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Catalytic Removal of Sulfur, Nitrogen, and Oxygen from Heavy Gas Oil

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Removal of sulfur, nitrogen, and oxygen from heavy gas oils is affected by the chemical composition of supported molybdate catalysts. Cobalt and nickel, when added to these catalysts, have a promoting effect on these reactions. However, the relative rates always follow the same trend; that is, the hydrodesulfurization is the fastest, followed by hydrodenitrogenation and hydrodeoxygenation.

SCOPE

Sulfur, nitrogen, and oxygen are present in various compounds in petroleum fractions. During catalytic hydrotreatments, the elements are removed simultaneously as hydrogen sulfide, ammonia, and water. Sulfur must be removed from products to avoid corrosion and to meet environmental requirements. Some nitrogen containing compounds may have a harmful effect on the properties of the products. Nitrogen bases are also effective poisons of the catalyst surface. Certain oxygen containing compounds are acidic, and their presence, especially in commercial petroleum products, is unwelcome.

To accomplish a high degree of refining, an active catalyst must be used. Supported molybdate catalysts, promoted by either cobalt or nickel, are the most frequently used. The hydrogen sulfide, ammonia, and water produced modify the catalyst surface. While hydrogen sulfide is responsible for sulfiding, ammonia, and to some extent also water, poisons the surface. The extent of these effects depends on the amount of the elments in feedstocks and on the relative rates of their removals. The rates might be dependent on relative stabilities of S, N, and O containing compounds present in the feed. The reactions occur on the catalyst surface, and as such they are not well understood. In the present study, these effects were compared under conditions similar to those encountered in industrial operations.

CONCLUSIONS AND SIGNIFICANCE

Relative rates of S, N, and O removal from a heavy gas oil are in qualitative agreement with the C-S, C-N, and C-O bond strengths; thus, the rate of hydrodesulfurization (HDS) is highest, followed by hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO). The comparison is based on heterocyclic compounds; that is, the O containing species which may be products of reactions between air and the feed are not included. These observations are supported by a number of mechanistic surface phenomena and other thermochemical considerations.

The presence of carbonaceous deposits on the catalyst surface had little effect on these trends. N and O accumulate in the deposits because N and O containing heterocyclic compounds resist the catalytic reactions. De-

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velopment of a catalyst possessing high activity for N and O removals may be the way to control deposit levels. The activity of molybdate catalysts used was affected by their chemical composition; however, the relative rates always maintain the same trend; that is, the HDS is the fastest, followed by HDN and HDO.

HDS, HDN, and HDO reactions usually occur during catalytic hydrotreatment of petroleum fractions. In scientific literature, these reactions are usually treated separately. Most attention has been paid to HDS because of the harmful effect of sulfur if present in products. HDS reactions have been reviewed several times, most recently by Schuit and Gates (1973).

The importance of HDN has been recognized in connection with poisoning of the catalyst surface by basic nitrogen compounds, thus slowing down some catalytic reactions, for example, HDS. Also, the stability of liquid products is affected by the presence of some nitrogen compounds because of the high rate of their autoxidation. Since it was observed that HDN reactions are beneficially affected by simultaneous HDS (Goudrian et al., 1973), some researchers have investigated HDN in relation to HDS. The most important information is that published by Satterfield and co-workers (1975).

There is a lack of information dealing with HDO. Removal of O during catalytic hydrotreatments is frequently assumed to be fast and complete. Recent results, however, indicate that some O containing compounds are very resistant to hydrogenolytic reactions (Rollmann, 1977), and complete HDO is not accomplished under conditions encountered in catalytic hydrotreatment operations (Furimsky, 1978). No work has appeared to date which deals thoroughly with HDO in relation to HDS and HDN.

Much of the information on HDS, HDN, and HDO available in the literature originates from model compounds studies. The experimental conditions applied in such studies are often different than those encountered in industrial operations, in which coke and metals deposit on the catalyst, greatly changing the active surface. Most of the coke is deposited during the initial period on stream (Oader and Duraiswamy, 1974). An operating catalyst is therefore covered by coke. Despite this, the catalyst maintains high activity during a long period of time. It is of practical importance that the relative rates of HDS, HDN, and HDO of the feed, where they occur simultaneously, are compared under such conditions.

