

# Investigation of the Reaction Network of Benzofuran Hydrodeoxygenation over Sulfided and Reduced Ni–Mo/Al<sub>2</sub>O<sub>3</sub> Catalysts

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The hydrodeoxygenation (HDO) network of benzofuran was investigated over alumina-supported Ni–Mo sulfided and reduced catalysts. The effect of reaction temperature, pressure, hydrogen sulfide feed concentration, and pretreatment procedure on the product distribution, hydrogenolysis, and hydrogenation activity of each catalyst was studied. The differences and similarities between the observed benzofuran HDO network and the networks proposed in the literature were examined. Parallels between HDO and hydrodenitrogenation (HDN) were investigated by comparing the benzofuran HDO findings with previous results obtained for indole HDN. Reaction studies were carried out in a fixed-bed vapor-phase reactor using a wide range of feed concentrations at 120–360°C and 300–800 psig. Over the sulfided catalyst, one major route is observed for the benzofuran HDO network; it starts with the hydrogenation of benzofuran to 2,3-dihydrobenzofuran followed by its hydrogenolysis to 2-ethylphenol. Over the reduced catalyst, however, an additional route is observed that begins with the hydrogenation of 2,3-dihydrobenzofuran. This route contains several other oxygen-containing intermediate species that are not observed over the sulfided catalyst, and hydrocarbon products are formed by this route at significantly lower temperatures. The product distribution for both catalysts is found to be a strong function of temperature and H<sub>2</sub>S feed concentration where the hydrogenolysis reactions were promoted and the hydrogenation reactions were inhibited by H<sub>2</sub>S in the feedstream. © 2002 Elsevier Science (USA)

**Key Words:** benzofuran; dihydrobenzofuran; hydrodeoxygenation; Ni–Mo sulfide.

## INTRODUCTION

Hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are the primary catalytic hydrotreating processes that have been heavily investigated because of the environmental concerns associated with the combustion of organonitrogen and organosulfur compounds and because these types of compounds are the major impurities in traditional petroleum feedstocks. HDS and HDN studies have led to a fairly good understanding of the mechanisms

involved in these reactions and effective catalysts have been developed for these two processes. The primary catalysts used for HDS and HDN are sulfided CoMo and NiMo catalysts that are supported on Al<sub>2</sub>O<sub>3</sub>. According to a widely accepted model proposed by Topsoe and co-workers, these catalysts consist of stacks of MoS<sub>2</sub> layers supported over alumina and the Ni or Co species are located on the edges of these stacks (i.e., CoMoS and NiMoS phases) (1–4).

Stricter environmental legislation on the allowable concentrations of nitrogen and sulfur compounds in fuel products and declining petroleum production rates in the United States have made it necessary to process heavier petroleum fractions and synthetic feedstocks such as coal-derived liquid, oil shale, tar sands, and biomass. This trend makes hydrodeoxygenation (HDO) processes very important since in these nonconventional feedstocks, organooxygen compounds constitute the primary impurities and their removal is essential to maintaining the stability of commercial fuels and achieving the purity levels required for chemical applications.

Since the majority of organooxygen compounds that are found in synthetic feedstocks have either a phenolic or a furanic structure (5–17), a good model compound for studying HDO reactions is benzofuran (BF). Benzofuran also has a structure similar to those of the most commonly studied organosulfur and organonitrogen compounds for HDS and HDN reactions, respectively and thus provides an analog that facilitates comparisons of HDO with these processes. The reaction network for HDO of benzofuran that is reported in the literature is shown in Fig. 1 (18–20). It was established from BF reaction experiments conducted over sulfided CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts. Reaction temperature and pressure for the experiments ranged from 200 to 350°C and from 1 to 100 atm, respectively. There is a general consensus that direct extraction of oxygen from benzofuran does not occur. The first step in the reaction network is the hydrogenation of the heterocyclic ring, which leads to the formation of 2,3-dihydrobenzofuran (DHBF). 2,3-Dihydrobenzofuran, in turn, is converted into 2-ethylphenol (EP) through a hydrogenolysis reaction, which then leads to the C–O bond cleavage that results in

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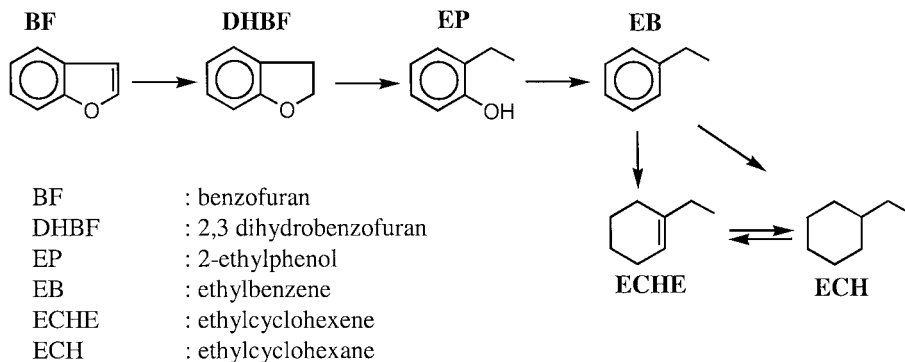


FIG. 1. Benzofuran HDO network proposed in the literature (18–20).

the formation of hydrocarbons. According to this network, ethylcyclohexene or ethylcyclohexane is formed only from hydrogenation of ethyl benzene (EB). Competitive adsorption between the organooxygen compounds and EB can strongly inhibit the reactivity of ethyl benzene.

The nitrogen analog of benzofuran is indole. The first step in the indole HDN network is hydrogenation of the heterocyclic ring which leads to the formation of indoline. Indoline undergoes hydrogenolysis, similar to 2,3-dihydrobenzofuran, but it is also hydrogenated to octahydroindole, providing an additional route in the indole HDN network that leads to the formation of hydrocarbon products (21–26). One major difference, therefore, between the indole HDN network and the BF HDO network is that the HDO reaction scheme includes only one route leading to the formation of hydrocarbons, whereas two routes are observed in HDN studies of indole. Therefore a key question regarding the benzofuran HDO network is whether a secondary route exists that involves saturation of the benzene ring before any hydrogenolysis step takes place and, if so, under what conditions this secondary route becomes favorable. Also of interest is whether the oxygen-containing intermediate species in this secondary route would undergo HDO more readily than their counterparts in the primary route.

