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Hydrodesulfurization and hydrogenation of aromatic compounds catalyzed by Ni–Mo/γ-Al_2O_3: effects of nickel sulfide and vanadium sulfide deposits

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A standard Ni–Mo/γ-Al_2O_3 catalyst containing 4 wt% Ni was modified by addition of nickel (2 wt%) and, alternatively, of vanadium (4 wt%) by contacting with a solution of the respective metal naphthenate. The catalysts were sulfided and tested in a batch reactor at 350°C and 165 bar for hydrogenation of naphthalene and for hydroprocessing of dibenzothiophene. Reaction networks were determined for each reactant, and the dependence of the pseudo first-order rate constants on the amount of nickel and of vanadium in the catalyst was used to determine the effects of nickel sulfide and of vanadium sulfide deposits on catalyst performance. For example, the nickel sulfide deposits only slightly affected the rate constants for hydrogenation in either network, but the vanadium sulfide deposits led to a decrease of at most 50% in the rate constants for hydrogenation reactions in the naphthalene network and to a doubling of the rate constants for hydrogenation reactions in the dibenzothiophene network. The nickel sulfide deposits led to almost no change in the rate constant for hydrogenolysis of dibenzothiophene (to give biphenyl), but the vanadium sulfide deposits led to a threefold decrease in the rate constant for this reaction. The nickel sulfide deposits have little activity for reactions giving lower-molecular-weight ("cracking") products, but the vanadium sulfide deposits have a relatively high activity for cracking, which suggests that they are acidic. The effects of the deposits are complex, as they both block catalytic sites and form new ones. The results indicate a need for representing the nickel and sulfide deposits separately in process models for heavy oil hydroprocessing.

Keywords: hydroprocessing; hydrogenation; hydrodesulfurization; poisoning; nickel sulfide deposits; vanadium sulfide deposits

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1. Introduction

Catalysts used for hydrodesulfurization and other hydroprocessing reactions, typified by sulfided Co–Mo/γ-Al_2O_3 and sulfided Ni–Mo/γ-Al_2O_3, are deactivated by deposits of coke and of nickel and vanadium sulfides [1] that are formed from soluble porphyrin-like compounds found in the gas oil and residuum fractions of petroleum. The effects of the metal sulfide deposits are complex and only partially understood. These deposits affect catalyst performance by (1) choking off pore mouths and limiting the access of reactants to the interior catalyst surface, (2) covering catalytic sites, (3) plugging catalyst beds, and (4) forming new catalytic sites.

Because the metal sulfide deposits are usually nonuniform within individual catalyst particles as a consequence of intraparticle mass transfer limitations in hydrodemetallization [1], because the nickel and vanadium sulfide deposits are formed simultaneously in catalytic hydroprocessing of petroleum, and because only few experiments have been done with separate nickel sulfide deposits and vanadium sulfide deposits [2], the effects of the nickel sulfide and vanadium sulfides have not been distinguished from each other. The goals of this research were to investigate hydroprocessing catalysts with uniform deposits of nickel sulfide and, separately, of vanadium sulfide to evaluate the separate effects. The catalyst performance in hydrogenation and hydrogenolysis was characterized by quantitative reaction networks for naphthalene hydrogenation and dibenzothiophene (DBT) hydrodesulfurization.

2. Experimental

2.1. CHEMICALS

The organic reagents (Aldrich, used without further purification) were dibenzothiophene (99+%), naphthalene (99+%), quinoline (98%), cyclohexane (99+%), and carbon disulfide (99.9+%). Nickel naphthenate (5 wt% in toluene) and vanadium naphthenate (2 wt% in toluene) were supplied by Wako Pure Chemical Industries (Japan). Hydrogen (99.999%, Matheson) was used without purification.

2.2. CATALYST PREPARATION

The Ni–Mo/γ-Al_2O_3 catalyst had a surface area of 255 m^2/g and a pore volume of 0.58 cm^3/g. It was used in the form of 1/16-inch cylinders. Samples containing vanadium or larger amounts of nickel than were present in the catalyst as supplied were prepared by the incipient wetness technique. Batches of catalyst were brought in contact with solutions of vanadium naphthenate or nickel naphthenate followed by drying to remove all the solvent, followed by calcination. Thus all the added nickel or vanadium remained in the catalyst.