Metals, particularly vanadium and nickel, are known offenders of catalyst surface. When present in the feed, they deposit on the surface and modify catalyst properties resulting in high hydrogen consumption. This would indicate that the metals deactivate HDS, HDN, and HDO rather than hydrogenation sites unless nickel promotes hydrogenation, a phenomenon which is not unusual for some nickel forms. Catalyst consumption during desulfurizing of residua also depends on the metals content and is high when the content is high (Nelson, 1976). In order to avoid these complications, the feedstock used in the present work contained no metals. Then, any differences caused by modified surface may be attributed to the presence of coke.

TABLE 1. PROPERTIES OF THE FEEDSTOCK

Boiling range	°C	345-525
Pitch (+524°C)	wt %	Nil
Pentane insolubles	wt %	0.3
Sulfur	wt %	3.69
Nitrogen	wt %	0.39
Oxygen	wt %	0.44
Ni + V	ppm	Nil

EXPERIMENTAL

The feedstock used in this study was prepared by thermally hydrocracking Athabasca bitumen obtained from Great Canadian Oil Sands, Limited, at Fort McMurray, Alberta. The 345° to 525°C heavy gas oil fraction of the hydrocracked product was used. Properties of the feedstock are listed in Table 1.

The hydrotreating experiments were performed in a bench scale fixed-bed reactor having a volume of 155 cm^3 and a length to diameter ratio of 12. The reactor was filled sequentially from the bottom with 42 cm^3 berl saddles, 100 cm^3 catalyst pellets, and 13 cm^3 berl saddles. The mixture of hydrogen and heavy gas oil flowed continuously into the bottom of the reactor and up through the catalyst bed. Each experiment was performed at a pressure of 1.39 MPa (2 000 lb/in.^{2}), a liquid hourly space velocity of 2 h^{-1}, and temperature of 400°C. The

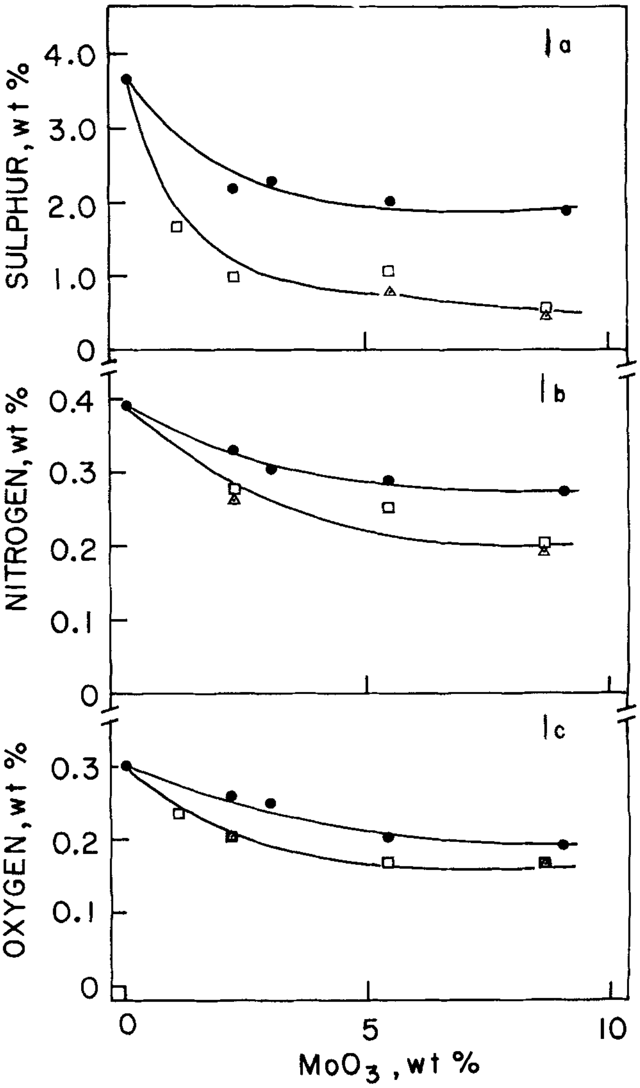

Fig. 1. Amount of sulphur, nitrogen and oxygen in products versus the concentration of MoO_3 in promoted (atomic Me/Mo ratio = 1.0; Me = Co or Ni) and unpromoted molybdate catalysts. ● = unpromoted; ☐ = Ni promoted; △ = Co promoted catalysts