Another key issue involving HDO reactions over the sulfided Ni–Mo catalysts is the catalytic functions of the active sites on Ni–Mo sulfide catalysts and, assuming that a parallel exists between the HDN and HDO mechanisms, whether the active site model proposed for indole HDN can account for the catalytic steps observed in benzofuran HDO. Figure 2 depicts the active site model that we have previously proposed for indole HDN (27) where hydrogenation sites are sulfur vacancies associated with Ni or Mo atoms and hydrogenolysis sites are formed by the adsorption and dissociation of  $\text{H}_2\text{S}$  molecules and are Brønsted acid centers associated with Mo atoms.

The HDO of organooxygen compounds under industrial conditions will always occur in the presence of organosulfur compounds. These compounds will be converted to  $\text{H}_2\text{S}$  by hydrodesulfurization. Therefore it is important to de-

termine the effect of  $\text{H}_2\text{S}$  or other sulfur compounds on hydrodeoxygenation reactions. Information about the catalyst active sites for HDO can also be obtained by investigating the effect of  $\text{H}_2\text{S}$  on the hydrogenation and hydrogenolysis reactions in the benzofuran HDO network. In this article, the HDO pathways of benzofuran were examined over reduced and sulfided Ni–Mo/ $\text{Al}_2\text{O}_3$  catalysts by using some of the reaction intermediates (i.e., 2,3-dihydrobenzofuran, 2-ethylphenol, and 2-ethylcyclohexanol) as probe molecules. X-Ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR) were used for pre- and postreaction characterization of the catalysts.

## EXPERIMENTAL

**Catalyst preparation.** The catalytic system used for this study was a NiMo (3% NiO–15%  $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ ) catalyst, which was prepared by wet coimpregnation of  $\gamma\text{-Al}_2\text{O}_3$  with aqueous solutions of ammonium heptamolybdate and

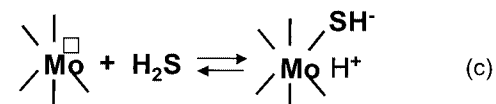
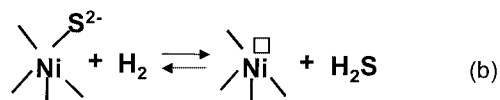
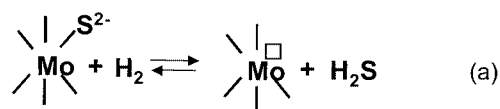


FIG. 2. Proposed catalytic active site model for Ni–Mo/ $\gamma\text{-Al}_2\text{O}_3$  catalyst: (a) Mo hydrogenation site, (b) Ni hydrogenation site, (c) Mo hydrogenolysis site.

nickel nitrate. The preparation procedures and characterization results were presented previously (27–29). The catalyst was in powder form. The loading of the catalyst in the reactor was kept constant at a total surface area of 50 m<sup>2</sup>. Before use, the oxide catalyst was either sulfided or reduced to activate it. Isothermal sulfidation was performed *in situ* at 400°C with 10% H<sub>2</sub>S in H<sub>2</sub> for 10 h. Isothermal reduction was performed *in situ* at temperatures ranging from 400 to 500°C with pure H<sub>2</sub> for 10 h.

**HDO reaction studies.** The reaction studies were carried out in a fixed-bed reactor system. The reactor was made out of 4-mm-i.d. stainless-steel tubing. Gas flow rates were controlled by Brooks 5850E mass flow controllers. Benzofuran and other reactants were introduced into the system by using diffusion tubes. The reactor pressure was controlled by a Tescom backpressure regulator with a control range of 0 to 1500 psig. The feed- and product streams were analyzed by an on-line HP 5890A gas chromatograph. The gas chromatograph was equipped with a 0.53-mm-i.d. fused silica (HP-1) capillary column and a flame ionization detector.

The reaction temperature was varied between 120 and 360°C and the pressure was varied between 300 and 800 psig. In addition to benzofuran HDO, experiments were also performed with 2,3-dihydrobenzofuran, 2-ethylphenol, and 2-ethylcyclohexanol. A wide range of feed concentrations were used for these reactants, with the balance being H<sub>2</sub> or H<sub>2</sub> and H<sub>2</sub>S. Reaction data were collected after steady-state conditions had been reached. The criterion for steady state was established by monitoring the product distribution and the reactant conversion level.

**XPS and TPR characterization.** The X-ray photoelectron spectrometer used for this study was an ESCALAB Mark II that was operated at 14 kV and 20 mA with MgK $\alpha$  radiation. All postsulfidation and postreaction XPS analyses of the catalysts were performed without exposing the catalyst to the atmosphere using a controlled atmosphere probe. Temperature-programmed reduction was performed using an apparatus built in-house, which has been described previously (29). One hundred milligrams of sample was heated at 10°C/min from 25 to 900°C and kept at 900°C for 20 min. The reducing agent was 10% H<sub>2</sub> in He.

## RESULTS

### HDO Reaction Studies over Sulfided Catalyst

In the earlier phases of this study, HDO of benzofuran was investigated over 3% Ni–15% Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sulfided catalysts. A wide range of temperature, pressure, and feed conditions were examined. Table 1 summarizes the conversions and product distributions obtained over this catalyst at pressures of 300 and 800 psig for the

TABLE 1

Variation with Temperature and Pressure of Benzofuran Conversion and Product Selectivity over Sulfided 3% Ni–15% Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

	200°C	240°C	280°C	320°C	360°C
<b>300 psig</b>					
BF conversion (%)	31.3	47.0	74.6	87.5	99.4
Selectivity (%)					
DHBF	64.5	37.2	7.4	1.7	0.0
EP	34.5	46.6	42.2	20.6	2.5
ECHE	0.0	5.3	4.7	3.2	0.0
EB	0.0	10.0	3.6	7.4	7.0
ECH	0.0	0.0	38.3	45.7	46.7
MCH	0.0	0.0	0.0	1.4	2.4
CH	0.0	0.0	3.5	19.8	40.7
<b>800 psig</b>					
BF conversion (%)	42.9	58.1	82.5	93.4	100.0
Selectivity (%)					
DHBF	62.2	36.1	8.5	1.1	0.0
EP	36.8	43.9	40.0	17.1	0.5
ECHE	0.0	6.0	1.2	0.5	0.0
EB	0.0	11.2	0.6	0.9	0.0
ECH	0.0	2.6	40.6	52.5	53.5
MCH	0.0	0.0	2.4	5.3	3.0
CH	0.0	0.0	6.0	22.3	42.6

temperature range 200–360°C with no H<sub>2</sub>S in the feed. The products observed under these conditions are DHBF; EP; three C8 hydrocarbons—ethyl benzene (EB), ethylcyclohexane (ECH), and ethylcyclohexene (ECHE); one C7 hydrocarbon—methylcyclohexane (MCH); and one C6 hydrocarbon—cyclohexane (CH). All of these species are present in the reaction network depicted in Fig. 1 except for the C7 and C6 hydrocarbons which are likely to be formed by dealkylation of the C8 hydrocarbons. As expected, BF conversion increased as temperature was increased and was always greater at 800 psig. No hydrocarbon production was observed at 200°C for either pressure. The overall hydrocarbon yield and the yield of saturated hydrocarbons for temperatures between 240 and 360°C was always greater at 800 psig. For temperatures between 280 and 360°C, the DHBF yield was significantly lower than the EP yield.

