

Nature of nitrogen specie in coke and their role in NO_x formation during FCC catalyst regeneration

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Abstract

NO_x emission during the regeneration of coked fluid catalytic cracking (FCC) catalysts is an environmental problem. In order to follow the route to NO_x formation and try to find ways to suppress it, a coked industrial FCC catalyst has been prepared using model N-containing compounds, e.g., pyridine, pyrrole, aniline and hexadecane–pyridine mixture. Nitrogen present in the FCC feed is incorporated as polyaromatic compounds in the coke deposited on the catalyst during cracking. Its functionality has been characterized using XPS. Nitrogen specie of different types, namely, pyridine, pyrrolic or quaternary-nitrogen (Q-N) have been discriminated. Decomposition of the coke during the catalyst regeneration (temperature programmed oxidation (TPO) and isothermal oxidation) has been monitored by GC and MS measurements of the gaseous products formed. The pyrrolic- and pyridinic-type N specie, present more in the outer coke layers, are oxidized under conditions when still large amount of C or CO is available from coke to reduced NO_x formed to N_2 . “Q-N” type species are present in the inner layer, strongly adsorbed on the acid sites on the catalyst. They are combusted last during regeneration. As most of the coke is already combusted at this point, lack of reductants (C, CO, etc.) results in the presence of NO_x in the tail gas.

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1. Introduction

Nitrogen oxides (NO_x) are harmful atmospheric pollutants [1]. Legislations to limit NO_x emissions are continually being introduced; 70–77% cut in NO_x emissions is targeted by the EU before 2009 [2]. NO_x emissions from a typical refinery are about 2000 tons/year, the fluid catalytic cracking (FCC) section contributes about 50% of this [3,4], and is thus an area of environmental concern.

Hydrocarbon feedstock for FCC units usually contains a variety of aromatic, N-heterocyclic compounds. During cracking, part of this N present is included in the coke that is deposited on the catalyst [3]. During regeneration of the catalyst, nitrogen in coke is released to the atmosphere as N_2 and NO_x . Typical levels of NO_x in the flue gas from fluid catalytic cracking regeneration units vary between 50 and

500 ppm, depending upon feed nitrogen content and regenerator conditions [5,6]. The major component (>95%) of NO_x is NO. Formation of N_2O and NO_2 is negligible under FCC regenerator conditions [3,6]. Reduction of NO_x levels in the exhaust gases is an essential part of the technology for a “green” refinery.

Real-life data from refineries show that correlations exist between nitrogen contents, basicity of nitrogen precursors present in the feed and NO_x emissions during regeneration [3,5]. Typically, N is present as (substituted poly-) aromatic compounds such as pyrroles ($=\text{C}-\text{NH}-\text{C}-$), pyridines ($-\text{C}=\text{N}-\text{C}=-$) or anilines ($=\text{C}-\text{NH}_2$). Of these, pyridine is a strong base, aniline and pyrrole are weaker bases because of the delocalization of the electron pair on N to the aromatic ring. Higher the basicity of the molecule, stronger is its adsorption on the acidic FCC catalyst and larger is the chance to be deposited in the coke during cracking.

The nature of N in coke and the mechanism of its conversion to NO_x or N_2 in the FCC regenerator are not very

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well understood. It is generally suggested, in analogy with coal combustion [7,8], that NO_x is formed via two routes: directly from nitrogen in coke (fuel NO_x) and through volatile nitrogen intermediates such as HCN and NH_3 (prompt NO_x) [5,6]. The mechanism of nitrogen transformation during coke or coal/char combustion is complex, and attempts to correlate nature of nitrogen functionality (its chemical environment) with the amount of NO_x released [9,10], have not been very successful. In the case of FCC catalysts such relationships are even less available.

Due to the very low nitrogen contents in coked FCC catalysts, the discrimination of nitrogen specie in coke is complicated. Presence of polar or non-polar type nitrogen has been reported, but no attempts have been made to relate this to NO_x formation during coke combustion in the FCC regenerator [11].

Aim of this work is to understand (i) if and how, the variations in the coking conditions and different types of N compounds present in FCC feed influence the nature of nitrogen in the coke and (ii) the transformation of the N specie in coke to N_2 and NO_x during oxidative regeneration. In order to establish this, reactions occurring in a FCC unit (cracking and regeneration) were carried out on lab scale using a commercial FCC catalyst and model N-heterocyclic aromatic compounds. The knowledge generated should be helpful in the development of catalyst systems to minimize NO_x emission from FCC regenerators.

