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Effect of Catalyst Acidity on the Hydrogenolysis of Anisole

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The reactions of anisole on sulfided $CoMo/Al_2O_3$ and $NiMo/SiO_2–Al_2O_3$ catalysts have been studied in a fixed-bed tubular reactor at 250–350°C, 5 MPa hydrogen pressure, and LHSV 2.0 h^{-1}. The acidity of the catalysts was modified by adding small amounts of pyridine or chloroform to the feed. Pyridine lowered the conversion of anisole appreciably. At the same time the selectivity of phenol increased at the expense of methyl-substituted phenols. Hydrodeoxygenation and hydrogenation selectivities were not markedly affected. The poisoning by pyridine was reversible. Chloroform first increased the conversion on the CoMo catalyst slightly, but soon, obviously due to permanent changes in the metal portion of the catalyst, the conversion began to fall and was not restored after discontinuing the addition of chloroform. The observed changes in catalyst acidities, as measured from the skeletal isomerization activity, were as expected: pyridine lowered and chloroform increased the acidity. A possible reaction mechanism for the hydrogenolysis of anisole is presented and the structure of the active sites is briefly discussed.

INTRODUCTION

It is generally accepted that hydrocracking catalysts are bifunctional in nature (*1*). The cracking activity is due to the acidity of the support while the metals play their major role in hydrogenation of the coke-forming precursors and thus prevent deactivation of the catalyst. Studies on the hydrocracking reactions of some aromatic oxygen compounds, including anisole and guaiacol, have been reported in a previous paper (*2*). The catalyst used contained sulfided Ni and Mo on a strongly acidic support. In the hydrocracking of anisole the first reaction step was the cleavage of the methyl carbon–oxygen bond. It was suggested that this carbon–oxygen bond-breaking might take place both on the metal part of the catalyst and on the acidic sites of the carrier, but through different reaction mechanisms. On the metal a homolytic splitting was supposed to occur followed by a rapid hydrogenation of the radicals formed. On the carrier a heterolytic scission was thought to be the dominating reaction. The methyl carbonium ion thus formed would attack the aromatic nucleus and due to a nonplanar adsorption state, preferentially the *ortho*-position.

The aim of the present work was to study further the validity of the proposed reaction scheme by changing the acidity of the catalyst. A hydrotreating catalyst which does not have a strongly acidic support was first tested. For this a $CoMo/Al_2O_3$ catalyst, widely used in hydrodesulfurization processes, was chosen. It is well known that although the alumina in this type of catalyst has weakly or moderately acidic sites (mainly of the Lewis type) it does not itself take part in the HDS reactions to any appreciable extent but has essentially the role of a support (*1*). Second, the acidity of the catalysts was modified *in situ* by adding to the feed small amounts of appropriate reactants. A decrease in the acidity can easily be achieved by poisoning a part of the most acidic sites with an organic base (*3*). For this purpose pyridine was chosen due to its well-known effect on acidic carriers (*3–5*) as well as catalysts (*6–8*). To increase the acidity of a catalyst–carrier system under reaction conditions is not so simple. In re-

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forming catalysts, for instance, the acidity of the alumina support is enhanced by introducing halide ions onto the surface (*9*). In the present work, chloride ions formed from the hydrogenolytic reactions of chloroform were used with this aim. It was, however, recognized that chloride ions could also interfere with the metals present on the catalyst.

Determination of surface acidity can be performed by many different methods (*3*, *10*). In the situation described above where the acidity of the catalyst is chemically changed *in situ*, a direct measuring method cannot be utilized because the state of the catalyst surface will be affected during such a measurement. Therefore, the model reaction method described by Benesi and Winquist (*10*) was applied. As a model reaction the skeletal isomerization of the six-carbon-atom ring to the five-atom ring was chosen. This reaction is generally believed to occur through a carbonium ion mechanism mainly on strongly acidic sites (*1*, *11*). Thus the ratio methylcyclopentane/cyclohexane in the reaction product (abbreviated i/n) is used as a measure of catalyst acidity. This ratio has a thermodynamic equilibrium value of about 4–5 under the reaction conditions studied here (*12*). In this context it should be noted that throughout the present work the two types of acidity, viz., Lewis and Brønsted acidity, are not treated separately. This is because even small amounts of water (formed, for example, from anisole) can transform a part of the Lewis acid sites to Brønsted sites (*3–5*) and, in addition, there is no means to measure the two types of acidity *in situ*.