Among the reaction parameters that had a strong effect on the product distribution is the presence or absence of H<sub>2</sub>S in the feed mixture. Figure 3 shows the effect of the presence of H<sub>2</sub>S (0.05%) on the reactivity of three organooxygen compounds encountered in this network at different temperatures over sulfided Ni–Mo catalysts. Figure 3a shows H<sub>2</sub>S to have an inhibition effect on benzofuran (BF: 0.04%, 300 psi) conversion. In contrast, when dihydrobenzofuran (DHBF: 0.03%, 600 psi) was substituted for benzofuran as the starting feed molecule, the effect was reversed where the rate of conversion of DHBF was

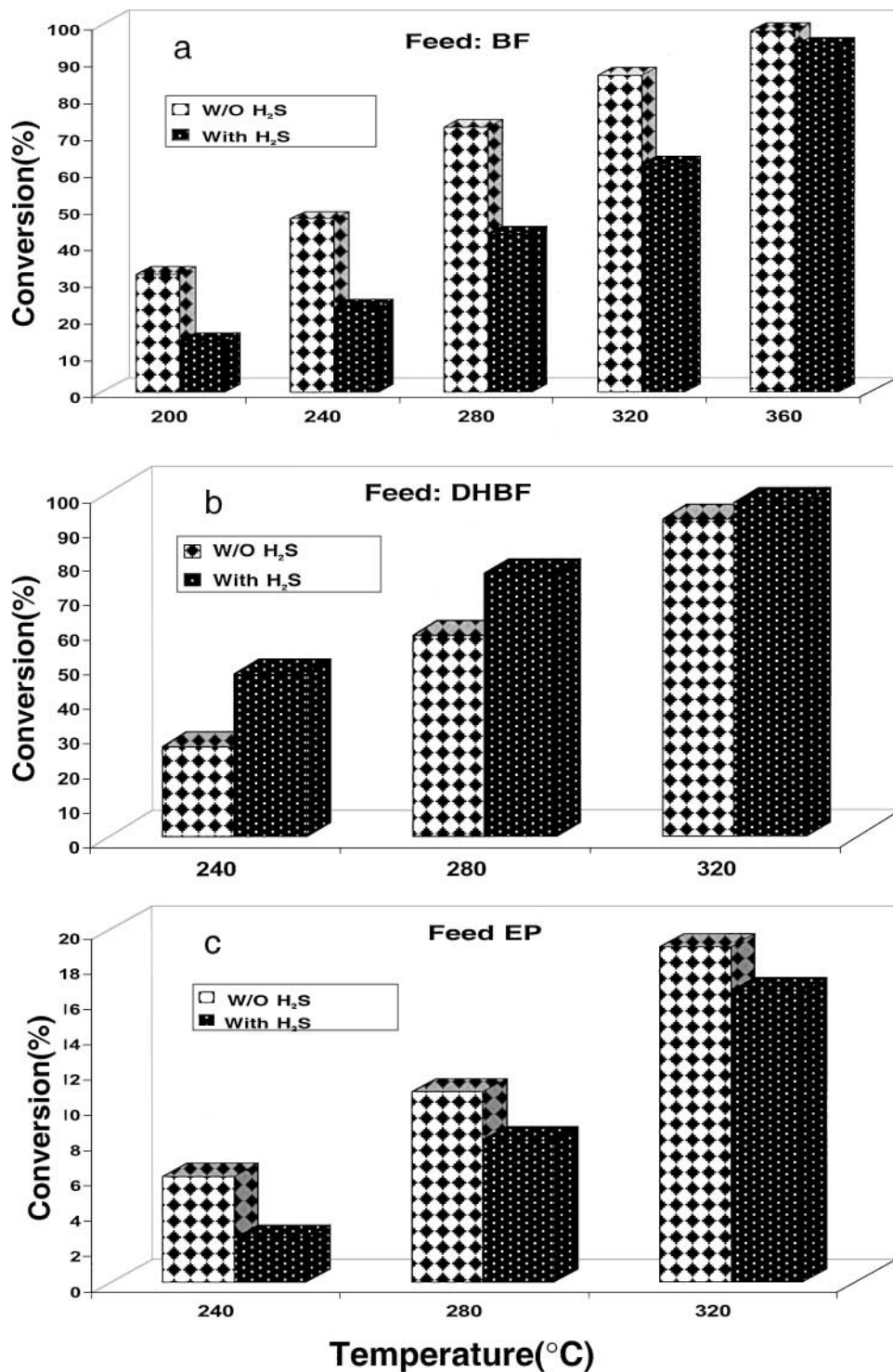


FIG. 3. Effect of H<sub>2</sub>S on percentage conversion using different feed molecules: (a) BF, (b) DHBF, (c) EP.

enhanced by the presence of H<sub>2</sub>S (Fig. 3b). When the next intermediate in the reaction network, EP (0.02%, 300 psi), was used as the starting material, the presence of H<sub>2</sub>S was seen to inhibit its conversion (Fig. 3c) as it did the conversion of BF.