Table 2. Relative Removal of S, N, and O from Heavy Gas Oil Over Unpromoted and Promoted Molybdate Catalysts

Active ingredients, wt %			S in products, wt %	Relative amounts in products			Relative amounts removed		
MoO_3	CoO	NiO		S/N	S/O	N/O	S/N	S/O	N/O
0	0	0	3.70	4.1	6.1	1.5	—	—	—
2.2	—	—	2.29	3.0	4.2	1.5	8.2	18.8	1.7
3.0	—	—	2.30	3.3	4.6	1.4	7.1	14.1	2.0
5.4	—	—	2.09	3.1	5.0	1.6	7.8	9.0	1.1
9.0	—	—	1.89	3.0	5.0	1.7	6.9	8.2	1.2
8.6	4.4	—	0.50	1.1	1.5	1.3	7.2	12.3	1.7
5.4	2.1	—	0.88	1.4	2.7	1.9	9.1	9.6	1.1
2.2	1.1	—	0.78	1.2	1.8	1.5	10.0	14.8	1.5
8.6	—	4.4	0.60	1.3	1.8	1.4	7.0	12.0	1.7
5.4	—	2.8	1.01	1.9	3.2	1.7	8.0	10.0	1.3
5.4	—	0.84	1.57	2.6	4.6	1.8	7.4	8.2	1.1
2.2	—	1.14	0.94	1.5	2.4	1.6	10.3	13.8	1.3

liquid products were collected after 36 Ks on stream and analyzed for S, N, and O.

The experimental catalysts were prepared by the impregnation of the support material with aqueous solutions of the appropriate metal salts. The detailed description of the methods and equipment used to make the catalysts has been published previously (Parsons and Ternan, 1977).

RESULTS AND DISCUSSION

The results on HDS, HDN, and HDO of the gas oil, obtained over a series of unpromoted molybdate catalysts, are shown in Figures 1*a*, *b*, and *c*, respectively. Over the pure alumina support (in Figure 1, the catalyst with 0 wt% molybdenum trioxide) almost no removal of S and N was observed. On the other hand, a rather large amount of O was removed (from 0.44 wt% in the feed to 0.30 wt% in the product). This contradicts some evidence supporting high stability of O containing heterocyclic compounds (Rollmann, 1977). The O removed must therefore originate from unstable, O containing compounds (alcohols, peroxides, ketones, aldehydes, etc.). Such compounds are products of autoxidation, that is, the reaction of oxygen with hydrocarbons (Howard, 1972) occurring while the feed is stored in contact with air. The products of autoxidation can hardly survive the conditions applied (high temperature and hydrogen pressure) even in the absence of catalyst. It is then apparent that HDS, HDN, and HDO cannot be compared on the basis of S, N, and O contents before and after hydrotreatment without paying special attention to the compounds involved. Ignoring this fact may lead to the erroneous conclusion that removal of O is faster than that of S and N. A starting point in the comparison of the relative rates of HDS, HDN, and HDO should be the concentrations of S, N, and O in the products obtained over a pure alumina support rather than in the feedstock (in Table 2 for catalyst with 0 wt% of active ingredients).

Quantitative results on relative rates of HDS, HDN, and HDO are summarized in Table 2. Calculations were based on the concentrations of S, N, and O in products, such as those shown in Figure 1. The amounts of these elements removed from the feed were determined as the difference between their concentrations in products and in the product obtained over pure alumina support. The relative amounts in Table 2 are the ratios of molar concentrations, assuming only one heteroatom per molecule. The concentrations of sulfur in products used for the calculations are summarized in the fourth column. Corresponding amounts of N and O are not included but can be easily back calculated. The actual values of relative rates of HDS, HDN, and HDO are those in the last three columns.

