FCC DeSO$_x$ and DeNO$_x$ additive technology

WEN Bin, HE Min-yuan *

(Research Institute of Petroleum Processing, SINOPEC, Beijing 100083, China. E-mail: wenzhang@bj.col.com.cn)

Abstract: The fluid catalytic cracking(FCC) is the principal gasoline-producing process in the refinery. Considerable amounts of harmful sulfur oxides and nitrogen oxides (SO$_x$ and NO$_x$) are generated with the FCC operation. Impacted by strengthening environmental regulations and the current global emphasis on environmental protection and pollution abatement, refiners have been meaning to look for effective ways to control and reduce SO$_x$ and NO$_x$ emissions. FCC DeSO$_x$ and DeNO$_x$ additives is the most promising measure. The present paper reviews the developments in FCC DeSO$_x$ and DeNO$_x$ additive technology based on the respective authors' works, the future directions of the technology are also discussed.
Key words: FCC; NO$_x$; SO$_x$; DeSO$_x$ additive; DeNO$_x$ additive

Introduction

In recent years, there has been an increasing concern worldwide for air pollution caused by industrial emissions. Sulfur oxides and nitrogen oxides(SO$_x$ and NO$_x$) are two main atmospheric pollutants, which are generally believed to be major precursors of acid rain and deplete the ozone layer. Their damaging effects on our health and environment are substantial. In response to the concern, worldwide action has been taken to reduce SO$_x$ and NO$_x$ emissions. In the United States, coal-fuel utility boilers account for about 65% of the SO$_x$ and 29% of the NO$_x$ emissions (Cusumano, 1992), petroleum refining operations are estimated to emit 6%—7% of the total SO$_x$ emissions and 10% of the NO$_x$ emissions(Nolan, 1998; Slack, 1971), more specifically from the fluid catalytic cracking(FCC) units(Seinfeld, 1986; Shannon, 1996). Processes used to decrease the emissions of SO$_x$ and NO$_x$ from effluent gases of the coal-fuel utility boilers have been developed successfully(Iwamoto, 1991a; 1991b), but they are not suitable for FCCU(FCC Unit) owing to the higher operation temperatures required in these units and the many other requirements associated with the FCC operation(Corma, 1992).

In the United States, the clean air act amendments(CAAA) and various local regulations regulate the emissions of SO$_x$ and NO$_x$. Each year new emission limitations are enforced by government. Current regulations controlling such pollution are becoming more stringent. Impacted by strengthening environmental regulations and the current global emphasis on environmental protection and pollution abatement, refiners have been meaning to look for effective ways including DeSO$_x$ and DeNO$_x$ additives to control and reduce SO$_x$ and NO$_x$ emissions generated by FCC processes. The current paper will mostly focus on the developments in FCC DeSO$_x$ and DeNO$_x$ additive technology, the future directions of the technology will also be discussed.

1   Reference criteria

California was the first state to set forth stringent standards for reducing SO$_x$ emissions from FCCU. Starting from the day of July 1, 1981, FCCU SO$_x$ emissions can not exceed 130 kg/1000 bbl of feed(Davey, 1996). SO$_x$ emissions from the FCCU have been under federal regulations since 1984, which limit emissions from a revamped FCCU to 9.8 kg SO$_x$ per 100 kg coke burned off or approximately 300 ppmv. The new source performance standards (NSPS) of the Environmental Protection Agency (EPA) went into effect in 1989. They cover new FCCU or modified units since January 1984. For FCCU SO$_x$ emissions regulation, the NSPS is, with added-on SO$_2$ control device, 50 ppmv SO$_2$ or 90% reduction of SO$_2$, without add-on SO$_2$ control device 9.8 kg SO$_2$ per 1000 kg coke burn-off(typically 250—300 ppmv) or 0.3% feed sulfur by weight(Gilman, 1998).

Recently, the south coast air quality management district (SCAQMD), has proposed a

---

* Corresponding author

significant reduction for the allowable level of FCC flue gas SO$_x$ emissions from the currently regulated level of 60 kg/1000 bbl of feed (issued in 1987, for a typical FCC unit this level corresponds to about 200—300 ppmv SO$_x$ in the FCC regenerator flue gas) down to 6 kg/1000 bbl of feed.

As to NO$_x$, they have received less attentions not long age due to their emissions are typically lower than uncontrolled SO$_x$ emissions from FCCU. The regulations in USA for FCC NO$_x$ emissions are < 10 ppmv without CO boiler, 100—200 ppmv withe CO boilers(Corma, 1994). The EPA has proposed that 22 eastern US States reduce 35 % of NO$_x$ emission by 2007.

