

Hydrodeoxygenation of benzofuran over sulfided and reduced Ni–Mo/ γ -Al₂O₃ catalysts: Effect of H₂S

Abdu Y. Bunch, Xueqin Wang, Umit S. Ozkan*

Department of Chemical Engineering, The Ohio State University, 140 West 19th Avenue,
Columbus, OH 43210, United States

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Abstract

Effect of H₂S on the catalytic performance of the reduced and sulfided Ni–Mo/Al₂O₃ catalysts in hydrodeoxygenation of benzofuran is studied. The steady-state reaction experiments showed a decrease in activity for both reduced and sulfided catalysts when H₂S was introduced into the feed. The reaction conversion of benzofuran over the reduced catalyst still remained superior to that of the sulfided catalyst in the presence of H₂S, however, at high reaction temperatures, the product distribution over the pre-reduced catalyst is similar to the sulfided catalyst. The studies with temperature-programmed desorption (TPD), temperature-programmed reaction (TPRxn) and X-ray photoelectron spectroscopy (XPS) techniques showed a partial sulfidation of the reduced catalysts when exposed to H₂S under reaction conditions, however, the catalyst does not go through a complete conversion to a molybdenum sulfide phase. Instead oxygen–sulfur exchange on the surface leaves behind oxysulfide species, with catalytic activity closely resembling that of the reduced catalysts. The effect of H₂S on the reaction performance is mainly coming from the competitive adsorption between H₂S and benzofuran and the formation of SH groups with decomposition of H₂S at high temperatures.

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Keywords: Benzofuran hydrodeoxygenation; Reduced Ni–Mo catalysts; Sulfided Ni–Mo catalysts; Effect of H₂S

1. Introduction

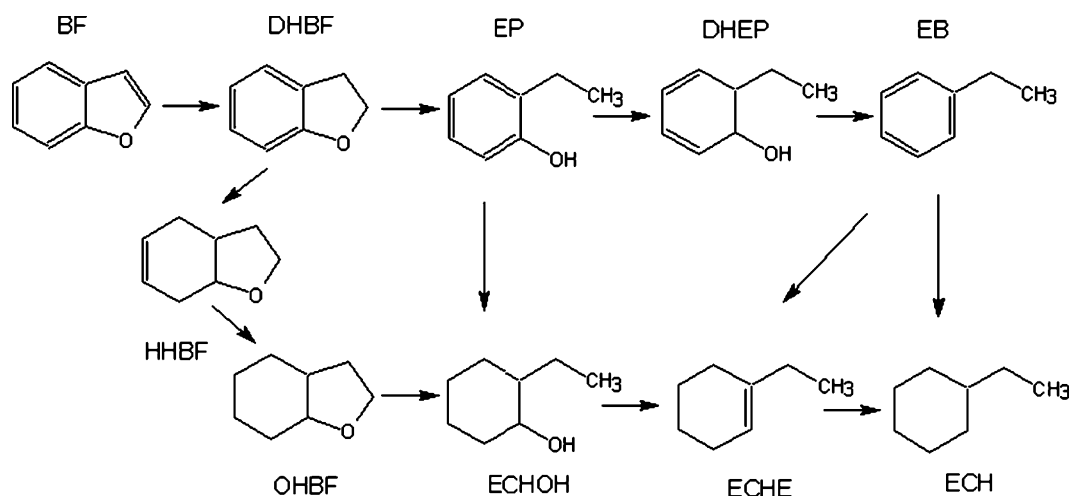
Hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are the primary catalytic hydrotreating processes that have been investigated extensively because of the environmental concerns associated with the combustion of organonitrogen and organosulfur compounds and because these types of compounds are the major impurities in traditional petroleum feedstocks. HDS and HDN studies have led to a fundamental understanding of the mechanisms involved in these reactions and effective catalysts have been developed for these two processes. As the primary catalysts used for hydrotreating processes, sulfided molybdenum and tungsten catalysts have been studied quite extensively [1–7]. The major catalysts used for HDS and HDN are sulfided Co–Mo and Ni–Mo catalysts that are supported on Al₂O₃. According to a widely accepted model proposed by Topsøe and coworkers, these catalysts consist of stacks of MoS₂

layers supported over alumina and the Ni or Co species are located on the edges of these stacks (i.e., CoMoS and NiMoS phases) [3,8–10].

While the primary catalytic hydrotreating processes are hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), removal of organooxygen impurities is also important, especially for nontraditional feedstocks, where the oxygen-containing heteroatom compounds may be in higher concentrations than their N-containing or S-containing counterparts. Sulfided Co–Mo and Ni–Mo catalysts that are supported on Al₂O₃ are also known to effectively catalyze the hydrodeoxygenation (HDO) reactions.

The majority of organooxygen compounds that are found in synthetic feedstocks have either a phenolic or furanic structure [11–15] and a good model compound for studying HDO reactions is benzofuran (BF). We have previously reported studies using BF and its derivatives, dihydrobenzofuran (DHBf), and ethylphenol (EP). The network consists of multiple steps of hydrogenation and hydrogenolysis [16] as shown in Scheme 1, which occur by β -hydrogen elimination (E₂) or nucleophilic substitution (S_N2). Much higher HDO activity for BF and

* Corresponding author. Tel.: +1 614 292 6623; fax: +1 614 292 3769.
E-mail address: ozkan.1@osu.edu (U.S. Ozkan).



Scheme 1. Proposed reaction network for HDO of benzofuran over sulfided and reduced Ni–Mo catalysts [16].

DHBF reactions was obtained when sulfided Ni–Mo catalyst was replaced with a reduced Ni–Mo catalyst. Hydrogenation route is the dominant pathway for benzofuran HDO over reduced Ni–Mo catalysts, while benzofuran HDO proceeds through the hydrogenolysis route over sulfided catalysts [16,17].

Since the hydrodeoxygenation of organooxygen compounds under industrial conditions will always occur in the presence of organosulfur compounds, which are likely to be converted to H₂S by hydrodesulfurization, it is important to determine the effect of H₂S or other sulfur compounds on hydrodeoxygenation reactions.

In this paper, the hydrodeoxygenation pathways of benzofuran (BF) are examined over reduced and sulfided Ni–Mo/Al₂O₃ catalysts in the presence and absence of H₂S in BF feed. The effect of catalyst pre-treatment on BF adsorption, reaction, and product formation was investigated through temperature programmed desorption (TPD) and reaction (TPR_{xn}) experiments. Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) and X-ray photoelectron spectroscopy (XPS) were used for characterization of the catalysts pre-treated at different conditions.

