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Effect of catalyst surface on decomposition of nitrogen heterorings during regeneration of hydroprocessing catalysts

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Abstract

Commercial CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts and γ-Al_2O_3 were deposited with pyrrole, pyridine and quinoline. The deposits were decomposed during the temperature-programmed experiments (from room temperature to 1000°C) in the gas mixture containing between 0 and 4 vol% O_2. For both catalysts (oxidic and sulfided), patterns in the formation of NH_3 and HCN indicate on participation of the Bronstedt acid sites during decomposition of the deposits contrary to a little involvement of these sites on γ-Al_2O_3. The pyrrole deposits were more reactive than pyridine and quinoline deposits. Also, the mechanism of decomposition of the latter differed from that of pyrrole, especially on γ-Al_2O_3. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Hydroprocessing catalysts; Regeneration; Nitrogen heterorings

1. Introduction

The oxidative regeneration of hydroprocessing catalysts has been practiced on a commercial scale for several decades. The objective is to reactivate a deactivated catalyst by removing the organic deposit, termed coke, using a carefully controlled oxidation to prevent temperature excursions. The literature on the removal of carbon, hydrogen and sulfur from the coke is quite extensive compared with that of nitrogen [1]. It was shown that during regeneration, the nitrogen in coke may be released as tar, N_2, NO, N_2O, NO_2, NH_3 and HCN [2]. Relative yields of these compounds depend on the O_2 concentration in the oxidizing gas. Part of the nitrogen is strongly bound in the catalyst and may not be removed during regeneration [3]. The main part of nitrogen in coke is in the form of 5- and 6-membered heterorings. Because of the conditions applied during hydroprocessing, amino groups can also be present in the coke. Yields of the N-containing compounds formed during the regeneration were measured using the spent catalysts used in the refining operations, as well as the catalysts deposited with model cokes produced by soaking fresh hydroprocessing catalysts in the liquids of pyrrole, pyridine and quinoline [2]. It was observed that the pyrrole deposit was much more reactive than that of pyridine and quinoline. Significant differences in the yields of products were observed between the oxidic and sulfided forms of a CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts. The trends observed during the decomposition of the same deposits on the γ-Al_2O_3 differed from those observed for the deposited catalysts. Although

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the effect of the catalyst surface structure on decomposition of the deposits was quite evident, detailed interpretations of these effects were not presented. In the present study, an attempt is made to interpret the experimental observations made during the temperature programmed pyrolysis and oxidation of the pyrrole, pyridine and quinoline deposits in line with the information on the structure of the oxidic and sulfided catalysts and alumina. It is assumed that both the Lewis and Bronstedt acid sites play an important role during the adsorption of the compounds on the catalyst surface, whereas the latter are important for the formation of NH_3, especially during the pyrolysis. The experimental conditions applied during this study are similar to those used during regeneration of hydroprocessing catalysts. Therefore, the observations and their interpretations contribute to the understanding of the mechanism of the regeneration process.

2. Experimental

2.1. Catalysts

An extrudate form of microporous $CoMo/Al_2O_3$ catalyst and chestnut burr-like form of macroporous $NiMo/Al_2O_3$ catalysts had the BET surface area of 210 and 140 m^2/g, respectively. Prickly burr structure of the latter resulted from the proprietary procedure applied during its preparation. Less than 100 Å diameter pores accounted for most of the pore volume of the $CoMo/Al_2O_3$ catalyst, whereas pores of diameter larger than 500 Å accounted for about half of the pore volume of the $NiMo/Al_2O_3$ catalyst. A lower acidity of the latter compared with that of the $CoMo/Al_2O_3$ catalyst was achieved by using a neutral γ-Al_2O_3 support. The sulfided form of the catalysts was obtained by sulfiding at 400°C using a 10% H_2S+H_2 balance mixture followed by cooling to room temperature in nitrogen. After cooling, no precautions were taken to avoid contact of the sulfided catalyst with air. The catalysts were placed in a wire basket and suspended in the liquid of pure N-compounds (pyrrole, pyridine and quinoline) for 20 min. To remove excess liquid, the baskets containing deposited catalysts were suspended in air for 2 h. Subsequently, the catalysts were treated at 150°C in a vacuum for 4 h. Activated γ-Al_2O_3 was low in alkalis and had a surface area of 175 m^2/g. It was deposited and treated in the same way as the catalysts.

2.2. Procedure and analysis

The fixed bed reactor used for the temperature programmed pyrolysis (TPP) and oxidation (TPO) experiments was made up of quartz and had 10 mm i.d. External heating was provided by a Lindberg furnace. In the reactor, the catalyst particles were supported by a quartz wool plug. About 0.5 g of accurately weighed sample was used for the experiments. The TPP experiments were performed in helium (0.6 l/min) from room temperature to 1000°C at the heating rate of 10°C/min. The same conditions were used for the TPO using the gas mixtures of O_2 concentrations varying from 1 to 4 vol%. Other details of the experimental system were published elsewhere [2,3].