As a measure of the hydrogenation activity of the catalysts the ratio of hydrogenated C_5–C_6 hydrocarbons to benzene (abbreviated ac/ar) is used. At equilibrium this ratio has a value greater than 1000 under the conditions studied (*12*). The HDO activity of the catalysts is described simply by the selectivity of hydrocarbon formation. The equilibrium of this reaction is entirely on the side of hydrocarbons.

EXPERIMENTAL METHODS

Chemicals. All chemicals were pure or analytical grade reagents. Hydrogen was laboratory grade and was used without further purification.

Catalysts. Two commercial catalysts were used, namely a hydrocracking catalyst (NiMo) and a HDS catalyst (CoMo). The composition and major properties of these catalysts are listed in Table 1. Both catalysts are normally run in sulfided form and this was also done in the present work. The sulfidation was carried out *in situ* in the reactor at 5 MPa hydrogen pressure. Two charges of both catalysts were used: charges CoMo I, CoMo II, and NiMo II were sulfided at 275°C with a feed containing 0.5 vol% CS_2 in benzene for 5–6 h, LHSV 2 h^{-1}. NiMo I was sulfided at 250°C with neat dimethyl sulfoxide for 3–4 h, LHSV 2 h^{-1}. The sulfur content of the catalyst charges after use was analyzed as $BaSO_4$ by the wet method (*13*).

Equipment and procedure. The small fixed-bed tubular reactor and its use have been described previously (*2*). The catalyst load was 5 cm^3. The feedstock was neat anisole containing usually 0.05 vol% CS_2 in order to maintain the catalyst in the sulfided state. In some runs small amounts of pyridine (0.1, 0.5, or 2.0 vol%) or chloroform (0.05, 0.25, or 1.0 vol%) were added to the liquid feed. Product analysis was carried out with gas chromatography, mainly as described earlier (*2*). Hydrocarbons were analyzed in this work by a Perkin–Elmer 452

TABLE 1

Composition and Properties of Catalysts

	Catalyst designation	
	CoMo	NiMo
Metal content (%)	Co 2.4 Mo 10.0	Ni 4.0 Mo 12.0
Carrier material	γ-Al_2O_3	SiO_2–Al_2O_3 (25 : 75 wt%)
Surface area (m^2/g)	200	180
Particle form	Tablets	Spherical
Particle size (mm)	3.2 × 3.2	1.68–2.00
Bulk density (g/cm^3)	1.0	0.66

gas chromatograph with a packed di(2-ethylhexyl) sebacate metallic column, length 1.83 m.

RESULTS AND DISCUSSION

A single run lasted usually 8–12 h. Some shorter runs were also made, particularly when the effect of temperature was studied by using a constant feed. It is evident that during these relatively short runs a steady state, in the strict sense of the word, could not be reached. However, as the results will show, after changing the reaction conditions the major changes in conversion and product distribution took place in about 3–4 h. Thus the results at the end of a run may well be attributed to the specific reaction conditions used. By applying the usual estimation methods (see, e.g., Ref. (*1*)) it was shown that intraparticle diffusion effects were negligible and no significant temperature or concentration gradients were present in the catalytic system studied.

Reaction Products

With both catalysts the reaction products identified were the same as found earlier (*2*), the main oxygen-containing compounds being phenol, *o*-cresol, and 2,6-dimethylphenol. Smaller amounts of *o*-methylanisole, *m*- and *p*-cresol, and some di- and trimethylphenols were also occasionally found. The HDO selectivity was quite low and varied between 5 and 30%. The most significant hydrocarbons formed were benzene, cyclohexene, cyclohexane, and methylcyclopentane, since these were used for the calculation of the acidity and the hydrogenation activity of the catalysts. Mainly C_7-hydrocarbons were found among other oxygen-free compounds. It is quite probable that these hydrocarbons originate from the successive reactions anisole → *o*-cresol → C_7-hydrocarbons, since toluene and methylcyclohexane have been reported as the main reaction products in the HDO of cresols (*14*).