2   The origin of SO$_x$ and NO$_x$ in the FCCU regenerator

The FCC unit, which is the principle gasoline-producing process in the refinery, converts heavy petroleum fractions to gasoline and lighter products. A diagram of the basic FCC unit is shown in Fig. 1(McArthur, 1981a; Thomas, 1983).

The FCC process consists of a reactor and a regenerator. Feed is injected into the riser section of the reactor where it mixed with catalyst and is cracked as it passes through the riser. Meanwhile, the catalyst is deactivated by coke and feed metal. After being stripped by steam, the cocked catalyst is directed to the regenerator. There, the coke on catalyst is arnold off, the sulfur and nitrogen in the coke originating from sulfur compounds and nitrogen compounds in the feed are transformed into SO$_x$ (ca. 90 % SO$_2$, 10 % SO$_3$; Byrne, 1984) and NO$_x$ (ca. 90 % NO, 10 % NO$_2$) and leave as flue gas from the regenerator during this time. The riser top temperature is between 480℃ and 570℃, typical regenerator temperature ranges from 650℃ to 760℃.

Emissions of the SO$_x$ and NO$_x$ in the flue gases of FCCU regenerator represent only a small fraction of the concentration of them in feed. Only about 5 % of the feed sulfur accounts for regenerator SO$_x$ emissions. Appproximately 2 %—4 % of the feed nitrogen is typically converted to NO$_x$, which depends primarily on the species and content of sulfur and nitrogen in the feed (Huling, 1975).

In FCCU regenerator, the SO$_x$ and NO$_x$ concentrations ranges are 100—1000 ppmv and 50—5000 ppmv respectively, which may be effected by variables such as process conditions, feedstock, and unit design. Since 1980, considerable progress has been made on determining the contribution of each of these variable to SO$_x$ and NO$_x$ emissions.

3   DeSO$_x$ additive technology

3.1   SO$_x$ control strategy for the FCCU

The SO$_x$ (SO$_2$ and SO$_3$) problem in FCCU has been the subject of extensive research. Generally, there are four principal options for abatement of FCC flue gas SO$_x$: flue gas scrubbing, feedstock desulfurization(hydrotreating), selection of low sulfur feedstock, and DeSO$_x$ additive.

Flue gas scrubbing is a tail-end control technology. If a refiner selects flue gas scrubbing, SO$_x$ emissions must be reduced by 90 % or emissions must be kept below 50 ppmv. But a flue gas scrubber requires a significant capital investment and operating costs, an has waste disposal problems. Then, the number of the refineries operating flue gas scrubbers is limited (Becker, 1997).

Both feedstock desulfurization and selection of low sulfur feedstock belong to prevention technology. Although hydrotreating preferentially removes non-thiophenic feed sulfur and provides benefits on the products side, the percent of the feed sulfur that goes to the flue gas as SO$_x$ is not reduced and it is a very capital intensive solution when reduction of FCC flue gas SO$_x$ emissions is the only incentive(Gilman, 1998).

Selection of low sulfur feedstock is usually also not an economically attractive alternative due to high sweet crude costs, a restriction of flexibility to optimize crude selection, and in some case vulnerability to uncertain crude supplies.

DeSO$_x$ additive belongs to in-process modification technology DeSO$_x$ additive (e. g. SO$_x$ transfer catalyst) is a co-catalyst, which is added directly to the FCCU catalyst inventory, where it traps SO$_x$ in the regenerator and releases it as H$_2$S in the reactor. The H$_2$S released in the reactor effluent results in 5% —20% increase in total H$_2$S, which can be handled in an existing gas concentration plant(Huling, 1975). In FCC process, catalyst circulating between the oxidizing atmosphere of the regenerator and the reducing atmosphere of the reactor makes the transfer of sulfur via a DeSO$_x$ additive possible.

3.2   Performing mechanism of DeSO$_x$ additive

The postulated chemistry of SO$_x$ removal by an DeSO$_x$ additive together with the changes of free energies of SO$_x$ transfer reactions with MGO, as reported in the literature(McArthur, 1981a; Thomas, 1983; Cheng, 1998; Bertolacini, 1974), is illustrated in Fig. 1.
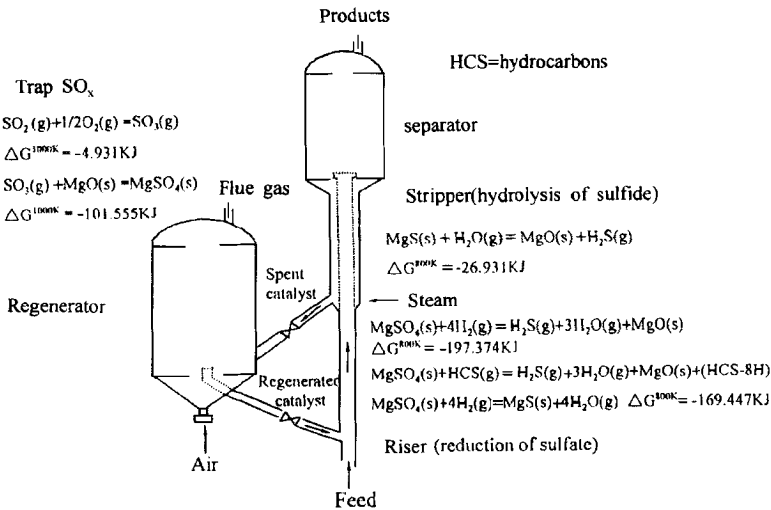