The analysis of NH_3 and HCN was performed using the dedicated on-line Bruel and Kjaer FTIR analyzer type 1301. The detection principle of the analyzer was based on a photoacoustic absorption. Analyses were carried out in 2 min intervals. The concentrations of NH_3 and HCN (in ppm) and volume of gas per unit of time were used to calculate their absolute yields normalized to STP conditions.

The standard combustion method used for the nitrogen determination in carbonaceous solids was used in this study. It is believed that this method requires some modifications to suit the analysis of nitrogen in spent catalysts. Thus, relatively short combustion period may not be sufficient to achieve a complete release of nitrogen from the solid suggesting that the obtained values represent an underestimate of the actual values. This prevented an accurate estimate of the relative reactivities of deposits.

3. Results and discussion

Conditions applied during the deposits formation suggest a uniform deposit distribution on the surface. The amount of deposited compounds shown in Table 1 approaches that required for a monolayer formation. Thus, the absolute amount of deposit on the $CoMo/Al_2O_3$ catalyst was greater than that on the $NiMo/Al_2O_3$ catalyst by a factor of 1.5 (ratio of the

Table 1
Amount of deposit, nitrogen and carbon per unit of catalyst surface

	Oxidic			Sulfided		
	Deposit (µmol/m^2)	Nitrogen (µmol/m^2)	Carbon (g/m^2 10^4)	Deposit (µmol/m^2)	Nitrogen (µmol/m^2)	Carbon (g/m^2 10^4)
CoMo						
Pyrrole	5.6	2.2	2.7	7.1	4.1	3.4
Pyridine	4.2	2.3	2.5	5.0	3.1	3.0
Quinoline	2.3	2.1	2.5	2.8	3.1	3.0
NiMo						
Pyrrole	5.9	3.6	2.8	7.4	7.3	3.6
Pyridine	4.4	2.9	2.6	5.9	1.8	3.5
Quinoline	2.3	2.8	2.5	3.2	2.7	3.5
γ-Al_2O_3						
Pyrrole	6.5	2.3	3.1			
Pyridine	4.8	1.4	2.9			
Quinoline	3.1	1.5	3.3			

catalysts' surface area). Gray and coworkers [4,5] have presented a method to calculate the amount of carbon required to form a monolayer from a particular compound involved. According to this method, the radius (r_M) of a compound can be calculated using the following formula:

$$r_M = \frac{(3M_w)^{1/3}}{N_A \rho 4\pi},$$

where M_w is the molecular weight, N_A is Avogadro's number (6.02×10^{26} molecules/kmol) and ρ is the density in kg/m^3. The radius values calculated by this method were 0.30, 0.32 and 0.44 nm, for pyrrole, pyridine and quinoline, respectively. The radius of the quinoline molecule is in good agreement with the values for similar molecules calculated by Tsai and coworkers [6,7] using bond lengths and bond angles. These values of radii were used to calculate the maximum carbon loading (M_{max}) required for a monolayer, i.e.,

$$M_{max} = \frac{M_w \chi_C}{N_A \pi r_M^2},$$

where χ_C is the mass fraction of carbon in the compound. Using these calculations, the amount of carbon (g/m^2) required to form a monolayer was 2.8×10^{-4}, 3.2×10^{-4} and 4.1×10^{-4} for pyrrole, pyridine and quinoline, respectively. This assumes a flat adsorption on the surface. A comparison of these results with the experimentally determined values in Table 1 (g of carbon/m^2) indicates that soaking the catalyst in the liquid compounds resulted in a nearly monolayer deposit. Also, the oxides of active metals, when combined with γ-Al_2O_3, affected the adsorption of the compounds on the catalyst surface. However, a consistently lower amount of carbon on the oxidic catalysts compared with that on the sulfided catalysts suggests either a lower adsorption or the metal oxides (e.g., MoO_3) aided decomposition of deposit during the vacuum treatment at 150°C of the former. Such a decomposition may be another reason for the lower than expected amounts of nitrogen in the catalysts. The increased amount of carbon on sulfided catalysts indicates that these effects were less pronounced.

