

Piperidine Hydrogenolysis on a Commercial Hydrocracking Catalyst

II. The Effects of Initial Piperidine Concentration, Temperature, Catalyst Presulfidation, and Hydrogen Partial Pressure on Catalyst Activity, Deactivation, and Coke Formation

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The formation of coke in the piperidine hydrogenolysis reaction over a fresh sulfided hydrocracking catalyst was examined at temperatures ranging from 281 to 321°C, hydrogen partial pressures of 11.2 to 15.9 atm (1.1 to 1.6 MPa), and initial concentrations of piperidine of 3.94×10^{-3} to 11.84×10^{-3} g mol/liter using elemental analysis, ¹³C NMR spectroscopy, and ESCA. The results indicated that most of the coke present on the catalyst after 17 h on stream was deposited in the initial 90 min of the reaction. Coke formation and hence catalyst deactivation were found to increase with both reaction temperature and initial concentration of piperidine. Reducing the catalyst instead of sulfiding it had no effect on the final coke content. Nitrogen was found to be present on the catalyst surface after reaction indicating that nitrogen-containing compounds were participating in the formation of coke. The H/C ratio of the coke decreased very slowly with reaction time and was invariant to changes in temperature, initial concentration of piperidine, or catalyst pretreatment method. Comparing the activity of reduced versus sulfided fresh catalysts in the hydrogenolysis of piperidine, it was found that under the present conditions, catalyst presulfidation increased the activity of the metallic catalyst function and decreased the rate of catalyst deactivation. Furthermore, decreasing the partial pressure of hydrogen resulted in an activity decrease of the metallic catalyst function and had a negative effect on the overall catalyst activity maintenance. The intrinsic activity of the acidic catalyst function was not affected by the change in hydrogen partial pressure. © 1992 Academic Press, Inc.

INTRODUCTION

One of the major technological and economic problems in petroleum refining is the catalyst deactivation caused by the formation of carbonaceous deposits (coke). It is therefore important to study the kinetics and mechanisms of coke formation and to determine its effects on the activity and selectivity of the catalysts (1). Of particular interest is of course the identification of the parameters that directly affect the formation of coke. The literature is rich with studies concerning the effects of variables such as reac-

tion temperature, contact time, hydrogen partial pressure, feed composition, and catalyst state (oxidic versus sulfidic) on catalyst deactivation and coke formation.

Pioneering work in coke formation was performed by Voorhies (2) who studied the cracking of gas oil feedstocks. Experimental results on the carbon content of natural and synthetic cracking catalysts as a function of process time were correlated with equations of the form

$$C_c = Gt_c^\nu \quad (1)$$

The exponent ν appeared to be about 0.5 and carbon formation on the catalyst increased mildly with cracking temperature but it was relatively independent of feed rate over the range of his experiments. Eberly *et al.* (3),

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however, in a study on the mechanism of coke formation on silica–alumina cracking catalysts showed that the rate of coke formation was a function of the feed rate. Also, values of the Voorhies exponent ranging from about 0.4 to 1.0 have been reported in various studies (3, 4). In addition, during the cracking of ethylene over a silica–alumina catalyst, Ozawa and Bischoff (4) observed a change in the slope of the \ln – \ln plot of Eq. (1), suggesting a relationship between coke deposition and the activity of the active center for coke formation. A change in slope in the Voorhies plot was also found by Butt *et al.* (5) for data on the cracking of cumene over a commercial H-mordenite catalyst at times on stream up to 6 h. In particular, two regions of the correlation were found in all cases. An initial rapid increase in coke content in the first 1 h to a near-equilibrium level of about 3.5 wt% and a subsequent very slow change in the amount of coke. The exponent ν in the Voorhies equation was reported to be about 0.5 in the initial region and 0.1 in the final region. The Voorhies equation has in general been useful in correlating coke formation in many systems; however, it should be regarded only as an empirical formulation (6).

Beuther and Schmid (7) investigated the deposition of carbon on a conventional desulfurization catalyst as a function of time, hydrogen partial pressure, and reaction temperature in the HDS processing of a vacuum residue. They reported that of the carbon deposited in 16 days of operation (20–30 wt%) one-half was deposited in the first 12 h. Furthermore, an increase in the hydrogen partial pressure reduced the equilibrium coke yield; however, the higher hydrogen pressure did not eliminate the initial rapid rate of coke formation. In addition, increasing the temperature resulted in an increase in the coke yield. Similar results were reported by Simpson (8) who examined the deactivation by coke deposition of a commercial HDN catalyst during hydrotreating of a vacuum gas oil feed. The hydrotreating was stopped at times from 0 to 60 h and

the catalyst was discharged and examined. Equilibrium carbon (toluene insolubles and total) deposition was achieved within only a few hours after feed introduction. Furthermore, the relative volume activity values for basic nitrogen removal initially showed a rapid decrease then decreased much more slowly; i.e., two regions of catalyst activity loss were observed.

In another study, Tanatarov *et al.* (9) examined the effect of catalyst presulfidation (with H_2S – H_2) on the deposition of coke on $\text{CoMo}/\text{Al}_2\text{O}_3$ in the hydrotreating of thermally cracked gasoline. The sulfur content of the catalyst was varied from 2.0 to 6.5 wt% by varying the sulfidation temperature and contact time. In addition to the sulfided samples, a catalyst in the oxide form was used for comparison. Their data indicated that as the amount of sulfur on the catalyst increased from 0 to 6.5 wt% the deposition of coke on the catalyst was reduced substantially. The decreased production of coke was accounted for by considering different extents of adsorption of the intermediate condensation products on oxidic and sulfided catalysts. In particular, it was proposed that the intermediate condensation products consist of unsaturated hydrocarbons whose bonding strength with the catalyst is governed by an electron pair. When the oxygen ions are replaced by sulfur ions, the valence of the metal is lowered and consequently the adsorption of unsaturated hydrocarbons on the active centers of the catalyst decreases (9).

The accelerated deactivation of an industrial sulfided $\text{CoMo}/\text{Al}_2\text{O}_3$ hydrotreating catalyst was studied by Arteaga *et al.* (10) by exposing it to a 1,3-butadiene or methylcyclopentane stream at 450°C in the presence of argon. The results indicated that the rate of coke deposition was higher when 1,3-butadiene was used as a coke precursor resulting in a sharp increase in the catalyst coke loading during 2 h of exposure. For the same precursor (1,3-butadiene), the coking rates increased when the space velocity decreased. In general, the extent of coke depo-

sition was found to markedly depend on the duration of coking.

Guisnet *et al.* (1) investigated the coking and aging rate of a HY zeolite catalyst during the cracking of *n*-heptane in a flow reactor at 450°C. The carbonaceous deposits were characterized by analysis of the solvent extracts obtained after dissolution of the zeolite by hydrofluoric acid. They observed fast deactivation of the zeolite, which lost 80% of its activity during the first 30 min of the reaction. The atomic H/C ratio of coke was found to decrease when the coke content increased. For 2–16 wt% coke the H/C ratio was below 1, a characteristic of polyaromatic compounds (1). In another study, Guisnet and co-workers (11) examined coke formation and deactivation of various Pt–zeolite catalysts for benzene hydrogenation at 80°C and reported that the percentage of carbonaceous compounds (coke) on the catalysts increased initially very rapidly with time on stream, then more slowly during 6 h of operation.