Fig. 1   FCC schematic with mechanism of reduction

The mechanism involves(1) the oxidation of SO$_2$ to SO$_3$; (2) the chemisorption and storage of SO as a sulfate in the additive(McArthur, 1981a); (3) the reduction and hydrolysis of sulfates to H$_2$S. Step 1 and 2 occur in FCC regenerator and under oxidizing conditions. Step 3 occurs in the FCC reactor under reducing conditions. Because each of the steps occurs in series, overall SO$_x$ transfer performance can be limited by any one of these three steps(Cheng, 1998).

Conditions within the regenerator have significant influence on additive performance. Depending on the FCCU operating conditions(McDaniel, 1992), 1 kg of a commercial additive can remove SO$_2$ in an amount between 8 and 60 kg. The higher the concentration of SO$_2$ and oxygen, the greater the reaction rate and the more efficient is the additive in removing SO$_x$. The effect of regenerator temperature on the efficiency of a DeSO$_x$ additive depends on thermodynamic equilibria, the rate of sulfation of the additive and the stability of the active SO$_x$ getting ingredient. At high temperatures, thermodynamics does not favor higher SO$_3$ concentration, but the rate of the reaction between SO$_3$ and the additive increases. The effect of oxygen and temperature on the equilibrium of the reaction (SO$_2$ + 1/2O$_2$ $\rightleftharpoons$ SO$_3$) is shown in Fig. 2 (Leppard, 1974). High regenerator temperatures can have detrimental effects on SO$_x$ gettering due to active sites destruction and decomposition of the sulfate species, especially in the presence of steam in the regenerator. Silica contained in FCC catalyst also can deactivate DeSO$_x$ additive due to both solid and vapor phase transport of silica under the conditions of regenerator(Byrne, 1984).

According to the mechanism, conditions of the FCCU, and the practical use, an effective SO$_x$

additive must have following properties:

Effectively capture SO_x under regenerator conditions; relatively completely release SO_x under reactor conditions; demonstrate excellent hydrothermal and thermal stability; ehibit good physical properties (to match in terms of particle size, density, and attrition properties with the FCC catalyst particles); minimize adverse effects on yields and octane; not increase FCC NO_x emissions; exhibit metals tolerance; demonstrate to be most cost effective.

Fig. 2 SO_2-SO_3 equilibrium

3. 3   The development of the DeSOx additive before 1984

The concept of DeSOx additive dates from at least 1973 when workers at Amoco applied for a patent which disclosed incorporating a Group IIA metal oxide (CaO or MgO) into a cracking catalyst for the purpose of reducing flue gas SO_x emissions (Bertolacini, 1974). Amoco announced the successful development of a new ultracat cracking process incorporating catalyst technology for reducing SO_x emissions by 60% —75% in 1997 (Vasalos, 1977), but has published little information on the system since then (Thomas, 1983). Following the SCAQMD's adoption of FCC SO_x limits in California, an extensive research and development effort to achieve a cost-effective SO_x reduction agent was initiated by Arco Petroleum Products Company in the mid. of 1970's. Prior to 1984, there were a number of patents and publications about DeSOx additives from oil industry.

The use of alumina as DeSOx additive has been discussed extensively in the patent literature. Patents designed to Chevron describe the use of reactive alumina (Blanton, 1978a; 1978b), silica-free alumina (Blanton, 1978c; 1978d), calcined alumina (Blanton, 1979) as well as alumina impregnated with sodium, manganese, or phosphorus (Blanton, 1981). These patents teach the use of alumina both admixed with or incorporated into the catalyst, and both with and without oxidation promoter. Patents assigned to Arco discuss the use of various alumina, preferably gamma alumina, with and without minor amount of silica, zirconia or magnesia (Mooi, 1981a; 1981b; 1981c; 1981d). A patent assigned to Texaco discloses the use of bismuth on alumina (Bartley, 1982), while a patent assigned to Union teaches the use of organ-aluminum compounds added to the FCC feed (McArthur, 1981b).