Dicyclics or other heavier products were not found. Of lighter compounds only methane and water (as a product of the HDO reaction) were identified. Normally, over 95% of the reaction product could be accounted for. The selectivities, calculated on the basis of anisole reacted, were normalized to 100% of the conversion, in order to smooth out possible random errors in the gas chromatographic analyses.

Sulfidation Level of the Catalysts

The maximum amount of sulfur which can be bound to the catalysts can be calculated on the basis of the metal content of the catalysts (see Table 1) and the stoichiometry of the stable sulfides under the reaction conditions (*15*). The values 7.7% S for the CoMo catalyst and 9.3% S for the NiMo catalyst are obtained in this way. The analyzed sulfur contents of the used catalyst charges are listed in Table 2 together with the total run times. As can be noted, the sulfur levels are only about 30 and 40–60% of the maximum for the CoMo and NiMo catalysts, respectively. According to Grimblot *et al.* (*16*), higher sulfidation levels (in the range of 70–90%) are easily reached by employing more severe sulfidation procedures than those used in this work. However, they report further that ca. 10–20% of Mo and ca. 50% of Co or Ni in commercial HDS catalysts are in the nonsulfided state after the usual sulfidation procedures. Gachet *et al.* (*17*) have reported a sulfidation level of over 90% for a commercial CoMo catalyst. On the basis of a ^{35}S radioisotope study they further postulate that only 20% of the sulfur is exchangeable

TABLE 2

Sulfur Content and Total Time on Stream of the Used Catalysts

Catalyst charge	Sulfur content (%)	Time on stream (h)
CoMo I	2.2	35
CoMo II	2.0	120
NiMo I	5.6	24
NiMo II	3.5	62

in the HDS reactions, the rest being fixed in the molybdenum and cobalt sulfide lattices so strongly that it cannot take part in the catalytic action.

Of the two catalysts studied in this work the NiMo catalyst is evidently the more easily sulfided. We now briefly discuss the influence of the sulfur level on the reactions of anisole and also the effect of CS_2 concentration in the feed.

NiMo/SiO$_2$–Al$_2$O$_3$ Catalyst

With the NiMo hydrocracking catalyst runs were made with neat anisole and with feeds containing pyridine. Increase of the catalyst acidity with a feed containing chloroform was not tried because the catalyst carrier was known to be strongly acidic as such. The results are summarized in Table 3 where the calculated values of the catalyst acidity (i/n) and hydrogenation activity (ac/ar) parameters are also shown.

The charges I and II were differently sulfided (see Experimental Methods). The effect of the sulfidation level is clearly noticed when the experiments without pyridine are compared with each other. The charge NiMo I, which was more strongly sulfided, gives an appreciably higher conversion than NiMo II, while the selectivities of the main O-compounds do not differ markedly. The most striking difference is found in the hydrogenation activities of the charges, that of NiMo I being about 10 times higher than of NiMo II. The increase of the hydrogenation activity due to the increase of the sulfidation level is a well-known effect (*15*). It has recently been observed also in a study concerning the hydrogenolysis of methoxyphenols on a $CoMo/Al_2O_3$ catalyst (*18*). The sulfidation level of the catalyst does not seem to have any clear influence on the HDO selectivity of the starting material. Moreover, the acidity parameter i/n and the methylation selectivity of the aromatic nucleus do not depend on the sulfidation level.

TABLE 3

Effect of Pyridine Poisoning on Reaction of Anisole on $NiMo/SiO_2–Al_2O_3$ Catalyst[a]