Results in Table 2 show large scatter when related to the concentrations of molybdenum trioxide. However, the addition of small amounts of molybdenum trioxide to the support results in a marked increase in S removal relative to that of N and O. At the same time, the HDO is least affected. With further increase in molybdenum trioxide concentration, HDO and HDN compete more successfully with HDS. This might be caused by more effective poisoning of HDS sites by basic nitrogen compounds which represent an important part of total nitrogen in the feed and the product (Furimsky et al., 1978). The increase in molybdenum trioxide concentration results in increased surface acidity (Parsons and Ternan, 1977). This favors interaction between basic compounds and acidic sites.

Several cobalt and nickel promoted catalysts are included in Table 2 as well. These values show large scatter and are inconclusive as to the relative promoting effects of cobalt and nickel. However, the order of S, N, and O removal is the same as with molybdenum trioxide alone, indicating that the rate of HDS is greater than that of HDN and HDO. The HDN is higher than the HDO for all the catalysts, although the difference is less pronounced than the difference between HDS and HDN.

The results in Table 2 confirm the high stability of O and N containing heterocyclic compounds under conditions of the catalytic hydrotreatment. The resistance of these compounds to HDO and HDN might result in their accumulation in the coke deposited on the catalyst surface. This was confirmed by the chemical composition of extracts obtained from catalyst pellets used in catalytic hydrotreatment of the heavy gas-oil feedstock. As the results in Table 3 show, the relative increase of O and N

Table 3. Chemical Analyses of Extracts Obtained by Successive Extractions of Used Catalyst Pellets

Solvent	Amount extracted, wt %	Content, wt % C	H	O	N	S
Pentane	16.7	86.8	10.32	0.40	0.23	2.5
Benzene	2.9	83.3	7.9	2.9	1.70	4.4
Benzene and methyl alcohol	2.8	75.3	7.8	5.4	2.45	8.4
Pyridine	1.0	74.6	6.5	5.3	5.0	6.6

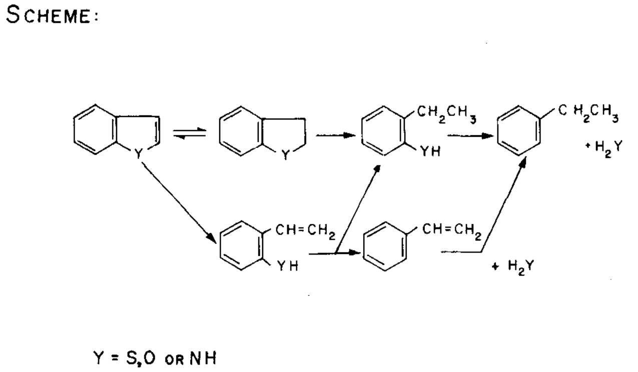

Fig. 2. Approximate reaction network for the removal of S, N and O from five membered heterorings in the presence of catalyst and hydrogen.

in all extracts, with the exception of that obtained by pentane extraction, was significantly larger than that of S. The material extracted by pentane probably corresponds to the feed and products left on the surface. The other extracts are heavier and result from downgrading of the feed on the catalyst surface. This indicates that the polar O and N containing compounds are strongly adsorbed on the surface, and while resisting HDO and HDN reactions, they are converted to larger molecules which accumulate in coke.

It is of interest to see how the present experimental results agree with expectations followed from information obtained on clean catalyst surface. Valuable information, particularly on the mechanistic aspects, is available in model compounds studies published in scientific literature. A number of other factors affect the relative rates of HDS, HDN, and HDO. For example, the presence of hydrogen suggests that some comparison can be made on the basis of thermochemical considerations using hydrogen and the S, N, and O containing compounds systems. Known surface phenomena and the influence of variations in the catalyst composition on the relative rates of HDS, HDN, and HDO are important as well.

THERMOCHEMICAL AND MECHANISTIC CONSIDERATIONS

Removal of S, N, and O from petroleum fractions, under reducing conditions and in the presence of industrial catalyst, is associated with elimination of hydrogen sulfide, ammonia, and water. Before this can occur, C—X (X = O, N or S) bonds must be broken, and the fission of one of these bonds may determine the rate. This suggests that the strength of the bonds may be some measure of the relative rates of HDS, HDN, and HDO. In aliphatic compounds such as alcohols, ether, mercaptans, sulfides, and amines, the strength of the bonds increases in the direction C—S → C—N and → C—O (Cottrell, 1958), indicating that the rate of O removal would be lowest and the rate of S removal highest. Other compounds, such as ketones, aldehydes, and amides, can be reduced and carboxylic acids decarboxylated. These compounds are all unstable and will hardly survive the conditions of thermal or catalytic hydrotreatments. On the other hand, heterocyclic S, N, and O containing rings are known for their high stability. Such compounds represent a substantial part of the heteroatoms containing species of the feed. The basic routes for HDS, HDN, and HDO of such molecules are shown in Figure 2.