#### *Characterization and HDO Reaction Studies over Reduced Catalyst*

Over the sulfided catalyst, only one oxygen-containing intermediate product, 2,3-dihydrobenzofuran, was produced

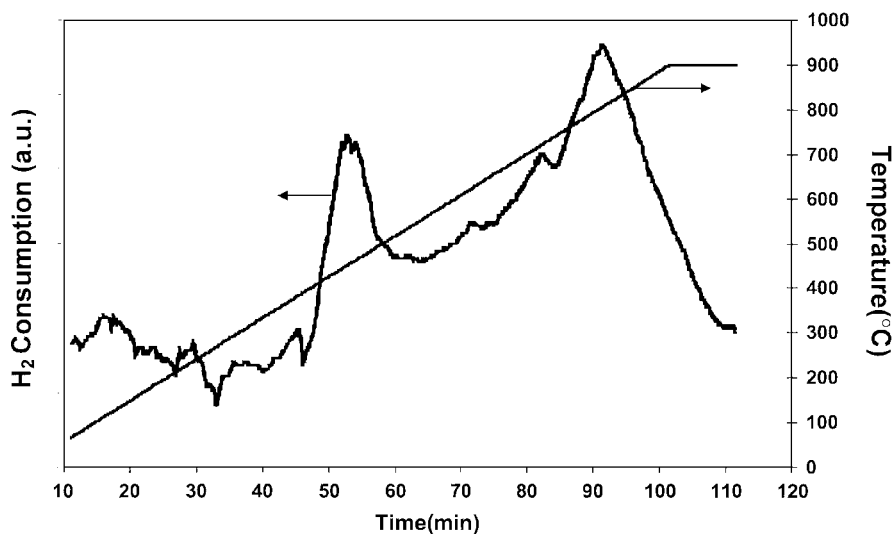


FIG. 4. Temperature-programmed reduction profile of 3% Ni-15% Mo oxide catalyst.

by hydrogenation. This step involves hydrogenation of the heterocycle. In contrast, in our earlier studies of indole HDN over sulfided NiMo/ $\text{Al}_2\text{O}_3$  catalysts, several nitrogen-containing intermediate products were produced by partial hydrogenation of the benzene ring. The reaction conditions for the indole experiments were similar to the conditions for the BF experiments. These observations led us to suspect that it should be possible to produce the oxygen analogs of these nitrogen-containing compounds during benzofuran HDO if the hydrogenation activity of the catalyst can be significantly enhanced. One possible way of increasing the hydrogenation activity is to reduce the catalysts so that the abundance of anionic vacancies associated with Ni and Mo sites is enhanced. It is conceivable that the function of the  $\text{SH}^-$  groups is fulfilled by  $\text{OH}^-$  groups. Earlier work in the literature points to the analogous behavior of reduced catalysts and sulfided catalysts in HDO reactions (8, 33).

To examine the reduction behavior of supported Ni-Mo catalysts, TPR experiments were conducted. Figure 4 shows the TPR profile obtained over the 3% Ni-15% Mo/ $\gamma\text{-Al}_2\text{O}_3$  oxide catalyst. The first major reduction feature occurs in the temperature range 400–500°C. Another reduction feature occurs above 700°C. Although we did not do an XPS analysis of the catalyst after it had gone through the TPR, we suspect this feature to be due to reduction of molybdenum oxide to metallic molybdenum. Since TPR experiments previously performed on bare alumina did not show a similar feature (30), the possibility of this feature being due to the alumina phase can be ruled out. Based on the TPR results, reduction of the oxide form of the catalysts was performed isothermally in the range 400–500°C. Figure 5 shows the deconvoluted Mo 3d X-ray photoelectron spectra of three 3% Ni-15% Mo/ $\gamma\text{-Al}_2\text{O}_3$  catalyst samples: oxide, reduced at 400°C, and reduced at 470°C. Mo is in the 6+ oxidation state in the oxide catalyst and it has

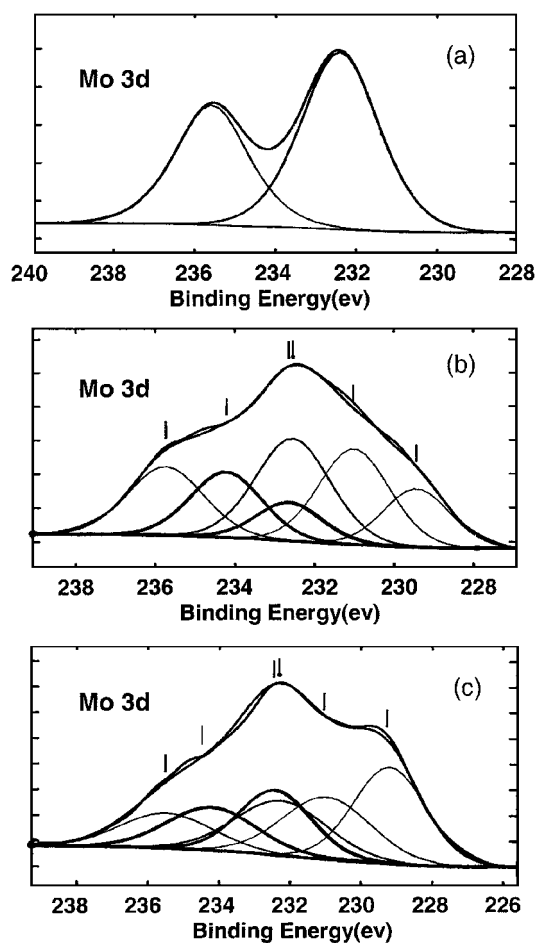


FIG. 5. X-Ray photoelectron spectra of Mo 3d region for prereaction 3% Ni-15% Mo catalysts: (a) oxide, (b) reduced at 400°C, (c) reduced at 470°C.

a coordination environment similar to that of  $\text{MoO}_3$ . Mo in the reduced catalysts is in the 6+, 5+, and 4+ oxidation states and the percentage of Mo in the lower oxidation states increases at higher reduction temperature. In the catalyst reduced at 400°C, the percentages of Mo in 5+ and 4+ oxidation states are 37 and 21%, respectively. In the catalyst reduced at 470°C, the corresponding percentages are 32 and 40%. The Ni  $2p_{3/2}$  binding energy for the oxide sample was 856.1 eV, which is characteristic of a  $\text{Ni}_2\text{O}_3$  phase structure. Therefore, Ni is primarily in a 3+ oxidation state. In the reduced samples, the Ni  $2p_{3/2}$  binding energy was 852.7 eV, which is very close to the binding energy for metallic Ni, although the presence of a substoichiometric nickel oxide phase cannot be ruled out. XPS measurements did not show the presence of a  $\text{NiAl}_2\text{O}_4$  phase in the reduced samples. As the active Ni sites in sulfided NiMo catalysts are believed to be part of the Ni–Mo–S structure, it is conceivable that Ni in the reduced catalysts exists as part of an analogous Ni–Mo–O structure.