Catalyst charge	I	I	II	II	II	II
Concentration of pyridine (vol%)	0	0.5	0	0.1	0.5	2.0
Conversion (%)	91.2	69.0	76.9	53.6	44.2	37.0
Selectivity (%)						
Phenol	64.2	72.2	59.6	73.3	80.8	85.0
o-Cresol	18.2	7.0	20.9	15.2	8.6	5.8
2,6-Dimethylphenol	4.2	0.5	5.6	2.3	0.6	+
Other O-compounds	0.8	+	2.9	0.1	+	+
Sum of O-compounds	87.4	79.7	89.0	90.9	90.0	90.8
Methylcyclopentane	3.9	1.4	1.9	2.0	0.6	0.3
Cyclohexane	4.4	11.6	2.3	3.3	4.0	3.7
Cyclohexene	1.2	2.6	0.5	1.4	2.3	2.6
Benzene	1.2	2.6	5.7	1.9	2.8	2.5
Other hydrocarbons	1.9	1.9	0.7	0.6	0.3	0.1
Sum of hydrocarbons	12.6	20.1	11.1	9.2	10.0	9.2
i/n	0.89	0.12	0.83	0.61	0.15	0.08
ac/ar	7.92	6.00	0.82	3.53	2.46	2.64
Catalyst age (h)	14	17	3	11	19	27

[a] Reaction conditions; $T = 300°C$, LHSV = 2.0 h^{-1}, $P = 5$ MPa, H_2/anisole ≃ 100 mol/mol, 0.05 vol% CS_2 in feed.

Effect of pyridine. This effect is as expected: the acidity decreases as the pyridine concentration in the feed increases. At the same time total conversion of anisole declines and the share of methylated products is very substantially reduced. For example, 2% of pyridine in the feed cuts the acidity parameter down to one-tenth of the original value, halves the conversion, and reduces the methyl substitution to a level at which only a small amount of *o*-cresol forms. This last finding indicates clearly, for this type of catalyst, the important role which the catalyst acidity plays in the alkylation of the aromatic nucleus. On the charge NiMo II pyridine does not have any effect on the HDO selectivity but on NiMo I a small increase can be observed. No clear effects on the hydrogenation activity are noted.

CoMo/Al$_2$O$_3$ Catalyst

More extensive runs were made with the CoMo catalyst, since the use of sulfided $CoMo/Al_2O_3$ catalysts for this type of experiment has not been reported before. In a recent study a CoMo–alumina catalyst was applied to the HDO of anisole and guaiacol (*19*), but the experiments were carried out

TABLE 4

Effect of Temperature and Pyridine Poisoning on Reaction of Anisole on CoMo/γAl_2O_3 Catalyst[a]

Temperature (°C)	275	300	325	275	300	325
Concentration of pyridine (vol%)	0	0	0	0.5	0.5	0.5
Conversion (%)	54.1	77.7	91.6	33.3	50.7	77.1
Selectivity (%)						
Phenol	50.9	50.4	43.8	68.2	61.2	48.7
o-Cresol	19.9	22.6	20.7	14.0	18.4	18.3
2,6-Dimethylphenol	6.8	8.5	9.5	2.0	2.7	6.8
Other O-compounds	+	0.1	0.4	−	+	+
Sum of O-compounds	77.6	81.6	74.4	84.2	82.3	73.8
Methylcyclopentane	1.1	0.2	1.3	0.7	0.4	0.4
Cyclohexane	3.6	5.0	7.1	5.5	5.1	6.9
Cyclohexene	1.1	1.4	1.8	1.9	1.8	2.2
Benzene	14.6	8.8	9.5	6.3	8.1	10.7
Other hydrocarbons	2.2	2.9	6.0	1.2	2.3	6.1
Sum of hydrocarbons	22.6	18.3	25.7	15.6	17.7	26.3
i/n	0.31	0.04	0.18	0.13	0.08	0.06
ac/ar	0.40	0.75	1.07	1.29	0.90	0.89
Catalyst age (h)	9	13	17	34	25	28

[a] Reaction conditions: LHSV = 2.0 h^{-1}, P = 5 MPa, H_2/anisole ≃ 100 mol/mol, 0.05 vol% CS_2 in feed, charge CoMo I.

batchwise in an autoclave using a dilute hydrocarbon solution and thus they are not directly comparable with the runs of the present work.

The results are summed up in Tables 4–6.

