containing 2307 ppm NH₃ and 769 ppm NO is contacted with a fixed bed of 1.0 g catalyst in the presence of 3 vol.% oxygen and the balance helium. The effluent gas was analyzed on-line by a mass spectrometer and/or IR analyzer, and the temperature of the catalyst bed was monitored by an Omega temperature logger. The percent reduction of NO at three temperatures is shown in Table 2. The results show that although a palladium/alumina and a vanadia/titania catalyst are effective at removing some NO_x, a copper-containing hydrotalcite, an iron-cerium-containing hydrotalcite and platinum/alumina are more effective catalysts for the removal of NO_x.

Table 1: Physical properties of catalysts

Catalyst	Average Particle Size (μm)	Surface Area (m^2/g)
1A	50	118
1B	72	91
1C	68	127
1D	71	105
1E	-	-

TABLE 2: Testing Results

Catalyst	NO Conversion (%)		
	250°C	300°C	350°C
1A	-	-	80
1B	90	100	-
95% 1A + 5% 1B	50	100	-
99% 1A + 1% 1B	10	100	-
95% 1C + 5% 1B	50	100	-
1D	-	-	10
1E	-	10	40

We claim:

1. A process for reducing the amount of nitrogen oxides (NO_x) discharged to atmosphere from a fluid catalytic cracking unit comprising a regenerator and a collecting means for collecting and supporting catalyst particles, wherein a flue gas containing NO_x is discharged from the regenerator and is then passed to the collecting means, said process comprising:

(a) adding a catalyst to the flue gas prior to entering the collecting means;

(b) precipitating the catalyst in the collecting means to form a catalyst bed in the collecting means;

(c) adding ammonia or an ammonia precursor to the flue gas prior to entering the collecting means, to the flue gas within the collecting means, or both;

(d) reacting NO_x in the flue gas with the ammonia or ammonia precursor at a temperature ranging from 200°C to 800°C in the presence of the catalyst bed to reduce the amount of NO_x in the flue gas; and

(e) discharging the flue gas containing a reduced amount of NO_x to atmosphere,

wherein the catalyst is one or more supported transition or lanthanide metal catalysts.

2. The process of claim 1 wherein the flue gas is cooled prior to entering the collecting means.

3. The process of claim 1 wherein the collecting means is an electrostatic precipitator.

4. The process of claim 1 wherein the collecting means is a bag filter.

5. The process of claim 1 wherein the collecting means is a sintered metal filter.

6. The process of claim 1 wherein the collecting means is a combination of a fast fluidized bed and a cyclone.

7. The process of claim 1 wherein the supported transition or lanthanide metal catalyst is a supported platinum catalyst.

8. The process of claim 7 wherein the supported platinum catalyst comprises platinum and an inorganic oxide.

9. The process of claim 8 wherein the supported platinum catalyst comprises platinum on alumina.

10. The process of claim 1 wherein the supported transition or lanthanide metal catalyst comprises (a) vanadium, tungsten, copper, iron, cerium, or mixtures thereof, and (b) a hydrotalcite, a clay, or a zeolite.

11. The process of claim 10 wherein the supported transition or lanthanide metal catalyst comprises copper and a hydrotalcite.

12. The process of claim 1 wherein NO_x in the flue gas is reacted with the ammonia at a temperature ranging from 200°C to 500°C.

13. The process of claim 1 wherein the catalyst has a mean particle size of 10 μm to 100 μm .

14. A process for reducing the amount of nitrogen oxides (NO_x) discharged to atmosphere from a combustion process comprising a combustion unit and a collecting means for collecting and supporting catalyst particles, wherein a flue gas containing NO_x is discharged from the combustion unit and is then passed to the collecting means, said process comprising:

(a) adding a catalyst to the flue gas prior to entering the collecting means;

(b) precipitating the catalyst in the collecting means to form a catalyst bed in the collecting means;

(c) adding ammonia or an ammonia precursor to the flue gas prior to entering the collecting means, to the flue gas within the collecting means, or both;

(d) reacting NO_x in the flue gas with the ammonia or ammonia precursor at a temperature ranging from 200°C to 800°C in the presence of the catalyst bed to reduce the amount of NO_x in the flue gas; and

(e) discharging the flue gas containing a reduced amount of NO_x to atmosphere,

wherein the catalyst is one or more supported transition or lanthanide metal catalysts.

15. The process of claim **14** wherein the combustion unit is a coal combustion unit, a fuel oil combustion unit, a wood product combustion unit, a fluid catalytic cracking unit, a fired heater, an ethylene heater, or a hydrogen heater.