CATALYTIC REMOVAL OF SULPHUR, NITROGEN AND OXYGEN
FROM HEAVY GAS-OILS

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SCOPE

Sulphur, nitrogen and oxygen are present in petroleum fractions in the form of various compounds. From the environmental and corrosion points of view, the presence of sulphur is of main concern. Nitrogen-containing compounds may have a harmful effect on the properties of the products. In addition to this, nitrogen bases are effective poisons of the catalyst surface. A number of oxygen-containing compounds are acidic in nature and their presence, especially in commercial petroleum products, is unwelcome.

An important step towards refined products is a catalytic hydro-treatment where these elements are removed simultaneously as H_2S, NH_3 and H_2O. To accomplish a high degree of refining an active catalyst must be used. Supported molybdate catalyst, promoted by either Co or Ni is generally used. Many reactions occurring on the catalyst surface are not well understood. Information concerning relative rates of S, N and O removal is incomplete as well.

CONCLUSIONS AND SIGNIFICANCE

Relative rates of S, N and O removals from a heavy gas oil are in qualitative agreement with the C-S, C-N and C-O bond strengths; thus the rate of desulphurization is highest, followed by denitrogenation and deoxygenation. The comparison is based on heterocyclic compounds; i.e., the O-containing species which may be products of reactions between air and the feed are not included. The resistance of N- and O-containing heterocyclic compounds to

the catalytic reactions might be an explanation for a high accumulation of N and O in carbonaceous deposits, as compared to S.

The activity of molybdate catalysts used, as well as relative rates of S, N and O removals, vary with the chemical composition of the catalysts. However, the relative rates always maintain the same trend; i.e., the desulphurization is the fastest, followed by denitrogenation and deoxygenation.

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Desulphurization (DS), denitrogenation (DN) and deoxygenation (DO) reactions usually occur during catalytic hydrotreatment of petroleum fractions. The majority of publications appearing in scientific literature treat these reactions separately. Most attention has been paid to DS because of the harmful effect of sulphur if present in products. DS reactions have been reviewed several times, most recently by Schuit and Gates (1973).

The importance of DN has been recognized in connection with poisoning of the catalyst surface by basic nitrogen compounds resulting in slowing down some catalytic reactions, for example, DS. Also the stability of liquid products is affected by the presence of some nitrogen compounds because of the high rate of their autoxidation. DN reactions are beneficially affected by simultaneous DS. Since this has been observed (Goudrian et al., 1973), some papers have appeared which investigate DN in relation to DS. The most important information is that published by Satterfield and his co-workers (1975).

There is a lack of information dealing with DO. Frequently, the assumption is made that removal of O during catalytic hydrotreatments is fast and complete. Recent results (Rollmann, 1977), however, indicate that

some 0-containing compounds are very resistant to hydrogenolytic reactions and complete DO is not accomplished under conditions encountered in catalytic hydrotreatment operations (Furimsky, 1978). No work has appeared so far which deals thoroughly with DO in relation to DS and DN.

The present survey is primarily concerned with a comparison of the relative rates of DS, DN and DO in feeds where they occur simultaneously. It starts with an attempt to understand their relative rates from consideration as to relative bond strengths of C-S, C-N and C-O. Since it is now known that the reaction networks for C-S and C-N fission are different it becomes necessary to take this into consideration examining the thermochemical aspects of the different pathways.

After a short discussion to illustrate the differences with catalysts in actual operation and in model studies, in particular the influence of coke formation, experimental results on the catalytic hydrotreatment of heavy gas-oil are discussed. The feed is essentially free of heavy metals so that the effects of coke formation can be shown more explicitly. The influence of variations in the catalyst composition on the relative rates of DS, DN and DO is discussed 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 H_2S, NH_3 and H_2O. 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 DS, DN and DO. In aliphatic compounds such as alcohols, ethers, mercaptans, sulphides and amines, the strength of the bonds increases

in the direction: C-S ⟶ C-N and ⟶ C-O, indicating that the relative rates of S, N and O removal would increase in the opposite direction to that above. Other compounds, such as ketones, aldehydes and amides, can be reduced and carboxylic acids decarboxylated. All those compounds can be classified as unstable and they will hardly survive the conditions of thermal or catalytic hydrotreatments.