The above results point to a complex dependency of coke formation on many parameters. In particular, the coke content is generally indicated to increase with temperature and to be a function of feed rate as well as of the composition of the feed. Increasing the hydrogen partial pressure was found to decrease the final wt% coke, and catalyst presulfidation was also shown to reduce the formation of coke. Of particular importance, however, was the relation of coke deposition with the time on stream. Two regions of coke formation have been identified with most of the coke being deposited in the initial (first) time period (region) resulting in a rapid activity decline, while the coke content increased and the activity decreased slowly in the second region. In addition, it was observed that as the amount of coke increases, its H/C ratio decreases.

In a recent correspondence (12), the reaction and deactivation kinetics of piperidine hydrogenolysis on a commercial hydrocracking catalyst and the feasibility of this reaction as a probe for catalyst characteriza-

tion were discussed. In these experiments, the catalytic activity decreased with time on stream, most probably due to coking; therefore, the reactant and/or products must have reacted to form carbonaceous deposits (coke). In the present work, the coke formation in the piperidine hydrogenolysis reaction is examined and the results are related to information from the literature. In particular, the effects of initial piperidine concentration, temperature, catalyst presulfidation, and hydrogen partial pressure on catalyst activity, deactivation, and coke formation as well as the nature of the coke precursors are discussed.

EXPERIMENTAL

Materials and Procedures

The catalyst samples used in this study were supplied by Amoco Oil Company. The fresh hydrocracking catalyst (NU-D) consists of Co and Mo oxides deposited on a support composed of crystalline aluminosilicates (ultrastable Y zeolite) dispersed in a porous matrix of silica–alumina. All the catalyst samples were crushed and screened to 0.2-mm average particle size and pretreated according to either method I* or II. In method I*, the catalyst was purged with nitrogen at room temperature for 1 h. It was then heated to 365°C and held at 365°C for 1 h under a flow of nitrogen. A mixture of 10% H₂S in H₂ was then passed through the catalyst bed at 40 cc/min (STP) and 365°C until the ratio of the mass of the catalyst to the mass of the H₂S passed was equal to unity. The catalyst was then cooled to room temperature under a flow of hydrogen for 1 h. Method II was the same as method I* except hydrogen was used instead of H₂S/H₂ mixture in the third step and the reactor was purged with hydrogen at 365°C for 1 h before the cooling step.

The experiments were carried out in a continuous-flow fixed-bed reactor system at temperatures ranging from 281 to 321°C, hydrogen partial pressures of 11.2 to 15.9 atm (1.1 to 1.6 MPa), initial concentrations of piperidine of 3.94×10^{-3} to 11.84×10^{-3}

gmol/liter, and catalyst times on stream of 90 to 1047 min. Space velocities were in the range of 1.07 to 3.57 h⁻¹. Details regarding experimental equipment and procedures as well as product distribution are given elsewhere (12, 13).

At the end of each experimental run, pure hydrogen at an increased flow rate was used to purge the reactor at reaction temperature until compounds detected via on-line gas chromatography in injected samples were negligible. The catalyst was then discharged from the reactor and analyzed for carbon and nitrogen using elemental analysis, ¹³C NMR spectroscopy, and ESCA. Several experimental techniques can be employed for the characterization of carbonaceous residues (14). However, as Maixner *et al.* (15) pointed out, cross-polarization/magic angle spinning ¹³C nuclear magnetic resonance (CP/MAS-¹³C NMR) spectroscopy appears to be among the most powerful tools for collecting information on the nature of coke on zeolite catalysts. CP/MAS measurements are made directly on the solid material, are nondestructive, and require little sample preparation. The NMR spectra of the catalyst samples used in the present work were recorded at ambient temperature on a Varian VXR-300 NMR spectrometer. Spinning rates between 2.5 and 4.5 kHz were applied. The spectra were measured using a 90° cross-polarization pulse width. Chemical shifts are given with respect to an external sample of solid hexamethylbenzene at 17.8 ppm. For assignment of the bands, reference was made to the ¹³C chemical shift ranges in organic compounds given by Breitmaier and Voelter (16). Spinning side bands resulting from the chemical shift anisotropy of aromatic carbon were identified by varying the spinning rate. Peaks identified as saturated and unsaturated carbon bands were denoted by S and U, respectively. The saturated and unsaturated carbon peak areas were assumed to be proportional to the change in the height of the integration line associated with the corresponding peaks. In this way, estimates of

the ratio of saturated to olefinic and aromatic carbon on each catalyst were obtained. The ESCA spectra were obtained using a VG Scientific ESCALAB Mark II equipped with a twin anode X-ray source (AlK α and MgK α radiation) and a spherical energy analyzer. For the present XPS measurements, the Al source was used at an emission current of 20 mA and a voltage of 15 kV. The analyzer energy was 50 eV.

Catalyst Activity Extrapolation Method

To offset effects of catalyst deactivation occurring during the piperidine hydrogenolysis kinetic experiments, a consistent means of determining fresh catalyst activity data was developed (13). Initial reaction rate parameters were obtained by (i) monitoring conversion as a function of time on stream; (ii) fitting the deactivation data to a catalyst decay correlation (Eq. (2) below); (iii) fitting the total conversion versus time on stream data to a reaction-deactivation model (Eq. (3) below); and (iv) applying Eqs. (4) and (5) for product *i*, where *i* stands for *N-n*-pentylpiperidine (2), *2-n*-pentylpiperidine (3), or decahydroquinolines (4).

$$x_i(t) = x_i(0) \exp(-a_i t^{0.5}) \quad (2)$$

$$\frac{1}{k_i^0 \tau} + \frac{k_d(C_{10})^{n^*} t}{k_i^0 \tau} = \left(\frac{1 - x_i}{x_i} \right) \quad (3)$$

$$k_{iI}^0 = \frac{x_{iII}^0}{x_{iI}^0} k_{iI}^0 \quad (4)$$

$$k_{iII}^0 = \frac{x_{iIII}^0}{x_{iII}^0} k_{iII}^0 \quad (5)$$

Figure 1 shows a simplified reaction scheme proposed for the hydrogenolysis of piperidine on the commercial hydrocracking catalyst (12) that accounts for the formation of the major products (2, 3, and 4) observed in this work. In all cases, the conversion versus time on stream data show the existence of two deactivation regimes which are denoted regions I and II (12, 13). Region I corresponds to a rapid initial activity decline step followed by a more gradual deactiva-

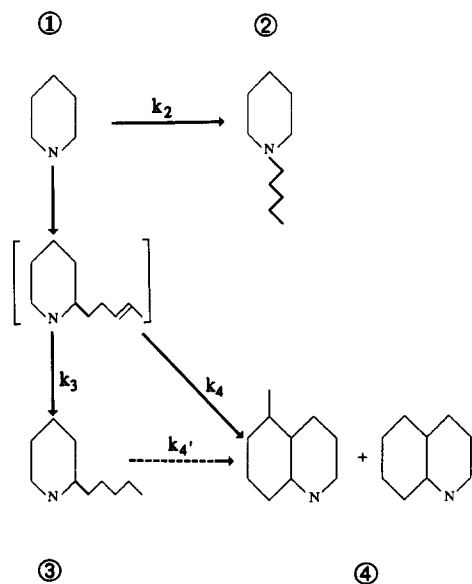


FIG. 1. A simplified reaction scheme for piperidine hydrogenolysis over the commercial hydrocracking catalyst.

tion rate (region II). Note that only k_{H}^0 and k_{H}^0 are the "true" initial rate constants, i.e., in the absence of deactivation (13); however, the conversion data in region II are also reported here for completeness.