3.1. *Decomposition of pyridine and quinoline deposits*

The literature on adsorption of pyridine on the surface of γ-Al_2O_3, Mo/Al_2O_3 and $Co(Ni)/Al_2O_3$ catalysts is quite extensive [8–11] compared with the little information on the other N-heterorings. It is generally accepted that for the oxidic Mo catalysts (unpromoted and/or promoted with Co and Ni), both Bronstedt and Lewis acid sites are present. The former can be detected by IR spectroscopy after the adsorption of pyridine or other bases. However, in the case of sulfided catalysts, the detection and/or involvement of Bronstedt acid sites required temperatures above 300°C and its intensity further increased when the temperature was increased to 400°C [11]. Below 300°C, most of the pyridine adsorption took place on Lewis sites of the support. Moreover, less adsorption was observed for the Mo/Al_2O_3 catalyst than that for the support presumably due to the coverage of Lewis sites by Mo species. This agrees with the present results for the oxidic catalysts and γ-Al_2O_3 (Table 1), i.e., for the latter the deposit was consistently higher than that for the oxidic catalysts. It is to be noted that in the present study, the deposits were formed by soaking the catalyst particles in pure liquid compounds rather than by depositing them from the vapor phase as is the case of the other studies. The amount of pyridine deposited by this method was greater by at least a factor of 3, compared with the deposition from the vapor phase [12]. It is believed that pyridine was initially uniformly deposited on the catalyst surface covering both the bare support and the support covered with the active metal oxides. Most likely, the pyridine and quinoline in excess of the monolayer were removed during the evacuation at 150°C. At the same time, the remaining deposit could have rearranged and approached the structure of that obtained during the deposition from the vapor phase. The highest adsorption was observed for the sulfided catalysts. This may be attributed to conversion of the uniformly distributed metal oxides to the slabs of MoS_2 resulting in more of the uncovered support surface. Otherwise, it would imply that pyridine adsorbed preferentially on the MoS_2 phase rather than on the support. The former mode of adsorption was proposed by Miciukiewicz et al. [13] during the pyridine poisoning studies of a $CoMo/Al_2O_3$ catalyst. The similar basicity of quinoline, as given by similar pK_a values, indicates a similar interaction with the catalyst surface as that of pyridine. However, the higher adsorption of quinoline compared with pyridine reported by Miciukiewicz et al. [13] is in line with the higher basicity of the former as determined by its ability to accept a proton [14].

The typical formation of NH_3 during the TPP of the pyridine deposit formed on the oxidic and sulfided $CoMo/Al_2O_3$ catalysts is shown in Fig. 1(a), whereas their cumulative yields are shown in Fig. 1(b). It is apparent that the NH_3 formation began at a temperature approaching that used during the vacuum treatment of the catalyst. This would confirm the loss of nitrogen during the treatment. The same trends in the NH_3 formation were observed during the TPP of quinoline. NH_3 was the only product analyzed during pyrolysis of the pyridine and quinoline deposits, i.e., no HCN was detected. For the sulfided catalyst, an additional region of NH_3 formation was observed compared with the oxidic catalyst. The same experiments were performed with the bare γ-Al_2O_3 support. However, as the results in Fig. 2 show, at least 400°C was required to detect NH_3 in the products. With further temperature increase, NH_3 formation reached a maximum at about 780°C indicating a strong interaction of N-rings with γ-Al_2O_3. This could be one of the reasons for the nitrogen content underestimate (Table 1). The results in Fig. 1(a) prove that during TPP of the catalyst deposited with pyridine and quinoline, a relatively large portion of the adsorbed N-heterorings will decompose into volatile products. A part of the undecomposed compounds may desorb as well. Desorption is generally accepted as the main

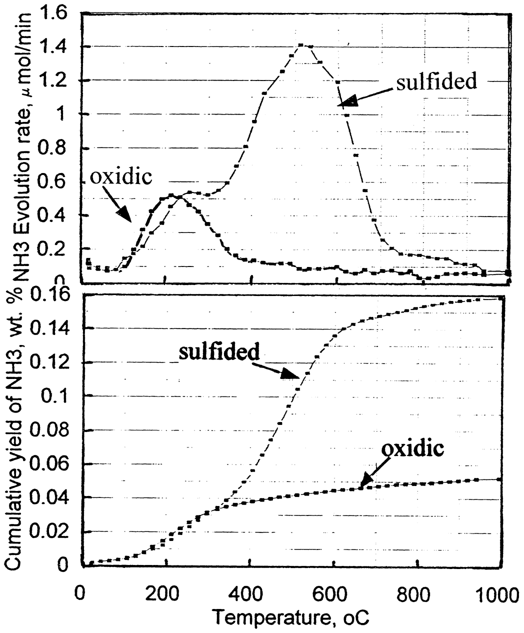

Fig. 1. Formation of NH_3 during TPP of pyridine deposited oxidic and sulfided $CoMo/Al_2O_3$ catalysts.