The activity of the reduced catalyst was found to be a function of reduction temperature. As reduction temperature increased, the hydrogenation and hydrodeoxygenation activities of the catalyst increased, possibly due to an increased concentration of oxygen vacancies. The results presented in this article are for the catalyst that was reduced at 470°C. Figure 6a shows the conversion and HDO percentages from the BF reaction over the reduced 3% Ni–15% Mo/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst in the absence of  $\text{H}_2\text{S}$  at three different temperatures. The BF feed concentration was 0.04 mol%. The term *HDO percentage* is used to denote the percentage of the feed BF that was converted to oxygen-free hydrocarbons. It should be noted that although the feed conditions used in the BF reactions over the reduced catalysts are the same as those used over the sulfided catalysts, the temperatures are much lower. The hydrogenation activity of the reduced catalyst was so high that the temperatures used for the BF reaction studies on the sulfided catalyst could not be used for the reduced catalyst since the reduced catalysts gave near-complete conversion, even at temperatures as low as 120°C. Although hydrocarbon production is not as high as conversion, it is still quite appreciable, giving an HDO percentage of 16% at 160°C. What is more striking is the product distribution, which shows three additional oxygen-containing intermediate species (Fig. 6b). These compounds, which were not observed during the reaction studies on sulfided catalysts, are hexahydrobenzofuran (HHBF), octahydrobenzofuran (OHBF), and 2-ethylcyclohexanol (ECHOH). Another major difference seen in this figure is the absence of EP, which was the primary component in the BF reactions over sulfided catalysts.

Figure 7 compares the conversion and HDO percentages for the DHBF reaction in the absence of  $\text{H}_2\text{S}$  over the reduced and sulfided catalysts. The DHBF feed concentration was 0.02 mol%. Significantly higher conversion levels were

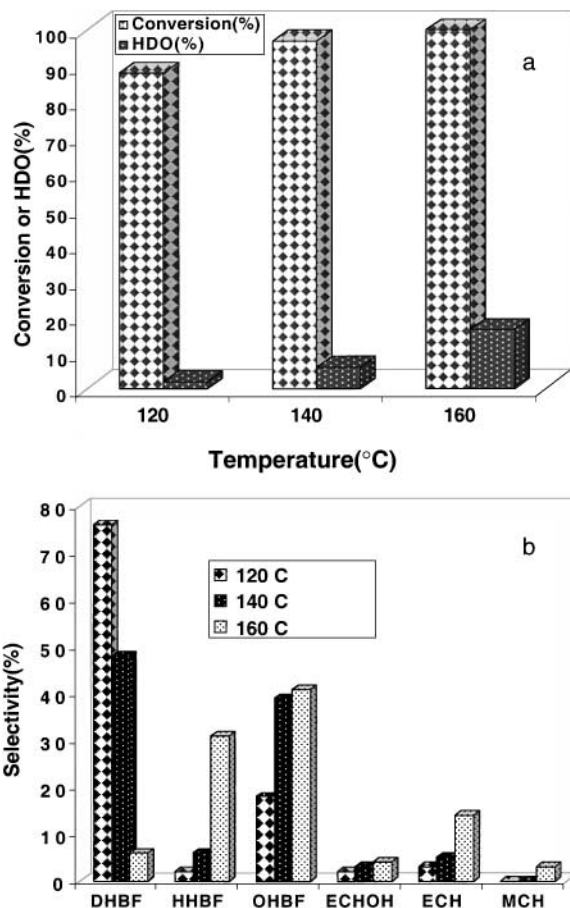


FIG. 6. Activity and product distribution over reduced Ni–Mo catalysts in BF reaction ( $P = 300$  psi): (a) % conversion and % HDO, (b) % product selectivity.

achieved for the reduced catalyst (Fig. 7a), especially at 240 and 280°C. But the difference between the two catalysts was even more striking when HDO percentages were compared. The sulfided catalyst showed essentially no cleavage activity, even at 280°C, while the reduced catalyst gave HDO percentages close to 90%. Figure 8 shows the product yields from the DHBF reaction at 300 psig in the absence of  $\text{H}_2\text{S}$  over the reduced and sulfided catalysts. Yield percentage is defined as the percentage of feed (BF or DHBF) converted to a given product. The product distributions are very different for the two catalysts. Only one major product (EP) was observed over the sulfided catalyst; no other oxygen-containing species were produced and hydrocarbon yield was very low. Over the reduced catalyst, on the other hand, there were three new oxygen-containing products that were not observed over the sulfided catalyst—ECHOH, OHBF, and HHBF—but there was no EP formation. Another important difference between the two catalysts was that the yield of hydrocarbons was substantial over the reduced catalyst, in contrast to the sulfided catalyst, which had little HDO activity under these conditions, even at 280°C.

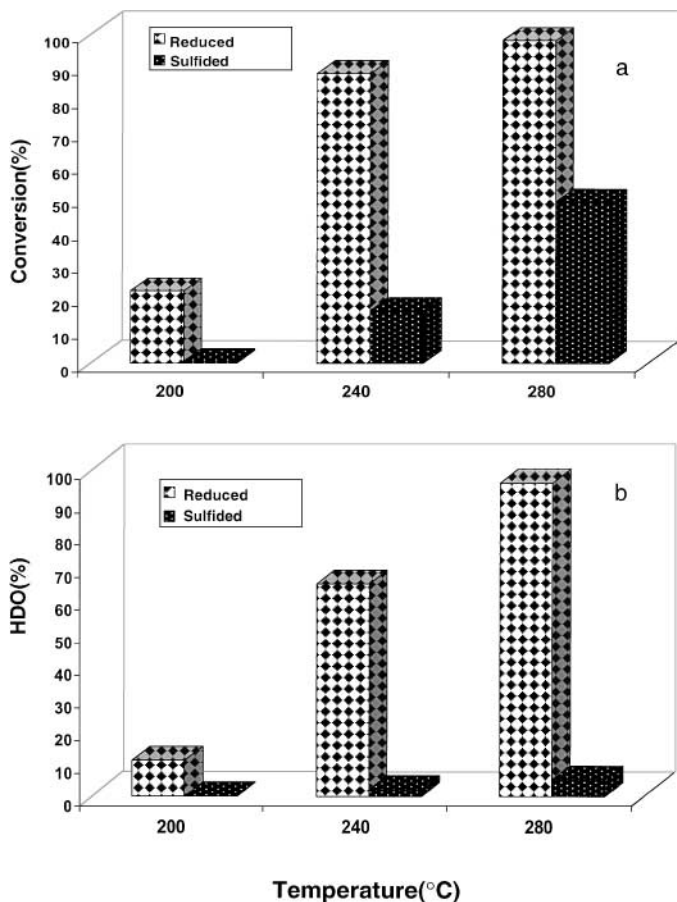


FIG. 7. Comparison of reduced and sulfided Ni-Mo catalysts in DHBf reaction ( $P = 300$  psi): (a) % conversion, (b) % HDO.