2. Experimental

2.1. Catalyst

Alumina-supported catalysts with 15%MoO₃ and 3%NiO loadings were prepared by wet co-impregnation of γ -Al₂O₃ (Harshaw-Filtre) with aqueous solutions of ammonium heptamolybdate [(NH₄)₆Mo₇O₂₄·4H₂O](Fisher) and nickel nitrate [Ni(NO₃)₂·6H₂O] (Mallinckrodt). The preparation procedure, which was reported previously [18,19] involved impregnation carried out at a pH of 8 and a temperature of 60 °C. The slurry was then dried at 60 °C under vacuum followed by drying in a drying oven over night at 110 °C. The resulting powder was calcined for 4 h at 500 °C under a continuous flow of pure oxygen. The surface area of oxidic samples 184 m²/g, was measured using BET method with a Micromeritics ASAP2010 automatically controlled instrument, using nitrogen as adsorbent

at liquid nitrogen temperature (–196 °C). Prior to reaction and characterization, the catalysts were sulfided at 400 °C for 10 h with 10% H₂S in H₂ or reduced at 475 °C for 10 h with H₂ followed by He flushing at the same temperatures. When the effect of H₂S on reduced catalysts was examined, the catalysts were reduced at 475 °C, followed by sulfidation at the desired temperature with 10% H₂S in H₂ for 10 h and followed by He flushing at 475 °C. The nomenclature used in naming the catalysts treated at different conditions is presented in Table 1.

2.2. 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. The catalyst was used in powder form. The loading of

Table 1
The nomenclature used in naming the catalysts

Nomenclature	Description
R-475-Al ₂ O ₃	Al ₂ O ₃ support reduced at 475 °C for 10 h with H ₂ .
R-475-clean feed	HDO of benzofuran without sulfur in the feed over Ni–Mo/Al ₂ O ₃ catalyst reduced at 475 °C for 10 h with H ₂ .
S-400-feed w/-S	HDO of benzofuran with H ₂ S in the feed over Ni–Mo/Al ₂ O ₃ catalyst sulfided at 400 °C for 10 h with 10%H ₂ S in H ₂ .
R-475-S-T	Ni–Mo/Al ₂ O ₃ catalyst reduced At 475 °C followed by sulfidation at T °C.
R-475-feed w/-S	HDO of benzofuran with H ₂ S in the feed over Ni–Mo/Al ₂ O ₃ catalyst reduced at 475 °C for 10 h with H ₂ .
S-400-He-475	Ni–Mo/Al ₂ O ₃ catalyst sulfided at 400 °C for 10 h with 10% H ₂ S in H ₂ following He flushing for 2 h at 475 °C.
S-Al ₂ O ₃	Al ₂ O ₃ support sulfided at 400 °C for 10 h with 10% H ₂ S in H ₂ .
R-T	Ni–Mo/Al ₂ O ₃ catalyst reduced at temperature T (°C) for 10 h with H ₂ .
O-500	Ni–Mo/Al ₂ O ₃ catalyst calcined at 500 °C for 4 h.

the catalyst in the reactor was kept constant at a total surface area of 50 m². Gas flow rates were controlled by Brooks 5850E mass flow controllers. Feed benzofuran (BF) was introduced to the system by using a diffusion tube. The reactor pressure was controlled by a Tescom back-pressure regulator with a control range of 0–1500 psig. The feed and product streams were analyzed by an on-line HP 5890A gas chromatograph. The GC 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 200 and 320 °C and the pressure was kept at 500 psig. Reaction data were collected after steady-state conditions had been reached. The criterion for steady-state was established through monitoring the product distribution and the reactant conversion level. The term HDO activity is used to denote the percentage of the feed BF that was converted to oxygen-free hydrocarbons. The yield percentage is defined as the percentage of the feed that is converted to a given product.

2.3. TPD and TPR_{xn} studies

Temperature programmed desorption (TPD) experiments were performed using an in-house built gas-flow system. For each of the TPD runs, 20 mg of sample was loaded in a quartz reactor. All samples were sulfided or reduced *in situ* using the same procedure as in reaction studies followed by He flushing and cooling down to 30 °C. Benzofuran adsorption was performed at 30 °C for 0.5 h, followed by flushing with He for 1 h. TPD was performed by heating the samples at a rate of 10 °C/min under a 30 cm³ (STP)/min He flow. For temperature programmed reaction (TPR_{xn}) experiments, the samples were heated at a rate of 10 °C/min under a 30 cm³ (STP)/min 20% H₂/He flow after adsorption and being flushed with He at 30 °C. The reactor effluent composition was continuously monitored as a function of sample temperature by a mass spectrometer (Shimadzu GC–MS QP 5050).

2.4. DRIFTS studies

Diffuse reflectance infrared Fourier transform spectroscopy experiments were performed using a Bruker IFS66 instrument equipped with DTGS and MCT (operated at –196 °C) detectors and a KBr beam splitter. Catalyst was placed in a sample cup inside a Spectrotech diffuse reflectance cell equipped with KCl windows and a thermocouple mount that allowed direct measurement of the surface temperature. Spectra for each experiment were averaged over 1000 scans in the mid-IR range (650–4000 cm⁻¹) to a nominal 3 cm⁻¹ resolution. The samples were sulfided or reduced in a reactor, which had two isolation valves on each end to allow its removal from the reaction system and air-free transfer for sulfided-sample characterization. The samples were transferred into DRIFTS cell in a glove box filled with Ar and the cell was isolated. After *in situ* pre-treatment of the samples with He for 1 h, the background spectra were taken under He flow. Adsorption process was carried out by introducing NO (5450 ppm in He) into the system at room temperature for 0.5 h. After adsorption, the system was subsequently purged for

1 h with He at a flow rate of 30 cm³/min. Spectra were collected under He flow and the background spectrum was subtracted from the post-adsorption spectra.

2.5. XPS studies

X-ray photoelectron spectroscopy analysis (XPS) was performed using an AXIS Ultra XPS spectrometer, operated at 13 kV and 10 mA with monochromator Al K α radiation (1486.6 eV). Sulfided and reduced catalysts were mounted on sample holder with conductive tape in dry glove box filled with Ar. The sample holder was then transferred to the analysis chamber of the spectrometer with a controlled-atmosphere transporter. Charge neutralization was used to reduce effect of charge build-up on samples. All binding energies were referenced to Al 2p of 74.4 eV.