Heterocyclic S-, N- and O-containing rings are known for their high stability. In this case, the heteroring is usually hydrogenated before C-X bond cleavage can occur. An example of the ring saturation is shown in the following reaction:

SCHEME insert here

Intermediates obtained after the first step should behave similarly to alkyl aryl ethers, sulphides and amines, respectively. 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 alkyl-phenols, -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 the hydrogenolysis.

The proposed scheme suggests that the ring opening is essential before any removal of heteratom can take place. This might occur either with or without preliminary heteroring hydrogenation. The ring saturation is important for the N-containing compounds (Satterfield and Cocchetto, 1975) while there are some indications that DS can be accomplished without it (Furimsky and Amberg, 1976). Rollmann (1977) assumed necessity of the ring

saturation also for furan compounds. Some support for this can be found in the ease with which furan can be converted to tetrahydrofuran (Nosovskii et al. 1973).

It is apparent that routes for DS, DN and DO are not necessarily the same. 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, for example the quinoline heteroring, 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 comparison indicates that, when the availability of hydrogen is becoming critical, the DN might be affected to the greatest extent. It was confirmed by Nelson (1977) that the amount of hydrogen required for DN is much larger than for DS.

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 Fig. 1, where log K is plotted against the reciprocal of the absolute temperature. Because of the lack of thermodynamic information, only mono-ring heterocyclic compounds can be compared. It is assumed that for the multi-ring compounds similar trends will be maintained. These results indicate the equilibrium limitations are greatest for the nitrogen compounds. For example, at 400°C the equilibrium constant for pyridine is about four orders smaller, while that of pyrrole is three orders of magnitude 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 favourable for the heterorings saturation. It is then clear that under the limitation conditions

the removal of N from the compounds will be slower as compared to 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 con-
firmed by Shih et al. (1977) the rate of DN levels off at pressures over
10.34 MPa (1500 psi). In view of the results in Figure 1 the rates of
DS and DO should be well off the region of limitations. This is why indust-
rial 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 DN with increase of temperature (Furimsky et al.,
1977). If the limitations were still in effect the opposite should be
observed. This conclusion is supported by the observation made by Goudrian
et al. (1973). These authors found that, over sulphided cobalt molybdate
catalyst at 400°C, more than 90% of pyridine DN was achieved already at
7.71 MPa pressure of hydrogen, i.e., a pressure much lower than 13.8 MPa
(2000 psi), applied in the present work. Then an assumption can be made
that the relative rates of DS, DN and DO are indeed given by the rates of C-X
bonds hydrogenolysis of saturated heterorings. If the reaction is controlled
by the C-X bond strength the DS should be the fastest, followed by DN and DO.

For larger molecules, for example, dibenzothiophene, dibenzofuran
and carbazol types, the mechanistic aspects are even less clear. Here the
hydrogenation of the heteroring, resulting in a decrease of strength of one
C-X bond, does not occur. This suggests that the ring is opened through
direct C-X bond scission unless the latter is weakened because of saturation
of the attached aromatic ring. The relative rates of the rings opening then