The simplified scheme suggests that the ring opening is essential before any removal of heteroatom can take place. This might occur either with or without preliminary heteroring hydrogenation. Ring saturation is important for N containing compounds (Satterfield and Cocchetto, 1975), while there is some experimental evidence that for the HDS both routes are possible (Furimsky and Amberg, 1976). Rollmann (1977) assumed that ring saturation is necessary also for furan compounds. Some support for this can be found in the case with which furan can be converted to tetrahydrofuran (Nosovskii et al., 1973). The difference in mechanisms is associated with the different amounts of hydrogen required for reactions to occur. The role of hydrogen as a reactant is often ignored in discussions. In order to open the quinoline heteroring, for example, three moles are needed, while two moles of hydrogen are needed for indol and benzofuran when preliminary ring saturation is considered. Without preliminary hydrogenation, as in the case of benzothiophene, one mole of hydrogen is sufficient to open the heteroring. This indicates that when the availability of hydrogen is becoming critical, the HDN might be affected to the greatest extent. It was confirmed by Nelson (1977) that much more hydrogen is required for HDN than for HDS.

The hydrogenation of the heteroring (step 1 in the above equation) is an equilibrium process. This was experimentally observed for benzothiophene (Givens and Venuto, 1970) and also for pyridine compounds (Satterfield and Cocchetto, 1975). The effect of temperature on the equilibrium is shown in Figure 3, where log K is plotted against the reciprocal of the absolute temperature. Because of the lack of thermodynamic information, only monoring heterocyclic compounds can be compared. It is assumed that for multiring compounds, similar trends will be maintained. These results indicate the equilibrium

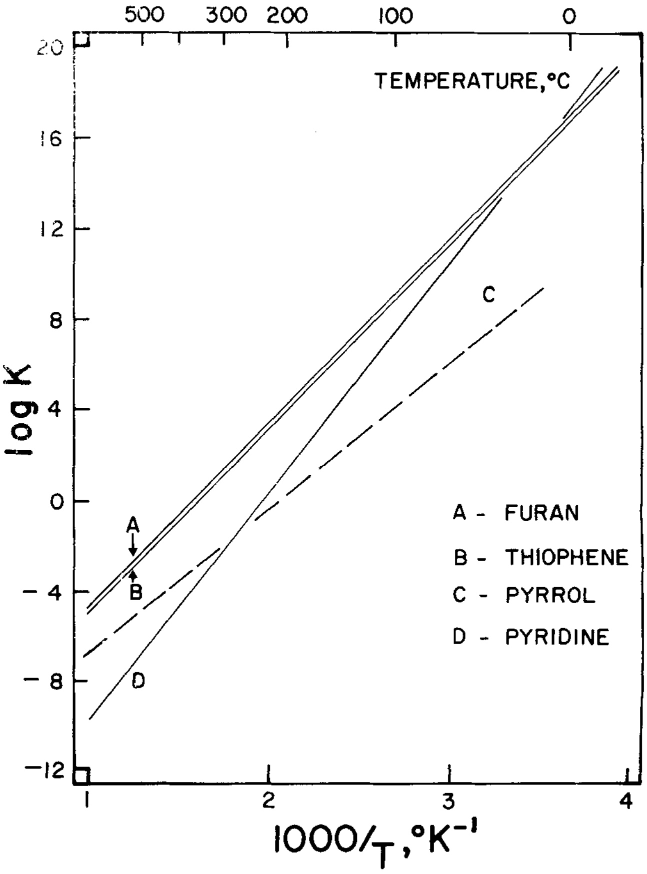

Fig. 3. Thermodynamic equilibria of furan, thiophene, pyrrol and pyridine with their hydrogenated derivatives.

limitations are greatest for the nitrogen compounds. For example, at 400°C, the equilibrium constant for pyridine is about four orders of magnitude smaller, while that of pyrrole is three orders smaller than those of thiophene and furan which are about equal. An increase of temperature results in a decrease of the constants, and the situation becomes less favorable for the heterorings saturation. It is then clear that under the limitation conditions the removal of N from the compounds will be slower compared with that of S and O.