Equation (2) is a modified form of the Voorhies correlation (Eq. (1)) proposed by Mahoney (17) and subsequently used by others (18–21). Equation (3) is a reaction–deactivation model derived by HadjiIoizou *et al.* (12) based on separable kinetics and the principles proposed by Szépe and Levenspiel (22, 23). Equations (4) and (5) were derived for the piperidine hydrogenolysis reaction system (12). The parameters of these correlations have been estimated by a linear regression method (12, 13). The results indicated that the catalyst deactivation rate increased with increasing reaction temperature, especially in region I. The deactivation in region I was also dependent on the initial concentration of piperidine with an order of dependency of about 1 (i.e., $n^* \approx 1$), whereas the data in region II indicated that deactivation was independent of C_{1_0} .

RESULTS AND DISCUSSION

Coke Formation and Nature of the Coke Precursors

To determine the effects of reaction time (here called catalyst time on stream), of the initial concentration of piperidine, and reaction temperature on carbon formation, catalyst deactivation, and possibly on the structure of coke, a series of experiments was performed where piperidine was hydrogenated over the sulfided hydrocracking catalyst (NU-D). Reaction data were also obtained with a catalyst sample reduced in H_2 (pretreatment method II). The used catalysts were then mostly analyzed by elemental analysis while some ^{13}C NMR spectroscopy and ESCA measurements were also performed. The data are presented in Table 1.

The relation between carbon on catalyst and time on stream of catalyst can be derived by comparing experiments 75, 42, and 52 of Table 1. The plot of wt% carbon on the catalyst versus catalyst time on stream is presented in Fig. 2 (fresh catalyst has 0.03 wt% C). The data clearly indicate that most of the carbon present on the catalyst after 17 h on stream was deposited in the initial 90 min of the reaction. Thus, two regions of coke formation can be seen in accordance with literature data; in the first region (I), coke deposition is very rapid while in the second region (II) much slower coke accumulation takes place. The exponent ν in the Voorhies equation (Eq. (1)) for the region after 90 min was found to be 0.05.

In the present work, ^{13}C NMR spectroscopy was used to characterize the coke deposits on the used catalyst samples from the above three experiments in order to possibly gain some insight into the structure of the deposits. These samples were fresh hydrocracking catalysts (NU-D) that have been used under the same conditions for piperidine hydrogenolysis but not for the same time on stream. The catalyst time on stream was varied between 90 and 1046 min in order to investigate how the ratio of saturated to

TABLE I

Coke Formation in the Hydrogenolysis of Piperidine over the Sulfided Commercial Hydrocracking Catalyst NU-D

Experiment	Catalyst time on stream (min)	Reaction temperature (°C)	Initial concentration of piperidine $\times 10^3$ (g mol/liter)	On catalyst				Q^a
				C (wt%)	N (wt%)	H/C (wt%/wt%)	H/N (wt%/wt%)	
75 ^b	90	301	4.13	4.78	0.87	0.30	1.64	2.6
42	725	301	3.94	5.19	0.69	0.29	2.17	2.6
52	1046	301	4.14	5.54	0.80	0.24	1.69	2.6
77 ^c	1047	301	4.15	5.33	0.83	0.23	1.45	—
56	1017	301	8.11	6.15	0.83	0.24	1.75	—
53	977	321	4.03	6.52	0.81	0.24	1.95	—
55	955	281	4.37	4.97	0.84	0.25	1.48	—

^a Q , Saturated carbon/olefinic and aromatic carbon, as determined by ^{13}C NMR.

^b Elemental results represent average values from three different analyses.

^c The catalyst was not presulfided but reduced in H_2 prior to reaction.

unsaturated carbon in the carbonaceous deposits changes during the reaction period (experiments 75, 42, and 52 of Table 1). A typical NMR spectrum of one of the catalysts used in the experiments (experiment 52) is shown in Fig. 3. A value of 2.6 for the ratio of saturated to olefinic and aromatic carbon on each catalyst was calculated in all cases indicating that little if any change occurs in the type of carbon on the catalyst

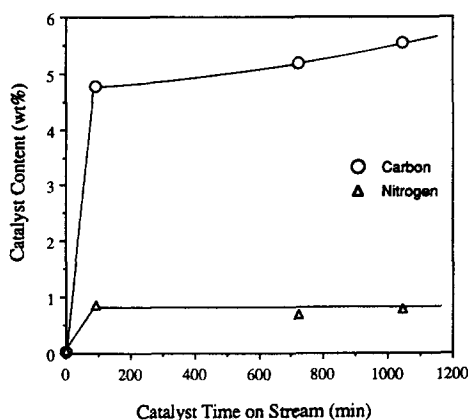


FIG. 2. Wt% carbon and nitrogen as a function of catalyst time on stream for NU-D at 301°C and an initial concentration of piperidine of about 4×10^{-3} g mol/liter.

as a function of time on stream. Indeed, elemental analysis results (Table 1) show only a small decrease in the H/C ratio with increasing catalyst time on stream, thus pointing to a very slow transformation of the coke structure to more unsaturated carbonaceous residues.

Considerable accumulation of nitrogen was also observed during the above experiments (Table 1; fresh catalyst has 0.04 wt% N) indicating that nitrogen is intimately involved in coke formation. The region I-II behavior mentioned above is also reflected in the plot of nitrogen on catalyst and time on stream, as shown in Fig. 2. The nitrogen accumulation was also confirmed by ESCA measurements. An example comparison between the fresh hydrocracking catalyst (NU-D) and the catalyst used in experiment 52 (0.80 wt% N) is illustrated in Fig. 4, where the molybdenum ($3p$) and nitrogen ($1s$) spectra are shown. A rather strong N $1s$ peak is seen to partly overlap with the Mo $3p_{3/2}$ peak in the used sample; however, the fresh sample does not show the nitrogen shoulder at 401 eV.

From the above results and those of prior work, the presence of two regions (I and II) in the coke formation and conversion data

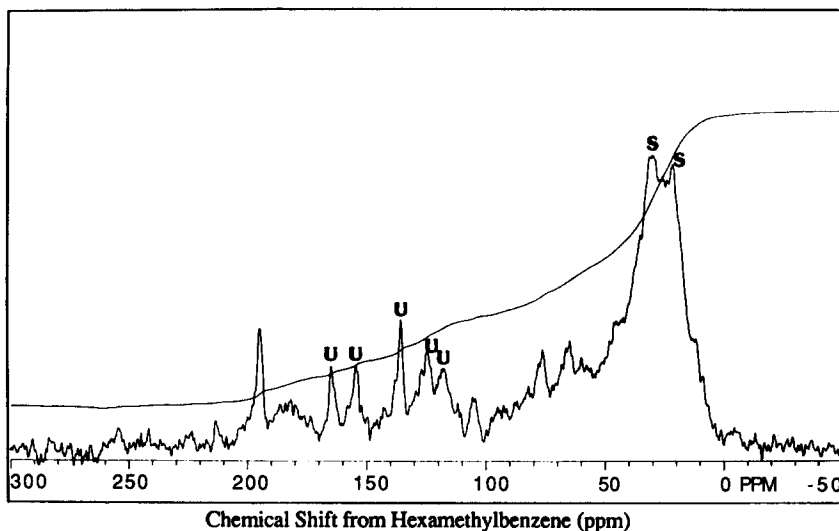


FIG. 3. CP/MAS-¹³C NMR spectrum of NU-D used in the hydrogenolysis of piperidine for 1046 min at 301°C and an initial concentration of piperidine of 4.14×10^{-3} g mol/liter; Table 1, experiment 52.