would increase from O- through N- to S-containing heterorings. Because the opening of an S-containing heteroring can occur even without preliminary hydrogenation (Furimsky and Amberg, 1976), little difference is expected between benzo- and dibenzo-thiophene. This was experimentally confirmed by Rollmann (1977) in his model compounds study. On the other hand, the rate constant for conversion of benzofuran was about three times larger than that of dibenzofuran. A similar comparison of nitrogen heterocyclics is not available in the literature. However, Cocchetto and Satterfield (1975) using thermodynamic considerations, predict the opening of the heteroring in carbazol to be much more difficult than that of indol. After the opening of heteroring is accomplished, the removal of S, N and O is governed by the stability of ortho-substituents of thiopenol, aniline and phenol. The thio-compounds 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 ortho-phenols 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. Then additional information on the behaviour of phenols and anilines under conditions of catalytic hydrotreatment would 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. In this case reactions occur on the surface of catalyst. Then the difference in the adsorption of reactants and products may be decisive. Smith et al. (1973) concluded from their deuterium exchange studies that the pyridine type compounds have a tendency to undergo flat adsorption on the

surface. This is supported by the ability of the compounds to form Ⅱ complexes with Mo. In the case of furan and thiophene compounds this trend is diminished because of the withdrawal of Ⅱ 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 DS and DO active sites. These authors also concluded, in agreement with Lipsch and Schuit (1969), that the sulphur and oxygen heterorings will be adsorbed on the surface via heteroatoms. This fact seems to be important when multi-ring compounds, such as dibenzothiophene and dibenzofuran are concerned. Here the adsorption will be more favourable for the sulphur compounds because of the larger size of the S heteroatom as compared to that of O, i.e., 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 regardless of from which heterocyclic compounds they were generated. For example, the same hydrocarbon may be formed from carbazol, dibenzofuran or dibenzothiophene. On the other hand, NH_3 will be strongly adsorbed on acidic sites, delaying their regeneration. Lipsch and Schuit (1969) observed strong adsorption of H_2O on the surface of cobalt molybdenum catalysts supported on alumina, resulting in poisoning of DS of thiophene and hydrogenation of butenes. This suggests that H_2O is adsorbed on sites where these reactions take place. The effect of H_2O on DN and DO is unknown. An interaction of H_2S 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 in-

dicates that relative concentrations of compounds may have an effect on DS, DN and DO. The heavy gas-oil chosen for the present comparison is a special feed, i.e., the relative mole ratio of S, N and O is approximately 4:1:1, assuming that there is one heteroatom per molecule. Then the S compounds will contact the surface more frequently. This is confirmed by the absolute amount of S removed relative to that of N and O (Table 2). Then the DS reaction may have a pronounced effect on a modification of the surface. Satterfield et al. (1975) confirmed that, at high temperatures, the thiophene present had a beneficial effect on pyridine DN. The effect was caused by the presence of H_2S (Goudrian et al., 1973), the product of DS. Information regarding a similar effect on DO is not available.

Catalysts in sulphided form are known to have higher activity. To explain this observation, only speculations can be made. At first more favourable conditions might exist for hydrogen transfer on the sulphided catalyst as compared to those on the oxidic one. It is believed that the O^{-2} or, in sulphided 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 Mo ions. This may decrease the interaction of II electrons from the N heterorings with Mo if the complexation mentioned above is in effect. Then less favourable conditions are created for surface poisoning by nitrogen bases.

EFFECT OF CATALYST COMPOSITION

It is expected that relative rates of DS, DN and DO may be affected by catalyst structure. This is indicated by different activities of catal-

ysts 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 effects on
the final properties of catalysts.

As far as catalysts with different chemical composition are con-
cerned, the supported Co and Ni molybdate types are of main interest.
Satterfield and Cocchetto (1975) investigated the two catalysts in a pyridine
DN study. They observed that the Ni-promoted catalyst is more active in the
first step, i.e., intermediate hydrogenation of the heteroring, while the Co
type is better in the next hydrogenolytic step. Because the first step is,
under equilibrium limitation conditions, the rate determining step, it appears
that the Ni-promoted catalyst is more active in DN than the Co one. These
results, as well as the majority of the results published in the literature,
were obtained under low hydrogen pressures where the limitations mentioned
were still in effect. In order 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 the cat-
alyst 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, Ni has a
tendency to diffuse faster to the support than Co during tempering operations
(Gates et al, 1978). When all these precautions were taken, an insignificant
difference in promoting effects of Ni and Co was observed in DN (Furimsky

et al., 1977) and DO (Furimsky, 1978) of the heavy gas-oil.