2. Experimental

2.1. Materials

FCC catalysts were obtained from Grace Chemicals, Germany. Reagent grade (>99%) pyridine, aniline, pyrrole and hexadecane (Aldrich Chemicals) were used as precursors for coking experiments.

2.2. Coking and regeneration experiments

Coking experiments were carried out at 550 °C. 0.4 g catalyst was placed between two quartz pugs in a quartz tubular reactor ($d = 4$ mm). The catalyst was preheated first in He (50 ml/min) at 550 °C for 30 min. Subsequently, coke precursors were introduced into the gas stream using a syringe pump. Flow of the liquid precursor was varied between 0.2 and 180 ml/h, coking time was varied from 10 s to 4 h. After

coking experiments, catalysts were either cooled to RT or allowed to age at 550 °C in He for varying durations. Catalyst regeneration experiments were carried out in a fixed-bed reactor (~0.2 g samples) in a temperature programmed oxidation (TPO) mode. TPO was carried out between 30 and 850 °C, using a heating rate of 10 °C/min and a gas mixture containing 2–4 vol.% O_2 ; 0–1 vol.% CO and balance He. Total flow rates were between 50 and 100 ml/min.

2.3. Analytical techniques

Elemental analyses (C, N and H) of coked catalysts were carried out on a Elemental Analyzer Carlo Erba EA1108. Thermo-gravimetric measurements were performed using a TGA/DSC (Mettler-Toledo) set-up. Typically, 50 mg sample and 30 ml/min flow of either 5% O_2 /He or pure He was used. During TPO, gas composition at the outlet was constantly monitored. N_2 , O_2 , CO, CO_2 and N_2O were analyzed by Varian 3300 GC, using a Valco 16 position ST valve, two columns (Heysep Q and MS 5A) and a TCD detector. The amounts of NO and NO_2 were determined by a NO_x analyzer (Thermo Environmental Instruments Inc. 42C). In addition, a Quadruple MS (Pfeiffer Vacuum) was used for continuous monitoring of the gas composition.

Coke formed on the catalyst was characterized (N1s, C1s) by XPS (Φ Quantera Scanning ESCA Microprobe spectrometer). C1s binding energy (BE) of 284.8 eV was used to calibrate the spectra. In order to differentiate the types of N specie present in coke, the non-symmetric N1s experimental envelopes were subjected to a de-convolution procedure using a minimal number of peaks, varying FWHM, position and intensities of the peaks to result in the best NLLS fit ($\chi^2 = 0.98$). A mix of Gaussian (80%) and Lorentzian (20%) functions, typical for XPS [12], was used.

3. Results

3.1. Coke formation and characterization

Table 1 gives the details of the “N” containing precursors used for coking experiments (see Section 2). $\text{p}K_{\text{base}}$ values of the precursors listed in the table show that acidity decreases in the order pyridine < aniline < pyrrole, i.e., pyridine is the most basic of the three components used. The table also gives the amount/composition of coke deposited on the catalysts after 4 h time on stream. No relation was observed

Table 1
Details of the coke precursors and coke formed on the catalysts^a

Coke precursor ^a	N/C atomic ratio for precursor	$\text{p}K_{\text{base}}$	Coke composition related to FCC catalyst (wt.%)		
			C (wt.%)	N (wt.%)	N/C atomic ratio
Pyridine	0.20	8.64	4.9 ± 0.1	0.90 ± 0.05	0.15
Aniline	0.16	9.38	7.3 ± 0.4	0.85 ± 0.05	0.10
Pyrrole	0.25	14.00	6.4 ± 0.1	0.85 ± 0.05	0.11

^a Total feed flow 100 ml/min containing 10 vol.% of coke precursor and He balance; coking time 4 h.

