JOURNAL OF CATALYSIS 84, 170–177 (1983)

Hydrodeoxygenation of 1-Naphthol: Activities and Stabilities of Molybdena and Related Catalysts

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Received March 16, 1983; revised May 25, 1983

Hydrodeoxygenation (HDO) of 1-naphthol catalyzed by Mo/γ-Al_2O_3 and Ni–Mo/γ-Al_2O_3 was investigated with a flow reactor operated at 225°C and 120 atm. The oxidic forms of the catalysts were more active than the sulfidic forms. The catalysts were deactivated during operation, evidently by water formed in the HDO reaction. The selectivity changed markedly during the deactivation, the HDO reactions becoming markedly slower and the hydrogenation reactions only slightly slower. The deactivated oxidic and sulfidic catalysts could be reversibly regenerated by treatment with H_2 and H_2S in H_2, respectively. The catalyst surfaces are suggested to incorporate two kinds of catalytic sites, one catalyzing direct HDO, the other aromatic ring hydrogenation. These sites are suggested to be anion vacancies, susceptible to inhibition by bonding of H_2O.

INTRODUCTION

The need for processing heavy oils, shale, and coal liquids has motivated intensive research on catalytic hydroprocessing, with most of the effort having been devoted to hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). Since some of the heavy fossil fuels have high concentrations of organo-oxygen compounds, there has been recent work on the characterization of hydrodeoxygenation (HDO) in the presence of standard hydroprocessing catalysts such as sulfided Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3. For example, reactivities of substituted phenols (*1*) as well as benzofuran and dibenzofuran (*2, 3*) have been reported, but quantitative comparisons are still largely lacking. Reaction networks have been determined for HDO of dibenzofuran (*5*) and of 1-naphthol (Fig. 1) (*6*). The relative rates of heteroatom removal from a mixture of sulfur-, nitrogen-, and oxygen-containing compounds were measured, the rate of HDO of 4-propylphenol and *o*-ethylphenol being large in comparison with the rates of HDO of dibenzofuran and hydrogenation of aromatic hydrocarbons. The rates of HDO, HDS, and HDN of various compounds were of the same order of magnitude, but the competitive inhibition effects were not resolved. Inhibition phenomena indicating competitive adsorption during simultaneous HDO and HDS and HDO and HDN were reported (*7, 8*); basic nitrogen-containing compounds are strong inhibitors. There has been little reported about catalyst deactivation during HDO, but son Bredenberg (*9*) mentioned a loss of activity in phenol HDO catalyzed by Ni–Mo/SiO_2–Al_2O_3.

In all these investigations of HDO, the catalysts were—at least initially—sulfidic hydroprocessing catalysts. Little is known about other catalysts or the fate of the sulfides in the presence of high concentrations of hydrogen with oxygen-containing compounds. The research reported here was intended to provide a preliminary comparison of hydroprocessing catalysts in both the ox-

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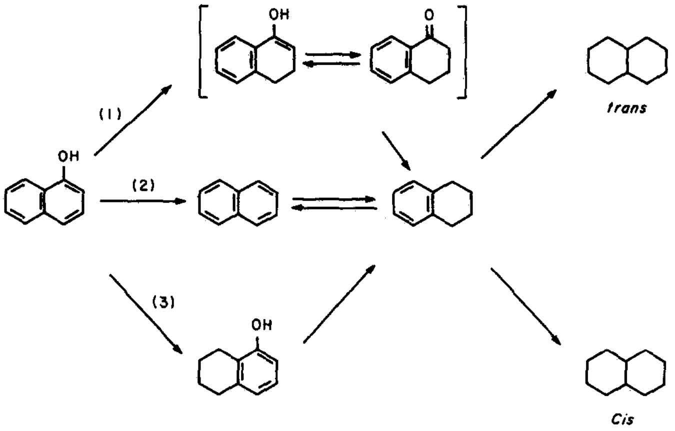

FIG. 1. Reaction network for hydrodeoxygenation of 1-naphthol catalyzed by sulfided Ni–Mo/γ-Al_2O_3 (*6*).

idic and sulfidic forms for HDO. The reactant chosen was 1-naphthol, a compound typical of the predominant organo-oxygen compounds in coal-derived liquids. The results provide evidence of the activities and stabilities of the catalysts and the changes in selectivity resulting from catalyst deactivation.