CATALYTIC HYDROTREATMENT OF HEAVY GAS-OIL

Much of the information on DS, DN and DO available in the litera-
ture originates from model compounds studies. The experimental conditions
applied in such studies are often different than those encountered in indust-
rial operations. In the latter case, catalysts have deposits of coke and
metals, i.e., the active surface is changed to a great extent. The main
part of the coke is deposited during the initial period on-stream (Qader and
Duraiswamy, 1974). This indicates that an operating catalyst is covered by
coke. Despite this, the catalyst maintains high activity during a long per-
iod of time. It is not easy to explain this residual activity because little
is known of the structure of the coke and metals deposits as well as the struc-
ture of the modified surface is unknown. The presence of a coke layer 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 ex-
plained also by the ability of active ingredients from cobalt-molybdate cat-
alysts 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 (Furimsky et al., 1978)
which results in reactivation of catalytic sites for reactions to occur.

As far as metals are concerned, Ni and V are of main interest. It
was shown by Nelson (1976) that catalyst consumption during desulphurizing
of residua depends on the metals content and is high when the content is high.
The metals deposits modify the catalyst surface resulting in high hydrogen

consumption. This would indicate that the metals deactivate DS, DN and DO rather than hydrogenation sites unless Ni promotes hydrogenation, a phenomena which is not unusual for some Ni forms.

The surface modified by coke and metals may be different as to the relative removal of S, N and O as compared to the clean surface encountered in model compounds studies. This may alter some conclusions reached on the basis of thermochemical, mechanistic and surface phenomena considerations. Extensive studies of catalytic hydrotreatment performed on the heavy gas-oil feedstock provide an opportunity to obtain some information on this subject. Because the amount of Ni and V in the feedstock is negligible, any differences, if observed, may be attributed to the presence of coke.

Experimental conditions, i.e., the methods and equipment used to make laboratory-prepared catalysts and to perform the reaction experiments, have been described in detail previously (Williams and Parsons, 1974). The properties of the feedstock investigated are listed in Table 1. The 343-524°C heavy gas-oil was a distillate fraction of the liquid product obtained by thermally hydrocracking Athabasca bitumen (Merrill et al., 1973). All results presented were obtained at a temperature of 400°C and hydrogen pressure of 13.8 MPa (2000 psi).

TABLE 1

Properties of the Feedstock

Boiling range	^{o}C	343-524
Pitch (+524°C)	wt %	Nil
Pentane insolubles	wt %	0.3
Sulphur	wt %	3.69
Nitrogen	wt %	0.39
Oxygen	wt %	0.44
Ni + V	ppm	Nil

The results on DS, DN and DO of the gas-oil, obtained over a series of unpromoted molybdate catalysts, are shown in Fig. 2a, b and c, respectively. Over the pure alumina support (in Fig. 2, the catalyst with 0 wt % MoO_3) 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. Then the O removed must originate from unstable O-containing compounds (alcohols, peroxides, ketones, aldehydes, etc.). Such compounds are products of autoxidation, i.e., the reaction of oxygen with hydrocarbons (Howard, 1972) occurring during the storage of the feed while the latter is 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 DS, DN and DO cannot be compared on the basis of S, N and O contents before and after the hydrotreatment without paying special attention to the compounds involved. Ignoring this fact may lead to the erroneous conclusion that the removal of O is faster than that of S and N. This indicates that a starting point in the comparison of the relative rates of DS, DN and DO should be the concentrations of S, N and O in the products obtained over a pure alumina support rather than in the feedstock. Then the S:N:O ratios (in Table 2 for catalyst with 0 wt % of active ingredients) will be different than those in the feed mentioned previously.