#### Postreaction Characterization of Reduced Catalyst

The reduced catalyst was kept on-line for 500 h. During this run, the pressure was kept constant at 300 psig and the feedstream was free of  $H_2S$ . The highest temperature to which the catalyst was exposed was 280°C. There was no change in the activity or the product distribution of the catalyst during the time-on-stream experiment, once steady state was reached. Steady state was usually reached within 3–4 h. There was no decrease in the hydrogenation activity and only a small decrease in the hydrogenolysis activity during the total time-on-stream period. The postreaction sample at the end of the time-on-stream experiment was characterized by XPS. The sample was transferred to the XPS chamber without exposure to atmosphere using a controlled-atmosphere probe. Figure 9 shows the Mo 3d X-ray photoelectron spectra of the pre- and postreaction samples. Mo exists in three different oxidation states in both pre- and postreaction samples. The percentages of Mo in the 6+, 5+, and 4+ oxidation states in the prereaction sample are 28, 32, and 40%, respectively. The corresponding percentages for the postreaction sample are 12, 23, and

65%, indicating a more reduced state for the postreaction sample. Although the reaction temperature was lower than the reduction temperature, it is possible that the higher pressure used for the reaction led to further reduction of the catalyst during the time-on-stream, explaining why the postreaction sample exhibits a more reduced state for molybdenum.

#### DISCUSSION

Our preliminary findings from benzofuran HDO studies on Ni-Mo sulfide catalysts were consistent with a reaction network proposed in the literature (Fig. 1), where the initial step is the hydrogenation of BF to DHBf. EP is the only other oxygen-containing product, suggesting only one route leading to the formation of hydrocarbons over the sulfided catalyst. As expected, higher pressure gave higher BF conversion and also led to greater hydrocarbon yields which contained more of the saturated products, ECH, MCH, and CH. When the effect of  $H_2S$  was examined in BF and DHBf reactions, adding  $H_2S$  to the feed caused

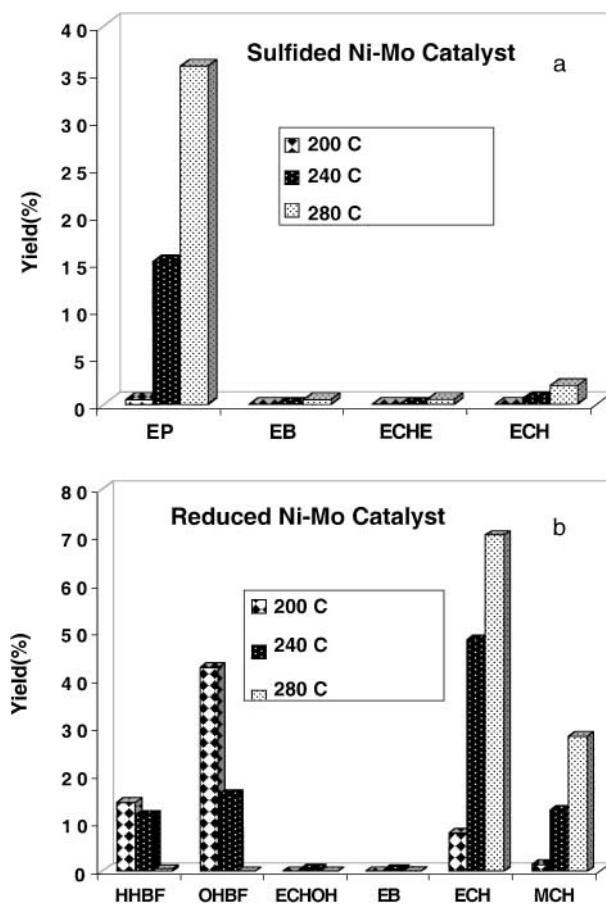


FIG. 8. Variation of product distribution with temperature in DHBf reaction ( $P = 300$  psi): (a) over sulfided Ni-Mo catalysts, (b) over reduced Ni-Mo catalysts.

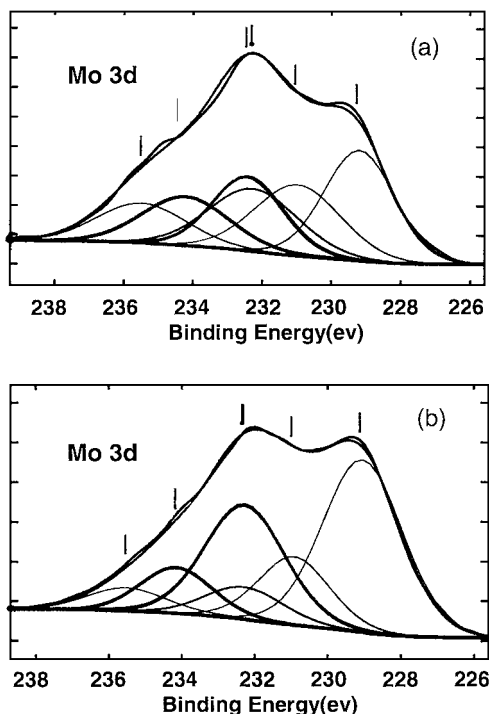


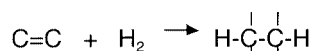
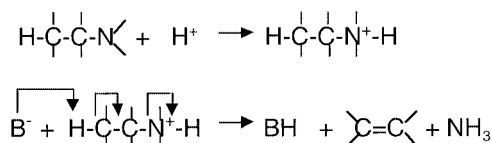
FIG. 9. X-Ray photoelectron spectra of Mo 3d region for pre- and postreaction 3% Ni–15% Mo catalysts: (a) reduced (470°C) prereaction, (b) reduced (470°C) postreaction.

a decrease in BF conversion, but an increase in DHBF conversion. Since BF and DHBF are converted by hydrogenation and hydrogenolysis reactions, respectively, adding H<sub>2</sub>S to the feed was observed to inhibit hydrogenation, but promote hydrogenolysis. This effect was quite similar to the effect of H<sub>2</sub>S observed in the indole HDN reaction studies (21–26) over the same group of catalysts, suggesting that the catalytic active sites responsible for hydrogenation and hydrogenolysis steps in the indole HDN network (i.e., anionic vacancies and Brønsted acid centers, respectively) may be performing similar functions in the benzofuran HDO network (Fig. 2).