EXPERIMENTAL

Materials. The catalysts were Mo/γ-Al_2O_3 (8% Mo) (*10*) and commercial Ni–Mo/γ-Al_2O_3 (American Cyanamid HDS-9A; 3.5% NiO, 18% MoO_3). The surface areas of the latter two catalysts in the initial oxidic forms were 185 and 149 m^2/g, respectively, and the pore volumes were 0.42 and 0.46 cm^3/g, respectively. Crushing and sieving provided particle sizes in the range of 80 to 100 mesh.

A saturated solution of 1-naphthol (>99%, Aldrich) in cyclohexane (reagent grade, Fisher) was used as a feed to a flow reactor. The concentration of 1-naphthol was 2.2×10^{-5} mol/g of solution. Hydrogen (Linde, 99.99%) was also present in the feed solutions; it was purified by flow through traps containing a copper deoxo catalyst and zeolite to remove oxygen and water, respectively.

The weak-acid fraction of SRC-II coal-derived liquid prepared from Powhatan No. 5 coal (a 0.25 wt% solution in cyclohexane) was used with hydrogen as the reactant in some experiments. The preparation of this fraction by liquid chromatography is described elsewhere (*11*). The fraction includes a number of weakly acidic compounds, typified by substituted partially hydrogenated naphthols and phenyl phenols; the detailed characterization is reported separately (*12*).

Catalytic reactions. The catalytic reaction experiments were carried out with a high-pressure microreactor, described elsewhere (*13, 14*), which operated nearly isothermally and with plug flow of the reactants. All the reactants were present in the liquid phase. Particles of catalyst (50 mg) were mixed with particles of inert alundum (100 mg) and placed in the isothermal region of the reactor; the upstream and downstream sections of the reactor were filled with alundum.

Sulfiding of some of the catalysts was done *in situ;* mixtures of 10% H_2S in H_2 flowed over the oxidic catalyst at atmospheric pressure and 400°C at a rate of 30 cm^3/min. In some experiments, the oxidic catalyst was not sulfided, but was instead reduced with H_2 under the same conditions. After sulfiding or reduction of the catalyst, the reactor was cooled to the desired reaction temperature for HDO of 1-naphthol

(225°C). This temperature was chosen because it allowed both a measurable conversion of the reactants and a measurable rate of catalyst deactivation. A higher temperature (350°C) was chosen for the experiment involving the coal–liquid fraction.

The reactant solution to be pumped to the flow reactor was prepared in an autoclave; it was purged to remove air by pressurizing and depressurizing 3 times with H_2; the feed was then saturated with H_2 at 86 atm. In all experiments with sulfided catalysts, CS_2 (0.1%) was present in the feed solution, its purpose being to maintain the catalyst in the sulfided state. In one experiment, 0.25 wt% CH_3OH was added to the feed prior to the saturation with hydrogen.

Immediately after the sulfiding or reduction procedure, the flow of feed was started with the reactor thermostated at 225°C. Typically, the flow continued for 36 h, during which time the product samples were collected every 2 h. All the experiments were done with a weight hourly space velocity (WHSV) of 0.4 (50 mg of catalyst, and 10 cm^3/h feed flow rate). The pressure in the reactor was maintained at 120 atm.

Product analysis. The coal–liquid product was analyzed for total oxygen by Microanalysis, Inc., Wilmington, Del. The other product samples were analyzed by gas chromatography with a SE-54 capillary column, 30 m in length. 2,6-Dimethylnaphthalene was used as an external standard.

RESULTS

Catalytic Activities and Catalyst Deactivation

Mo/γ-Al_2O_3 and Ni–Mo/γ-Al_2O_3 catalysts, both in the oxidic and sulfidic forms, were active for hydrodeoxygenation of 1-naphthol. The products observed in all the experiments were the same as those found (*8*) in an investigation of the reaction network (Fig. 1). Tetralin was the organic product formed in highest concentration; naphthalene, 1-tetralone, and 5,6,7,8-tetrahydro-1-naphthol were observed in lower concentrations. The hydrogenation and HDO reactions were accompanied by a keto-enol conversion involving 1,2-dihydronaphthol and tetralone. The rates of formation of *cis*- and *trans*-decalin were negligible at the conversions observed.