of piperidine hydrogenolysis can be interpreted in the following way. At the beginning of the reaction (region I), the strongly basic nitrogen compounds remain adsorbed on the most active acid sites and develop

into coke precursor molecules. This seems clear from the data presented in Fig. 2 and the results on nitrogen surface coverage for this system reported previously (12). This causes a fast deactivation of the catalyst,

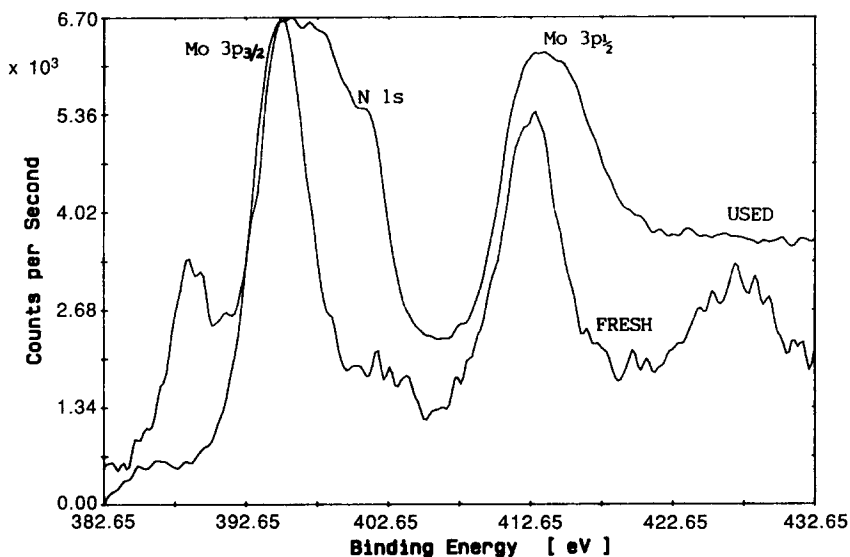


FIG. 4. ESCA spectra for molybdenum and nitrogen on the fresh hydrocracking catalyst and the catalyst used in the hydrogenolysis of piperidine for 1046 min at 301°C and an initial concentration of piperidine of 4.14×10^{-3} g mol/liter; Table 1, experiment 52.

assuming the main reactions and coke formation occur on the same sites. Oligomerization, alkylation, cyclization, and hydrogen transfer are all reactions that probably participate in the conversion of the coke precursor molecules into coke-like products which also cover the hydrogenation sites adjacent to the acid sites. During this whole process a rapid accumulation of coke on the catalyst takes place resulting in a sharp increase in the carbon content, and this constitutes region I. When the most active sites are covered, the formation of other coke molecules becomes very slow and region II begins. In this stage, the increase in coke content is then essentially the result of the increase in the size of the coke molecules. The coke formation and catalyst deactivation rate are in this region much slower. This is partly explained in terms of the difficulty associated with the bimolecular reactions required to increase the size of the coke molecule, since one of the reactants practically cannot move (1). As the number of active acid sites covered by the coke molecules increases very little during this stage, the coke toxicity (activity decrease per gram of coke) is obviously lower than in region I. The above deactivation process is closely related to that proposed by Absil (20) for cumene disproportionation on ultrastable Y zeolites, as discussed elsewhere (13), and to the discussion reported by Guisnet *et al.* (1) regarding the two-stage coke formation on a HY zeolite during *n*-heptane cracking. The very slow decrease in the H/C ratio on the catalyst as a function of time indicates that a transformation of the coke layer to graphitic structures seems unlikely to be the reason, as proposed by Shum *et al.* (24), for the two observed deactivation regimes. Furthermore, a comparison of the H/C ratios of the present study with values reported by Franck and Martino (25) for various hydrocarbons, petroleum cuts, coal liquids, coals, and coke deposits obtained in different processes indicates that the carbon deposits in the piperidine hydrogenolysis work are not highly unsaturated.

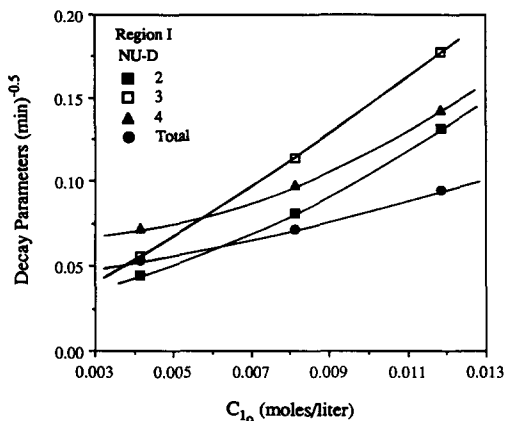


FIG. 5. Decay parameters, a_i , for NU-D as a function of initial concentration of piperidine in region I at 301°C.

Reducing the catalyst instead of sulfiding it had practically no effect on the H/C ratio, the wt% N, and the wt% C (experiments 52 and 77 of Table 1). On the contrary, doubling the initial concentration of piperidine (experiments 52 and 56) resulted in a substantial increase in the final carbon content. This is in agreement with the results of the kinetic study (13), which indicated that in region I of the data the deactivation rates were higher when the initial concentration of piperidine was increased, as illustrated by the increase in the decay parameters for individual species, a_i (Eq. (2)), shown in Fig. 5. After most of the coke has been deposited and region II begins, the kinetic study showed that overall catalyst deactivation was mostly independent of C_{1_0} ($n^* \approx 0$), as also indicated by the rather unchanged values of the decay parameters in this region shown in Fig. 6. Thus, the increase in the piperidine concentration results in deposition of more coke initially, which increases not only the rate of deactivation but also the final coke level.

The reaction temperature was also found to have a considerable effect on the final coke content (experiments 52, 53, and 55; the small differences in catalyst time on stream are not expected to contribute much to any trends, based on the earlier results).

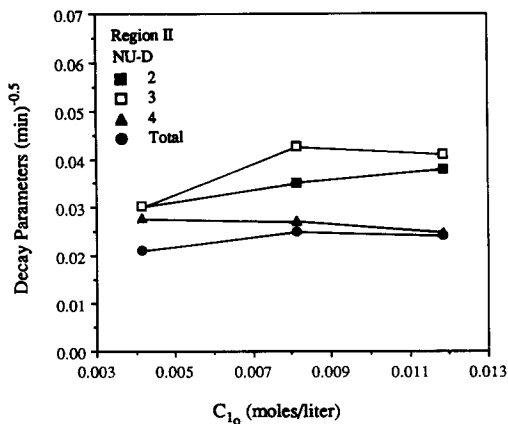


FIG. 6. Decay parameters, a_i , for NU-D as a function of initial concentration of piperidine in region II at 301°C.

