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Mechanisms of hydrodenitrogenation of alkylamines and hydrodesulfurization of alkanethiols on NiMo/Al_2O_3, CoMo/Al_2O_3, and Mo/Al_2O_3

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Abstract

The simultaneous hydrodenitrogenation (HDN) of alkylamines and hydrodesulfurization (HDS) of alkanethiols, with the NH_2 and SH groups attached to primary, secondary, and tertiary carbon atoms, were studied at 270–320 °C and 3 MPa over sulfided NiMo/Al_2O_3, CoMo/Al_2O_3, and Mo/Al_2O_3 catalysts. Pentylamine and 2-hexylamine reacted by substitution with H_2S to form alkanethiols and with another amine molecule to form dialkylamines. Alkenes and alkanes were not formed directly from pentylamine and 2-hexylamine, but indirectly by elimination and hydrogenolysis of the alkanethiol intermediates, as confirmed by their secondary behavior and the similar alkene/alkane ratios in the simultaneous reactions of amines and thiols. Only 2-methyl-2-butylamine, with the NH_2 group attached to a tertiary carbon atom, produced alkenes as primary products by E1 elimination. NiMo/Al_2O_3 and CoMo/Al_2O_3 have a higher activity for the HDS of alkanethiols than does Mo/Al_2O_3; H_2S has a negative influence. This shows that the thiols react on vacancies on the catalyst surface (Lewis acid sites). Mo/Al_2O_3 is the best HDN catalyst; H_2S has a positive influence on the HDN of amines with the NH_2 group attached to a secondary and a tertiary carbon atom. This indicates that the HDN of alkylamines occurs on Brønsted acid sites.

Keywords: Pentylamine; 2-Hexylamine; 2-Methyl-2-butylamine; NiMo/Al_2O_3; CoMo/Al_2O_3; Mo/Al_2O_3; HDN; HDS; Hexanethiol; 2-Pentanethiol; 2-Methyl-2-butanethiol

1. Introduction

Future environmental legislation will require the further reduction of the sulfur content of gasoline and diesel fuel to 10 ppm. Deep hydrodesulfurization (HDS) technology must be implemented to attain this low level of sulfur. Nitrogen-containing compounds are harmful in deep HDS, as they inhibit the HDS of sulfur-containing compounds through competitive adsorption [1–3]. Therefore, it is important to know how nitrogen-containing molecules are removed by hydrotreating catalysts. Nelson and Levy were the first to suggest mechanisms for the hydrodenitrogenation (HDN) of alkylamines and that nucleophilic substitution and Hofmann β-H elimination are responsible for HDN [4]. Evidence of these mechanisms has been published [5–8], and it has been concluded that they depend on the alkylamine as well as on the catalyst [7]. We found that, over sulfided NiMo/Al_2O_3, the substitution mechanism dominates in the HDN of alkylamines with the NH_2 group attached to a primary or secondary carbon atom [9,10]. Hofmann β-H elimination rarely occurs in these alkylamines. Nevertheless, a large amount of alkene is formed in the HDN of an alkylamine by fast decomposition of the corresponding alkanethiol, which is formed by the substitution of the alkylamine with H_2S. On the other hand, the HDN of tertiary amines occurs via an E1 mechanism [10].

Cattenot et al. concluded that the HDN mechanism depends not only on the alkylamine, but also on the catalyst [7]. Different metal sulfides may have different acidities

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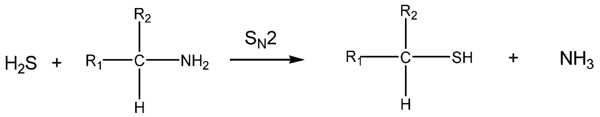


Scheme 1. Direct substitution of an alkylamine to an alkanethiol by nucleophilic attack (acid–base catalyzed).

and, therefore, different catalytic properties. According to their results for unsupported metal sulfides, the acidity decreases in the order $NbS_3 > MoS_2 > RuS_2 > Rh_2S_3$. The HDN reaction of alkylamines might help to discriminate among the acidic properties of $NiMo/Al_2O_3$, $CoMo/Al_2O_3$, and Mo/Al_2O_3. In the HDN of an alkylamine, the products are a dialkylamine, an alkanethiol, alkenes, and an alkane. They can be formed, in principle, by acid–base catalysis (Scheme 1). The amine group reacts with a proton or a Lewis acid, and, at the same time, a nucleophile attacks the α-carbon atom. The ammonia is split off, and a substitution product is formed. Acid–base chemistry can take place at metal sulfide surfaces, as confirmed by FTIR spectroscopy of pyridine adsorbed at high temperature [11]. Maugé and coworkers found evidence that H_2S adsorption leads to a substantial increase in the Brønsted acidity of the sulfide phase [12–14].