Individual catalyst particles were characterized by electron microprobe analysis with a Jeol model JXA733 instrument to determine profiles of Mo, Ni and V. Line profiles were measured with wavelength dispersive spectroscopy.

Performance of catalysts was evaluated with a 1 ℓ autoclave reactor designed for nearly isothermal, high-pressure semibatch reaction experiments. The pressure was kept nearly constant as H_2 was introduced approximately as fast as it was consumed in the catalytic reactions. The apparatus was designed so that the catalyst and solvent cyclohexane (500 ml) could be brought to the desired reaction temperature in the autoclave prior to the rapid injection of the reactants with high-pressure H_2. Each sample of catalyst was introduced into the reactor with the cyclohexane and CS_2 to keep the catalyst in the sulfided state. The catalyst mass was 2.00 g when the catalyst was used without added nickel or vanadium. When nickel or vanadium was added, the mass of catalyst excluding the added components was again 2.00 g. CS_2 (2.0 ml) was added to the mixture to presulfide the catalyst upon the addition of H_2; the CS_2 (1.5 ml) was converted rapidly into methane and H_2S. The reactor was then pressurized with H_2 at 42 bar, heated over a period of 2 h to 350°C, and held for 2 h at this temperature. Each catalytic reaction experiment was carried out following the sulfiding of the catalyst. The reactant mixtures contained naphthalene $+ H_2$, DBT $+ H_2$, or naphthalene + DBT + quinoline $+ H_2$. The organic reactants were introduced into the reactor in solutions of cyclohexane, with the total volume added being 20 ml. The amounts of the organic reactants were either zero or the following: naphthalene, 1.05 g (8.20 mmol); DBT, 0.700 g (3.80 mmol); quinoline, 0.443 g (3.43 mmol). The reaction temperature was 350 ± 1°C, and the total pressure 165 ± 3 bar.

The liquid products were analyzed by gas chromatography. The peaks were almost all well separated, the exceptions being relatively light cracking products, e.g., benzene. An analysis to determine the amount of any cyclohexane that might have been produced was not possible because this solvent was present in large excess in the reactant mixtures.

3. Results

3.1. CATALYST CHARACTERIZATION

The nickel content was either 4.0 or 6.0 wt%. The vanadium content was either 0 or 4.0 wt%. The electron microprobe analyses all showed that the distributions of molybdenum, nickel, and vanadium in the catalyst particles were nearly uniform.

3.2. CATALYST PERFORMANCE

Catalysts were reused several times in the reaction experiments, and the product distributions and activities remained unchanged within experimental error. Thus

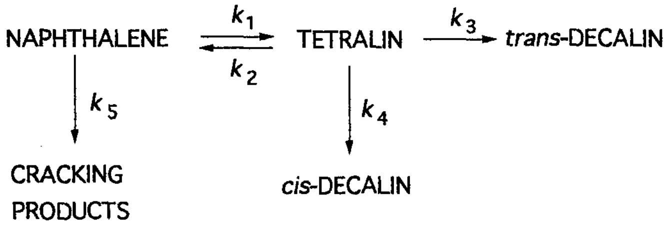

Fig. 1. Approximate reaction network for hydrogenation of naphthalene. The reactions are represented as pseudo first order in the organic reactant. The rate constants, represented by the k_i values, are summarized in table 1. The reactant H_2 is omitted from the depiction to simplify the representation.

the deactivation taking place during the semibatch reactor experiments is concluded to have been negligible.

The products of naphthalene conversion were tetralin, the two isomers of decalin, and lighter products that are lumped as cracking products. The mass balances closed within the range 96–101%. The initial rate of formation of tetralin was greater than zero for each catalyst, and the concentration passed through a maximum after about 3–4 h for each; thus tetralin is identified as a primary product. The initial rate of formation of decalins was zero for each catalyst, and the concentration increased monotonically with time; thus, decalins are identified as nonprimary products. The cracking products were formed from the beginning, and the lump is represented as a primary product.