Increasing the temperature resulted in more coke as was also reported by others (7). As with the increase in the piperidine initial concentration, the increase in temperature produces more carbon in region I which deposits rapidly on the catalyst, increasing the rate of deactivation as illustrated by the increase in the decay parameters in this region, shown in Fig. 7. In region II, the decay parameters did not show any change or indicative trend within experimental error

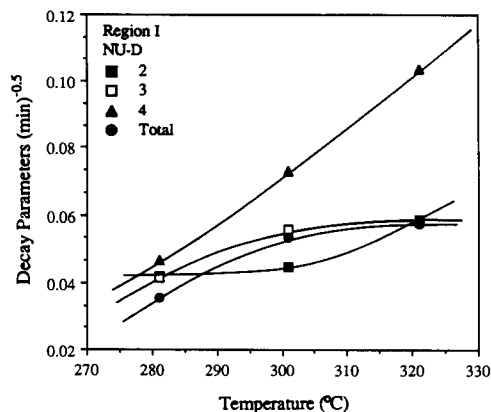


FIG. 7. Decay parameters, a_i , for NU-D as a function of temperature in region I at an initial concentration of piperidine of about 4×10^{-3} g mol/liter.

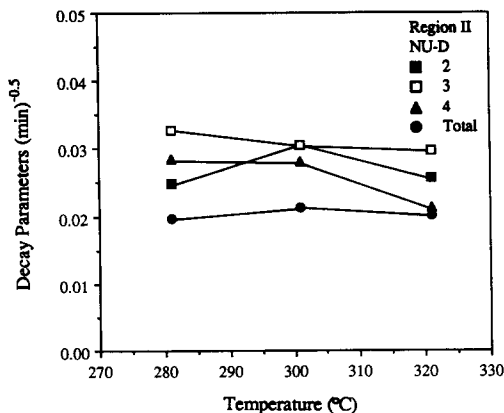


FIG. 8. Decay parameters, a_i , for NU-D as a function of temperature in region II at an initial concentration of piperidine of about 4×10^{-3} g mol/liter.

with increasing temperature (Fig. 8). Again the results here are in agreement with observations on the deactivation kinetics reported previously (12, 13), which showed that the overall deactivation rate in region II was much less activated by temperature than in region I. Interestingly, the wt% N and H/C ratio did not seem to be functions of either the initial concentration of piperidine or temperature.

All these results are consistent with the concept that a nitrogen compound (piperidine or reaction product) is participating in the formation of the coke precursor. Heterocyclic nitrogen compounds have indeed been reported to act as precursors in coke formation. For example, Mills *et al.* (26) investigated the adsorption of quinoline on cracking catalysts and reported that at temperatures of 425°C and above as the adsorption time was extended to several hours the catalyst ($\text{SiO}_2\text{-Al}_2\text{O}_3$) gradually picked up more quinoline. At the same time, the catalyst's color turned black and it was concluded that under the prevailing conditions a slow decomposition of quinoline on the catalyst surface took place, thus forming coke. Therefore, heterocyclic aromatic nitrogen compounds, like their hydrocarbon analogs, can undergo condensation and coupling reactions to form coke (27). This was

also verified by Appleby *et al.* (28) when cracking of the nitrogen bases quinoline and acridine at 500°C and atmospheric pressure over a SiO₂-Al₂O₃ catalyst produced coke as the chief product. The nitrogen contents of the feed and products, including coke, indicated that nitrogen was retained in the ring. Distillation of the quinoline product left a residue which was in good agreement in elemental analysis with biquinoline (28). Furthermore, Furimsky (29) studied the catalytic removal of sulfur, nitrogen, and oxygen from heavy gas oil and reported that oxygen- and nitrogen-containing heterocyclic compounds were more stable than sulfur-containing compounds under catalytic hydrotreatment conditions. It was suggested that the resistance of these compounds to HDO and HDN reactions resulted in their accumulation in the coke deposited on the catalyst surface. This was confirmed by the high content of O and N heteroatoms in the extracts obtained from catalyst pellets used in catalytic treatment of the heavy gas oil feedstock (30).

A possible route to coke formation in the present study is provided by the compound Δ^1 -piperidine (3,4,5,6-tetrahydropyridine), an imine, which is a product in the hydrogenolysis of piperidine (13). This compound does not usually exist as only a monomer, but it forms two trimers that are geometric isomers, called α - and β -tripiperidine, which exist in equilibrium with the monomer (31, 32), as illustrated in Fig. 9. This polymerization reaction is enhanced by strong Brønsted acid sites on the catalyst and the resulting trimer (I) formed on the surface is a plausible coke precursor. An analogous reaction mechanism was proposed by Yang and Satterfield (33) for coke formation during the hydrodenitrogenation of 5,6,7,8-tetrahydroquinoline. In this case, the intermediate undergoing polymerization is 3,4,5,6,7,8,9,10-octahydroquinoline (II), as also shown in Fig. 9. Note that in the present work decahydroquinoline was one of the major products in the reactions; dehydrogenation of the latter could have pro-

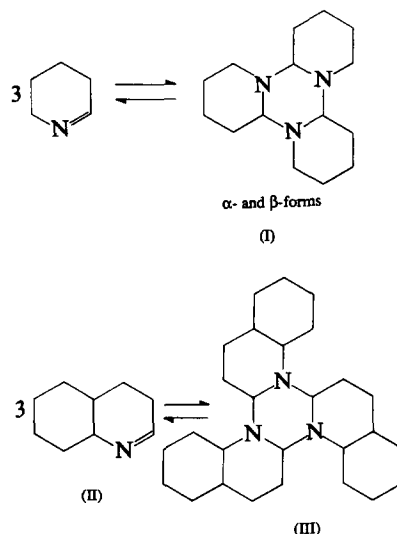


FIG. 9. Formation of coke precursors during the hydrogenolysis of piperidine over the commercial hydrocracking catalyst.

duced compound (II) which upon polymerization yielded the coke precursor trimer (III) (Fig. 9).

Evidence pointing to the above mechanisms as possible routes to coke formation can be obtained as follows. For example, if the dehydrogenation of piperidine to tetrahydropyridine was significantly increased allowing the latter to form in a greater amount than normal, then that would have increased the degree of formation of the trimer (I) hence producing more coke. The results here and those reported by Hadjiloizou (13) clearly indicate that as the reaction temperature and initial concentration of piperidine increased the coke buildup and rate of deactivation also increased. The yield (gram moles of product produced per gram moles of piperidine initially) of products 5 and 6 (tetrahydropyridine and pyridine) as a function of time on stream also showed a marked increase with temperature and initial concentration of piperidine, as shown in Figs. 10 and 11, in agreement with the above discussion and proposals. Therefore, the reactions depicted in Fig. 9 are indeed possible routes to coke formation in the piperidine hydrogenol-

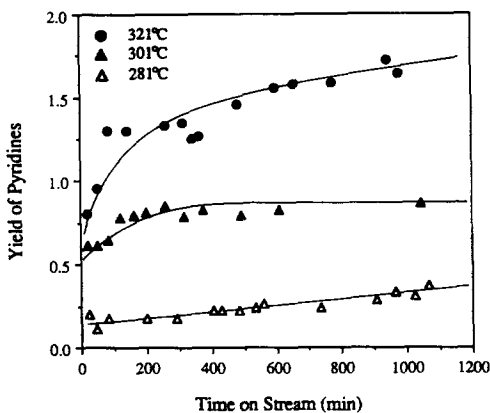


FIG. 10. Yield of pyridines on NU-D as a function of time on stream and temperature at an initial concentration of piperidine of about 4×10^{-3} g mol/liter.

lysis reactions over the commercial hydrocracking catalyst. Hydrogenolysis products such as unsaturated C_5 's, which were also detected (13), can also be participating in the coke formation reactions. Olefins can react to form aromatics; they may also condense with aromatics to form more coke.