TABLE 5

Effect of Pyridine Poisoning on Reaction of Anisole on CoMo/γ-Al_2O_3 Catalyst[a]

Concentration of pyridine (vol%)	0[b]	0	0.1	2.0	0[c]
Conversion (%)	81.7	79.7	67.3	43.2	77.9
Selectivity (%)					
Phenol	51.3	49.9	53.6	66.9	48.6
o-Cresol	22.0	21.5	21.2	15.9	23.9
2,6-Dimethylphenol	8.7	10.6	7.6	2.8	11.1
Other O-compounds	2.2	2.5	1.5	+	2.6
Sum of O-compounds	84.2	84.5	83.9	85.6	86.2
Methylcyclopentane	0.6	0.6	0.2	0.1	0.5
Cyclohexane	5.1	5.2	5.2	4.4	4.3
Cyclohexene	1.2	1.3	1.6	2.0	1.4
Benzene	5.6	5.1	6.2	6.3	4.6
Other hydrocarbons	3.3	3.3	2.9	1.6	3.0
Sum of hydrocarbons	15.8	15.5	16.1	14.4	13.8
i/n	0.12	0.12	0.04	0.02	0.12
ac/ar	1.23	1.39	1.13	1.03	1.35
Catalyst age (h)	11	23	35	47	71

[a] Reaction conditions; T = 300°C, LHSV = 2.0 h^{-1}, P = 5 MPa, H_2/anisole ≃ 100 mol/mol, 0.05 vol% CS_2 in feed (see below), charge CoMo II.

[b] 0.5 vol% CS_2 in feed.

[c] After regenerating the catalyst for 24 h with neat anisole.

TABLE 6

Effect of Chloroform on Reaction of Anisole on CoMo/γ-Al_2O_3 Catalyst[a]

Concentration of chloroform (vol%)	0	0.05	0.25	1.0	0[b]
Conversion (%)	77.9	80.1	75.9	73.1	67.5
Selectivity (%)					
Phenol	48.6	50.8	54.1	58.8	52.8
o-Cresol	23.9	25.4	24.7	24.2	26.8
2,6-Dimethylphenol	11.1	11.3	10.2	8.5	11.5
Other O-compounds	2.6	3.0	3.1	3.6	3.1
Sum of O-compounds	86.2	90.5	92.1	95.1	94.2
Methylcyclopentane	0.5	0.5	0.5	0.4	0.3
Cyclohexane	4.3	2.4	1.6	0.7	0.9
Cyclohexene	1.4	1.3	1.0	0.4	0.9
Benzene	4.6	3.4	3.1	2.4	2.7
Other hydrocarbons	3.0	2.0	1.7	1.0	0.9
Sum of hydrocarbons	13.8	9.6	7.9	4.9	5.7
i/n	0.12	0.21	0.31	0.57	0.33
ac/ar	1.35	1.24	1.00	0.63	0.78
Catalyst age (h)	71	83	95	107	119

[a] Reaction conditions as in Table 5.

[b] After regenerating the catalyst for 12 h with neat anisole.

The effect of pyridine at different temperatures was studied with charge CoMo I (Table 4). Charge CoMo II was used to study the influence of different levels of pyridine and chloroform at a constant temperature of 300°C (Tables 5 and 6). The effect of sulfur level in the feed was also studied with this charge. These experiments were carried out uninterruptedly during 5 days. The performance of the catalyst during these runs is illustrated in Fig. 1. Comparison of the results with those of the NiMo catalyst shows that the conversion of anisole is the same for both catalysts when sulfided by the same method. The acidity parameter i/n is much lower for the CoMo catalyst, as was expected. The selectivities differ somewhat, the CoMo catalyst showing a higher activity in HDO and, strikingly, in nuclear methyl substitution. This finding that the less acidic CoMo catalyst shows a higher extent of nuclear substitution is not compatible with the reaction scheme outlined earlier (see Introduction and Ref. (*2*)). The discrepancy, however, can be explained by taking into account the fact that two different types of reaction are considered when the concept of acidity is applied: first, there