Substitution may be catalyzed by metallic sites as well as by acidic sites [15]. Several groups have discussed the electronic properties of the ideal reactive MoS_2 surface and pointed out that this surface has an electron acceptor property and that it is metallic [16–22]. As shown in Scheme 2, a sequence of dehydrogenation of amine to imine, H_2S addition, ammonia elimination, and hydrogenation of the thioaldehyde transforms an alkylamine into an alkanethiol.

For these reasons, we compared the HDN and HDS mechanisms in the simultaneous reactions of pentylamine and hexanethiol, the simultaneous reactions of 2-hexylamine and 2-pentanethiol, the HDN of 2-methyl-2-butylamine, and the HDS of 2-methyl-2-butanethiol in the presence of hexylamine over the three molybdenum sulfide-based catalysts.

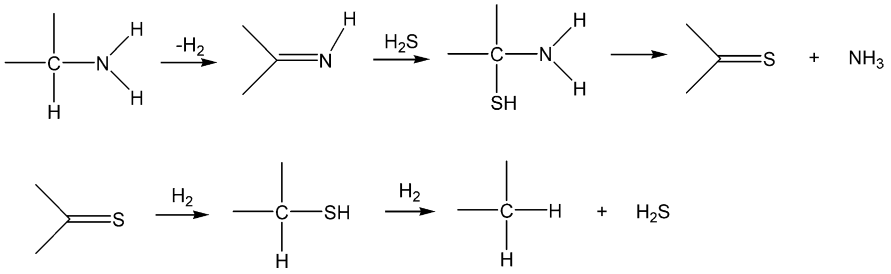
2. Experimental

HDN and HDS experiments were carried out in a continuous-flow reactor with $NiMo/Al_2O_3$, $CoMo/Al_2O_3$, and Mo/Al_2O_3 catalysts, prepared by sequential pore-volume impregnation of γ-Al_2O_3, as described elsewhere [9,23]. The catalysts were sulfided in situ and used immediately, without exposure to nitrogen or air. The total pressure in the HDN and HDS experiments was 3 MPa; the partial pressure of the alkylamines was 5 kPa. The HDS of alkanethiols was studied because they are intermediates in the HDN of alkylamines. They were studied at 5 kPa in the simultaneous reaction with 5 kPa of the relevant alkylamine to simulate the conditions necessary for an alkanethiol to form as an intermediate in the HDN of an alkylamine. The experiments were carried out at 270 and 320 °C with a H_2S partial pressure of 10 or 100 kPa. When the partial pressure of H_2S was changed, the hydrogen pressure was adapted to keep the total pressure constant. The weight time τ is defined as the ratio between the catalyst weight and the total molar flow to the reactor and is expressed in g min/mol ($1\ \text{g min/mol} = 0.68 \times 10^{-3}\ \text{g h/l}$). To study the influence of weight time on the product distribution, we changed the weight time by varying the flow rates of the liquid and the gaseous reactants with respect to the amine, while keeping their ratio constant. The accuracy of the measured conversion was 2% (relative).

Pentylamine (Aldrich), hexanethiol (Fluka), 2-hexylamine (Lancaster), 2-pentanethiol (Aldrich), 2-methyl-2-butylamine (Aldrich, 98%), 2-methyl-2-butanethiol (ABCR), and cyclohexane (Fluka, puriss.) were all used as purchased. The gases were hydrogen (PanGas 4.0) and a mixture of 10% H_2S in H_2 (Linde). Mass spectrometry was used to identify the reaction products. The MS analysis was performed with an Agilent 6890 gas chromatograph equipped with an HP-5MS capillary column (cross-linked 5% PH ME siloxane, 30 m × 0.25 mm × 0.25 µm) and with an Agilent 5973 mass selective detector. The temperature of the injector was 270 °C, and the initial temperature of the column oven was 80 °C; heating to 300 °C started after 2 min at 20 °C/min.

3. Results

As we showed for sulfided $NiMo/Al_2O_3$ [9,10] and as we will show here for sulfided Mo/Al_2O_3 and $CoMo/Al_2O_3$, the HDN of alkylamines is not a simple reaction, but is the sum of two parallel reactions, each of which consists of several consecutive reactions. We will use two methods to disentangle this complex network of reactions. One method is



Scheme 2. Indirect substitution of an alkylamine to an alkanethiol by metal catalysis.