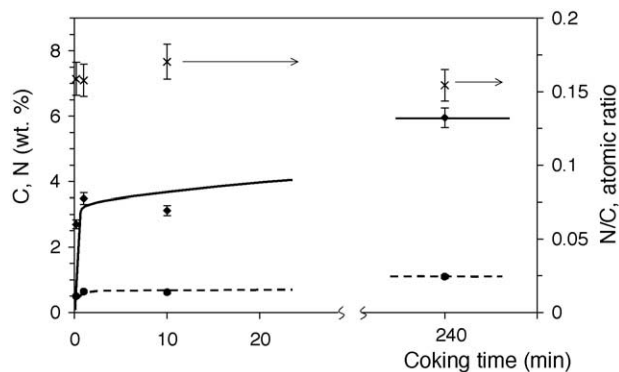


Fig. 1. Amount and composition of coke over the FCC catalyst as a function of time. Pyridine was used as the coke precursor; total feed/catalyst ratio is 2 ml/g; $T = 550\text{ }^{\circ}\text{C}$. Left X-axis: (\blacklozenge) carbon content; (\bullet) nitrogen content in the coke formed; right Y-axis: (\times) N/C atomic ratio.

between the relative amount of N (indicated by N/C) in the coke precursor and in the coke deposited on the catalyst. As expected, the more basic compound, pyridine, causes higher percentage of N in the coke and detailed studies were undertaken with pyridine.

Fig. 1 shows the extent of coking with pyridine at $550\text{ }^{\circ}\text{C}$ as a function of time. It can be seen from the figure that majority of the carbon and nitrogen is deposited on the catalyst at short times on stream. In the 4 h coking experiment shown, 70% of the total coke was deposited during the first 60 s. No significant deviation in the coke composition (N/C ratio) was observed during this coking period. Further heating at the coking temperature ($550\text{ }^{\circ}\text{C}$) in an inert atmosphere (He) up to 6 h did not cause any additional changes. In order to check if the nature of the “N”

in coke varied with coking time, XPS spectra in the region of N1s BE were recorded for catalyst samples coked with varying times on stream. Typical N1s experimental spectra are shown in Fig. 2.

It can be seen from the figure that position and shape of the N1s peaks changed with coking time. Thus, increase of coking time from 10 s to 4 h caused a shift in the spectra position from 400.8 to 400.0 eV as well as broadening of the peak. In order to probe the changes in the spectra in terms of different types of “N” specie, experimental N1s spectra were de-convoluted with multiple peaks as described in the experimental section. The details of the fit results, viz. positions of the individual peak maxima and their relative intensities are summarized in Table 2. The best fit for the experimental N1s spectra, in all cases, was obtained with two individual components (Fig. 2a–d). BE of these two peaks did not depend on way coke was formed (coking time, precursor). Furthermore, FWHM of each peak varied only within the accuracy of the binding energy determination. The results indicate, probably, two types of nitrogen specie to be present in the coke and characterized by BE at 399.9 and 402 eV. Relative amounts of a nitrogen species corresponding to these were estimated from the integral intensity of the peaks and are presented in Table 2.

In the case of coking experiments with pyridine, the contribution of the peak corresponding to the “N” specie characterized by the higher BE (402 eV) decreased from 58 to 20% with increasing the coking time from 10 to 600 s. Further, independent of the precursor used, longer coking (4 h) or further ageing times (6 h) resulted in low intensities of this peak, i.e., between 10 and 17% of total integral intensity of N1s experimental peak (Table 2).

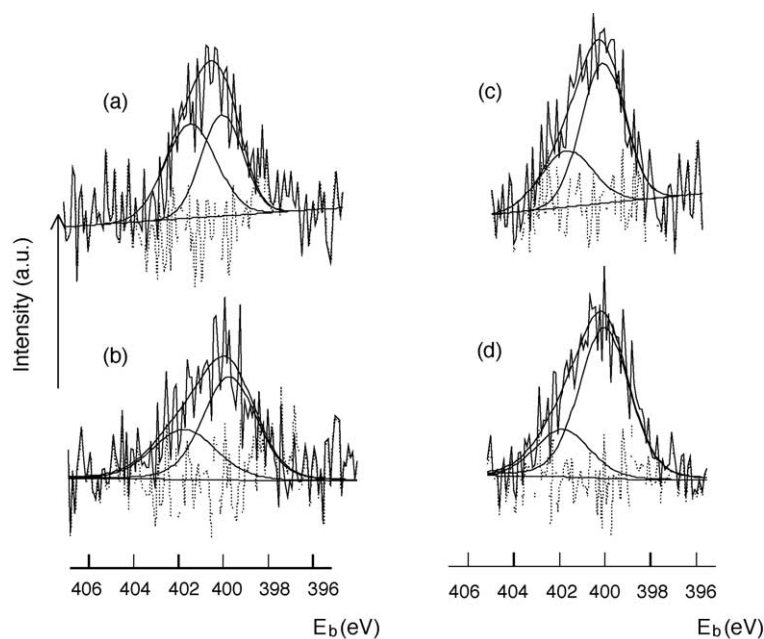


Fig. 2. N1s experimental XPS spectra of coked FCC catalyst. Experimental curves are fitted with two individual peaks. Shown spectra are after catalyst coked for 10 s (a), 60 s (b), 600 s (c) and 4 h (d).