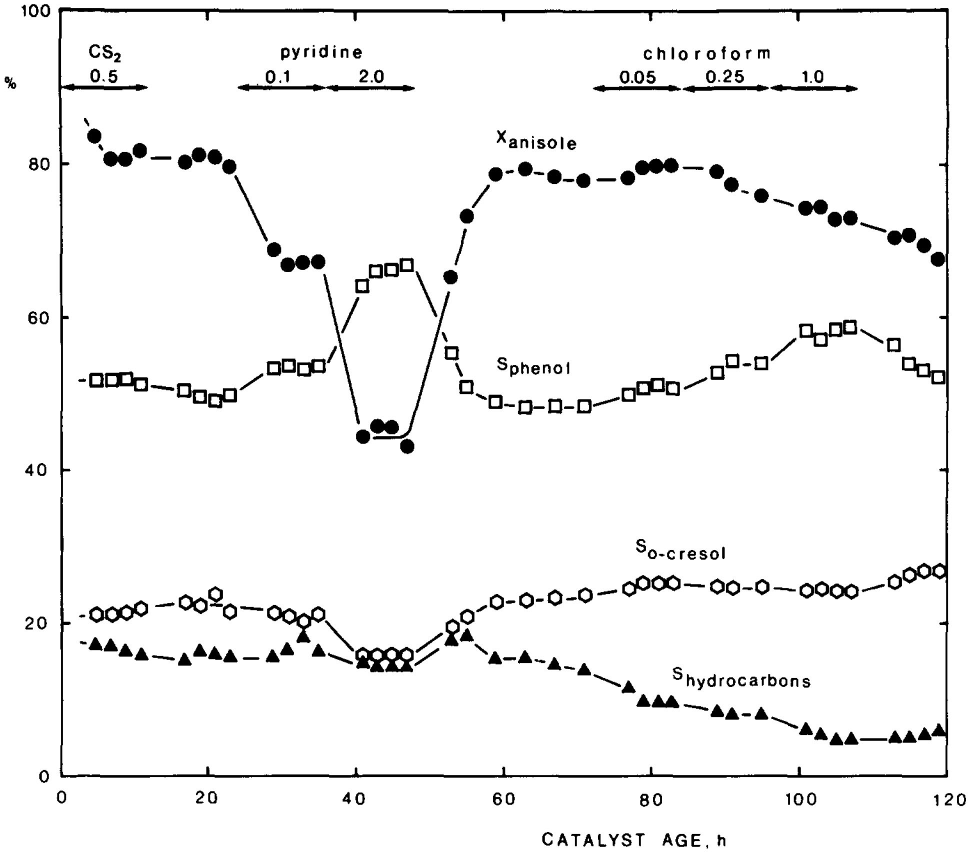


FIG. 1. Effect of pyridine and chloroform on the performance of the CoMo catalyst. × = conversion (%), S = selectivity (%). Reaction conditions as in Table 5. Concentrations of added reactants in vol% of liquid feed.

is the skeletal isomerization of a hydrogenated ring (as the measure of acidity) and second, the methyl substitution of the aromatic nucleus. The former reaction obviously requires stronger acid sites. Thus, nuclear substitution may occur to a higher extent on the CoMo catalyst, although the skeletal isomerization is faster (and therefore the acidity parameter higher) on the NiMo catalyst.

It is well known that the metal sulfides used in HDS catalysts are very stable at the reaction temperatures generally applied (*15*). Hence only a very low partial pressure of H_2S is needed to suppress the decomposition or reduction of these sulfides. In this work H_2S is generated *in situ* from the hydrogenolysis of CS_2 added to the feed. The possible influence of H_2S on the reactions of anisole was tested by using in one run 0.5 vol% of CS_2 in the feed, a concentration 10 times higher than the usual one. However, no changes in conversion or product distribution could be noted (see Table 5 and Fig. 1). Thus the sulfur level of the feed employed in the present study and earlier (*2*) is quite appropriate and on no account too high.

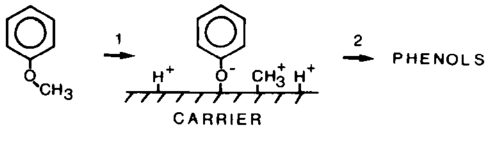
Effect of pyridine. The effect of pyridine is similar in the entire temperature range studied (Table 4). Critical examination is therefore focused on the results obtained at 300°C where the bulk of the runs were carried out. On the CoMo catalyst the influence of pyridine is not as strong as in the case of the NiMo catalyst, i.e., the conversion does not drop as steeply and nuclear substitution is not reduced to the same extent. This might be due to the lower acid strength of the CoMo catalyst carrier. On the NiMo catalyst pyridine may be adsorbed so strongly that most of the acidic sites are occupied. This retards the adsorption of anisole and particularly the nuclear substitution which takes place mainly on strong acid sites. The decrease of the acidity parameter i/n due to pyridine can be readily distinguished, although the initial value is already very low. As with the NiMo catalyst, pyridine does not change the HDO selectivity. The hydrogenation activity, however, is slightly lowered.