In addition, the kinetic experiments showed that tetrahydropyridine is also produced by thermal dehydrogenation of piperidine (12, 13). The thermal conversion increased rapidly especially at temperatures higher than about 320°C . Upon identification of tetrahydropyridine as a possible intermediate toward coke formation the importance of keeping the reaction temperature at or below 321°C in the kinetic study is evident. As was observed during the study, at temperatures higher than 321°C deactivation was indeed very rapid, thus possibly indicating the increased contribution not only of catalytic reactions but also of thermal dehydrogenation toward coke formation. A small fraction of the coke formed in the experiments discussed here could have indeed been the result of thermally produced pyridines.

Activity, Stability, and Selectivity of Reduced versus Sulfided Catalyst

We have previously demonstrated that the piperidine hydrogenolysis reaction ex-

hibits the desired property of bifunctionality. In particular, the formation of products 2 and 3 can be attributed exclusively to the metallic catalyst function while the acidic catalyst function is mainly responsible for the formation of product 4 (12, 13). To examine the activity and stability of the metallic and acidic functions of the fresh hydrocracking catalyst when reduced in H_2 at high temperature, the piperidine hydrogenolysis reaction over a catalyst pretreated according to method II was investigated. The results were analyzed using Eqs. (2) through (5) as outlined above. The reaction and decay parameters for products 2, 3, and 4 are compared with those of the corresponding sulfided catalyst and are tabulated in Table 2. The yield of products 2, 3, and 4 as a function of time on stream for the reduced and sulfided samples are shown in Figs. 12 and 13, respectively.

The data indicate that the metallic function of the reduced catalyst is less active than that of the sulfided sample. This resulted not only in a lower conversion of piperidine to products 2 and 3 but also in higher catalyst deactivation rates. This is evident from the decay parameter of product 2 in region I, as listed in Table 2, and also from the sharp decrease in the initial yield of product 4, as shown in Fig. 12. The

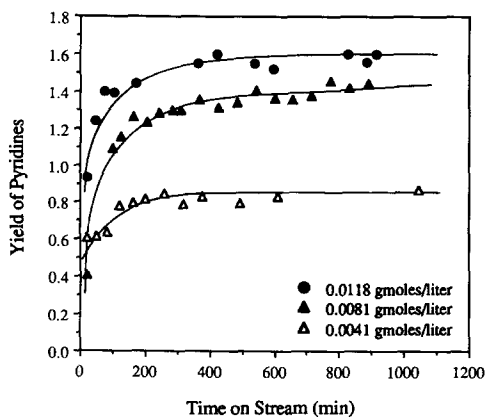


FIG. 11. Yield of pyridines on NU-D as a function of time on stream and initial concentration of piperidine at 301°C .

TABLE 2

The Effect of Catalyst Presulfidation on Piperidine Hydrogenolysis over NU-D

Experiment ^a	52	77
Catalyst pretreatment method	I*	II
Reaction temperature (°C)	301	301
Space velocity × 10 ⁴ (g mol pip/g cat/min)	2.099	2.099
Initial partial pressure of piperidine (atm)	0.195	0.195
Partial pressure of hydrogen (atm)	15.7	15.8

Region I^b

x_{2I}^0	0.208	0.0751
a_{2I}	0.0448	0.0784
x_{3I}^0	0.131	
a_{3I}	0.0560	
x_{4I}^0	0.102	0.0515 ^c
a_{4I}	0.0729	0.0371 ^c
k_{2I}^0	3.32	0.959
k_{3I}^0	2.09	
k_{4I}^0	1.64	0.658 ^c

Region II^b

x_{2II}^0	0.161	0.0378
a_{2II}	0.0305	0.0342
x_{3II}^0	0.0780	0.0031
a_{3II}	0.0305	0.0188
x_{4II}^0	0.0474	0.0347
a_{4II}	0.0280	0.0208
k_{2II}^0	2.12	0.486
k_{3II}^0	1.03	0.041
k_{4II}^0	0.624	0.447

^a See Table 1.

^b a_i in $\text{min}^{-0.5}$, k_i^0 in $\text{liter}^2/\text{g mol/g cat/min}$.

^c Order of magnitude values.

observed higher deactivation rates on the reduced catalyst possessing a weaker metallic function are expected, since one of the roles of the metal sites is to hydrogenate the coke precursors and decrease catalyst deactivation (34). Thus, decreasing the activity of the metallic function increases catalyst deactivation. Furthermore, the longer equilibration period for product 3 and the very fast initial deactivation of the acidic function resulted in difficulties when applying the extrapolation technique to the reduced catalyst in region I for products 3

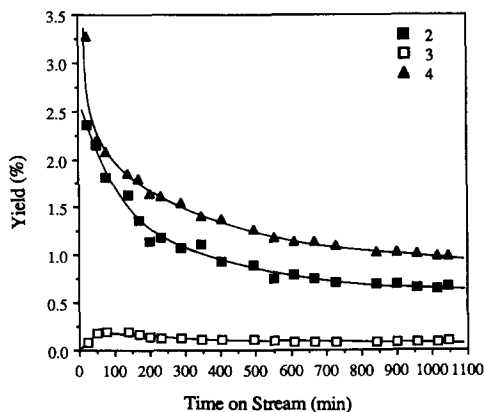


FIG. 12. Yield of *N-n*-pentylpiperidine (2), 2-*n*-pentylpiperidine (3), and decahydroquinolines (4) in the hydrogenolysis of piperidine on reduced NU-D at 301°C as a function of time on stream.

and 4. In particular, extrapolation back to zero time on stream could not be performed for product 3, and the decay parameter calculated for product 4 seems to indicate a lower deactivation rate on the reduced sample than on the sulfided one. However, as shown in Fig. 12, the acidic function of the reduced catalyst deactivated initially very fast and the initial conversion and rate constant to product 4, as listed in Table 2, seem lower than with the sulfided sample because

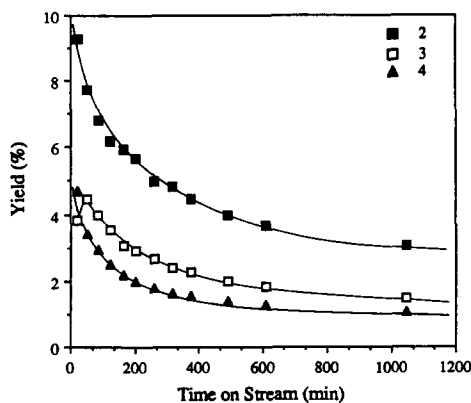


FIG. 13. Yield of *N-n*-pentylpiperidine (2), 2-*n*-pentylpiperidine (3), and decahydroquinolines (4) in the hydrogenolysis of piperidine on sulfided NU-D at 301°C as a function of time on stream.

they only reflect the activity of the acidic function after undergoing an initial drastic deactivation. Contrary to the metallic function, catalyst presulfidation should have little or no effect on the intrinsic activity of the acidic catalyst function under the present conditions, as discussed in detail elsewhere (13).