Relative rates of DS, DN and DO are summarized in Table 2 where the concentrations of S, N and O in the products as well as those removed from the feed are compared. The molar concentration values were obtained under an assumption that there is only one heteroatom per molecule.

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	–	.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

Results in Table 2 show large scatter when related to the concentrations of MoO_3. However, one observation is rather interesting, i.e., the addition of small amounts of MoO_3 to the support results in a marked increase in S removal relative to that of N and O. At the same time the DO is least affected. With further increase in MoO_3 concentration, DO and DN compete more successfully with DS. This might be caused by more effective poisoning of DS sites by basic nitrogen compounds which represent an important part of total nitrogen in the feed and the product (Furimsky et al., 1977). The increase in MoO_3 concentration results in an increase of surface acidity (Parsons and Ternan, 1977). This is favourable for an interaction between basic compounds and acidic sites to occur.

Several Co and Ni promoted catalysts are included in Table 3 as well. These values show large scatter and are inconclusive as to the relative promoting effects of Co and Ni. This suggests that additional and more precise work on this matter is needed. However, the order of S, N and O removal is unchanged, indicating that the rate of DS is larger than that of DN and DO. The DN seems to be higher than the DO for all the catalysts although the difference is less pronounced.

The results in Table 2 are in support of high stability of O- and N-containing heterocyclic compounds under conditions of the catalytic hydrotreatment. The resistance of these compounds to DO and DN 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 in all extracts, with the exception of that obtained by pentane extraction, was significantly larger than that of S. The material extracted by pentane corresponds, most likely, to the feed left on the surface. The other extracts are heavier and result from a downgrading process of the feed on the catalyst surface.

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

This indicates that the polar O- and N-containing compounds are strongly adsorbed on the surface and while resisting DO and DN reactions they are converted to larger molecules which accumulate in the coke.

In conclusion, the relative rates of DS, DN and DO of the heavy gas-oil seem to be in agreement with predictions following from some thermochemical, mechanistic and surface phenomena considerations based on the assumption that heterocyclic compounds represent the major part of S-, N- and O-containing compounds in the feed. This excludes O compounds present as a result of a reaction between the feed and air. Then the DS is fastest, followed by DN which is slightly faster than DO. These conclusions cannot be generalized unless the observation is confirmed on several feedstocks with variable relative concentrations of S-, N- and O-containing compounds. For instance, the heavy gas-oil used in this study might have a concentration of nitrogen bases too low for an effective poisoning of the catalyst surface to occur.