When the effect of H<sub>2</sub>S was examined using EP as the starting molecule, the results could no longer be explained by the simple reaction network shown in Fig. 1. These results show that adding H<sub>2</sub>S to the feed causes a decrease in EP conversion (Fig. 3). Since H<sub>2</sub>S promotes the conversion of 2,3-dihydrobenzofuran, it should also promote the conversion of 2-ethylphenol if it is converted directly into EB by a direct hydrogenolysis step. The fact that the result observed was just the opposite suggests that the step involved here is not a direct cleavage step. The aromatic type C(*Sp*<sup>2</sup>)–O bonds in BF and EP are stronger than the aliphatic type C(*Sp*<sup>3</sup>)–O bond in DHBF. Although direct cleavage of the C(*Sp*<sup>2</sup>)–O bond in EP cannot be ruled out, it is likely to occur to a very limited extent, especially at low reaction temperatures. Similar to BF, EP may have to

be hydrogenated before C–O bond cleavage occurs. The primary mechanisms for C(*Sp*<sup>2</sup>)–N bond cleavage (Fig. 10) are a Hofmann-type elimination reaction (E2) and a nucleophilic substitution reaction (S<sub>N</sub>2) (34). It is conceivable that C–O bond cleavage also occurs through these two reactions. In both mechanisms the amino group is quaternized by a Brønsted acid (H<sup>+</sup>) which creates a more labile “leaving group.” In the E2 reaction, a base such as the SH<sup>−</sup> group promotes the elimination by removing a β hydrogen. For the E2 reaction, it is necessary for the carbon atoms in the α and β positions with respect to the nitrogen atom to be saturated. In the S<sub>N</sub>2 reaction, nucleophilic substitution of the amine group by SH<sup>−</sup> is followed by hydrogenolysis of the C–S bond. The S<sub>N</sub>2 mechanism requires only that the carbon atom in the α position with respect to the oxygen atom be saturated. Unlike DHBF, EP cannot directly undergo either mechanism because both carbons in the α and β positions are unsaturated. It is possible that there is an intermediate species between EP and EB that is formed by the hydrogenation of EP. The fact that EP conversion decreased by the addition of H<sub>2</sub>S to the feed provides supporting evidence for this suggestion. Hydrogenation of EP would saturate the carbons in the α and β positions and EB could be produced by an E2 reaction. Figure 11 is a modified benzofuran HDO network over Ni–Mo sulfided catalysts. It includes a new intermediate species called dihydroethylphenol that is formed by the hydrogenation of EP. Although this species was not observed in the product

Hofmann type elimination (E2):



Nucleophilic Substitution (S<sub>N</sub>2):

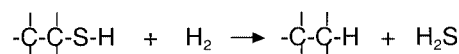
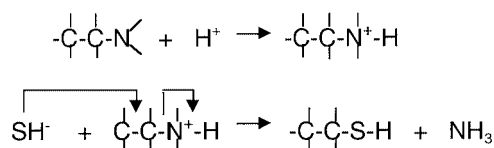


FIG. 10. C–N bond cleavage mechanisms (34).



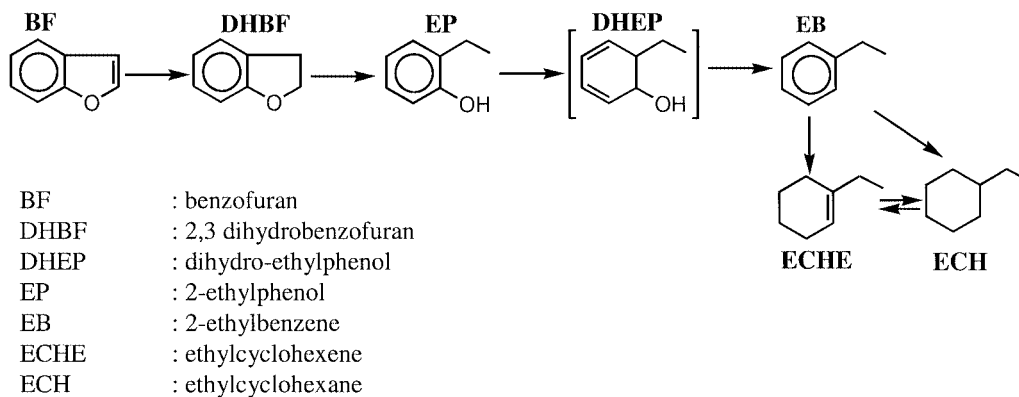


FIG. 11. Proposed benzofuran HDO network over sulfided Ni–Mo catalysts.

stream, adding it to the network is consistent with the effect of H<sub>2</sub>S on EP conversion and with the theory explaining how C–O or C–N bond breaking occurs. In addition, dihydroethylphenol would be a very reactive species and may readily react to produce EB before it desorbs from the catalyst. A similar intermediate, dihydroorthoethyl aniline, which would be analogous to dihydroethylphenol, has also been suggested in the indole reaction network (21–26).

The major difference between benzofuran HDO and indole HDN over sulfided Ni–Mo catalysts is that two distinct routes were observed that lead to the formation of hydrocarbons in the indole HDN network, but only one route was proposed for the benzofuran HDO network. For indole HDN, the hydrogenation activity of the sulfided catalyst was high enough that the aromatic ring of indoline, which is analogous to 2,3-dihydrobenzofuran in the benzofuran network, was hydrogenated. On the other hand, in the benzofuran reaction the aromatic ring of 2,3-dihydrobenzofuran was not hydrogenated over the Ni–Mo sulfided catalyst. To promote the saturation of the aromatic ring in DHBF, reduction was used as a form of pretreatment. Earlier work in the literature (8, 30) points to the analogous behavior of reduced catalysts and sulfided catalysts where reduction increases the number of anionic vacancies, and it is possible that the function of the SH<sup>−</sup> groups is fulfilled by OH<sup>−</sup> groups. By increasing the hydrogenation activity of the catalyst, we expected that 2,3-dihydrobenzofuran would be hydrogenated more easily, forming additional oxygen-containing intermediate species. These partially and fully saturated species, in turn, would undergo C–N bond cleavage more readily than EP since they will have saturated carbon atoms in the  $\alpha$  and  $\beta$  positions.