Typical results are shown in Fig. 2, where 1-naphthol conversion is plotted as a function of time on stream, determined in experiments with Mo/γ-Al_2O_3 and Ni–Mo/γ-Al_2O_3 catalysts originally in the oxidic and in the sulfidic forms. (There was CS_2 in the feed when the reactor contained a sulfidic catalyst.) The oxidic Mo/γ-Al_2O_3 catalyst had a relatively high initial activity and underwent slow deactivation. The oxidic Ni–Mo/γ-Al_2O_3 catalyst had a higher initial activity and underwent a relatively rapid deactivation for approximately 25 h, after which the rate of deactivation leveled off.

The sulfidic Mo/γ-Al_2O_3 catalyst had a low initial activity and underwent little deactivation. The sulfidic Ni–Mo/γ-Al_2O_3 catalyst had a lower activity than the oxidic form but a higher initial activity than the sulfided Mo/γ-Al_2O_3 catalyst. After roughly 20 h onstream, the conversion of 1-naphthol catalyzed by the sulfidic Ni–Mo/γ-Al_2O_3 approached that catalyzed by the sulfidic Mo/γ-Al_2O_3.

In summary, the oxidic forms of each catalyst were initially more active than the sulfidic forms. The rate of decrease of activity of the Mo/γ-Al_2O_3 was lower than that of the Ni–Mo/γ-Al_2O_3, independent of whether the catalysts were in the oxidic or sulfidic form.

The oxidic Mo/γ-Al_2O_3 catalyst was reactivated by treatment with H_2 for 2 h at 400°C. The reactivated catalyst regained almost all its initial activity. A complementary experiment was done with the sulfidic Ni–Mo/γ-Al_2O_3 catalyst. Complete reactivation was observed after a H_2S/H_2 treatment at 400°C for 2 h. We conclude that both the oxidic Mo/γ-Al_2O_3 and the sulfidic Ni–Mo/γ-Al_2O_3 catalysts could be deactivated and reactivated reversibly.

Hydrodeoxygenation of the weak-acid fraction of the SRC-II coal-derived liquid

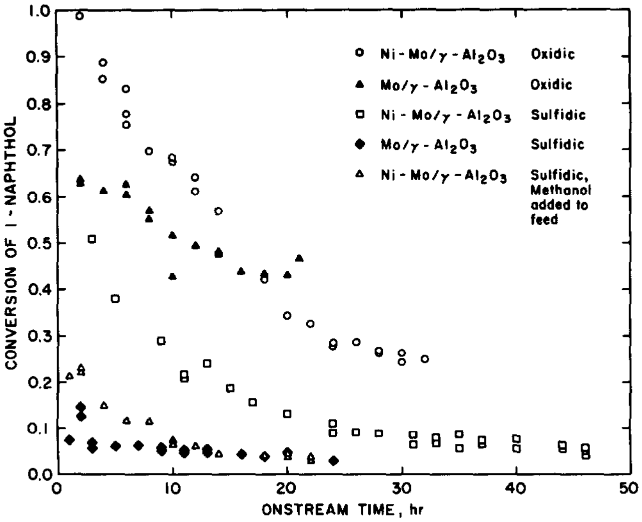

FIG. 2. Catalyst deactivation during hydrodeoxygenation of 1-naphthol. Temperature = 225°C; pressure = 120 atm; WHSV = 0.4. The feed contained 2.2 × 10^{-5} mol of 1-naphthol/g of solution.

was investigated with the sulfided Ni–Mo/γ-Al_2O_3 catalyst. The change in the fractional removal of oxygen (determined by elemental analysis of the products) with time onstream is shown in Fig. 3. Part of the initial catalytic activity was lost in a period of roughly 10 h, after which the deactivation was almost negligible; this behavior is qualitatively like that observed with the 1-naphthol, evidently confirming the appropriateness of this model reactant.