LEGEND OF FIGURES

Figure 1   Thermodynamic equilibria of furan, thiophene, indole and
            pyridine with their hydrogenated derivatives.
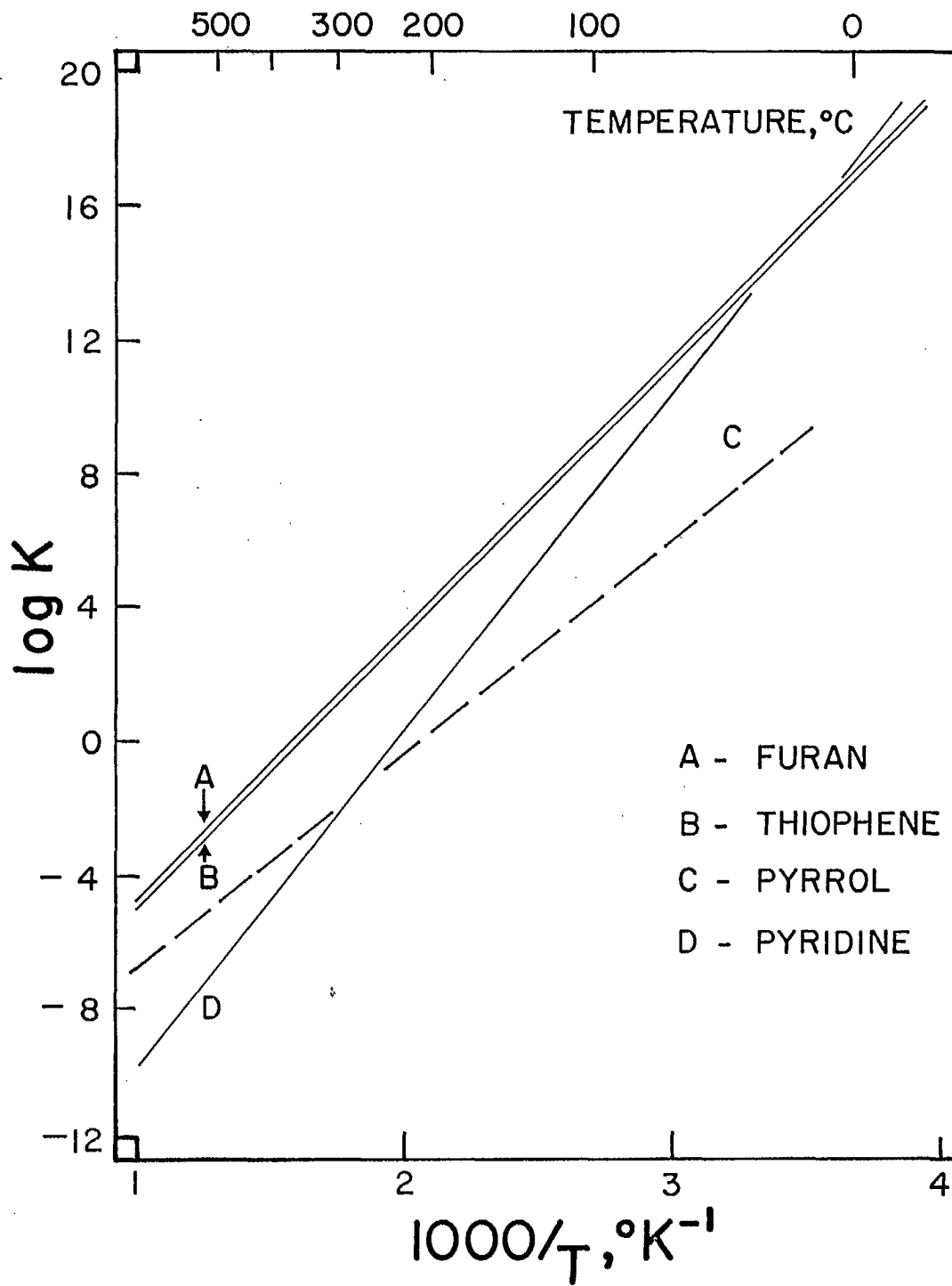
Figure 2   Amount of sulphur, nitrogen and oxygen in products versus
            the concentration of MoO_3 in promoted (atomic Me/Mo ratio =