The reaction results from reduced Ni–Mo studies proved our postulate to be valid in that the hydrogenation and HDO activities of the reduced catalyst were indeed much greater than the corresponding activities of the sulfided catalyst. This difference is exemplified by the significantly lower temperatures required for benzofuran conversion

and hydrocarbon formation over the reduced catalysts compared with the sulfided catalysts. While the sulfided catalyst did not show much activity for BF conversion below 200°C, the reduced catalyst was active even at temperatures as low as 120°C (Fig. 6). In addition to exhibiting high activity for benzofuran conversion through the initial hydrogenation step, the reduced catalysts also yielded substantial levels of hydrocarbon, indicating significant hydrogenolysis activity. These results confirmed our postulate that the reduced catalyst not only can have increased hydrogenation activity due to an increase in the anionic vacancies, but it can also carry out the hydrogenolysis function of the sulfided catalyst, by having OH<sup>−</sup> groups operate in a fashion similar to that of SH<sup>−</sup> groups. Perhaps the most striking difference in the performance of the reduced catalysts was the formation of new reaction intermediates that were not observed over the sulfided catalyst (Fig. 8). The presence of new oxygen-containing intermediates (e.g., ECHOH, OHBF, and HHBF) led us to suggest that a second route that involves saturation of the aromatic ring is available over the reduced catalyst. Figure 12 shows the modified reaction network for benzofuran HDO over the reduced catalyst in the absence of H<sub>2</sub>S. This network contains a second route that begins with the hydrogenation of 2,3-dihydrobenzofuran and leads to the formation of hydrocarbons through ECHOH, OHBF, and HHBF intermediates. The lower hydrogenation activity of the sulfided catalyst does not allow saturation of the aromatic ring and the conversion of DHBF leads predominantly to EP. Over the reduced catalyst, on the other hand, EP is essentially nonexistent since saturation of the aromatic ring is by far the dominant step in this case because of the high hydrogenation activity of the catalyst. The primary products over the reduced catalyst when the DHBF conversion level was low were HHBF and OHBF. ECHOH was also produced but it was not a significant product because it is a very reactive species. The main reason the hydrocarbon yield is much higher over the reduced catalyst is that the oxygen-containing species in the secondary route can readily undergo a S<sub>N</sub>2

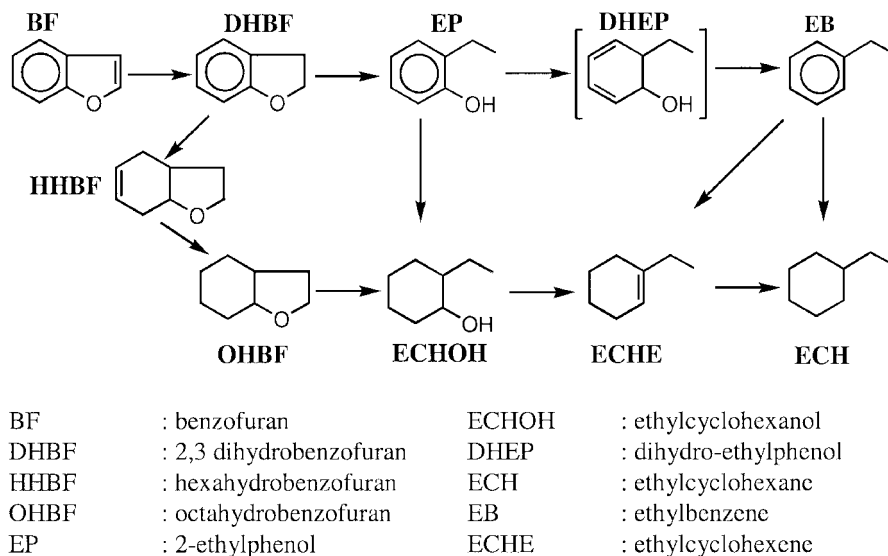


FIG. 12. Proposed benzofuran HDO network over reduced Ni-Mo catalysts.

reaction, E2 reaction, or even direct cleavage. Over the sulfided catalyst, hydrocarbon formation is tied to the reactivity of EP, which does not directly undergo a  $S_N2$  or E2 reaction. Consequently, 2-ethylcyclohexanol is much more reactive than EP and the deoxygenation activity of the reduced catalyst in the absence of  $H_2S$  is significantly greater than that of the sulfided catalyst. It should be noted that, although the secondary route which is included in the reaction network has not previously been reported in the literature, a similar route has been reported in HDN literature for the denitrogenation of indole, which is the nitrogen-containing analog of benzofuran.

Although the steps shown in the reaction network of Fig. 12 can conceivably be reversible under some conditions, they were represented as irreversible under the conditions used in this study. Hydrogenolysis steps are less likely to be reversible than hydrogenation steps, and as expected, there was no DHBF formation when EP was used as the feed molecule. Even the initial hydrogenation of BF, which is a fast reaction step likely to be controlled by thermodynamic equilibrium, was found to be irreversible under these conditions since the reaction where DHBF was used as the feed molecule showed no BF formation.

## CONCLUSIONS

The benzofuran HDO network consists of multiple steps of hydrogenation and hydrogenolysis which occurs by  $\beta$  hydrogen elimination ( $E_2$ ) or nucleophilic substitution ( $S_N2$ ). The network has two routes that lead to the formation of hydrocarbons. One route starts with the hydrogenation of 2,3-dihydrobenzofuran and the other starts with the hydrogenolysis of 2,3-dihydrobenzofuran. Hydrocarbons are produced at much lower temperatures when the

primary route is the one that starts with hydrogenation. Which route is favored depends on the hydrogenolysis and hydrogenation activities of the catalyst which are both strong functions of catalyst pretreatment conditions.

Over sulfided Ni-Mo catalysts, the hydrogenolysis route was observed but not the hydrogenation route. Adding  $H_2S$  to the feed causes a decrease in the HDO rate primarily because the hydrogenation of benzofuran is inhibited, but also because EP does not directly undergo hydrogenolysis by a  $S_N2$  or  $E_2$  mechanism to form EB. The aromatic ring of EP has to be partially saturated before hydrogenolysis will occur; therefore EP conversion decreases as feed  $H_2S$  concentration increases. Over the sulfided catalyst hydrocarbon production depends on the conversion of EP. Since EP is relatively unreactive, especially when  $H_2S$  is added to the feed, significant HDO activity is obtained only at higher reaction temperatures.

Over the reduced catalyst in the absence of  $H_2S$ , only the hydrogenation route is observed. The reduced catalyst has significant hydrogenation activity because many Ni- and Mo-associated vacancies are formed during reduction. The hydrogenation route contains partially and fully saturated oxygen-containing compounds. Unlike EP, these compounds—hexahydrobenzofuran, octahydrobenzofuran, and 2-ethylcyclohexanol—can directly undergo an  $E_2$  or  $S_N2$  reaction and hydrocarbons are produced over the reduced catalyst at temperatures for which the sulfided catalyst is unreactive.

The proposed mechanism, although qualitative in nature, helps explain the different reaction behavior observed over catalysts with different hydrogenation versus hydrogenolysis activities. The effect of  $H_2S$  on the HDO performance of reduced catalysts will be presented in the next article in this series.

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