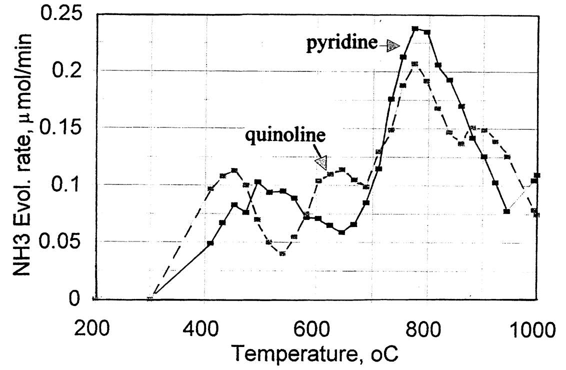

Fig. 2. Formation of NH_3 during TPP of γ-Al_2O_3 deposited with pyridine and quinoline.

cause for the weight decrease during TPP. The present results suggest that this may not be the case. NH_3 formation requires the presence of surface hydrogen. The –OH groups attached to aluminum cations are the main hydrogen containing groups present on the surface of γ-Al_2O_3 support. Five types of –OH groups of varying acidic strength are usually present [15]. Their relative concentrations depend on the type of γ-Al_2O_3. However, it is unlikely that such groups could be the source of hydrogen required for NH_3 formation, at least in the temperature region where most of the NH_3 was formed, for both oxidic and sulfided catalysts. On the oxidic catalyst, some of the –OH groups are capable of donating proton and as such can behave as Bronstedt acidic sites. This suggests that the protonation of N-heterorings may be the first step in NH_3 formation. In the case of sulfided catalysts, –SH groups attached to Mo cations may be an important source of hydrogen. It was proposed by Topsoe et al. [11] that such groups can be formed during sulfidation by the dissociative H_2S reaction shown in Fig. 3. Conditions of the catalyst sulfidation used in the present study approached those used by the authors. Such groups can donate protons and as such behave as Bronstedt acidic sites. These authors have shown that the proton donating ability of the –SH groups is enhanced significantly above 400°C. These groups are believed to be responsible for the NH_3 formation above 400°C shown in Fig. 1(a) for the sulfided catalyst. The relatively low S–H bond strength suggests that hydrogen could be supplied via radical abstraction if the latter are formed during the ring decomposition. Such hydrogen abstraction is less likely to occur for –OH groups because of the significantly greater O–H bond strength compared with the S–H bond. Based on this discussion, protonation of pyridine and quinoline is the first step in the formation of NH_3 on both the oxidic and sulfided catalysts. Some –OH groups on the bare support could have taken part as well. However, the proton donating ability of such groups may exist above the temperature regions of the main NH_3 formation for the oxidic and sulfided catalysts. For the sulfided catalyst, the appearance of the second NH_3 peak above 400°C supports participation of Bronstedt acid sites formed on sulfidation [11].

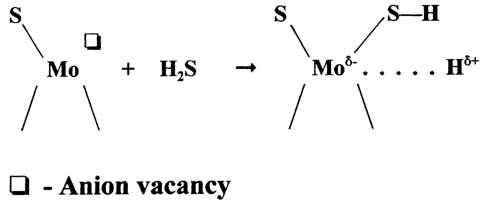

Fig. 3. Tentative mechanism of dissociative decomposition of H_2S on Mo catalysts [11].

Correlations, such as those shown in Fig. 1(b), are suitable for estimating the number of moles of NH_3 formed in the different temperature regions. These results are summarized in Table 2. For the oxidic $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts, most of the NH_3 was formed below 360°C. Assuming that

Table 2
Yield of NH_3 in $\mu mol/m^2$ during TPP of deposits

Deposit	Oxidic	Sulfided	
		Below 360°C	Total
$CoMo/Al_2O_3$ catalyst			
Pyridine	0.19	0.13	0.57
Quinoline	0.20	0.12	0.43
$NiMo/Al_2O_3$ catalyst			
Pyridine	0.48	0.15	0.26
Quinoline	0.48	0	0.15
γ-Al_2O_3[a]			
Pyridine	0.14		
Quinoline	0.12		

[a] NH_3 formation began above 650°C.

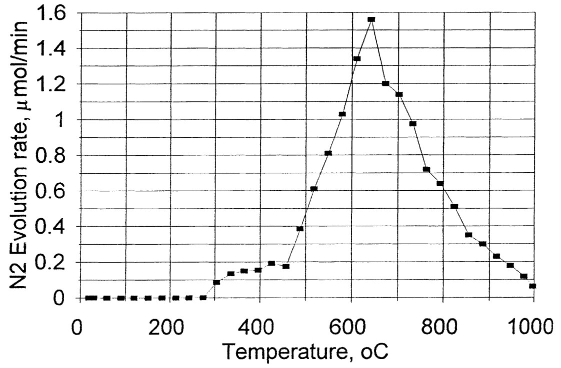

Fig. 4. Formation of N_2 during TPP of quinoline deposited sulfided $CoMo/Al_2O_3$ catalyst.