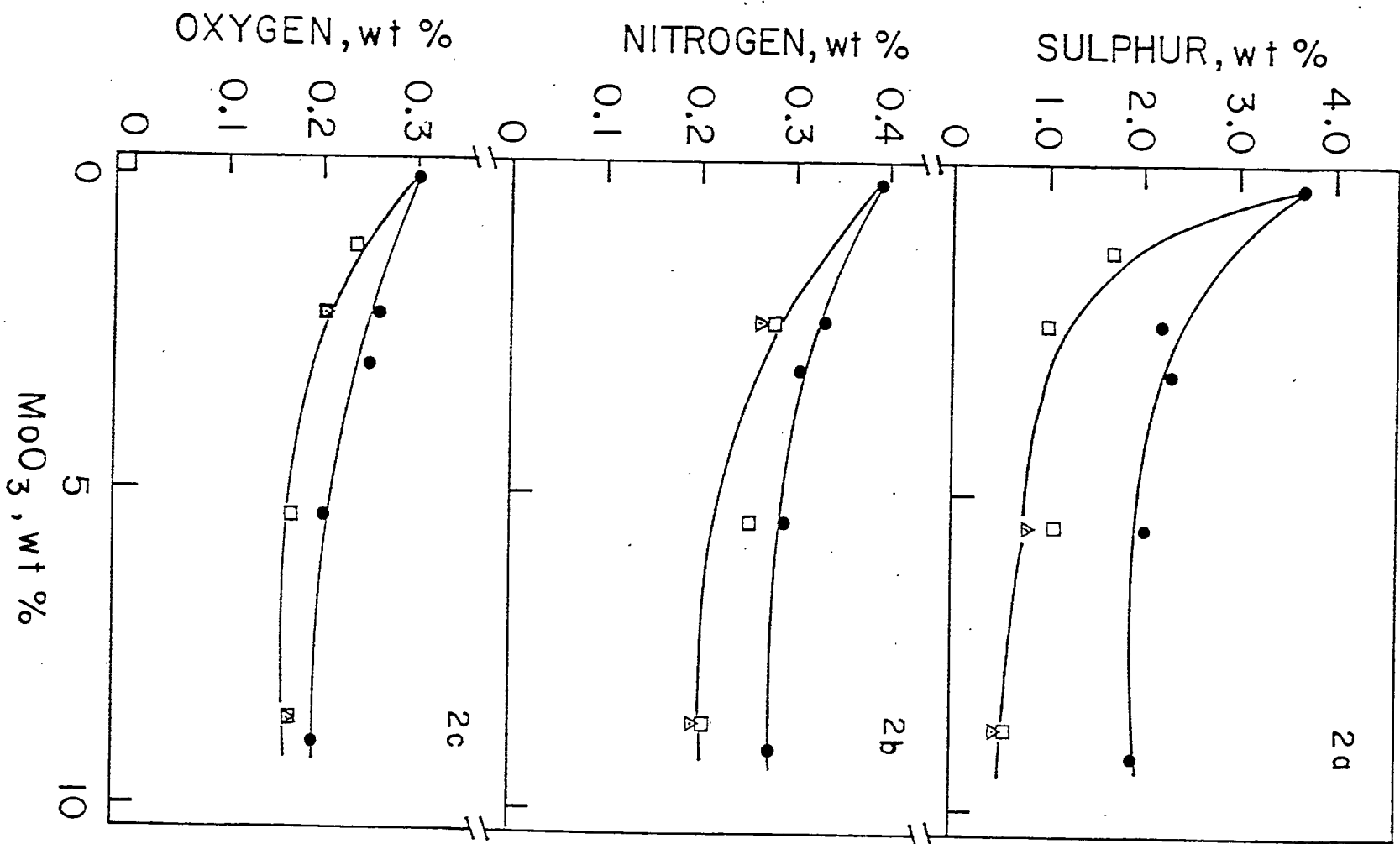   1.0; Me = Co or Ni) and unpromoted molybdate catalysts.

            ● – unpromoted; ☐ – Ni promoted; △ – Co promoted catalysts

Scheme:

Y = S, O or NH

OXYGEN, wt %

NITROGEN, wt %

SULPHUR, wt %

MoO₃, wt %

2c

2b

2a
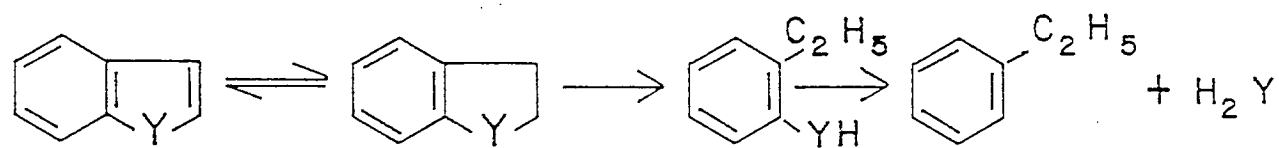
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