The influence of pyridine was found to be practically reversible (see Table 5 and Fig. 1). After changing from pyridine-containing feeds to neat anisole, selectivities were restored in 24 h. The small drop in conversion can be accounted for by normal aging of the catalyst. These findings are in accordance with the view of Weisser and Landa (*15*). However, different results have also been reported. Sonnemans *et al.* (*6*) stated that on an oxidic $CoMo/Al_2O_3$ catalyst a part of the pyridine is irreversibly adsorbed. Very recently Miciukiewicz *et al.* (*20*) found that pyridine and some other N-compounds are strongly adsorbed on a sulfided $CoMo/Al_2O_3$ catalyst and cannot be removed completely by H_2 at 350°C even after several days. A reasonable explanation for these results is the low hydrogen pressure used; viz., only 0.1 MPa compared to 5 MPa in the present work. High hydrogen pressure is essential in hydrogenation of pyridine to piperidine which in turn is quite readily hydrogenolyzed to ammonia and other desorbable products (*6*). Unfortunately, the reversibility of the pyridine poisoning was not tested in the case of the NiMo catalyst and thus comparisons in this regard cannot be made. If the concept of a stronger adsorption of pyridine on the carrier of the NiMo catalyst is accepted, it is clear that the regeneration will not take place as fast as in the case of the CoMo catalyst.

Effect of chloroform. Addition of chloroform increases the acidity of the catalyst, as was outlined earlier. The increase, as measured with the acidity parameter i/n, is not, however, particularly high. In addition, a part of the increase may be due to kinetic reasons, because the selectivity of hydrocarbon formation is considerably decreased. On nuclear substitution chloroform has no significant effect. At the lowest level used (0.05 vol%) chloroform increased the conversion slightly. When higher concentrations were employed a continuous decline in conversion was observed. This decline did not end after stopping the addition of chloroform, although most of the selectivities were shifted back toward their initial values (Table 6 and Fig. 1). A plausible explanation for this phenomenon is the reaction of the metal sulfides of the catalyst with HCl formed from chloroform. It is also possible that carbon laydown, caused by the enhanced acidity of the carrier, is partly responsible for the catalyst deactivation. However, this possibility could not be verified as the carbon contents of the catalysts were not analyzed.

Reaction Mechanism

The results obtained in the present work support the reaction scheme formerly proposed for the hydrocracking of anisole (see Introduction and Ref. (*2*)). The scheme also describes well the hydrogenolytic reactions of anisole on the HDS catalyst studied. The main reactions occurring on the acidic carrier are illustrated by Scheme 1. The adsorption (stage 1) is a dissociative heterolytic process leading to the formation of a negative phenoxide ion and a positive methyl carbonium ion on the surface of the carrier. The adsorption site for the phenox-

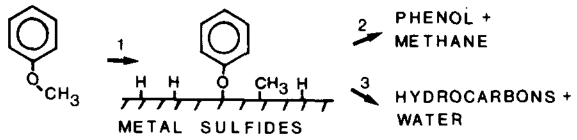


SCHEME 1

ide ion is most probably an acidic center, whereas the methyl carbonium ion is bound to a neighboring oxide ion, coordinated to aluminum. In stage 2 (after possible nuclear substitution reactions) desorption of a phenol, formed from a phenoxide ion and a surface proton, takes place. The formation of *o*-cresol may be partly regarded as an intramolecular rearrangement reaction occurring on the acidic surface of the catalyst carrier. The formation of 2,6-dimethylphenol, however, is a distinct proof of an intermolecular reaction and of the mobility of the methyl carbonium ions.

The preference of the *ortho*-position for the nuclear substitution is clear evidence for a nonplanar orientation of the phenoxide ion. The *m*- and *p*-positions are obviously too far from the catalyst surface to be substituted by a methyl cation. The HDO reaction does not seem very probable on the carrier because it would lead to excessive coke formation and rapid catalyst deactivation and this was not observed.