no intramolecular migration of hydrogen towards nitrogen has occurred, the formation of each mole of NH_3 would require three hydrogen atoms from the surface of the catalyst. However, after the elimination of NH_3 from the ring, part of the nitrogen depleted hydrocarbon residue will remain on the catalyst and as such may be an additional source of hydrogen. It is believed that the hydrogen in residue at least partly contributed to the NH_3 formation on the bare γ-Al_2O_3 (Fig. 2). The presence of such a residue is confirmed by the results in Fig. 4 showing the formation of N_2 after the formation of NH_3 almost completely ceased. This N_2 originated from a deposit still present on the catalyst. Nevertheless, if all or most of the hydrogen required to form NH_3 is supplied by the catalyst surface, the results in Table 2, when multiplied by 3, would indicate the approximate number of Bronstedt acid sites on the catalyst used during the overall decomposition of the ring leading to NH_3 formation. The results in Table 2 indicate the difference between the effect of the $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts on the decomposition. For the former, the NH_3 yield increased significantly on sulfidation, presumably because of the additional Bronstedt acid sites formed on sulfidation. The first NH_3 peak, which coincides with that for the oxidic catalyst decreased but was not completely eliminated. This may suggest that some Bronstedt sites associated with the Mo oxide were still present as the result of an incomplete sulfidation and/or a chemisorbed oxygen while the catalyst was exposed to air [16]. For the sulfided $NiMo/Al_2O_3$ catalysts, the NH_3 yield was decreased on sulfidation mainly due to the marked decrease and/or complete elimination of the NH_3 portion formed below 360°C. It is evident that the Bronstedt sites formed on sulfidation could not compensate for the loss of the Bronstedt sites associated with the oxidic catalyst. As indicated by the amount of NH_3 formed above 400°C, the number of Bronstedt sites formed during the sulfidation of the $NiMo/Al_2O_3$ catalyst was much smaller than that during the sulfidation of the $CoMo/Al_2O_3$ catalyst. This agrees with the results published by Topsoe et al. [11] who have shown that more Bronstedt sites are formed on sulfided $CoMo/Al_2O_3$ catalyst than that on the sulfided $NiMo/Al_2O_3$ catalyst.

3.2. *Pyrolysis of pyrrole deposit*

Little information is available on interaction of the 5-membered rings with the catalyst surface though, it was reported that indole can be a poison [17]. However, the poisoning effect of the 5-membered rings is much less evident than that of the 6-membered rings. Also, based on the significantly lower resonance energy of the pyrrole ring compared with that of the pyridine ring [14], a higher reactivity of the former is expected.

The formation of NH_3 during TPP of the pyrrole deposited catalysts and γ-Al_2O_3 is shown in Fig. 5. In this case, small amounts of HCN (about 3% of the NH_3 yield) were also formed contrary to the total absence of HCN during TPP of the pyridine and quinoline deposited catalysts. For the $CoMo/Al_2O_3$ catalyst, sulfiding had similar effects as observed during TPP of the 6-membered rings, i.e., below 360°C, NH_3 formation decreased though the NH_3 peak which coincided with that for the oxidic catalyst was still quite evident. Moreover, an additional NH_3, with the peak maximum above 400°C was formed. For the sulfided $NiMo/Al_2O_3$ catalyst, NH_3 formation below 360°C was almost eliminated and most of the NH_3 was formed above 360°C. TPP of the pyrrole deposited γ-Al_2O_3 differed significantly from that deposited with pyridine and quinoline (Fig. 2). Thus, the NH_3 build-up began at about 200°C and reached the first maximum at 390°C. The second NH_3 maximum was observed at about 700°C. The yields of NH_3 estimated in the two temperature regions from similar correlations, as shown in Fig. 1(b), are shown in Table 3.

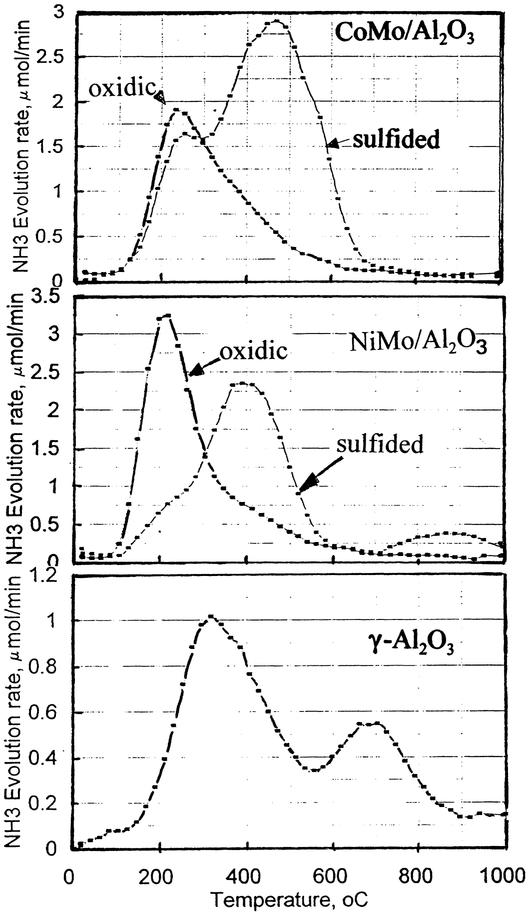

Fig. 5. Formation of NH_3 during TPP on the pyrrole deposited catalysts and γ-Al_2O_3.