3. Results and discussion

3.1. HDO of benzofuran over sulfided and reduced Ni–Mo/Al₂O₃ catalysts

Fig. 1 shows the effect of reaction temperature on BF conversion for hydrodeoxygenation of benzofuran over sulfided and reduced Ni–Mo/Al₂O₃ catalysts in the absence and in the presence of H₂S (0.03%) in the feed. The BF feed concentration was 0.05 mol% in H₂. Reduced catalyst shows much higher BF conversion than sulfided catalyst. The apparent activation energy of BF HDO, which proceeds mainly through a hydrogenation route over the reduced catalyst (65.5 kJ/mol) is lower than the one over the sulfided catalyst (192.4 kJ/mol), which takes place

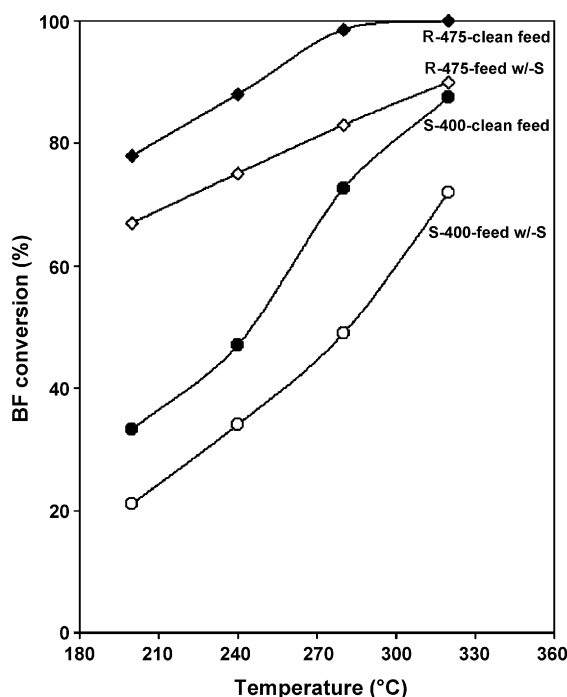


Fig. 1. Effect of H₂S in the feed on conversion of BF over reduced and sulfided catalysts.

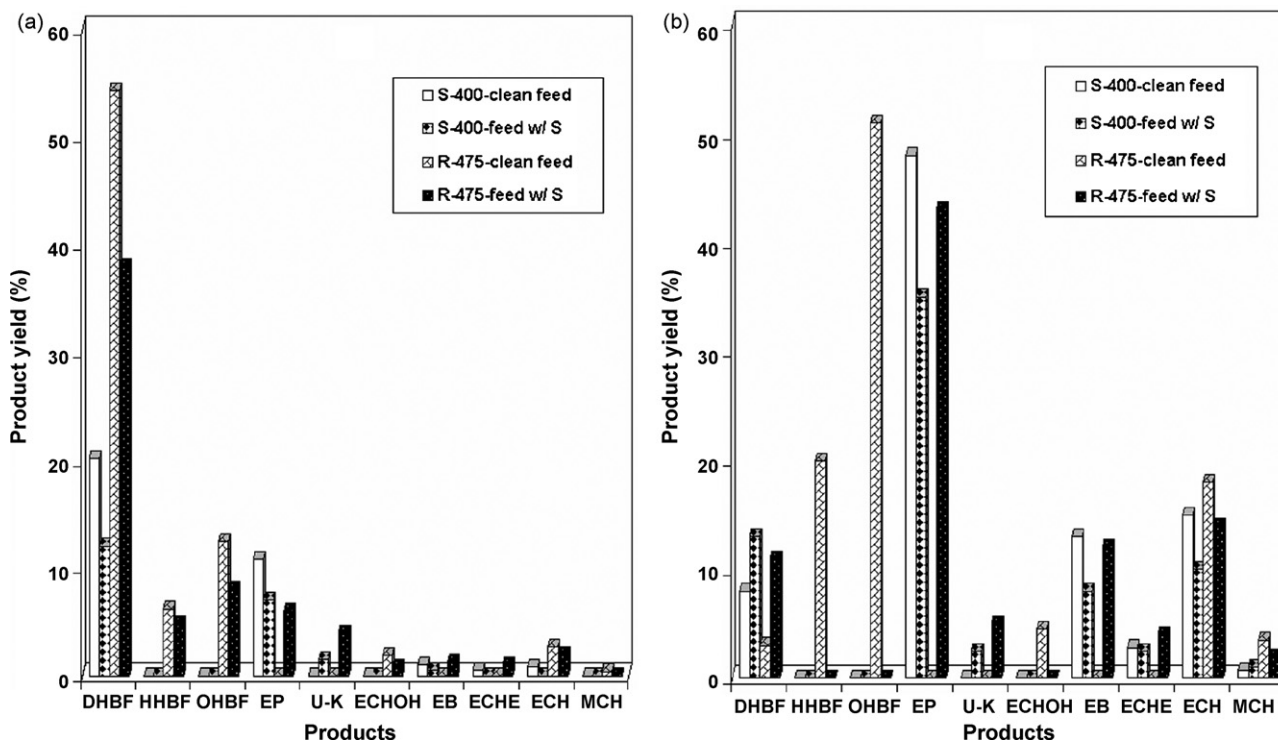


Fig. 2. Effect of H₂S in the feed on the product distribution in BH HDO reaction over reduced and sulfided catalysts (a) 200 °C, (b) 320 °C.

mainly through hydrolysis route. The apparent activation energies are based on the data taken at 240 °C and below, away from conditions that lead to near complete conversion. This can be seen easily by the sharp increase in conversion with increasing temperature over the sulfided catalyst. With the presence of H₂S in the feed (high ratio of H₂S/BF = 0.03/0.05), the BF conversion for both reduced and sulfided catalysts decreases noticeably. However, the activity of the reduced catalyst still remains higher than that of the sulfided catalyst.

Fig. 2 shows the comparison of product distribution for HDO of BF over reduced and sulfided Ni–Mo/Al₂O₃ catalysts in the absence and presence of H₂S in the feed. At a reaction temperature of 200 °C (Fig. 2a), the main products over the sulfided catalyst are DHBF and EP. HHBF and OHBF are observed only in trace amounts. The main products over the reduced catalyst are DHBF, HHBF, and OHBF. No significant EP and EB are observed. These results are consistent with the proposed reaction network (Scheme 1), where the major reaction pathway of BF HDO over sulfided catalyst follows a hydrogenolysis route while the major pathway of BF HDO over reduced catalyst is through the hydrogenation of the benzene ring.

With H₂S in the feed, the product distribution of BF HDO over the sulfided catalyst is similar to those with clean feed except for some decrease in the product yields. Over the reduced catalyst, however, EP and EB were observed to form, accompanied with a decrease in the yields of other products, suggesting that the two reaction routes (hydrogenolysis and hydrogenation) exist in parallel for BF HDO over the reduced catalyst in the presence of H₂S in the feed. There were also small quantities of some unknown products (denoted as U-K) detected when a high

ratio of H₂S/BF is used for both sulfided and reduced catalysts. Possibly they are sulfides formed from the reaction of H₂S with phenolic intermediates.

At a higher reaction temperature (320 °C, Fig. 2b), the main product over the sulfided catalysts from clean feed is EP, giving a yield of close to 50%. EB and ECH with lower yields are also observed. No HHBF or OHBF is observed. The main product from clean feed over the reduced catalyst is OHBF with a yield over 50%. HHBF and ECH are also produced with yields close to 20% each. No EP or EB is observed. The reaction pathways still follow the proposed reaction network (Scheme 1).