The naphthalene conversion results are in good agreement with the literature [3,4] and consistent with the sequential reaction network of fig. 1. For simplicity and consistent with earlier work [3,4], the order or each reaction in the organic reactant is approximated as unity. The conversion–time data were used to estimate the pseudo-first-order rate constants shown in this network. The best-fit estimates of the rate constants determined with a multi level single linkage algorithm are shown in table 1. The network provides a good fit of the data and is regarded as an accurate representation except for the cracking reaction; since the cracking conversion was low, there was insufficient information for determining the pathways for cracking, and the simplest approximation was adopted, namely, that all the crack-

Table 1
Rate constants characteristic of reactions in the naphthalene hydrogenation network (fig. 1)

Ni content (wt%)	V content (wt%)	$10k_1$ [a]	10^2k_3 [a]	10^3k_4 [a]	10^3k_5 [a]
4.0	0.0	4.0	2.9	8	8
6.0	0.0	4.1	2.9	8	3
4.0	4.0	2.7	1.5	5	23

[a] Units: ℓ/(g-catalyst h) based on the mass of unsulfided catalyst without any nickel or vanadium in addition to that present in the catalyst as supplied, which contained 4.0 wt% Ni and no V.

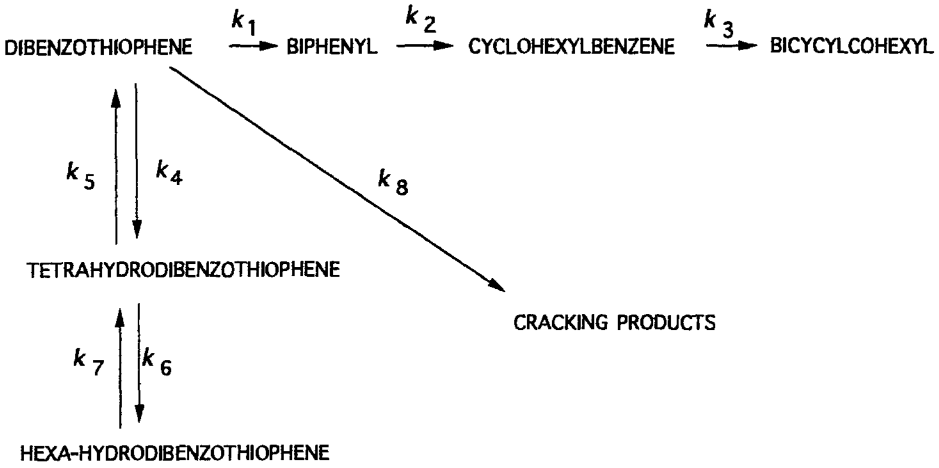

Fig. 2. Approximate reaction network for hydroprocessing of dibenzothiophene. The reactions are represented as pseudo first order in the organic reactant. The rate constants, represented by the k_i values, are summarized in table 2. The reactant H_2 is omitted from the depiction to simplify the representation.

ing products were formed from naphthalene itself. More details and a statistical evaluation will be reported elsewhere [5].

The observed products of DBT conversion were biphenyl, cyclohexylbenzene, bicyclohexyl, hydrogenated dibenzothiophenes (believed on the basis of earlier reports [4,6]) to be hexahydrodibenzothiophene and tetrahydrobenzothiophene, and light byproducts (referred to as cracking products) including toluene and ethylbenzene. The light products were not fully resolved by the gas chromatographic analysis. The mass balances closed within a range of about 100 ± 5% in experiments carried out with the catalyst to which no nickel or vanadium had been added, but when vanadium was present in the catalyst, there were high yields of unidentified light products, and the closures were in the range of about 100 ± 25% at the highest conversion.

The DBT conversion data are consistent with the reaction network of fig. 2, and the data analysis was carried out with the algorithm used for the naphthalene network. The best-fit pseudo-first-order rate constants are summarized in table 2.