Table 3
Yields of NH_3 (μmol/m^2) during TPP of pyrrole deposited catalysts

Oxidic	Sulfided	
	Below 360°C	Total
$CoMo/Al_2O_3$ catalyst		
0.50	0.31	0.92
$NiMo/Al_2O_3$ catalyst		
1.93	0.21	1.05
γ-Al_2O_3		
0.31[a]		
0.49[b]		

[a] Yield below 600°C.
[b] Total yield.

These results indicate similar trends as observed for the 6-membered rings (Table 2), i.e., for the $CoMo/Al_2O_3$ catalyst, sulfiding increased the NH_3 yield, whereas for the $NiMo/Al_2O_3$ catalyst, the NH_3 yield decreased on sulfiding. For every catalyst and γ-Al_2O_3, the NH_3 yields were significantly higher from the pyrrole deposits compared with those from the pyridine and quinoline deposits. The lower stability of the pyrrole ring compared with that of the pyridine and quinoline rings [14] may be one of the reasons for the higher NH_3 yields, in the case of the former. It is believed that NH_3 formation during the TPP of pyrrole involves a different mechanism than that from the pyridine and quinoline. Thus, the protonation of the pyrrole is limited to very strong acids, e.g., concentrated H_2SO_4 and CF_3COOH or superacids [18].

The occurrence of the first NH_3 peak for the pyrrole deposited γ-Al_2O_3, compared with its absence for that deposited with the 6-membered rings indicates a significant difference in the adsorption mode. It is believed that the role of the Lewis acid sites in the adsorption of pyrrole is much less important compared with the pyridine. A flat adsorption on the catalyst surface may be more favorable for the interaction of the pyrrole ring with the surface –OH groups resulting in the formation of a polymer. It is well established that pyrrole readily forms polymers. In such a case, the originally uniform deposit of pyrrole would be converted to islands of polymer molecules which could be an additional source of hydrogen required for NH_3 formation.

3.3. *Oxidative decomposition of N-heterorings*

In this case, the decomposition was performed using gas mixtures varying in O_2 concentration from 1% to 4%. For the $CoMo/Al_2O_3$ catalyst, the effect of O_2 concentration on NH_3 conversion is shown in Fig. 6. These conversions were estimated from the yields of NH_3 at the end of the TPP and TPO runs. Similar trends were observed for the $NiMo/Al_2O_3$ catalysts. For the oxidic form, the NH_3 yield gradually decreased with an increase in O_2 concentration, contrary to a more abrupt decrease in the NH_3 yield for the sulfided catalyst. The latter observation is attributed to the oxidation of the inorganic sulfur, which results in

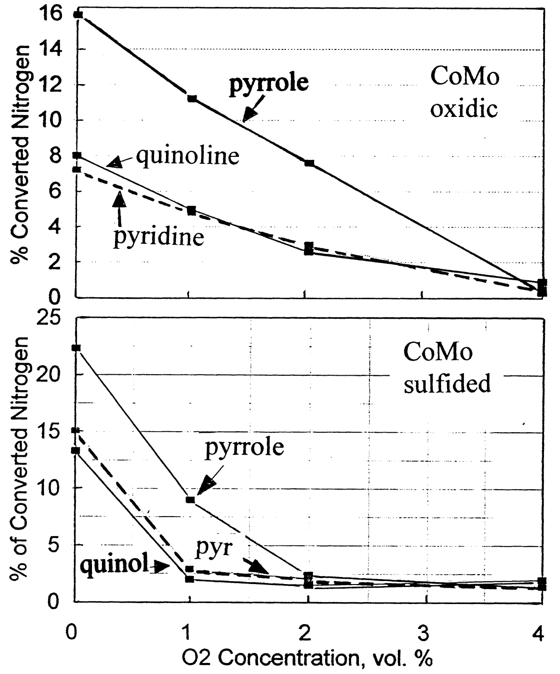

Fig. 6. Effect of O_2 concentration on conversion of coke's nitrogen to NH_3 ($CoMo/Al_2O_3$ catalyst).