During this period, bastanaesite (Bron, 1982a; 1982b), spinel (Magnabosco, 1983; Powell, 1984; Siefert, 1985; Yoo, 1982; 1984a; Tamborski, 1985), lanthanides (Vasalos, 1979; 1980a; 1980b; 1980c), and rare earth ores (Baron, 1982; 1982a; 1982b) also had been used to reduce FCC SOx emissions.

From the year 1981 to 1983, substantial progress had been made in reducing FCCU SO_x emission. All the major catalyst manufactures offered SO_x catalysts and/or additives. In addition, many oil companies had developed technology for reducing SO_x emissions. Table 1 lists the various commercially available materials for reducing FCCU SO_x emissions during this period (Aitken, 1985).
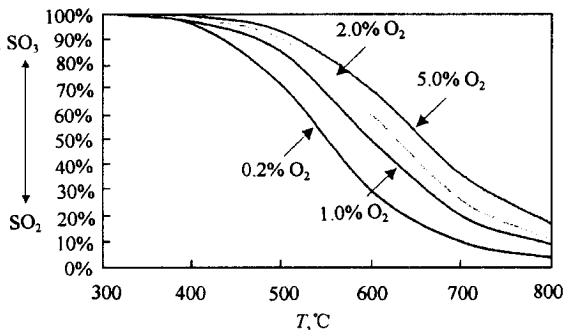
Table 1   Commercial SO_x additives(catalysts) for SO_x emissions from the year 1981 to 1983

Company	Designation	Type	Year Introduction	Number Commercial trial
Arco	HRD-276	Additive	1983	2
Grace Davison	R	Additive	1981	
Grace Davison	DAS	Catalyst	1981	12
Chevron	TransSO$_x$	Catalyst	1982	2
Engelhard	UltraSO$_x$	Additive	1983	5
Katalistiks	DESOX	Additive	1984	1
Union	UniSO$_x$	Catalyst	1981	3

Though the commercialization of many $DeSO_x$ additives(catalysts), some disadvantages of these additives such as large addition rates into FCCU, irreversible regeneration, and the adverse effect on the products, still existed. So, great efforts had been made to develop a highly efficient DeSOx additive.

3.4   The further study $DeSO_x$ additive and it's mechanism

As referred above, to be a successful additive, the $DeSO_x$ additive should contain catalytic ingredients that promote the oxidation reaction of SO_2 to SO_3 in the regenerator and assist in the reduction of metal sulfates in the reactor. Considerable research has been done about the ingredients. It was found that cerium oxide is effective for the oxidation of SO_2 (Bhattacharyya, 1987) and some transition metal oxides(especially, copper and vanadium) are active for the reduction of the sulfates(Krylov, 1970; Corma, 1994). The role and mechanism of the transition metal such as vanadium, iron and chromium on the oxidation and SO_2 to SO_3 and reduction of sulfated additive were investigated (Yoo, 1992). The formation of sulfate species on copper/alumina for SO_2 removal were also studied(Waqif, 1991), it allows a better understanding of the nature and the evolution of sulfate species on the catalyst during consecutive cycles of sulfation-regeneration.

The reductive species used for the reduction of the sulfates were also studied. It was doubt that H_2S is the most powerful reducing series for sulfated r-Al_2O_3 at 500℃ by thermogravimetric measurements(Andersson, 1990). Because of the short residence time in the riser, it was concluded that most of the reduction reaction take place in the stripper(Andersson, 1985). Pure hydrogen was also used as the reductive species(Bhattacharyya, 1988), the release of sulfur from sulfated $CeO_2/Mg_2Al_2O_5$ was found to be sufficient at 650℃. When the bastnaesite was used for FCC $DeSO_x$ additive, among the H_2S, hydrogen, LPG and water vapor, H_2S was found to be the most active for the reduction of sulfated bastnaesite(Andersson, 1990).

Meanwhile, in order to enhance $DeSO_x$ activity, an additive should have larger surface areas to improve the contact between the sulfur oxides containing gas with solid. The following technologies took some of above factors into considerations.

From the year of 1984, a series of patents were assigned to Arco and UOP respectively for $DeSO_x$ in FCCU regenerator(Yoo, 1984b; 1985a; 1985b; 1985c; 1985d; 1985e; 1990a; 1990b). These patents focus on the materials of spinel and pervoskite, and some technologies had been commercialized. The composition(Van Broekhoven, 1989; 1990) containing anionic clay which has a hydrotalcite, and ettringite or a hydrocalumite structure, and the composition(Kim, 1994) comparising coprecipitated magnesia-banthana-alumina, combined with a catalytic oxidation and/or reduction promoter such as cerium, vandia and titania, were also used as $DeSO_x$ additives for FCC process. Recently, collapsed compositions(Bhattacharyya, 1995; 1998) which is substantially composed of microcrystallites containing Mg, Al, Ce and V were claimed to have excellent properties to remove SOx from a gas mixture in FCC processes.