Table 2
Rate constants characteristic of reactions in the dibenzothiophene hydrodesulfurization network (fig. 2)

Ni content (wt%)	V content (wt%)	$10k_1$ [a]	$10k_2$ [a]	10^2k_3 [a]	10^2k_8 [a]
4.0	0.0	2.9	1.1	2	2
6.0	0.0	2.7	1.5	3	2
4.0	4.0	1.0	2.3	4	7

[a] Units as in table 1.

Again, the network is an accurate approximation except for the cracking reaction pathways, which are unidentified and for simplicity represented as only a reaction of DBT itself. The values included in the table are those that could be determined with a sound statistical basis. The rate constants that could not be estimated on this basis are omitted from the table; the goodness of fit was barely affected by the omission. Details and a statistical evaluation will be reported elsewhere [5].

4. Discussion

Because the reaction networks of figs. 1 and 2 represent the data well for all the catalysts, we infer that the added nickel and vanadium did not substantially change the reaction networks, although they did affect the values of the rate constants for the individual reactions in the networks (tables 1 and 2). Because the deposits of nickel and vanadium sulfides were nearly uniform in the catalyst particles and because the nickel and vanadium were added in separate batches of catalyst, the results provide the sought-for resolution of the effects of nickel and vanadium sulfides on the catalytic activity.

The addition of nickel (increasing the nickel content of the catalyst from 4.0 to 6.0 wt%) led to only slightly changed rate constants for hydrogenation, both in the naphthalene network (table 1) and in the DBT network (table 2). In contrast, the addition of 4.0 wt% vanadium led to a decrease in the rate constants for hydrogenation in the naphthalene network (to about 1/2–2/3 of the values for the catalyst as supplied) and to an increase (an approximate doubling of the rate constants) for the hydrogenation reactions in the DBT network (table 2). These results indicate that the vanadium sulfide deposits are catalytically active for hydrogenation, and that the nickel sulfides are less active for these reactions. The results suggest that the loss of activity resulting from coverage of surface sites in the original catalyst by nickel sulfide is approximately compensated by the activity of the deposited nickel sulfide.

The added nickel sulfides led to almost no change in the rate constant for the hydrogenolysis reaction in the DBT network (the reaction giving biphenyl from DBT), but the addition of vanadium caused approximately a threefold decrease in the rate constant for this reaction. These results are consistent with the suggestion that the deposited nickel sulfide was catalytically active for hydrogenolysis, with the coverage of the surface of the original catalyst being compensated by the activity of the deposits. The data suggest that the vanadium sulfides are poisons for the hydrogenolysis reaction.

The contrasting roles of the vanadium sulfides deposits for hydrogenation and hydrogenolysis reactions implies that the catalytic sites for hydrogenation of aromatic hydrocarbons on these deposits are different from those for hydrogenation of sulfur-containing aromatic compounds, which are more strongly adsorbed than the hydrocarbons, possibly (in part) as a consequence of bonding through the electron-rich sulfur atom [7].

The reactions described as cracking in both reaction networks are those forming lower-molecular-weight hydrocarbon products, not all of which were identified. Thus the designation is only approximate. The added nickel led to a decrease in the cracking in the naphthalene network (by a factor of about three) and to almost no change in the cracking in the DBT network. In contrast, the vanadium caused approximately a tripling of the cracking rate constants in both the naphthalene and the DBT network. Thus we conclude that the nickel sulfide deposits have little activity for cracking and the vanadium sulfide deposits have a high activity for cracking.

Because they are active for cracking reactions, the vanadium sulfide deposits are suggested to incorporate acidic sites. In agreement with this suggestion, addition of the strong base quinoline to the feed markedly decreased the effect of the vanadium sulfide deposits as cracking catalysts; data demonstrating the effect will be reported elsewhere [5]. There are precedents in the literature for the acidity and cracking activity of vanadium sulfides [8].

In summary, the results of this work demonstrate that the deposits of nickel and of vanadium sulfides in hydroprocessing catalysts have significantly different effects on catalyst performance. The results imply that process models for heavy oil hydroprocessing could be improved by the incorporation of parameters to account for the separate effects of these two kinds of deposits.

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