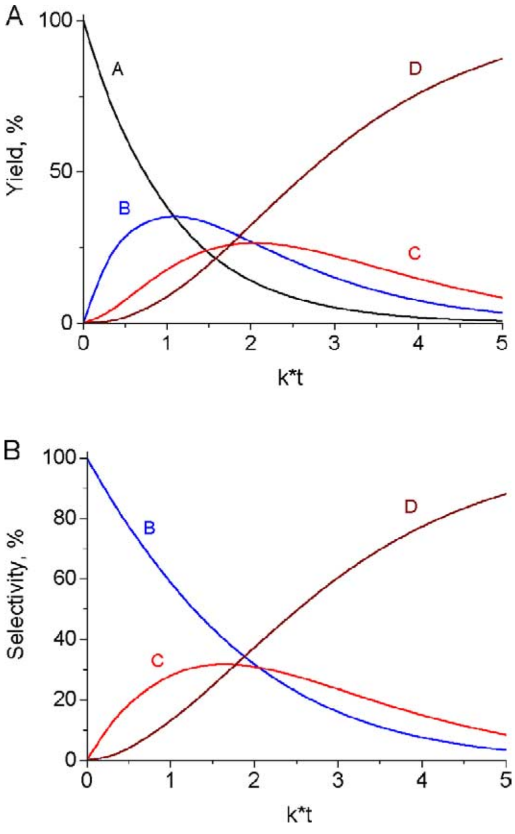


Fig. 1. Product selectivities and yields in a consecutive reaction from reactant A to product D (with equal rate constants for each reaction step).

to concentrate on selectivities instead of yields. The advantage is that selectivities make it easier to distinguish between primary and secondary products. For instance, in a series of consecutive reactions from reactant A to product D, in which the adsorption–desorption rates of reactant, intermediate, and product molecules are much faster than the rates of the chemical reactions of the adsorbed species,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$$

the yield of the primary product B and the yield of the secondary product C initially increase with reaction time (Fig. 1A), but this behavior would also be observed for parallel reactions of A to B and A to C. Only if one can measure in a very short time will it be possible to distinguish between consecutive and parallel reactions and to prove the secondary character of C. By plotting the same experimental results as selectivities, however, the selectivity of B decreases and that of C increases initially with time for a consecutive reaction (Fig. 1B), whereas both selectivities increase in parallel reactions of A to B and C. Even though the product yields are initially low and, thus, the uncertainty of the selectivities quite high, it is easy to distinguish between an increase or a decrease in the selectivity with time. Therefore, we will use selectivities to explain the reaction mechanisms.

The second method is to compare the alkene/alkane ratio in the HDN of an alkylamine with the alkene/alkane ratio in the HDS of a similar alkanethiol. The reason for this is that if an alkylamine were to react to alkenes and an alkane without going through an intermediate alkanethiol, the alkene/alkane ratio would not be the same as that in the HDS of the alkanethiol. If, on the other hand, the alkylamine reacted first to an alkanethiol, which would then react to a mixture of alkenes and alkane, the alkenes/alkane branching ratio would be determined by the alkanethiol. Thus, the branching ratio would be the same in HDN and HDS. The branching ratio proved to be quite sensitive to the presence and partial pressures of alkylamine and alkanethiol, apparently because they influenced the coverage of the catalyst surface. Therefore, in the HDS of alkanethiols, this ratio was always determined in the presence of an amount of alkylamine equivalent to that used in HDN. Nevertheless, the conditions in HDS and HDN were not identical, because in the HDN the thiol is relatively slowly created but reacts fast, whereas during HDS the initial thiol concentration is high. As a consequence, we found that the alkene/alkane branching ratio could vary by 50%. As we shall see in the following, this still allows us to confirm the nucleophilic substitution mechanism, because when the mechanism switches to direct elimination of ammonia from the alkylamine the branching ratios in HDS and HDN differ by a factor between 7 and 30. Finally, the branching ratios in HDS and HDN should only be compared at low weight time, because the alkanethiol reaction is complete within 2 or 3 g min/mol; after that the only reaction is the hydrogenation of the resulting alkene to the alkane. This hydrogenation explains why the branching ratio decreases with weight time.

3.1. Simultaneous reaction of pentylamine and hexanethiol

The conversion of 5 kPa pentylamine in the simultaneous HDN and HDS at 320 °C in the presence of 5 kPa hexanethiol and 10 kPa H_2S was 12% at $\tau = 1.6$ g min/mol and 60% at 8.9 g min/mol over $NiMo/Al_2O_3$ (Fig. 2); the conversion over $CoMo/Al_2O_3$ was similar. The conversion over both catalysts decreased slightly when the H_2S pressure was increased from 10 to 100 kPa. Over Mo/Al_2O_3, the conversion of pentylamine was much higher than it was over $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$; it decreased substantially as the H_2S pressure increased from 10 to 100 kPa H_2S.