The picture in region II is similar, although what happens at longer times on stream certainly depends on the catalyst behavior in region I. Overall, prereducing the hydrocracking catalyst resulted in a profound decrease in the activity per se of the metallic function while the intrinsic activity of the acidic function was more or less unaffected, as seen in Table 2. The slight decrease in the initial conversion and rate constant to product 4 on the reduced catalyst in region II is probably the result of the rapid deactivation the acidic function underwent in region I. In region II the catalyst deactivation during formation of products 2, 3, and 4 was much slower than in region I and did not show any dependence on catalyst pretreatment. The decay parameter for product 3 was slightly lower on the reduced sample than on the sulfided one in region II which might reflect the fact that larger errors are associated with the extrapolation technique at such low conversions.

The results discussed previously indicated that the deposition of carbon during catalyst deactivation in the present study takes place to a large extent in the initial period of the experiments, i.e., in region I. This is consistent with the results presented here that show higher deactivation rates in region I than in region II. Furthermore, from the above results we expect that more carbon should have been deposited initially on the reduced catalyst than on the sulfided sample, resulting in a higher final equilibrium coke content. However, the results in Table 1 (experiments 52 and 77) indicate practically no change of final coke content or coke structure with the catalyst pretreatment conditions. Thus, although the reduced catalyst initially deactivates faster

than the sulfided one the coke content on both samples after 17 h on stream is the same. This points to a higher toxicity of coke (activity decrease per gram of coke) on the reduced catalyst.

Higher deactivation rates of reduced versus sulfided catalysts have also been reported elsewhere, as for example in hydrocarbon conversion reactions over reforming PtRe/Al₂O₃ catalysts (35). Furthermore, in hydrotreating, sulfided catalysts are known to have higher activity than the catalysts in oxide form (29). The higher activity of sulfided hydrotreating catalysts is partly attributed to more favorable conditions that might exist for hydrogen transfer on these catalysts. Thus, it is believed that the O²⁻ or, in sulfided form, S²⁻ ions on the catalyst surface participate in the transfer through -OH or -SH groups (36). The transfer must be much faster through the latter because of the significantly lower S-H bond strength as compared to that of the O-H (29).

The Effect of Hydrogen Partial Pressure on the Hydrogenolysis of Piperidine

It is hard to say whether this should have been discussed with respect to the analysis of the reaction kinetic model (12) or with respect to catalyst deactivation, since hydrogen plays such an important role in both. Here we examine a combination of the two.

To examine the effect of the partial pressure of hydrogen (P_{H_2}) on the initial catalyst activity in the hydrogenolysis of piperidine, two experiments were compared. Both were performed under similar conditions except at partial pressures of hydrogen differing by about 4.5 atm. In addition, the experiment at the lower P_{H_2} was terminated at 6 h after initiation, while the other experiment lasted 17 h. The conditions employed for both experiments are listed in Table 3. The yield of products 2, 3, 4, and 5 + 6, as a function of time on stream is shown in Figs. 14 through 16. From the results it can be concluded that lowering the partial pressure of hydrogen resulted not only in an activity decrease of the metallic function but also in higher deac-

TABLE 3

Experiments for the Effect of Hydrogen Partial Pressure on the Hydrogenolysis of Piperidine over NU-D

Experiment	52 ^a	78
Catalyst pretreatment method	I*	I*
Reaction temperature (°C)	301	301
Space velocity $\times 10^4$ (g mol pip/g cat/min)	2.099	2.098
Initial partial pressure of piperidine (atm)	0.195	0.195
Partial pressure of hydrogen (atm)	15.7	11.2

^a See Table 1.

tivation rates for both functions of the hydrocracking catalyst. In fact, the deactivation rates were so fast at the lower hydrogen partial pressure that the extrapolation to zero time on stream technique using Eq. (2) was unreliable. The higher deactivation rates observed when decreasing the P_{H_2} are consistent with the higher yield of pyridines obtained in the latter case (Fig. 16); tetrahydropyridine is identified above as a possible coke precursor.

Absil *et al.* (37) also examined the effect of hydrogen on catalyst deactivation during a cumene disproportionation study over the

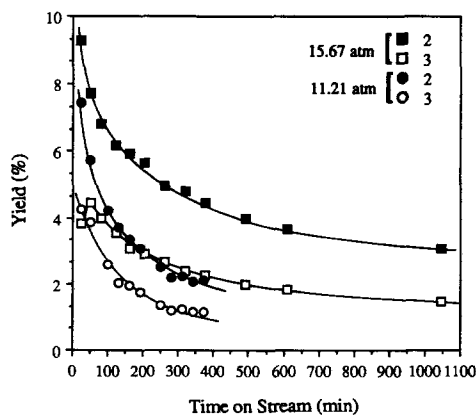


FIG. 14. The effect of hydrogen partial pressure on the metallic function of the sulfided hydrocracking catalyst at 301°C.

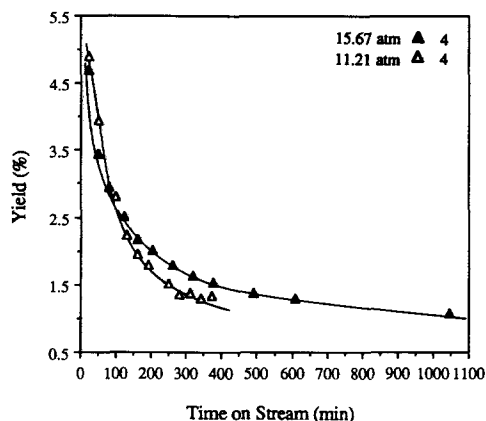


FIG. 15. The effect of hydrogen partial pressure on the acidic function of the sulfided hydrocracking catalyst at 301°C.

commercial cobalt molybdate hydrocracking catalyst. In particular, the catalyst deactivation rate was examined at 185°C as a function of cumene partial pressure and carrier gas (hydrogen versus helium). When hydrogen was used as the carrier gas the rate of catalyst deactivation was reduced over the entire range of cumene partial pressures.

Since the extrapolation technique could not be applied in the present case (for experiment 78), a different procedure was used to calculate and compare the reaction rate

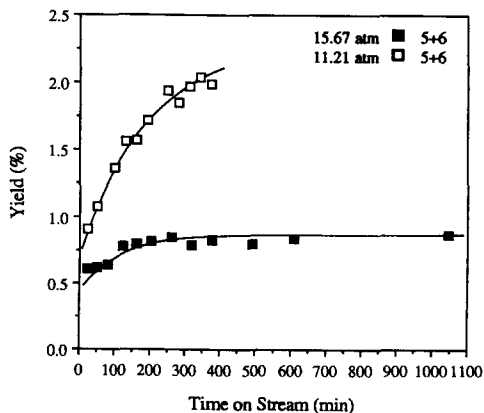


FIG. 16. The effect of hydrogen partial pressure on the yield of pyridines during the hydrogenolysis of piperidine on sulfided NU-D at 301°C.