Scheme 2 shows the major reactions occurring on the metal part of the catalysts:



SCHEME 2

In this case the adsorption (stage 1) is immediately followed by a homolytic splitting. Anion (sulfur) vacancies are the most probable adsorption sites for the phenoxy radicals. The methyl species may be bonded to the metal or they may react very rapidly with adsorbed hydrogen to methane. In the main reaction 2 the phenoxy and methyl radicals formed are hydrogenated to phenol and methane which desorb. In the HDO reaction 3 the bond between the aromatic ring and the oxygen atom is broken and a hydrocarbon forms. The oxygen atom bonded to the surface is further hydrogenated to water. The breaking of the C–O bond may take place before or after the aromatic ring has been hydrogenated. As it is known that benzene is hydrogenated on the NiMo hydrocracking catalyst only to a very small extent (*2*), it can be concluded that both routes to hydrocarbons are important under the conditions studied because both aromatic and alicyclic hydrocarbons are obtained in significant amounts.

It has recently been reported that on a sulfided Mo/Al_2O_3 catalyst pyridine chemisorbs unselectively on both the alumina and the molybdena portions of the surface (*21*). Thus it is clear that both the main reactions, taking place on different parts of the catalyst surface, are markedly retarded on the type of catalyst studied. Further work concentrated on the reactions of anisole on pure carrier materials as well as on unsupported metal sulfides is in progress and will be reported in the near future.

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REFERENCES

1. Satterfield, C. N., "Heterogeneous Catalysis in Practice." McGraw–Hill, New York, 1980.
2. Bredenberg, J. B., Huuska, M., Räty, J., and Korpio, M., *J. Catal.* **77**, 242 (1982).
3. Tanabe, K., "Solid Acids and Bases." Academic Press, New York, 1970.
4. Schwarz, J. A., *J. Vac. Sci. Technol.* **12**, 321 (1975).
5. Parry, E. P., *J. Catal.* **2**, 371 (1963).

6. Sonnemans, J., van den Berg, G. H., and Mars, P., *J. Catal.* **31,** 220 (1973).
7. Segawa, K.-I., and Hall, W. K., *J. Catal.* **76,** 133 (1982).
8. Furimsky, E., *Erdoel Kohle* **35,** 455 (1982).
9. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes." McGraw-Hill, New York, 1979.
10. Benesi, H. A., and Winquist, B. H. C., "Advances in Catalysis," Vol. 27, p. 97. Academic Press, New York, 1978.
11. Pines, H., and Haag, W. O., *J. Amer. Chem. Soc.* **82,** 2471 (1960).
12. Stull, D. R., Westrum, E. F., and Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds." Wiley, New York, 1969.
13. Vogel, A. I., "A Text-book of Quantitative Inorganic Analysis, Theory and Practice," 2nd ed., Longmans, Green, London, 1957.
14. Odebunmi, E. O., and Ollis, D. F., *J. Catal.* **80,** 56 (1983).
15. Weisser, O., and Landa, S., "Sulphide Catalysts: Their Properties and Applications." Pergamon, New York, 1973.
16. Grimblot, J., Dufresne, P., Gengembre, L., and Bonnelle, J.-P., *Bull. Soc. Chim. Belg.* **90,** 1261 (1981).
17. Gachet, C. G., Dhainaut, E., de Mourgues, L., Candy, J. P., and Fouilloux, P., *Bull. Soc. Chim. Belg.* **90,** 1279 (1981).
18. Bredenberg, J. B., Huuska, M., and Toropainen, P., Proceedings of the IX Iberoamerican Symposium on Catalysis (Lisbon, 1984), p. 650. J. Fernandes, Lisbon, 1984.
19. Hurff, S. J., and Klein, M. T., *Ind. Eng. Chem., Fundam.* **22,** 426 (1983).
20. Miciukiewicz, J., Zmierczak, W., and Massoth, F. E., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. II, p. 671. Verlag Chemie, Weinheim, 1984.
21. Valyon, J., Schneider, R. L., and Hall, W. K., *J. Catal.* **85,** 277 (1984).