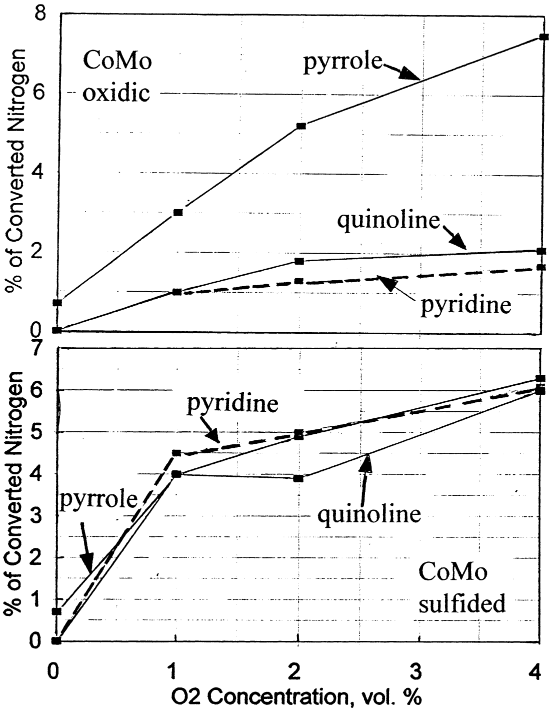

Fig. 7. Effect of O_2 concentration on conversion of coke's nitrogen to HCN ($CoMo/Al_2O_3$ catalyst).

the destruction of the surface –SH groups. The decrease in the NH_3 yields, shown in Fig. 6, was complemented by the appearance of HCN. These results are shown in Fig. 7. It is noted again that no HCN was formed during the TPP of the pyridine and quinoline deposits, whereas a small amount of HCN was formed during that of the pyrrole deposit. A comparison of the results in Figs. 6 and 7 shows that the appearance of HCN did not account for the decrease in the NH_3 yield during the oxidation runs. This is evident especially for the sulfided $CoMo/Al_2O_3$ catalyst, in which case, the appearance of HCN accounted only for about half of the NH_3 formed during the TPP runs. It is obvious that NO and N_2O, which are formed during the oxidation, were responsible for the part of the unaccounted NH_3 [2,3]. It is also evident that, to a certain extent, the mode of the N-heteroring decomposition changed in the presence of O_2, favoring the formation of HCN relative to that of NH_3.

Fig. 8 shows effect of O_2 concentration on NH_3 formation during the decomposition of the deposits on the γ-Al_2O_3. There is a significant difference between the effects on the decomposition of the pyrrole deposit on one hand, and that of the pyridine and quinoline deposits on the other. During the TPO of the pyridine and quinoline deposits, all NH_3 was formed above 600°C, similarly as during their TPP. As it is shown in Fig. 5(c), two peaks of the NH_3 formation were observed during TPP of the pyrrole deposit on γ-Al_2O_3, i.e., one having its maximum at about 300°C and the other at about 670°C. In 1% O_2, the first peak increased and the second decreased. With a further increase in the O_2 concentration to 2% and 4%, the first peak further increased while the second peak completely disappeared. Moreover, only a very small amount of HCN was formed during TPO of the pyrrole deposit and no HCN during that of the pyridine and quinoline deposits. This contrasts with the increase in HCN yield under the same conditions in the case of the deposits on both oxidic and sulfided $Co(Ni)Mo/Al_2O_3$ catalysts. These observations suggest that below about 600°C, the γ-Al_2O_3 support had an insignificant effect on the decomposition of the pyridine and quino-

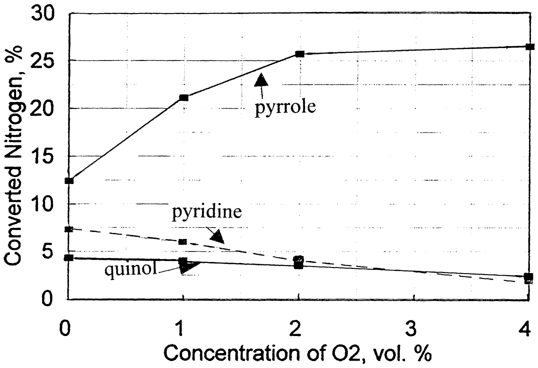

Fig. 8. Effect of O_2 concentration on conversion of coke's nitrogen to NH_3 (γ-Al_2O_3).

line deposits compared with that of the pyrrole deposit. However, during the TPP and TPO, decomposition of the former was significantly enhanced by both the oxidic and sulfided form of the Co(Ni)Mo metals.

The increased NH_3 yield during TPO of the pyrrole deposit on γ-Al_2O_3 compared to its TPP appears to be anomalic. Thus, it is not easy to reconcile the increase in the availability of the hydrogen as indicated by the increase in the NH_3 yield during TPO. It is unlikely that the –OH groups on the γ-Al_2O_3 surface are a source of the hydrogen in the case of the pyrrole deposit and not for the pyridine and quinoline deposits, although adsorption of the 5-membered N-rings on the surface may differ from that of the 6-membered rings. A possible explanation can be based on the different reactivity of the pyrrole compared with that of the pyridine and quinoline. It was shown by Gossauer and Nesvadba [19] that the former undergoes an autoxidation when exposed to O_2. It was proposed that the mechanism of the autoxidation involves the formation of the endoperoxide as an intermediate. In this case, O_2 is disassociatively adsorbed at the 2,5 positions. Subsequently, the endoperoxide group breaks and the 2,5 hydrogens migrate to the 3,4 positions of the pyrrole ring. This results in the formation of the succinimid, which was identified among the products. Then, the fully hydrogenated 3,4 positions of the modified ring appear to be a potential source of the hydrogen required for the NH_3 formation. In this case, the radical-like N-containing species formed initially would abstract hydrogen from these groups. A similar autoxidation of the 6-membered N-rings does not occur.