With H₂S in the feed, the product yields of BF HDO over sulfided catalyst decrease except for DHBF. The increased yield of DHBF is not due to increased production of this species, but due to the suppressed activity of the catalyst for further reaction of DHBF. Over the reduced catalyst, the product distribution becomes similar to those over the sulfided catalyst, while HHBF and OHBF completely disappear. This implies that, at high reaction temperatures and in the presence of H₂S in the feed, the hydrogenolysis route is the dominant pathway for BF HDO over the reduced catalyst. The unknown product yields increase slightly.

3.2. Temperature-programmed desorption studies

Fig. 3 shows benzofuran TPD profiles obtained over reduced Al₂O₃ support and Ni–Mo/Al₂O₃ catalysts after different pre-treatments. The pre-treatments are sulfidation (S-400), reduction (R-475) and reduction followed by sulfidation (R-475-S-400). Reduced Al₂O₃ shows a large desorption feature at 78 °C, which is the benzofuran adsorbed on Al₂O₃ surface. Over sulfided and

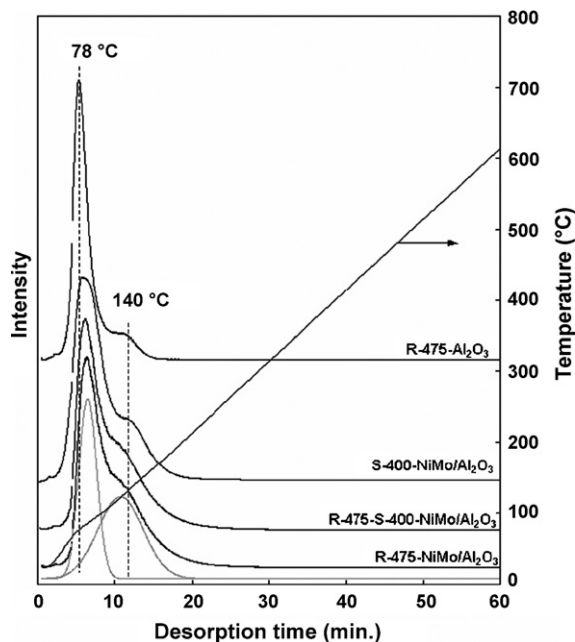


Fig. 3. TPD of BF over 3%Ni–15%Mo catalysts pre-treated at different conditions. TPD of BF over reduced Al_2O_3 is included for comparison.

reduced Ni–Mo/ Al_2O_3 catalysts, two bands were observed at around 85 and 140 °C. The desorption feature at around 85 °C can be assigned to BF from Al_2O_3 surface left exposed after the sulfidation process. This peak shifts to a higher temperature (from 78 to 85 °C) compared to the pure Al_2O_3 support. As expected, the intensity of the peak from Al_2O_3 surface is lower over Ni–Mo/ Al_2O_3 catalysts than over Al_2O_3 support only. The desorption feature at around 140 °C is the BF adsorption on CUS, as discussed in another article [17]. The intensity of desorption feature from anion vacancy sites (CUS) is higher over the reduced catalyst than over the sulfided catalyst. When the peaks are deconvoluted, the ratios of $\text{Area}(\text{CUS})/\text{Area}(\text{Al}_2\text{O}_3)$ are 1.13 and 0.73, for reduced and sulfided catalysts, respectively. BF TPD profile over the catalyst reduced at 475 °C followed by sulfidation at 400 °C (with a ratio of $\text{Area}(\text{CUS})/\text{Area}(\text{Al}_2\text{O}_3)$ is 1.10) is very similar to that over the catalyst reduced only at 475 °C. These findings are consistent with the chemisorption results of CO_2 and NO, which are suitable methods for measuring Al_2O_3 surface and coordinatively unsaturated sites, respectively [20]. A very small feature at 140 °C is also observed over reduced Al_2O_3 support, which may be due to a trace amounts of CUS existing on Al_2O_3 after being reduced at 475 °C (the ratio of $\text{Area}(\text{CUS})/\text{Area}(\text{Al}_2\text{O}_3)$ is 0.16).

Fig. 4 shows TPD profiles following consecutive adsorption of H_2S and BF over the catalyst reduced at 475 °C and sulfided at 400 °C. In the TPD experiment, the catalyst was reduced at 475 °C, sulfided at 400 °C and cooled down to room temperature under the flow of the same sulfidation mixture (10% H_2S in H_2). After flushing the system with He for 1.0 h, BF was introduced into the reactor for 30 min followed by He flushing for 1 h. The temperature program was started after He flushing. The TPD profile shows a large H_2S desorption peak centered at 200 °C. Compared to TPD profile of BF over reduced cat-

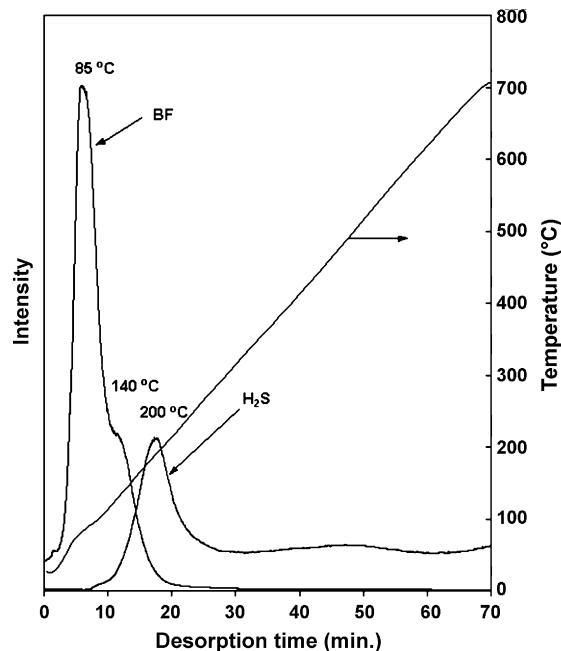


Fig. 4. TPD profile following consecutive adsorption of H_2S and BF over the catalyst reduced at 475 °C followed by sulfidation at 400 °C.

alyst in Fig. 3, it can be seen that the intensity of the peak at around 140 °C, which represents desorption of BF from CUS, decreases significantly, as indicated by the decrease in the ratio of $\text{Area}(\text{CUS})/\text{Area}(\text{Al}_2\text{O}_3)$ from 1.13 to 0.48. This finding implies that BF and H_2S competitively adsorb at CUS. It also explains the reaction results, which showed that the BF DHO activity decreased over all catalysts (reduced and sulfided) in the presence of H_2S in the feed.

3.3. Temperature-programmed reaction studies

Benzofuran TPRxn profile over sulfided Ni–Mo/ Al_2O_3 catalyst is shown in Fig. 5. Trace amount of DHBF was observed at 155–200 °C, followed by a broad peak from OHBF at around 280 °C that was formed by hydrogenation of DHBF. More intensive peaks centered at 440 and 450 °C appear from desorption of DHBF and EP. EP was produced through hydrolysis of DHBF. Two points that should be noted from this experiment are that over the sulfided Ni–Mo/ Al_2O_3 catalyst, the reaction of BF proceeds mainly through the hydrolysis route and the hydrolysis reaction needs higher activation energy than the hydrogenation reaction.