Table 2

Details of coking procedures, N1s BE of “N” specie and composition of gaseous products formed during oxidative regeneration

Coke precursor	Coking time/ageing time in He	N1s BE (eV) ^a	Peak area ratio (%)	Distribution of C and N in gaseous products during regeneration of the coked catalyst (vol.%)				
				Carbon		Nitrogen		
				As CO ₂	As CO	As N ₂	As NO	
Pyridine	10 s/0 s	401.9	399.9	58:42	85.4	14.6	61.7	38.3
Pyridine	60 s/0 s	402.1	400.0	32:68	69.7	30.3	75.2	24.8
Pyridine	600 s/0 s	402.2	400.1	20:80	60.3	39.7	85.6	14.4
Pyridine	4 h/0 h	402.0	399.9	16:84	65.4	34.6	78.0	22.0
Pyridine	4 h/1 h	402.3	400.0	19:81	79.4	20.6	76.6	23.4
Pyridine	4 h/6 h	402.0	400.0	12:88	75.1	24.9	80	20
Pyrrrole	4 h/0 h	401.9	399.9	10:90	62.2	37.8	87.0	13.0
Aniline	4 h/0 h	401.9	400.0	14:86	53.7	46.3	89.1	10.9
Hexadecane:pyridine (3.6:1 v/v)	4 h/0 h	Low intensity peaks, not quantified			50.0	50.0	81.6	18.4

^a Reproducibility in the individual N1s peak position is ± 0.2 eV.

3.2. Catalyst regeneration

Coke combustion was followed by TGA (catalyst coked with pyridine at 550 °C for 4 h) in 5% O₂/He (data are not shown). Complete coke removal (by oxidation) was observed within the temperature interval 450–750 °C for different samples. The observed weight loss corresponded to the amount of coke determined by chemical analysis.

Evolution of gaseous products during oxidative regeneration (TPO) of catalyst coked with pyridine at 550 °C for 4 h is shown in Fig. 3. The trend is typical for other samples also; the main gaseous products observed during the TPO were CO₂, CO, N₂ and NO. Only very small amounts NO₂, NH₃, HCN or N₂O were observed.

It can be seen from Fig. 3 that the order of appearance of the gases with respect to temperature is CO₂ \approx CO < N₂ < NO. This trend was the same for all samples studied. Further, in all cases, coke combustion started between 450 and 500 °C and was accompanied by oxygen consumption and CO₂ and CO formation. Between 550 and 600 °C in addition to CO₂/CO, formation of molecular N₂ was also observed. Maximum in N₂ release was observed around

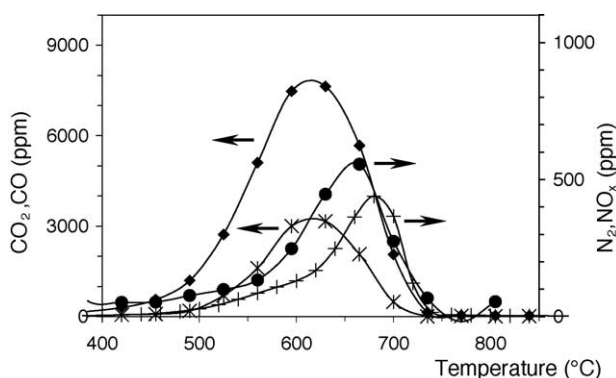


Fig. 3. Evolution of gases during temperature programmed oxidative regeneration of the FCC catalyst coked with pyridine (4 h). Heating rate 10 °C/min, amount of catalyst 100 mg. (◆) CO₂; (×) CO; (●) N₂ and (+) NO concentration.

675 °C. Formation of NO occurred at higher temperatures (650–750 °C) coinciding with the decrease in CO and CO₂.