Selectivities of Catalysts

Accompanying the deactivation of the catalysts in all the experiments with 1-naphthol, there were changes in selectivity. The Ni–Mo/γ-Al_2O_3 in both the sulfidic and oxidic forms catalyzed formation of products that did not react further to give tetralin in any significant concentration. Therefore, assuming that the network of Fig. 1 is valid for both forms of the catalyst, we infer the pattern of changes in selectivity for hydrogenation vs HDO as a function of time on stream. The results are illustrated in Fig. 4 for the sulfidic Ni–Mo/γ-Al_2O_3 catalyst. The concentration of naphthalene (the hydrodeoxygenation product) decreased with time on stream, and the concentration of 5,6,7,8-tetrahydro-1-naphthol (the hydrogenation product) decreased slightly with time on stream. In contrast, the concentration of 1-tetralone increased; only little 1-tetralone was found in the product for approximately the first 10 h, but a high concentration of 1-tetralone was maintained later in the experiment, decreasing at times beyond 40 h onstream.

The change in selectivity observed with the oxidic Ni–Mo/γ-Al_2O_3 catalyst was less but followed much the same pattern. The concentrations of the products naphthalene, 1-tetralone, and 5,6,7,8-tetrahydro-1-naphthol all maintained higher values than

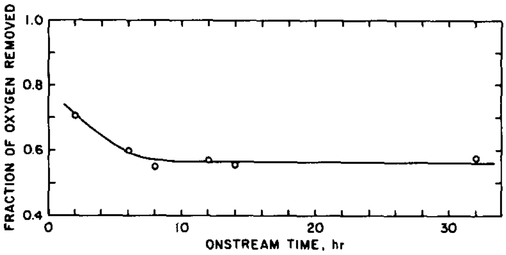

FIG. 3. Hydrodeoxygenation of the weak-acid fraction of SRC-II coal-derived liquid catalyzed by sulfided Ni-Mo/γ-Al_2O_3. Temperature = 350°C; pressure = 120 atm; WHSV = 0.64 (g of catalyst · h)/(g of weak acid fraction).

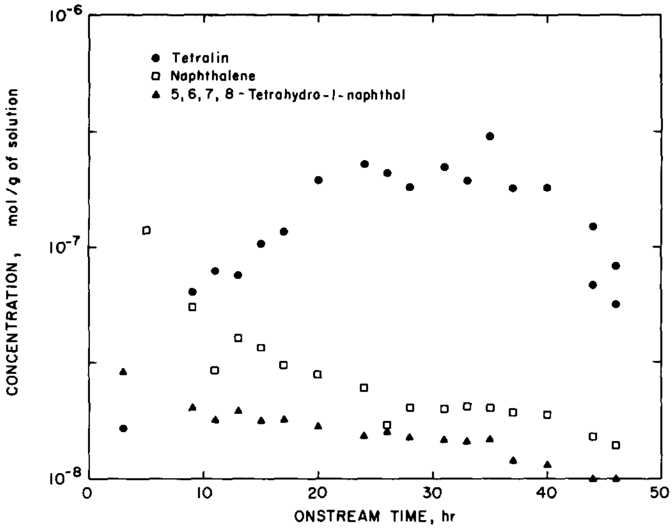

FIG. 4. Product distribution during hydroprocessing of 1-naphthol catalyzed by sulfided Ni–Mo/γ-Al_2O_3: mass of catalyst = 50 mg; WHSV = 0.4; temperature = 225°C; pressure = 120 atm.

those observed with the sulfidic form of the catalyst.

When the oxidic Mo/γ-Al_2O_3 catalyst was used, the concentrations of these products were negligible; the only observed organic product was tetralin. When the sulfidic Mo/γ-Al_2O_3 catalyst was used, negligible concentrations of naphthalene and 5,6,7,8-tetrahydro-1-naphthol were again observed, but the 1-tetralone concentration was measurable, having a nearly constant value, less than that observed with the sulfidic Ni–Mo/γ-Al_2O_3 catalyst.

In summary, assuming the general validity of the reaction network shown in Fig. 1, we infer that the catalytic activity for the HDO reaction decreased to a greater extent during the deactivation of the catalyst than did the activity for hydrogenation. This pattern of selectivity change was more pronounced for the sulfidic than the oxidic catalysts.