The main factor affecting the equilibrium in step 1 in the above equation is the concentration of hydrogen. If sufficient hydrogen pressure is maintained, complications due to the limitations can be avoided. As confirmed by Shih et al. (1977), the HDN rate levels off at pressures over 10.34 MPa (1 500 lb/in.^{2}). In view of the results in Figure 2, the rates of HDS and HDO should be well off the region of limitations. This is why industrial catalytic hydrotreatment operations are performed under high hydrogen pressure. It is now assumed that experimental results presented in this work were obtained under conditions free of these limitations. This is confirmed, for example, by improved HDN with increase of temperature (Furimsky et al., 1977). If the limitations were still in effect, the opposite should be observed. This is supported by the observation made by Goudrian et al. (1973), who found that over sulfided cobalt molybdate catalyst at 400°C, more than 90% of pyridine HDN was achieved already at 7.71 MPA pressure of hydrogen, that is, a pressure much lower than 13.8 MPa (2 000 lb/in.^{2}), applied in the present work. The relative rates of HDS, HDN, and HDO can thus be assumed to be given by the rates of C—X bonds hydrogenolysis of saturated heterorings. If the reaction is controlled by the C—X bond strength, the HDS should be the fastest, followed by HDN and HDO.

Intermediates obtained after the first step should behave similarly to alkyl aryl ethers, sulfides, and amines. Then the two C—X bonds in the intermediates have different strengths. The bond between the heteroatom and aromatic structure is stronger. Consequently, the hydrogenolysis of the saturated heteroring will occur predominantly through the weaker C—X bond, resulting in formation of alkylphenols, -anilines, and -thiophenols. In the compounds, the C—X bond strength decreases in the same direction, suggesting that the thiophenols will be least resistant and phenols most resistant to hydrogenolysis.

For larger molecules such as dibenzothiophene, dibenzofuran, and carbazol types, the ring is opened through the C—X bond scission either directly (Houalla et al., 1977) or after the latter is weakened by saturation of the attached aromatic ring (Qader et al., 1968). The relative rates of ring opening then would increase from O through N to S containing heterorings (Cottrell, 1958). After the heteroring opens, removal of S, N, and O is again governed by the stability of orthosubstituents of thiopenol, aniline, and phenol. The thiocompounds are unstable, and it is highly unlikely that they can survive the conditions applied in catalytic hydrotreatments of heavy oils. On the other hand, corresponding orthophenols and -anilines are stable, as shown by Rollmann (1977) and Shih et al. (1977), respectively. This suggests that such compounds might concentrate in the products. Additional information on the behavior of phenols and anilines under conditions of catalytic hydrotreatment would then be of great value.

SURFACE PHENOMENA

In the presence of a catalyst, many other factors besides those mentioned above must be considered when the removals of S, N, and O are compared. Because reactions occur on the catalyst surface, the difference in the adsorption of reactants and products may be decisive. Smith et al. (1973) concluded from deuterium exchange studies that the pyridine type of compounds have a tendency to undergo flat adsorption on the surface. This is supported by the ability of the compounds to form Π complexes with molybdenum. In the case of furan and thiophene compounds, this trend is diminished because of the withdrawal of Π electrons from the heteroring because of the electronegative nature of S and O heteroatoms. The flat adsorption results in the coverage of a larger part of the surface and presumably the blocking of HDS and HDO active sites. These authors also concluded, in agreement with Lipsch and Schuit (1969), that the sulfur and oxygen heterorings will be adsorbed on the surface via heteroatoms. This fact seems to be important when multiring compounds, such as dibenzothiophene and dibenzofuran, are concerned. Here the adsorption will be more favorable for the sulfur compounds because the S heteroatom is larger than that of O; that is, the adsorption of the latter might be sterically hindered by attached aromatic rings.