4 $DeNO_x$ additive technology

FCC regenerator poses a very challenging problem for controlling NO_x(Zhao, 1997). Other

than NO, the high-temperature flue gas contains O_2, CO, CO_2, SO_2, SO_3, H_2O, and possibly other nitrogen oxygen species. Any NO$_x$ control technology has to be designed in a way that it neither interferes with the catalytic cracking reaction in the riser nor substantially increases the emissions of other pollutants. NO is the primary components of NO$_x$ from the FCC regenerator. NO_2 is formed only after being released to the air, while N_2O exists typically at very low levels. So, it should be understood that NO$_x$ control and control of NO in the FCCU regenerator is in practice the same thing. NO is mainly produced in the regenerator during the burning of nitrogen in the coke. Most of the NO formed in the dense bed is further reduced to N_2 by the reaction which either CO or carbon on spent catalyst.

4.1   The actors affecting NO concentration

The concentration of NO emissions from the FCC regenerator relates to the type and content of feed nitrogen, the used of CO combustion promoter, and the content of excess oxygen.

The nitrogen content in most FCC feed is quite low, typically from 0.05 to 0.5 wt.%. A high nitrogen feed produces more NO emission. The types of the nitrogen compounds are typically distinguished by their basicity(Zhao, 1997). According their molecular structure, most of the nitrogen compounds fall into following four groups with decreasing basicity: amines, pyridine derivatives, pyrrole dericatives, and amides. Most of the amine and pyridine types of nitrogen compounds are considered to be basic and are expected to be absorbed on the acidic sites of the catalyst and converted to coke during the cracking process. Very little of nitrogen in the coke(ca. 10%—30%) is oxidized to NO, most is concerted to N_2 in the regenerator. It is different from that of sulfur, nearly all of sulfur in the coke is oxidized to sulfur oxides(Wormsbecher, 1993).

The effects of CO combustion promoter and higher excess oxygen content on NO emissions form the regenerator are especially pronounced, as illustrated in Fig. 3 and Fig. 4(Davey, 1996). The reason is not entirely understood. Based on current understanding, the CO promoter an higher excess oxygen content deplete the concentration of reductants such as CO, COK and NH_3 in both the dense and the dilute phase, less reductant is available to reduce NO to N_2. Briefly, the effects can be expressed by following equation:

$$NO_x = 40 + 0.2N + 1.25O_2 + 105Pt.$$

Where NO$_x$ is the concentration of NO$_x$ in the flue gas (ppmv), O_2 is the excess oxygen(v%), Pt represents the amount of Pt in the FCC catalysts(ppm wt.).
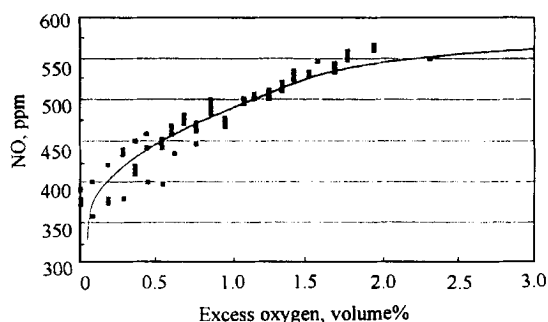

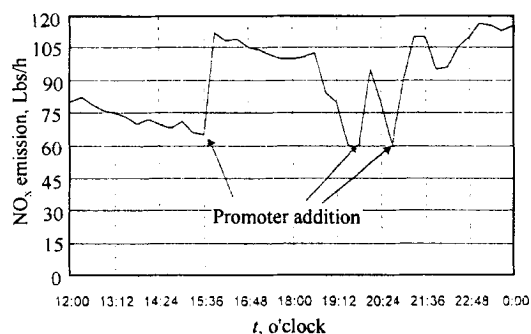Fig. 3   Commercial FCC flue gas analysis NO production vs. excess oxygen

Fig. 4   Impact of conventional CO promoter on NO$_x$ formation

4.2   NO control technology for the FCCU

There are many methods can be used to control the NO$_x$ emissions from the regenerator. Process modifications such as Kellog countercurrent regenerator design(Scott, 1982a; Miller, 1996; Mann, 1993) two and three-stage FCC regenerator(Hall, 1983; Scott, 1982b), can be used to control regenerator NO$_x$ emissions due to the presence of a higher concentration of reductant

at the top of the regenerator catalyst bed and more reductant in one of stages, respectively.

NO_x reduction can also be achieved by changes of operation conditions, including pretreatment of crude by hydrotreating or choosing appropriate crude oils, partial combustion, and prudent use of combustion promoters(Meguerian, 1981; 1982).