TABLE 4

The Effect of Hydrogen Partial Pressure on the Metallic and Acidic Functions of Sulfided NU-D^a

Reaction parameter (liter ² /g mol/g cat/min)	Partial pressure of hydrogen (atm)		<i>m'</i> ^b
	15.7	11.2	
<i>k</i> ₂	2.89	2.07	1.0
<i>k</i> ₃	1.68	1.38	0.5
<i>k</i> ₄	1.16	1.28	0
<i>k</i> _{<i>i</i>}	6.51	5.74	~0.4

^a Results at 50.1 min on stream.

^b Dependence of *k_i* on hydrogen partial pressure.

parameters of both experiments. Namely, to avoid the initial equilibration period for product 3, the conversions to products 2, 3, and 4 as well as the total conversion were determined for both experiments at the second data point (50.1 min on stream), and then

$$\frac{WC_{1_0}^2}{F_{1_0}} = \frac{1}{k_i^0 s_i} \left(\frac{x_i}{1 - x_i} \right) \quad (6)$$

derived elsewhere (12), was used to calculate the overall reaction rate constant

$$k_i = \frac{F_{1_0}}{WC_{1_0}^2} \left(\frac{x_i}{1 - x_i} \right) \quad (7)$$

From the overall reaction rate constant and the individual conversion values, reaction rate constants for products 2, 3, and 4 were calculated using an equation similar to Eq. (4) namely,

$$k_i = \frac{x_i}{x_t} k_t \quad (8)$$

The resulting reaction parameters are tabulated in Table 4. Since the experimental reproducibility results indicated average deviation of 14.4% in the parameters listed in Table 4 (13), it can be concluded that under the present conditions the hydrogen partial

pressure has no effect on the intrinsic activity of the acidic function (see *k₃* values in Table 4). Furthermore, using the power law dependence

$$k_i = k_i^0 (P_{H_2})^{m'} \quad (9)$$

for products 2, 3, and for the overall reaction, one obtains the dependencies on hydrogen partial pressure as listed in Table 4. A typical plot of Eq. (9) is shown in Fig. 17 for product 2. The results indicate that the rate of formation of product 2 is first order in hydrogen under the present conditions, in agreement with the reaction mechanism and kinetic correlation for piperidine disproportionation proposed by Hadjiloizou *et al.* (12). The dependence on hydrogen partial pressure of the rate constant for product 3 suggests the participation of one adsorbed hydrogen (from the dissociation of H₂) in the rate-limiting step of the reaction. The 0.4-order dependence of the overall reaction rate constant on hydrogen partial pressure probably reflects the fact that overall conversion lumping includes individual hydrogenolysis, alkylation, cyclization, cracking, hydrogenation, and dehydrogenation reactions, each of which has kinetics that can differ substantially in magnitude. While the above orders are based on only a

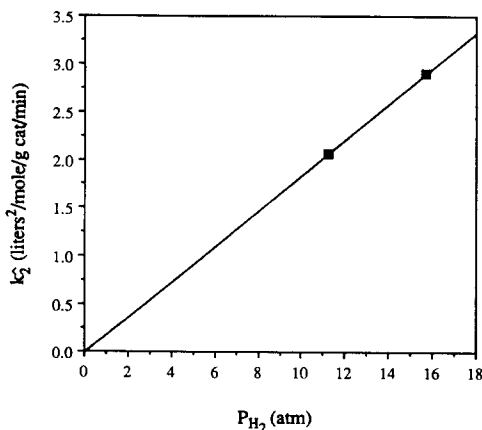


FIG. 17. Plot of *k*₂ versus *P*_{H₂} for sulfided NU-D; data at 50.1 min on stream and 301°C.

two-point correlation, they are reasonable values and can be used in the absence of a more extensive data base. However, the above-mentioned procedure used to compare the reaction rate constants from the two different experiments should be regarded with caution, since the comparison was made not at zero time on stream but at a point in time where the two catalysts could have undergone different changes in activity.

CONCLUSIONS

(i) The results on the formation of coke during the hydrogenolysis of piperidine and the proposed nature of the coke precursors are in agreement not only with the literature but also with the data obtained in the kinetic study over the fresh hydrocracking catalyst.

(ii) Most of the coke on the catalysts initially increases very rapidly with time on stream, then much more slowly. Coke formation is found to increase with both reaction temperature and initial concentration of piperidine.

(iii) In agreement with the known role of heterocyclic nitrogen compounds as being significant coke precursors, experimental evidence here indicates that nitrogen-containing compounds are participating in the formation of coke during the reactions. However, it still seems that correlations related to carbon (coke) content are reliable in estimation of catalyst activity, regardless of the coke precursor.

(iv) Under the conditions employed in these experiments, there is no significant conversion of initial coke to more graphitic structures, even after relatively long times on stream.

(v) Catalyst presulfidation increases the activity of the metallic catalyst function and decreases catalyst deactivation in the piperidine hydrogenolysis reaction.

(vi) Increasing the partial pressure of hydrogen has a positive effect on the activity of the metallic function and on the overall catalyst activity maintenance.

APPENDIX: NOMENCLATURE

a_i	Decay parameter for the formation of product i , $\text{min}^{-0.5}$.
a_{iI}, a_{iII}	Decay parameter for the formation of product i in region I and II, respectively, $\text{min}^{-0.5}$.
C_c	Weight percent carbon on catalyst.
C_{1_0}	Initial concentration of piperidine, g mol/liter.
F_{1_0}	Reactor inlet molar flow rate of piperidine, g mol/min.
G	Empirical constant in Voorhies equation.
i	Index.
k_d	Rate constant of overall deactivation reaction, liter/g mol/min or min^{-1} .
k_i, k'_i	Rate constants of formation of product i , as used in Eqs. (8) and (9).
k_i^0	Initial reaction rate constant of formation of product i , liter ² /g mol/g cat/min.
k_{iI}^0, k_{iII}^0	Initial reaction rate constant of formation of product i in region I and II, respectively, liter ² /g mol/g cat/min.
k_i	Rate constant of overall reaction, as used in Eqs. (7) and (8).
k_i^0	Initial rate constant of overall reaction, liter ² /g mol/g cat/min.
k_{iI}^0, k_{iII}^0	Initial rate constant of overall reaction in region I and II, respectively, liter ² /g mol/g cat/min.
m'	Order of reaction with respect to hydrogen.
n^*	Order of concentration dependency of deactivation.
P_{H_2}	Partial pressure of hydrogen, atm.
pip	Piperidine.
Q	Ratio of saturated to unsaturated carbon on catalyst, as determined by ¹³ C NMR.
s_t	Activity of catalyst at time on stream t for overall reaction.
t	Time on stream, min.
t_c	Catalyst time on stream.
W	Weight of catalyst, g.

- $x_i, x_i(t)$ Conversion of piperidine to product i at time on stream t , g mol of piperidine reacted to i /g mol of piperidine initially.
- $x_i(0)$ Initial conversion of piperidine to product i .
- x_{iI}^0, x_{iII}^0 Initial conversion of piperidine to product i in region I and II, respectively.
- x_t Total conversion of piperidine at time on stream t .
- x_{tI}^0, x_{tII}^0 Initial total conversion of piperidine in region I and II, respectively.

Greek Symbols

- ν Empirical constant in Voorhies equation.
- τ Space time = WC_{10}^2/F_{10} , g mol · g cat · min/liter².

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