Fig. 6 shows BF TPRxn over reduced Ni–Mo/ Al_2O_3 catalyst. Compared to the BF TPD profile over the same catalyst (Fig. 3), BF peak at around 140 °C (representing desorption from CUS) has completely disappeared, implying that all BF adsorbed on CUS has been converted. The major products are DHBF and OHBF centered at 175 and 225 °C, respectively. A small amount of EP was observed around 260 °C. These results confirm that the hydrogenation of the benzene ring is the primary route for BF reaction over the reduced Ni–Mo catalysts.

The BF TPRxn results over sulfided and reduced catalysts are consistent with steady-state reaction results and agree with

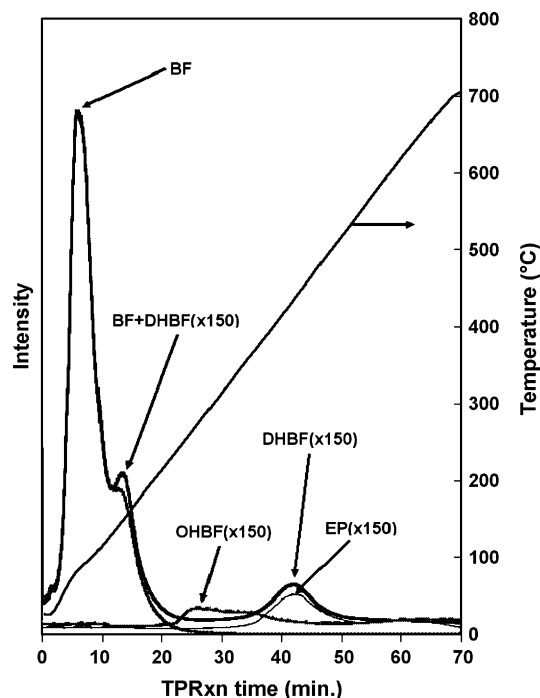


Fig. 5. TPRxn profile of BF over Ni–Mo/Al₂O₃ catalyst sulfided at 400 °C.

the proposed reaction scheme for BF HDO over Ni–Mo/Al₂O₃ catalysts (Scheme 1).

Fig. 7 shows BF TPRxn profile over catalyst reduced at 475 °C followed by sulfidation at 400 °C and H₂S adsorption at 30 °C. Peaks from desorption of BF and H₂S are similar to H₂S–BF TPD profile. Small peaks centered at 440, 450 °C from DHBF and EP are close to those observed over the sulfided catalyst.

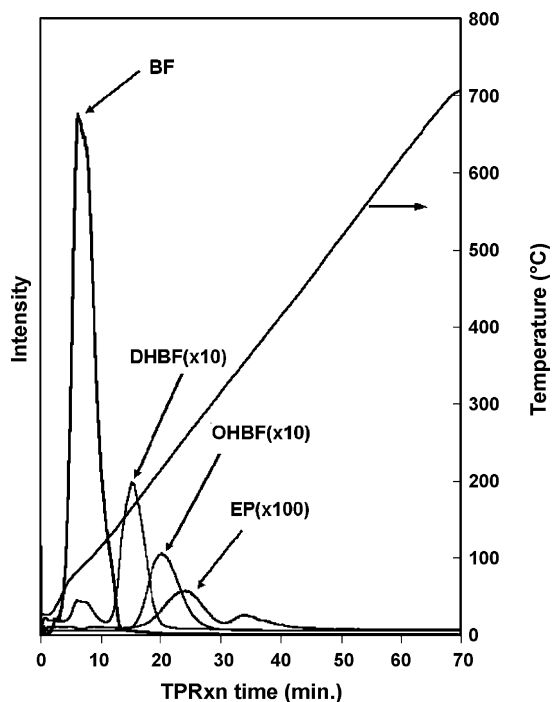


Fig. 6. TPRxn profile of BF over Ni–Mo/Al₂O₃ catalyst reduced at 475 °C.

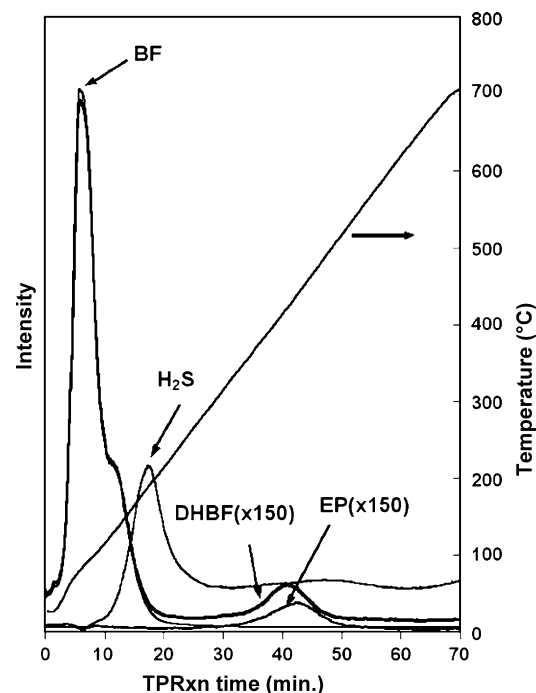


Fig. 7. TPRxn profile of BF over Ni–Mo/Al₂O₃ catalyst reduced at 475 °C followed by sulfidation at 400 °C.

3.4. DRIFTS studies of NO adsorption

Fig. 8 shows DRIFT spectra of NO adsorbed on Ni–Mo/Al₂O₃ catalysts that have been exposed to different pre-treatment steps, namely sulfidation at 400 °C (S-400), reduction at 475 °C (R-475) and reduction at 475 °C followed by

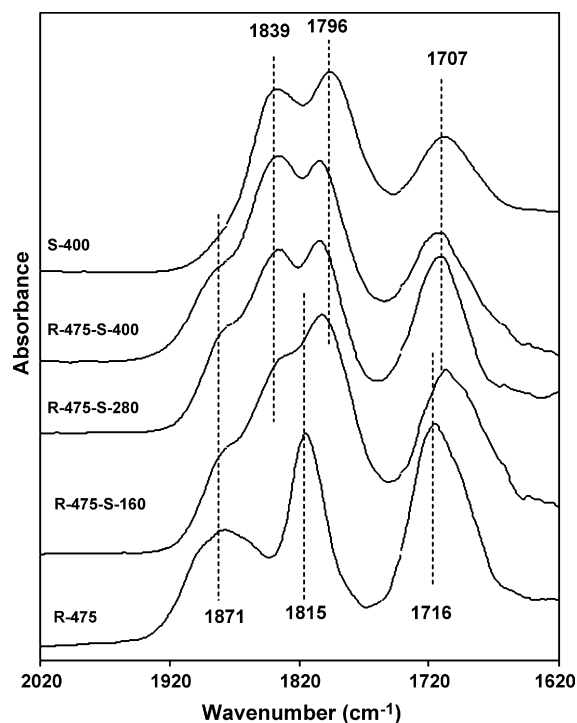


Fig. 8. DRIFTS of adsorbed NO over Ni–Mo/Al₂O₃ catalysts pre-treated at different conditions.