Quantitative data on the carbon (CO and CO₂) and nitrogen (N₂ and NO) containing gaseous products formed during coke combustion (TPO) are presented in Table 2. It is interesting to note that the relative amount of NO formed decreases from 38 to 22% if coking time is increased from 10 s to 4 h. This is in line with the changes in N1s peak areas in XPS spectra of the coked catalysts and will be discussed in the next section.

It can be seen from Table 2 that the relative amounts of CO vary inversely with those of NO. In order to check the influence of CO on the formation of NO/N₂ during combustion, TPO experiments were carried out with CO in the feed. Results of these experiments are shown in Table 3. It is observed that in the presence of 1 vol.% CO the amount of NO is about two times lower than if only O₂ were present in the regeneration feed.

In order to simulate conditions in an FCC regenerator in the laboratory, isothermal coke combustion experiments were performed. Results of these experiments are shown in Fig. 4. Contacting the catalyst with 2% O₂/He at 600 °C resulted in a rapid evolution of CO₂ and was complete by 90–100 min. At this time removal of coke from the catalyst was also complete. The NO peak followed the CO₂ peak with a time delay.

4. Discussions

The aim of the current study is to follow (i) the nature of “N” specie present in coke, (ii) the factors that influence

Table 3

Effect of CO on the formation of N₂ and NO during combustion coked catalyst followed by TPO

Regeneration conditions	Total N products released (%)	
	NO	N ₂
2 vol.% O ₂ + He (balance)	24.8	75.2
2 vol.% O ₂ + 1 vol.% CO + He (balance)	13.9	86.1

The catalyst was coked with pyridine during 60 s.

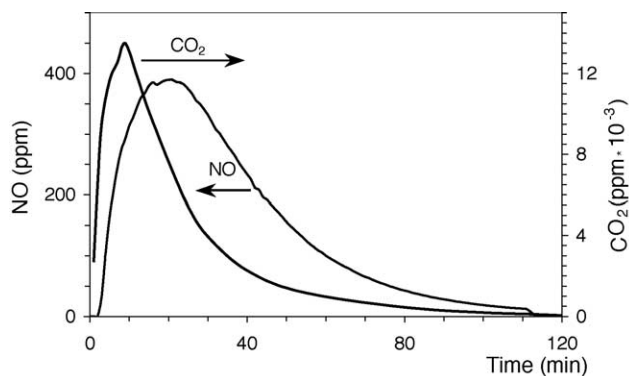


Fig. 4. Isothermal oxidative regeneration of the coked catalyst at 600 °C. Catalyst coked with pyridine at 550 °C for 4 h; gas flow 5% O₂/He, switched at $t = 0$.

their formation and (iii) if any correlations exist between the nature of the “N” in coke and formation of N₂/NO_x during regenerative combustion of coke. This information will help in the modification of FCC catalyst and in optimization of the regeneration procedure in order to minimize NO_x emissions during catalyst regeneration.

First of all, in agreement with what is reported, coke formed from the more basic compounds such as pyridine, retains a higher relative amount of nitrogen. This is significant, as all the NO_x formed during regeneration originates from the N in coke (no thermal NO_x is formed during regeneration). Analysis of coked catalysts by XPS allowed us to discriminate two types of nitrogen specie based on the different N1s BE (Fig. 2, Table 2) observed. The XPS technique has been used before to discriminate different types of nitrogen functionalities in coals and model chars. Kapteijn et al. [13] reported nitrogen-containing species in char-type materials schematically to be as in Fig. 5. Based on N1s BEs, different authors [10,11,13–16] have suggested the following “N” specie to be present in chars, i.e., pyridinic (“Py-N”) ($E_{BE} = 398.7 \pm 0.2$ eV); pyrrolic (“Pr-N”) ($E_{BE} = 400.3 \pm 0.2$ eV); quaternary-nitrogen (Q-N, $E_{BE} = 401.4 \pm 0.2$ eV). As shown in Fig. 5, “Q-N”

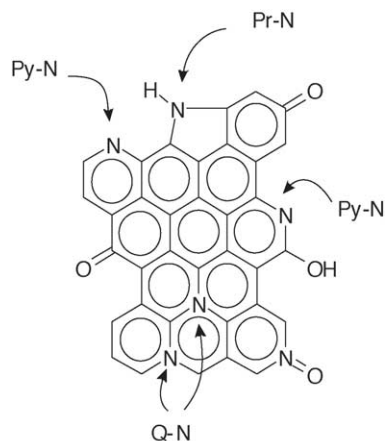


Fig. 5. Schematic representation of nitrogen functionalities in char [13].