In selective catalytic reduction(SCR) (Erickson, 1985; Dimpfl, 1984), NO_x is reduced by ammonia or hydrocarbons(for instance, C_3H_8) in the presence of O_2 at a temperature ranges of 150℃ to 400℃. In the presence of the catalyst, ammonia or hydrocarbons selectively react with the NO_x to form nitrogen and water. The catalyst is typically an extrudated or coated monolith containing vanadia supported on titania.

None of the approaches described above provides a perfect solution for NO_x abatement. Process methods such as countercurrent or multistage regenerators require revamping of the FCC regenerator. It is not generally desirable to sacrifice CO conversion or to increase coke on regenerated catalyst for the purpose of NO_x reduction. For SCR, excess ammonia, which itself is an air pollutant, may be released. Therefore, the majority of refineries began to pay their attention to $DeNO_x$ additive technology.

4.3   The development of $DeNO_x$ additive

$DeNO_x$ additive is a co-catalyst which can reduce NO_x emissions from the FCCU regenerator by its catalytic performance. In commercial operation, a $DeNO_x$ additive must maintain activity in repeated redox cycles under severe hydrothermal environment of the FCC unit and in the presence of other gases such as CO, CO_2, SO_2, O_2 and H_2O. Meanwhile, it must have no detrimental effect on products and have required physical properties matched with FCC catalysts.

Various perovstikit oxides(Teraoka, 1990) have been used as $DeNO_x$ additive, but due to their low surface areas, the $DeNO_x$ activity is low and large amounts of additive are required to achieve high NO_x conversions. In order to overcome this disadvantages, pervoskite/spinel additive (Yoo, 1994; Dieckmann, 1994) is developed, in which an active components such as copper or magnesia cation is added to enhance catalytic stability of the additive. The additive reduces NO_x, in the presence of SO_2 and oxygen, by catalyzing the reaction of NO with reductants to form N_2. Zinc compounds(Chin, 1991a), especially ZnO, and antimony oxides(Chin, 1991b) were also found to have activity to reduce NO_x emissions from regenerator. Particles(Gree, 1990a; 1990b; Robert, 1992) containing zeolite in a matrix consisting predominately of titania, zirconia or a mixture impregnated with copper and rare earth cations have been claimed as a NO_x additive. A new $DeNO_x$ additive(Davey, 1996; Peters, 1996; 1998) designated as DENOX^{TM} has been developed by Grace Davision. Commercial testing has confirmed that DENOX^{TM} reduces FCC NO_x emissions by more than 50% in a unit using contentional platinum based promoter for after combustion control. Lanthanum or Yttrium oxides, or lanthanum titanate(Chin, 1991c) have been found to be effective in reducing NO_x in laboratory fixed-fluirized-bed studies. Some commercially available SO_x additives (Yoo, 1993) have also been used as $DeNO_x$ additives, for example, DESOX^{TM} of Katalistiks can reduce NO emission by 30% to 35% at ca. 1 wt. % addition to the FCC catalyst in the commercial FCC unit (Tamborski, 1985). The operation of DESOX^{TM} is not entirely understood, one possibility is that the additive catalyzes the reaction of NO with either CO or coke.

5   The future

The important chemistry occurring in FCCU regenerator involves coke combustion, followed by subsequent homogeneous gas phase and heterogeneous(gas-solid) catalyzed and non-catalyzed reactions. These reactions are all extremely complicated and are not completely understood, especially for the nitrogen chemistry (McArthur, 1981a). A better understanding of the SO_x transfer mechanism and the relationship between coke combustion chemistry and the formation or destruction of NO_x would no doubt help the development of new and improved $DeSO_x$ and $DeNO_x$

additives.

The elimination of SO$_x$ requires the presence of O$_2$ in order to oxidize the SO$_2$ to SO$_3$ that is chemisorbed on the additive as sulfate, the used of combustion promoter favor the reaction. In contrast, the DeNO$_x$ technologies rely on the reduction of NO by the reducing agents available in the regenerator. So the excess oxygen and the used of combustion promoter will reduce the DeNO$_x$ efficiency, that is, Desk$_x$ additives typically work better in a more oxidizing regenerator environment, while most of the DeNO$_x$ additives work better in a more oxidizing regenerator environment, while most of the DeNO$_x$ additives work better in a more reducing regenerator

Fig. 5   SO$_x$ vs. NO$_x$ emissions commercial data

environment. There is an inverse correlation of concentration between SO$_x$ and NO$_x$. In Fig. 5 (Aitken, 1985), the graph of SO$_x$ versus NO$_x$ missions can directly indicates the relationship between SO$_x$ and NO$_x$ emissions.

It is a great challenge to develop an additive for simultaneous reduction of SO$_x$ and NO$_x$ in the FCCU regenerator. Though some efforts have been made towards this field (Cormsa, 1997), there are non satisfactory results for the time being. It is expected that this problem would be solved in the not-too-distant future.