sulfidation at 160, 280 and 400 °C (R-475-S-160, R-475-S-280, R-475-S-400). Over the reduced catalyst, three NO adsorption bands are observed. Those at 1716 and 1815 cm^{-1} are from Mo-related sites and the one at 1871 cm^{-1} is from Ni-related sites [21]. Following sulfidation, the intensity of the NO adsorption bands on Mo-related sites decreases and shifts to lower frequencies; the NO adsorption band on Ni-related sites also decreases and a new band appears, which has the same vibrational frequency as the band from Ni-related sites over the sulfided catalyst, implying the exchange of O atoms with S atoms [20]. With increasing sulfidation temperature, the three characteristic bands from Mo-related and Ni-related sites shift closer to the features seen over the catalyst which underwent sulfidation only. However, even after sulfidation at 400 °C, the pre-reduced catalyst still shows a NO adsorption band from reduced Ni-related sites, indicating that the pre-reduced catalyst does not get sulfided completely.

3.5. XPS studies

Figs. 9–11 present X-ray photoelectron spectra for Mo, Ni, and S species in Ni–Mo/Al₂O₃ catalysts treated at various reducing or sulfiding conditions. The nomenclature used in naming the catalysts is already presented in Table 1. Quantification of different species based on deconvolution of the spectra is listed in Tables 2–4. The deconvolution was achieved with Gaussian curve-fitting following background correction by interactive polynomial method.

Mo 3d-S 2s regions of the X-ray photoelectron spectra for these catalysts are presented in Fig. 9. The catalyst reduced at

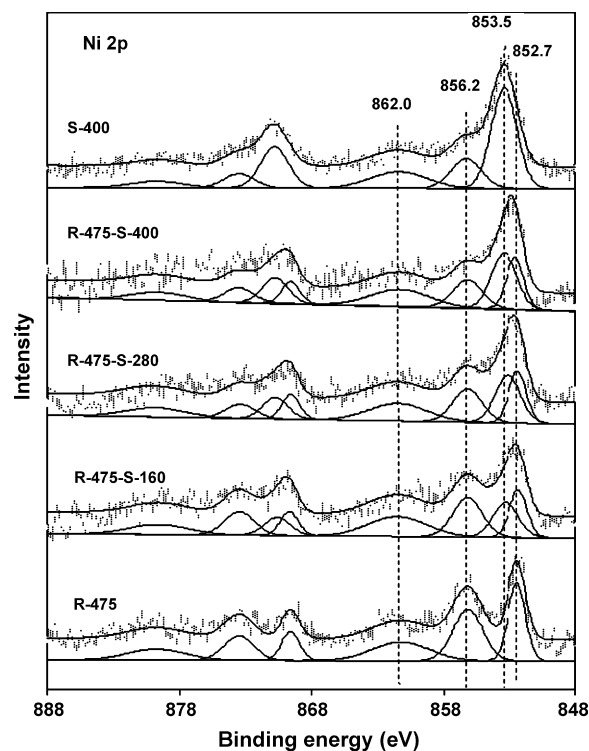


Fig. 10. X-ray photoelectron spectra (Ni 2p region) of Ni–Mo/Al₂O₃ catalysts pre-treated at different conditions.

475 °C (R-475) shows Mo species to exist in three different oxidation states, +6, +5 and +4. When these catalysts are sulfided at 160 °C with 10% H₂S in H₂ for 10 h (R-475-S-160), an S²⁻ species appear with a 2s binding energy of 226.1 eV. The con-

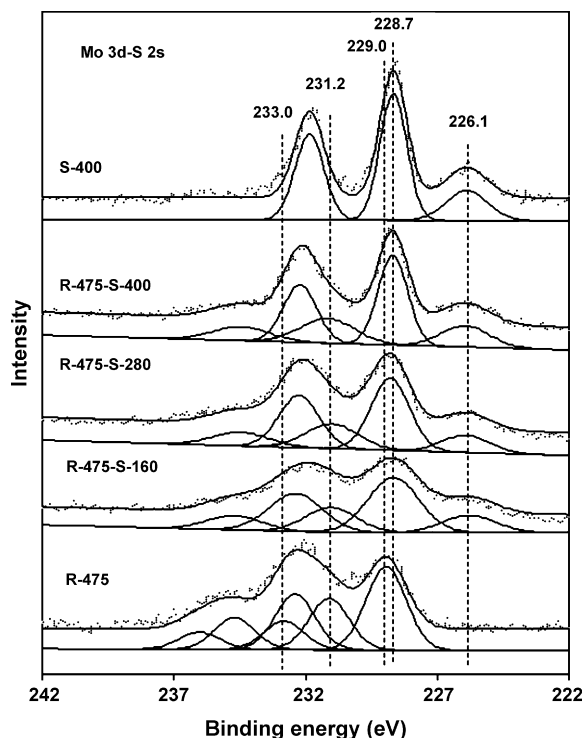


Fig. 9. X-ray photoelectron spectra (Mo 3d-S 2s region) of Ni–Mo/Al₂O₃ catalysts pre-treated at different conditions.

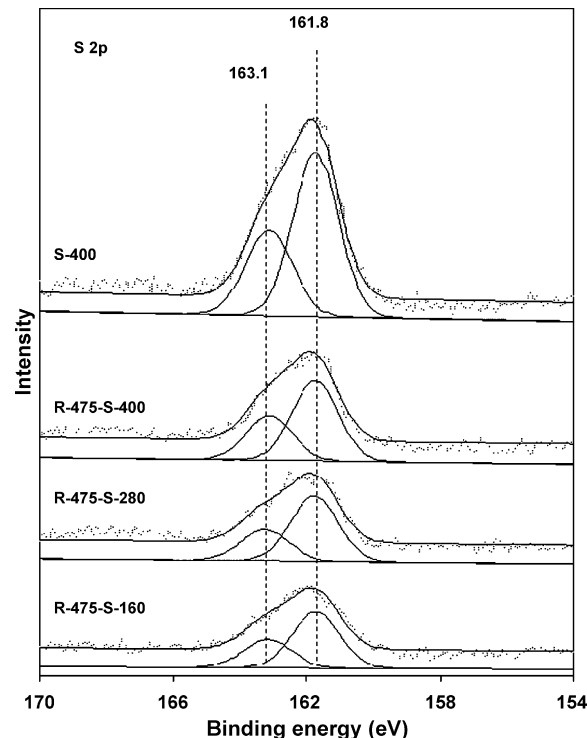


Fig. 11. X-ray photoelectron spectra (S 2p region) of Ni–Mo/Al₂O₃ catalysts pre-treated at different conditions.