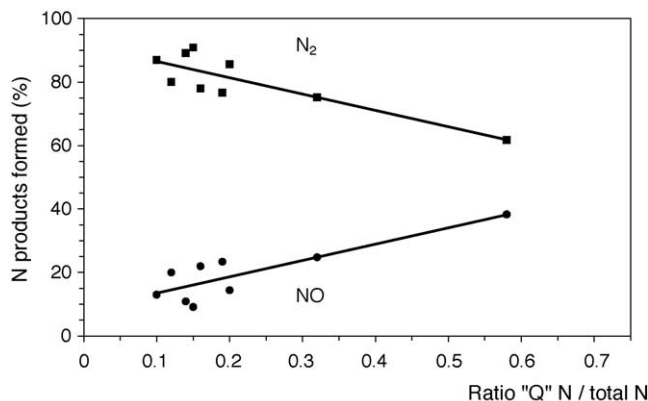
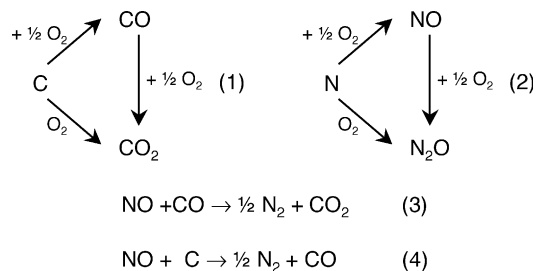


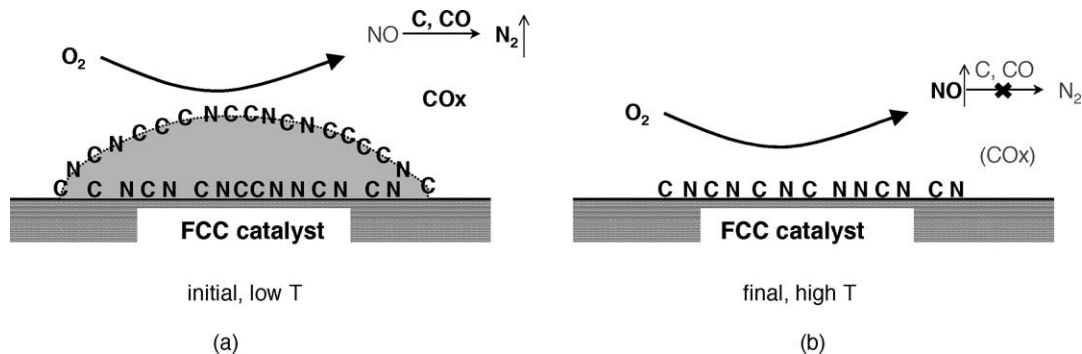
Fig. 6. Correlation between the type of nitrogen specie and the selectivity towards NO_x formation under oxidative regeneration of the FCC coked catalyst.

is represented by nitrogen which substitutes for carbon in the “graphene” type structure. For FCC catalysts, coked under industrial conditions, such discrimination has been difficult due to the low nitrogen content in the coke. In our experiments, the N contents in coke are high because we use model compounds. For the sake of argument, we assume that this (large amount of hydrocarbon coke) does not affect the nature of “N” specie in coke. Extensive characterization of catalysts prepared in this study, have been carried out by Barth et al. [4]. Using IR, MAS NMR and MALDOTOF, they show that N in coke is present as polyaromatic species such as carbazole, imidazole or porphyrine derivatives, adsorbed on acid sites. This is in agreement with what has been suggested in literature [13,16], that the nature of chars and FCC coke are similar. We will thus use the model used for “N” specie in model chars to characterize catalysts coked in this study.

In accordance with the BE observed in our case and those reported, we ascribe the “N” species with BE around 399.9/400.1 as similar to pyridinic/pyrrolic types located at the edges of the carbon structure shown in Fig. 5 [13]. During catalytic cracking, feed molecules or their cracked fragments are adsorbed at the catalyst surface, especially via the strong interaction of nitrogen with the surface acid (Lewis and Bronsted) sites [17]. The shift in electron density away from N to the acid site will result in an increase in N1s BE. Further, based on BE, these specie are similar to the “Q-N” nitrogen species shown in Fig. 5. We, therefore, propose that the acid sites on the catalyst are responsible for the



Scheme 1. Simplified reaction pathways during coke combustion.