References:

Aitken E J, Baron K, MaArthur D D, Mester I C, 1985. The Katalistick' 6th annual fluid cat cracking symposium[M]. Munich. Germany.

Andersson S, Pompe R, Vannerberg N-G, 1985. Appl Catal[J], 16:49—58.

Andersson S, Pompe R, Vannerberg N-G, 1990. Appl Catal[J], 65:21—29.

Baron K, McArthur D P, 1982. US patent[P], 4366083.

Baron K, McArthur D P, 1982a. US patent[P], 4311581.

Baron K, McArthur D P, 1982b. US patent[P], 4341661.

Bartley B H, Petty R H, 1982. US patent[P], 4344926.

Becker J S, LaCour M J, Davey S W, Haley J T, 1997. Oil and Gas[J], 95:76—80.

Bertolacini R J, Lehmann G M, Wollaston E G, 1974. US patent[P] 3835031.

Bhattacharyya A A, Wolterman G M, Karsch J A, Cornir W E, 1987. ASC meeting[C].

Bhattacharyya A A, Wolterman G M, Yoo J S, Kareh H A, Cormier W E, 1988. Ind Eng Chem Rest[J], 27:1356—1360.

Bhattacharyya A A, Foral M J, Reagan W J, 1995. US patent[P]. 5426083.

Bhattacharyya A A, Foral M J, Reagan W J, 1998. US patent[P], 5750020.

Blanton W, Flanders R L, 1978a. US patent[P], 4071436.

Blanton W, Flanders R L, 1978b. US patent[P], 4115249.

Blanton W, Flanders R L, 1978c. US patent[P], 4115250.

Blanton W, Flanders R L, 1978d. US patent[P], 4115251.

Blanton W, Jaffe J, 1979. US patent[P], 4116787.

Blanton W, 1981. US patent[P], 4243556.

Byrne J W, Speronello B K, Levenberger E L, 1984. Oil and Gas Journal[J], 82:101—103.

Cheng W C, Kim G, Peters A W, Zhao X, Rajagopalan K, 1998. Catal Rev Sci Eng[J], 40:39—79.

Chin A A, 1991a. US patent[P]. 4988432.

Chin A A, 1991b. US patent[P]. 5002654.

Chin A A, 1991c. US patent[P]. 5021146.

Corma A, Kluger E L, 1992. Progress FCC catalysts[M]. Catalytical Studies Division.

Corma A, Palomres A E, Rey F, 1994. Applied Catalysis B[J], 4:29—43.

Corma A, Palomares A E, Rey F, Marquez F, 1997. J Catal[J], 170:140—149.

Cusumano J A, 1992. Chemtech[J], 22:482—489.

Davey S W, Haley J T, 1996. Intentional catalyst conference & exhibition[C]. Feberary 1—2, 1996. Houston, Texas.

Dieckmann G H, Labrador E Q, 1994. US patent[P]. 5364517.

Dimpfl W L, Blanton W A, 1994. US patent[P]. 4434147.

Erickson D C, 1985. US patent[P]. 4521389.

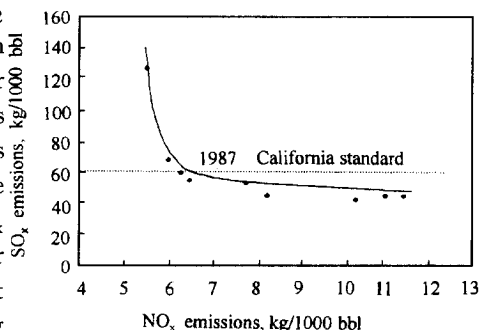Gilman K R, Vincent H B, Walker T F, 1998. Proceedings of the 1988 NRPA annual meeting[C], San Francisco, California.

Green G L, Shihabi D S, Yan T Y, 1990a. US patent[P], 4980052.

Green G L, Shihabi D S, Yan T Y, 1990b. US patent[P], 4973399.

Hall R N, Carison F B, Thomson W J, 1983. US patent[P], 4413573.

Huling G P, McKinney J D, Readal T C, 1975. Oil and gas Journal[J], 73:73—79.

Iwamoto M, Yahiro H, Tanda K, Mizuno N, Mine Y, Kagawa S J, 1991a. Phys Chem[J], 95:3727—3730.

Iwamoto M, Hamada H, 1991b. Catal Today[J], 10:57—71.

Kim G, 1994. US patent[P], 5288675.

Krylov O V, 1970. Catalysis by nonmetals[M]. New York: Academic Press.

Leppard W R, 1974. Report No. EPA-460/3-75-001-a, No. 1974(NMS No. PS 240995).