Table 2
Distribution (%) of Mo and Ni oxidation states in Ni–Mo/Al₂O₃ catalysts treated at different conditions

Samples	Mo species			Ni species		
	233.1 eV (Mo ⁺⁶)	231.2 eV (Mo ⁺⁵)	228.8–229.0 eV (Mo ⁺⁴)	856.2 eV (A)	853.5 eV (B)	852.7 eV (C)
R-475	25	32	43	55	–	45
R-475-S-160	–	30	70	37	29	34
R-475-S-280	–	26	74	30	39	31
R-475-S-400	–	24	76	24	48	28
S-400	–	–	100	25	75	–

Table 3
Surface atomic ratios of Mo/Al, Ni/Al, and Ni/Mo of Ni–Mo/Al₂O₃ catalysts treated at different conditions

Pre-treatment	A _{Mo} /A _{Al} (×10 ²)	A _{Ni} /A _{Mo}	A _S /A _{Mo}
O-500	13.2	0.30	–
R-475	9.6	0.31	–
R-475-S-160	9.4	0.35	1.0
R-475-S-280	9.3	0.38	1.2
R-475-S-400	9.3	0.39	1.4
S-400	9.4	0.39	2.4

tribution from the Mo⁺⁶ (23.0 eV) disappears completely upon exposure to the sulfiding atmosphere. With increasing sulfidation temperature, the Mo⁺⁴ peak shifts to lower binding energies and sharpens, becoming closer to the peak in the sulfided catalyst. The deconvolution results show that the percentage of Mo⁺⁴ species increases slightly. However, even when the pre-reduced catalyst was sulfided at 400 °C, Mo⁺⁵ species still exists, although the catalyst sulfided at 400 °C without pre-reduction has only Mo⁺⁴ species on the surface. As indicated in the literature [22–24], complete sulfidation of the suboxide species is much more difficult than sulfidation of the fully oxidized (Mo⁺⁶) species. However, exchange of surface oxygen with sulfur is likely to take place upon exposure to H₂S, forming oxysulfide species [21].

Fig. 10 shows Ni 2p region of the X-ray photoelectron spectra for the same set of Ni–Mo/Al₂O₃ catalysts. The reduced catalyst exhibits two different Ni species, one seen in a fully oxidized sample with characteristic lines at 856.2 and 873.8 eV for 2p_{3/2} and 2p_{1/2} binding energies and strong shake-up lines at 862.0 and 879.6 eV. These Ni species are denoted as Ni-A in Table 2. The second feature corresponds to a Ni–Mo–O structure with 2p binding energies at 852.7 and 870.3 eV. These species are shown as Ni-C in Table 2. When reduced catalysts are exposed to H₂S, the Ni-A and Ni-C species decrease significantly, while a new

Table 4
Estimation of sulfur intake over the reduced catalysts exposed to H₂S

Samples	S atoms per 100 moles of Mo on the surface			S/Mo calculated
	Mo ⁺⁴ Type I	Mo ⁺⁴ Type II	Ni ⁺² Ni-B	
R-475-S-160	43	54	10	1.1
R-475-S-280	43	62	15	1.2
R-475-S-400	43	66	19	1.3
S-400	–	200	29	2.3

feature appears with 2p_{3/2} and 2p_{1/2} binding energies at 853.5 and 871.1 eV, respectively. This specie, which is denoted as Ni-B in Table 2 is the same as that observed for the sulfided catalysts (S-400) and is believed to be part of a Ni–Mo–S structure [21]. With increasing sulfidation temperature, the percentage of Ni-B species gradually increases while the percentage of Ni-A species decreases. The percentage of Ni-A species reaches the same value observed in the fully sulfided sample (~25%), but does not decrease any further. As discussed previously [21], the portion of Ni which is left unsulfided is most likely a NiAl₂O₄ phase, which cannot easily be reduced or sulfided. With increasing sulfidation temperature, Ni-C species decreases slightly, but does not completely disappear. This finding is consistent with the observation from the NO adsorption studied with DRIFTS technique which showed that the Ni-associated coordinatively unsaturated sites did not disappear when the pre-reduced catalysts were exposed to H₂S even at high temperatures (Fig. 8).

Fig. 11 shows the S 2p region of the X-ray photoelectron spectra for the same set of catalysts. For all catalysts that are exposed to sulfur species, the peak positions and shapes are identical, corresponding to S^{–2} species. Although the peak intensity for pre-reduced catalysts that are subsequently sulfided increases slightly with increasing in sulfidation temperatures, it is much lower than that observed over the sulfided sample without pre-reduction. There are no other sulfur species identified on the surface. Although formation of elemental sulfur on the surface at lower temperatures is a possibility, based on the sulfidation mechanisms suggested in the literature [25,26], in the presence of H₂, elemental sulfur is expected to be converted back to H₂S, as shown through temperature programmed sulfidation experiments reported by Moulijn and coworkers [25].

Table 3 shows the surface atomic ratios of Mo/Al, Ni/Al, and Ni/Mo of Ni–Mo/Al₂O₃ catalysts analyzed by XPS. Reduction caused a significant decrease of Mo/Al ratio, similar to what was observed for the sulfided catalysts, possibly due to the formation of stacks. Exposure of the reduced catalysts to H₂S does not change the Mo/Al ratio pronouncedly, but it increases the Ni/Mo ratio slightly. It is possible that the same effect observed in the sulfidation of the oxide, where migration of the Ni species to the surface is envisioned [21,27], is in operation for the pre-reduced catalyst as well.

Table 4 presents the results of an attempt to quantify the sulfur intake during the sulfur exposure of the reduced catalyst at different temperatures. The calculation was performed with several assumptions, as described previously [20]. The calculated S/Mo ratios (Table 4) are very similar to the ones obtained from XPS

analysis (Table 2). Starting out with a basis of 100 moles of Mo atoms on the surface and using the percent distribution of different oxidation states presented in Table 2 and the Ni/Mo atomic ratios of Table 3, moles of sulfur atoms that would be inserted into the reduced catalyst through different sulfur treatments are estimated. The calculations assume that the Mo^{+4} species over the reduced catalysts are primarily on the outermost surface and exchange only their terminal oxygen with sulfur, ending up with a S/Mo ratio of 1:1, while maintaining their +4 oxidation state (Type I species). Similar arguments have been forwarded earlier, citing the difficulty of completely sulfiding reduced Mo species [20,25,24]. The other assumption is that the remaining Mo^{+4} species found in the R-475-S-T samples (Type II species) are in a molybdenum sulfide matrix with an S/Mo ratio of 2:1 and they are formed mostly from the Mo^{+6} (or some of the Mo^{+5}) species that were left behind in the reduced sample. Using the distributions in Table 2, the amount of sulfur associated with the two different types of Mo species in reduced/sulfided catalysts are estimated. The amount of S on the surface associated with Ni sites is estimated using the Ni/Mo ratios of Table 3 and the percentage of Ni-B species of Table 2. An S/Ni ratio of 1:1 is used for all Ni-B species, consistent with earlier reports from the literature [28–31]. When the S/Mo ratios calculated using these assumptions (Table 4) are compared to those measured from XPS analysis (Table 3), they are found to be quite similar. These calculations, which are based on several assumptions, are nevertheless, useful in explaining the XPS results through a model where Mo^{+4} species are envisioned to exchange only their terminal oxygen with S in the pre-reduced catalysts upon sulfur exposure, leaving behind an oxysulfide matrix. It appears that these materials, which do not completely get converted to a sulfide phase, exhibit catalytic behavior much closer to that of the reduced catalysts than that of the sulfided catalysts.