4. Conclusions

The γ-Al_2O_3 support plays an important role during the adsorption of the N-heterorings on the surface of hydroprocessing catalysts. However, its role during their pyrolysis and oxidative decomposition appears to be rather minor. A relatively large conversion of pyrrole on the γ-Al_2O_3 was attributed to its autoxidation, yielding hydrogen donating groups rather than to the participation of the –OH groups on the surface. Neither pyrolysis nor oxidative decomposition of the γ-Al_2O_3 deposited with pyridine and quinoline was observed in the temperature region typical of that employed during regeneration. As Fig. 2 shows, above 600°C, some –OH groups may be capable of donating a proton as the initial step for the decomposition of the 6-membered rings.

Co(Ni)Mo metals, when added to the γ-Al_2O_3, enhance both pyrolysis and oxidative decomposition as evidenced by the significantly greater yields of NH_3 for the catalysts shown in Fig. 5. As a result of their catalytic actions, decomposition of the deposits occurred in the temperature region typical of regeneration. The formation of NH_3 as the main product of the pyrolysis of pyridine and quinoline was attributed to the participation of the Bronstedt acid sites by donating their proton to the N-heterorings. It is unlikely that other source of hydrogen could take part in the reaction leading to NH_3 formation. Upon sulfidation, most of the Bronstedt acid sites present on the oxidic catalysts were converted to new types of Bronstedt acid sites associated with the –SH groups. However, these sites require temperatures above 400°C before they can participate in the protonation of the 6-membered N-heterorings. Also, if the radicals are formed during the early stages of decomposition, the –SH groups may participate in the hydrogen abstraction reactions, leading to the hydrogen enriched species. It is proposed that such reactions are more important for decomposition of the pyrrole deposit than that of the pyridine and quinoline deposits because the Bronstedt sites on both oxidic and sulfided catalyst may not be strong enough to achieve protonation of the pyrrole ring.

References

[1] E. Furimsky, F.E. Massoth, Catal. Today 17 (1993) 537.

[2] E. Furimsky, M. Nielsen, P. Jurasek, Energy and Fuels 9 (1995) 439.

[3] E. Furimsky, Ind. Eng. Chem. Res. 12 (1996) 4406.

[4] M.R. Gray, in: Upgrading Petroleum Residues and Heavy Oils, Marcel Dekker, New York, 1994.

[5] S.M. Richardson, H. Nagaishi, M.R. Gray, Ind. Eng. Chem. Res. 35 (1996) 3940.

[6] C.H. Tsai, F.E. Massoth, S.Y. Lee, J.D. Seader, Ind. Eng. Chem. Res. 30 (1991) 22.

[7] S.Y. Lee, J.D. Seader, C.H. Tsai, F.E. Massoth, Ind. Eng. Chem. Res. 39 (1991) 1683.

[8] P. Ratnasamy, H. Knozinger, J. Catal. 54 (1978) 155.

[9] K.I. Segawa, W.K. Hall, J. Catal. 76 (1987) 133.

[10] S.M. Riseman, S. Bandyopadyhya, F.E. Massoth, M. Eyring, Appl. Catal. 16 (1985) 29.

[11] N.-Y. Topsoe, H. Topsoe, F.E. Massoth, J. Catal. 119 (1989) 252.

[12] R. Ramachandran, F.E. Massoth, Chem. Eng. Commun. 11 (1982) 239.

[13] J. Miciukiewicz, W. Zmierczak, F.E. Massoth, in: Proceedings of the Eight International Congress on Catalysis, Berlin 1984, vol. 2, Verlag Chemie, Basel, 1984, p. 671.

[14] E. Furimsky, Erdöl und Kohle 35 (1982) 455.

[15] R. Ratnasamy, H. Knozinger, Catal. Rev.-Eng. Sci. 18 (1978) 31.

[16] F.E. Massoth, C.-S. Kim, J.-W. Cui, Appl. Catal. 58 (1990) 199.

[17] F.E. Massoth, K. Balusami, J. Shabtai, J. Catal. 122 (1990) 256.

[18] A.H. Jackson, in: Heterocyclic Compounds-Pyrrole, vol. 48 (1), 1990, p. 305.

[19] A. Gossauer, P. Nesvadba, in: Heterocyclic Compounds-Pyrrole, vol. 48 (1), 1990.