Role of Water in Catalyst Deactivation

Since water was a product in all the aforementioned experiments, it was considered to be a possible cause of the catalyst deactivation. To test this assumption, we added methanol (0.1 wt%) to the feed in some experiments. Methanol was chosen because it is (slightly) soluble in the feed and expected to decompose readily in the presence of the catalyst to form water and methane. Since methane is expected to be virtually inert, any change of activity or selectivity is inferred to be caused by the water.

The activity of the sulfided Ni–Mo/γ-Al_2O_3 catalyst decreased as a result of the addition of methanol to the feed. The product distribution observed initially in the experiment with added methanol was nearly the same as that observed with the same catalyst after it had been deactivated by operating for 25 h on stream, as shown in Fig. 4. The degree of activity loss caused by the methanol was also the same as that of the catalyst after 25 h of operation without added methanol. All these results are consistent with the hypothesis that water caused the decrease in activity and the change in selectivity of the catalyst.

DISCUSSION

Since the deactivation of the catalyst took place similarly for 1-naphthol and the complex coal–liquid mixture, we infer that the pattern of initial relatively rapid deactivation followed by slow deactivation may be general for hydroprocessing of oxygen-containing fossil fuels. The results show that for both the oxidic and sulfidic catalysts, the Ni–Mo/γ-Al_2O_3 has a higher initial activity than the Mo/γ-Al_2O_3. After approximately 25 h on stream, however, there was only little difference, suggesting that after the catalyst underwent a break-in, the role of the nickel was sharply diminished.

Since methanol accelerated the decline in activity, we infer that water is the cause of the rapid deactivation observed in the break-in period. We suggest that during this period, in the presence of water, the catalyst underwent significant structural changes. Since the catalysts may be used in the presence of H_2S as well as H_2O, we may expect both the oxidic and sulfidic forms to occur, depending on the processing conditions.

To explain the difference between the Ni–Mo/γ-Al_2O_3 and Mo/γ-Al_2O_3 catalysts with respect to their degree of deactivation, we propose that there are two different types of sites on the Ni–Mo/γ-Al_2O_3 catalysts. One type is also presumed to be present on the Mo/γ-Al_2O_3. As a result of formation of water on the catalyst surface, one type of site on Ni–Mo/γ-Al_2O_3 is presumed to be deactivated, the remaining site being that present on the Mo/γ-Al_2O_3. This simple hypothesis provides an explanation for the result that the Ni–Mo/γ-Al_2O_3 and Mo/γ-Al_2O_3 catalysts had about the same activity in the deactivated state following the break-in period. The effect of added methanol is consistent with this suggestion, i.e., the sulfidic Mo/γ-Al_2O_3 catalyst in the presence of methanol had about the same activity as the deactivated catalyst. Both types are (partly) deactivated by water, but the sites associated with Mo appear to be less susceptible to deactivation than those associated with Ni.

A simple explanation for the deactivation follows from the assumption that an active site consists of an anion vacancy next to a transition metal ion; the site can become saturated by adsorption of H_2O or H_2S. Consequently, we suggest, the site can either operate in direct HDO [as has been suggested by Lipsch and Schuit (*15*) for HDS] or in aromatic ring hydrogenation [as suggested by Kwart *et al.* for HDS (*16*)]; in each case, two H atoms are donated to the reactant molecule. Desikan and Amberg (*17*), working with sulfidic catalysts, concluded that the two reactions needed different types of anion vacancies, an assumption that is widely accepted (*18*). This requirement leads to the inference that the rates of deactivation should be different for the hydrogenation reactions (1 and 3) on the one hand, and for the HDO reaction (2) on the other (Fig. 1). Indeed, with the sulfidic catalysts, the activity for reaction 2 is more readily lost than that for reactions 1 and 3. We might infer, then, that Lipsch's site and Kwart's site are different, e.g., because [as assumed by Stevens *et al.* (*18*)] the Kwart site is located on the crystal edge and the Lipsch site on the basal plane of MoS_2. The oxidic catalyst, on the other hand, does not show this difference: the Lipsch site and the Kwart site might therefore be more nearly the same. The deformed rutile symmetry of MoO_2 (*19*) would probably present many slightly different surface sites but not the sharp difference between edge site and basal plane site of the MoS_2 layer structure.