Scheme 2. Schematic representation of coke combustion over coked FCC catalyst at initial (low temperature) (a) and final (high temperature) (b) stages. Main products are shown in black; products, which are formed to a less extent, are shown in grey.

formation of the “Q-N” type species. With increase of coking time, nitrogen-containing groups, with N1s BE close to pyridinic/pyrrolic structures and located at the edge of coke particle are continually formed. However, at the same time, the acid sites on the catalyst surface sites are progressively consumed and are unavailable after a while. Thus, the “Q-N” type N specie shows a relative decrease with time in the XPS spectra. This would explain our experimental observation that, with increase in coking time the relative intensity of this “Q-N” type specie (N1s $E_B = 401.9$) actually decreases (Table 2).

In Fig. 6, we see that there is a strong correlation between the amount of “Q-N” type species and the selectivity towards NO_x . This implies that the presence of large amount of “Q-N” type specie can be related to higher NO_x formation during regenerative combustion. Despite a large number of publications regarding regeneration of coked FCC catalysts, the actual reaction mechanism is not clear yet, but it is generally accepted that in a simplified way the coke combustion reactions can be represented by Scheme 1 [7]. A similar mechanism was also proposed for combustion of coal and model chars [8,10]. We have not included in the scheme, the formation of volatile nitrogen compounds like NH_3 and HCN (as definite intermediates), these are believed to be intermediates for N_2 and NO_x formation [8,10]. We only observed traces of NH_3 and HCN in our experiments.

In order to explain the formation of NO_x and its relation to “N” specie nature, it is essential to understand what happens during coke combustion.

It is generally agreed that, during combustion of coal, chars and diesel particulates [8,13], oxidation begins from the outside of a coke particle. Oxidation of nitrogen-containing specie in the coke particle starts at the outer surface, which is easily accessible for oxygen (see Scheme 2a). The pyrrolic- and pyridinic-type N specie present more in the outer layers are oxidized under conditions when still large amount of C or CO is available from coke. As shown earlier (Scheme 1) sequential reduction of NO to N_2 (reactions (3) and (4)) by CO is feasible under these conditions. As a result, N_2 is seen in the earlier stages of combustion (Fig. 3, N_2 pattern). As the “Q-N” type specie are those which are directly interacting with the catalyst via

the acid sites and limited to the inner layers of coke, their combustion at the earlier stages of the catalyst regeneration is limited most probably due to lack of oxygen availability.

At later stages of the coke oxidation, i.e., in the deeper layers, the availability of possible reductants, C and CO become limited and feasibility of the reactions (3) and (4) is diminished. Further, we notice that oxidation of C in coke is more facile than N (Fig. 3, CO_x , N_2 and NO patterns). This is in agreement with data of chemical analysis of partially regenerated industrially coked FCC catalyst [3,6], i.e., partial coke removal results in the increase nitrogen content in the coke remaining. Thus, nitrogen specie, which is combusted last during regeneration are those strongly bound to the catalyst surface, i.e., “Q-N” type. As most of the coke is already combusted at this point, lack of reductants such as CO, results in the appearance of NO_x in the gas phase as this is not completely reduced to N_2 (Scheme 2b). Since coking or ageing time does not strongly influence the extent of formation of “Q-N” type specie, the only way to reduce NO_x formed during combustion is its sequential reduction.

5. Conclusions

Using model compounds, it is possible to follow the reaction pathways of N present in FCC feed, as heterocyclic compounds, to its incorporation in coke as polyaromatic specie. Coke formed from the more basic compounds, e.g., pyridine, retains a higher relative amount of nitrogen. Analysis of coked catalysts by XPS allows characterization of the N specie present in coke, namely pyridinic, pyrrolic or quaternary-nitrogen. The pyrrolic- and pyridinic-type N specie, present more in the outer layers, are oxidized under conditions when still large amount of C or CO is available from coke and N_2 is the main product. “Q-N” type species are those strongly adsorbed on the acid sites on the catalyst and limited to the inner layer of deposited coke. Thus, “Q-N” type specie is combusted last during regeneration. As most of the coke is already combusted at this point, lack of reductants, such as CO, results in the appearance of NO_x in the gas phase. In this way, larger amount of “Q-N” type

specie present on the coked FCC catalyst is related to higher NO_x formed during regenerative combustion of the coke.

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