It is conceivable that the anion vacancies over the reduced sample are maintained when exposed to sulfur because of the larger size of sulfur as opposed to oxygen, creating a steric hindrance effect. Reduced Ni–Mo/Al₂O₃ catalyst, which possesses more active sites than sulfided catalyst [21], shows higher BF HDO activity than sulfided catalyst even in the presence of H₂S in the feed. The decrease in activity in the presence of H₂S in the feed for both reduced and sulfided catalysts is likely to be from the competitive adsorption of H₂S and BF on CUS. The effect of competitive adsorption of H₂S on the reaction becomes more significant at higher temperatures since H₂S adsorbs stronger on CUS as identified by TPD-TPR_{xn} studies. At high temperatures, adsorbed H₂S on pre-reduced catalysts may dissociate and form sulfhydryl (SH) groups, leading to a performance similar to that observed over the sulfided catalyst.

4. Summary

TPR_{xn} studies support the proposed reaction scheme for BF HDO where, over sulfided Ni–Mo/Al₂O₃ catalysts, HDO mainly proceeds through a hydrolysis route, while over reduced Ni–Mo/Al₂O₃ catalysts, the primary route involves hydrogenation

of the benzene ring before any heteroatom removal takes place. The presence of H₂S in the feed mixture leads to a decrease in HDO of BF for both reduced and sulfided Ni–Mo/Al₂O₃ catalysts, mainly due to the competitive adsorption between H₂S and BF species, which decreases the number of anion vacancies available for hydrogenation step(s) and increases the number of SH groups at high temperatures promoting the hydrolysis route. When exposed to H₂S at different pressures [20] and temperatures, the pre-reduced Ni–Mo catalysts gets partially sulfided, however, it is not completely converted to a molybdenum sulfide phase, since sulfiding suboxides of molybdenum requires much higher temperatures. Instead oxygen–sulfur exchange on the surface leaves behind oxysulfide species, with catalytic activity closely resembling that of the reduced catalysts.

References

- [1] G.C.A. Schuit, B.C. Gates, *AIChE J.* 19 (1973) 417.
- [2] P. Grange, *Catal. Rev. - Sci. Eng.* 21 (1980) 135.
- [3] H. Topsøe, B.S. Clausen, *Catal. Rev. - Sic. Eng.* 26 (1984) 395.
- [4] R. Prins, V.H.J. de Beer, G.A. Somorjai, *Catal. Rev. - Sci. Eng.* 31 (1989) 1.
- [5] R.R. Chianelli, M. Daage, M.J. Ledoux, *Adv. Catal.* 40 (1994) 177.
- [6] H. Topsøe, B.S. Clausen, F. Massoth, in: J.R. Anderson, M. Boudart (Eds.), *Science and Technology*, vol. 11, Springer, Berlin, 1996.
- [7] D.D. Whitehurst, T. Isoda, I. Mochida, *Adv. Catal.* 42 (1998) 345.
- [8] H. Topsøe, B.S. Clausen, R. Candia, C. Wivel, S. Morup, *J. Catal.* 68 (1981) 433.
- [9] R.C. Wivel, R. Candia, B.S. Clausen, S. Morup, H. Topsøe, *J. Catal.* 87 (1984) 497.
- [10] H. Topsøe, B.S. Clausen, *Appl. Catal.* 25 (1986) 273.
- [11] J.R. Katzer, Sivasubramanian, *Catal. Rev. - Sci. Eng.* 20 (2) (1979) 155.
- [12] J.B. Bredenberg, M. Huuska, P. Toropainen, *J. Catal.* 120 (1989) 401.
- [13] E. Furimsky, *Ind. Eng. Chem. Prod. Res. Dev.* 22 (1983) 34.
- [14] E. Furimsky, *Appl. Catal.* 6 (1983) 159.
- [15] E. Laurent, B. Delmon, *Appl. Catal.* 109 (1994) 97.
- [16] A.Y. Bunch, U.S. Ozkan, *J. Catal.* 206 (2002) 177.
- [17] A.Y. Bunch, X. Wang, U.S. Ozkan, *J. Phys. Chem.*, submitted for publication.
- [18] U.S. Ozkan, S. Ni, L. Zhang, E. Moctezuma, *Energy Fuels* 8 (1994) 249.
- [19] U.S. Ozkan, L. Zhang, S. Ni, E. Moctezuma, *J. Catal.* 148 (1994) 181.
- [20] X. Wang, R.Y. Saleh, U.S. Ozkan, *Appl. Catal.* 286 (2005) 111.
- [21] X. Wang, U.S. Ozkan, *J. Phys. Chem. B* 109 (5) (2005) 1882.
- [22] Y. Okamoto, H. Tomioka, Y. Katoh, T. Imanaka, S. Teranishi, *J. Phys. Chem.* 84 (14) (1980) 1833.
- [23] P. Arnoldy, J.A.M. van den Heijcant, G.D. deBok, J.A. Moulijn, *J. Catal.* 92 (1985) 35.
- [24] L. Portela, P. Grange, B. Delmon, *J. Catal.* 156 (1995) 243.
- [25] P. Arnoldy, J.A.M. van den Heijcant, G.D. deBok, J.A. Moulijn, *J. Catal.* 92 (1985) 35.
- [26] L.P. Nielsen, M. Schonning, S.V. Christensen, S.V. Hoffmann, Z. Li, P. Hofmann, F. Besenbacher, B.J. Clausen, *Catal. Lett.* 73 (2) (2001) 85.
- [27] K.T. Ng, D.M. Hercules, *J. Phys. Chem.* 80 (1976) 2094.
- [28] L.P. Nielsen, S.V. Christensen, H. Topsøe, B.S. Clausen, *Catal. Lett.* 67 (2000) 81.
- [29] L.S. Byskov, B. Hammer, B.S. Norskov, B.S. Clausen, H. Topsøe, *Catal. Lett.* 47 (1997) 177.
- [30] L.S. Byskov, B.S. Norskov, B.S. Clausen, H. Topsøe, *Catal. Lett.* 187 (1999) 109.
- [31] S. Helveg, J.V. Lauritsen, E. Legsgaard, I. Steensgaard, J.K. Norskov, B.S. Clausen, H. Topsøe, *Phys. Rev. Lett.* 84 (2000) 951.