In order to renew catalytic sites, the rate of products desorption must be considered. It is expected that there is little difference in the desorption of hydrocarbons irrespective of the heterocyclic compounds from which they were generated. For example, the same hydrocarbon may be formed from carbazol, dibenzofuran, or dibenzothiophene. On the other hand, ammonia will be strongly adsorbed on acidic sites, delaying their regeneration. Lipsch and Schuit (1969) observed strong adsorption of water on the surface of cobalt molybdenum catalysts supported on alumina, resulting in poisoning of HDS of thiophene and hydrogenation of butenes. This suggests that water is adsorbed on sites where these reactions take place. The effect of water on HDN and HDO is unknown. An interaction of hydrogen sulfide with the catalyst surface will be discussed in more detail later.

It is evident that a catalytic reaction will occur after the contact between the surface and the reactant molecule has been made. This indicates that relative concentrations of compounds may have an effect on HDS, HDN, and HDO. The heavy gas oil chosen for the present comparison is a special feed; that is, the relative mole ratio of S, N, and O is approximately 4:1:1, assuming one heteroatom per molecule. The amount of hydrogen sulfide produced should therefore be significantly larger than that of ammonia and water. Then the hydrogen sulfide produced will have a pronounced effect on a modification of the surface, as confirmed by Goudrian et al. (1973). Satterfield et al. (1975) reported that hydrogen sulfide formed in HDS of the thiophene had a beneficial effect on the simultaneous HDN of pyridine. Information regarding a similar effect on HDO is not available.

Sulfided catalysts are known to have higher activity than the catalysts in oxidic form. To explain this observation, only speculations can be made. At first, more favorable conditions might exist for hydrogen transfer on the sulfided catalyst. It is believed that the O^{-2} or, in sulfided form, S^{-2}, ions on the catalyst surface participate in the transfer through —OH or —SH groups (Schuit and Gates, 1973). 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. Also, the replacement of O by S results in an increase of distance between the surface and molybdenum ions. This may decrease the interaction of Π electrons from the N heterorings with molybdenum if the complexation mentioned above is in effect. Then less favorable conditions are created for surface poisoning by nitrogen bases.

EFFECT OF CATALYST COMPOSITION

It is expected that relative rates of HDS, HDN, and HDO may be affected by catalyst structure, as indicated by different activities of catalysts having the same chemical composition. This suggests that the selectivity and activity of catalysts can be controlled to some extent during preparation. In the case of supported catalysts, the nature of the support, the way of layering the active ingredients, the temperature of drying and calcining, the rate of cooling, preconditioning, etc., may have pronounced effecs on the final properties of catalysts.

As far as catalysts with different chemical composition are concerned, the supported cobalt and nickel molybdate types are of main interest. It is usually believed that nickel has a promoting effect on HDN, while cobalt has a similar effect on HDS. However, most published results were obtained under low hydrogen pressures where the limitations mentioned previously were still in effect. To obtain a true comparison, conditions must be applied which are similar to those encountered in industrial operations. It is also essential that activity be determined after catalysts reach steady state. During the initial period on stream, catalyst activity changes rapidly, and any comparison at this stage is rather meaningless. Also, during catalyst preparation, a procedure must be applied which ensures that the same concentrations of active ingredients are present on the support. It is known that at high concentrations of active ingredients on the support, nickel has a tendency to diffuse faster to the support than cobalt during tempering operations (Gates et al., 1978). When all these precautions were taken, an insignificant difference in promoting effects of nickel and cobalt was observed in HDN (Furimsky et al., 1977) and HDO (Furimsky, 1978) of the heavy gas oil.

In conclusion, the present experimental results are in qualitative agreement with a number of facts followed from surface phenomena, mechanistic, and thermochemical considerations. The effect of coke on relative rates of HDS, HDN, and HDO is therefore not a major one. The coke layer on the catalyst surface does not have to be harmful assuming that it is either in a porous form or has a large number of fissures. In either case, reactant molecules can reach and contact an active surface. The activity of catalysts covered by coke is explained also by the ability of active ingredients from cobalt-molybdate catalysts to penetrate into the coke layer and serve as active sites (Stanulonis et al., 1976). It is believed that two coke forms, reactive and unreactive, exist on the catalyst surface. The former is assumed to be an intermediate form which is slowly hydrogenated to liquid products (Ternan et al., 1978), resulting in reactivation of catalytic sites.

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