Magnabosco L M, Powell J W, 1983. Katalistiks fourth annual fluid cat cracking symposium[C]. Amsterdam, The Netherlands.

Mann R, 1993. Catal Today[J], 18: 509—528.

AcArthur D P, Simpson H D, Baron K, 1981a. Oil and Gas Journal[J], 79:55—60.

McArthur D P, 1981b. US patent[P], 4259175.

MaDaniel J, Neuman D J, 1992. Proceedings of the 1992 NPRA annual meeting [C], New Orleans, Louisiana.

Meguerian G H, Lorntson J M, Vasalos I A, 1981. US patent[P], 4300997.

Meguerian G H, Lorntson J M, Vasalos I A, 1982. US patent[P], 4350615.

Miller R B, Johnson T E, Santner C R, Avidan A A, Beech J H, 1996. Proceedings of the 1996 NPRA annual meeting[C], San Antonio, Texas.

Mooi J, 1981a. US patent[P], 4252636.

Mooi J, 1981b. US patent[P], 4285806.

Mooi J, 1981c. US patent[P], 4297244.

Mooi J, 1981d. US patent[P], 4316795.

Nolan P S, Hendriks R V, Koresovich N, 1998. The first combined FGD and dry SO_2 control technology symposium[C], St. Louis, MO.

Peters A W, Koranne M, Pereira C *et al* ., 1996. Control and origin of NO_x in the FCCU regenerator, ACS annual meeting[C]. Orland, FL.

Peters A , Zhao X, Yaluris G *et al* ., 1998. NPRA annual meeting[C]. San Fracisco, California.

Powell J W, Chao J, Edison R R *et al* ., 1984. NRPA annual meeting[C]. San Antonio, Texas.

Robert P L, Bowes E, Green G L *et al* ., 1992. US patent[P], 5085762.

Scott J W, 1982a. US patent[P], 4313848.

Scott J W, 1982b. US patent[P], 4325833.

Seinfeld J H, 1986. Atmospheric chemistry and physics of air pollution[M]. New York: Willey.

Shannon I J, Rey F, Sankar G *et al* ., 1996. J Chem Soc Farady Trans[J], 92: 4331—4336.

Siefert K S, Chuang K G, Foster R L, 1985. 78th annual meeting of their pollution control association[C]. Detroit, Michigan.

Slack A V, 1971. Pollution control review No. 4[M]. New Jersey: Noyes Data Copeoration.

Tamborski G A, Magnabosco L M *et al* ., 1985. 6th annual fluid cat cracking symposium[C]. Munich, Germany.

Teraoka Y, Fukuda H, Kagura S, 1990. Chem Lett[J], 1:1—4.

Thomas Habid E, 1993. Oil and Gas Journal[J], 81:111—113.

Van Broekhoven E H, 1989. US patent[P], 4866019.

Van Broekhoven E H, 1990. US patent[P], 4952382.

Vasalos I A, Strans E R, Hsieh C K R, 1977. Oil and Gas Journal[J], 75:141—147.

Vasalos I A, Ford W D, Hsieh C K R, 1980a. US patent[P], 4221677.

Vasalos I A, Ford W D, Hsieh C K R, 1980b. US patent[P], 4238217.

Waqif M, Saur O, Lavalley J C *et al* ., 1991. J Phys Chem[J], 95:4051—4058.

Wormsbecher R F, Weatherbee G D *et al* ., 1993. NDRA annual meeting[C], San Antonio, Texas.

Yoo J S, Jaecker J A, 1982. European patent[P], 45170

Yoo J S, Jaecker J A, 1984a. US patent[P], 4469589.

Yoo J S, Jaecker J A, 1984b. US patent[P], 4472267.

Yoo J S, Jaecker J A, 1985a. US patent[P], 4492677.

Yoo J S, Jaecker J A, 1985b. US patent[P], 4492678.

Yoo J S, Jaecker J A, 1985c. US patent[P], 4495304.

Yoo J S, Jaecker J A, 1985d. US patent[P], 4495305.

Yoo J S, Jaecker J A, 1985e. US patent[P], 4522937.

Yoo J S, Karch J A *et al* ., 1990a. US patent[P], 4957718.

Yoo J S, Radlowski C A *et al* ., US patent[P],4963520.

Yoo J S, Bhattacharyya A A *et al* ., 1992. Appl Catal B[J]: 1:169—189.

Yoo J S, Bhattacharyya A A *et al* ., 1993. New frontiers in catalysis[M](Ed. by J Guczi). Amsterdam: Elsevier.

Yoo J S, Radlowske C A, Karch J A, 1994. Preprints of the 207th ACS national meeting. Vol. 39.

Zhao X, Peter A W, Weatherbee G W, 1997. Ind Eng Chem Res[J], 36:4535—4542.