Reaction 3 can be written in terms of a Kwart mechanism followed by a fast keto-enol tautomerization; the ultimate product should be tetralin formed by HDO of tetralone. The water formed in the reaction inhibits the tetralone–tetralin reaction, and, as a consequence, tetralone becomes the main product. The keto-enol tautomerization is catalyzed by traces of bases or acids (*20*). The surface of an alumina support containing –OH groups would therefore catalyze this reaction. Instead of being inhibited by water, this reaction could actually be facilitated as water reacts with the Al_2O_3 surface to increase the –OH group concentration.

The blocking of sites by H_2O or H_2S can be considered as simple ligand association with an anion vacancy, represented schematically as follows:

$$O^{2-}\square_a + H_2O \rightleftarrows 2OH^- \qquad (4)$$

$$S^{2-}\square_a + H_2O \rightleftarrows SH \cdot OH \qquad (5)$$

where $\square_a$ is an anion vacancy.

An alternative model is given by an oxidative addition:

$$2Mo^{3+} + O^{2-}\square_a + H_2O \rightleftarrows 2Mo^{4+} + 2O^{2-} + H_2 \qquad (6)$$

$$2Mo^{3+} + S^{2-}\square_a + H_2S \rightleftarrows 2Mo^{4+} + 2S^{2-} + H_2 \qquad (7)$$

where O^{2-} and S^{2-} are anions located on the surface but belonging to the bulk structure. Similar equations are feasible for $Ni^0 \rightarrow Ni^{2+} + 2e^-$, etc. The oxidative addition is similar for the catalyzed HDO and HDS reactions; it appears to offer the better possibilities for explaining the observed effects. For instance, the difference in activity between oxidic and sulfidic catalysts (the latter being less active) could be a consequence of the Mo in the sulfidic catalyst remaining in a higher oxidation state because of the continuous addition of CS_2. As a result, reaction (7) would be driven to the right (fewer anion vacancies, less tendency for electron donation, and therefore less activity). A pretreatment with H_2, on the other hand, would be expected to drive reaction (6) to the left (more vacancies and greater activity). On the other hand, adding H_2O would be expected to have a much greater effect on reaction (6) than on reaction (7), because the latter reaction is already driven to the right because of the earlier presence of H_2S.

The thermochemistry of some of these reactions can be estimated from enthalpies of formation given in the literature (*21*, *23*): MoO_3, −180; MoO_2, −140; NiO, −57; MoS_2, −66; Ni_3S_2, −52; NiS, −22; and $H_2O(g)$, −58 kcal/mol. We estimate roughly the following values for Mo_2O_3, −210, and Mo_2S_3, −100 kcal/mol. The following enthalpies of reaction, ΔH_r, are then estimated (all in kcal/mol):

	ΔH_r, kcal/mol
$Mo_2O_3 + H_2O \rightleftarrows 2MoO_2 + H_2$	−12
$Ni + H_2O \rightleftarrows NiO + H_2$	+1
$Ni_3S_2 + H_2O \rightleftarrows NiO + 2NiS + H_2$	+10
$Mo_2S_3 + H_2O \rightleftarrows \frac{3}{2}MoS_2 + \frac{1}{2}MoO_2 + H_2$	−11

The reactions written from right to left are expected to occur during pretreatment, while those written from left to right are expected to represent the interaction with H_2O, i.e., the deactivation. Reduction to the active state is apparently more difficult for molybdenum compounds than for nickel compounds, so that nickel-containing species would be more active for the catalytic reaction; however, they would become more readily deactivated by H_2O. Obviously, given the uncertainties in the estimates of the enthalpies, this line of reasoning should be considered speculative. At best, it is an indication that the oxidative addition mechanism may be considered a viable alternative to the simple ligand association.

ACKNOWLEDGMENTS

We thank S. K. Starry and S. K. Banerjee for experimental assistance and W. K. Hall for providing the $Mo/\gamma\text{-}Al_2O_3$ catalyst. The work was supported by the U.S. Department of Energy.

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