The HDN products of pentylamine over the three catalysts were pentanethiol, dipentylamine, pentenes (i.e., the sum of the two pentene isomers), and pentane (Figs. 3–5). The selectivities for dipentylamine and pentanethiol increased in the order NiMo $<$ CoMo $<$ Mo, whereas the reverse order was observed for pentane and the pentenes. Dipentylamine behaved as a primary product over all three catalysts. The amount of dipentylamine was much larger over Mo/Al_2O_3 than over $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$. The selectivity of pentanethiol over the $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ catalysts increased with decreasing weight time, suggesting that pentanethiol is a primary product as well. The Mo/Al_2O_3 catalyst behaved differently at 100 kPa H_2S (Fig. 5). As the weight time decreased, the selectivity

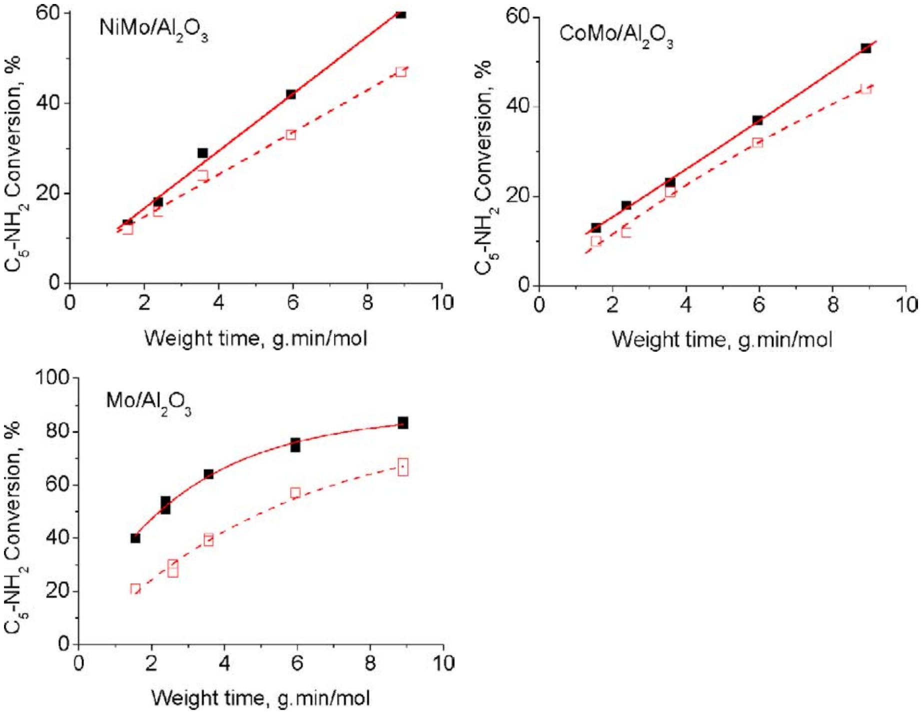


Fig. 2. Conversion of pentylamine in the presence of hexanethiol at 10 (■) and 100 (□) kPa H_2S, and 320 °C over sulfided NiMo/Al_2O_3, CoMo/Al_2O_3, and Mo/Al_2O_3 catalysts.

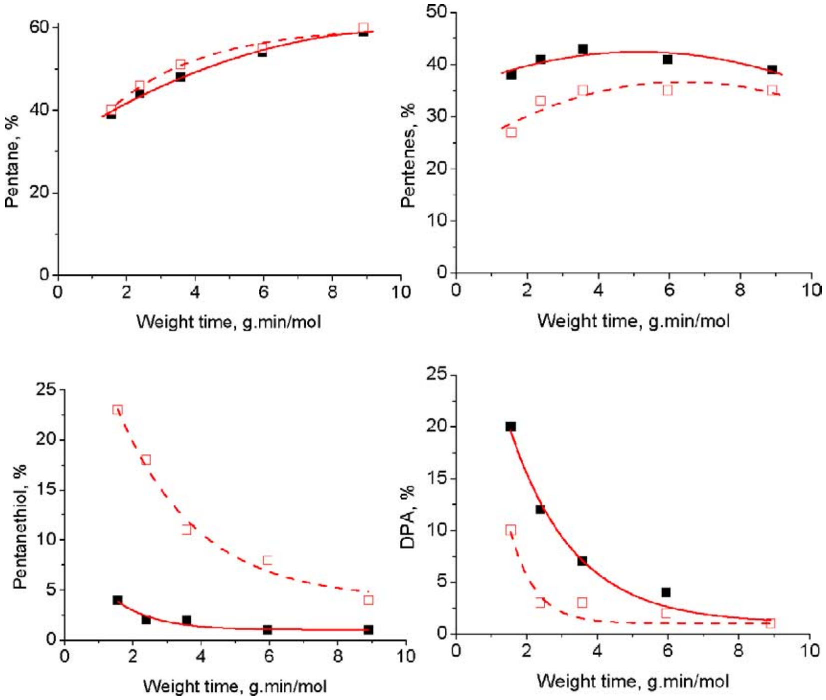


Fig. 3. Product selectivities in the HDN of pentylamine in the presence of hexanethiol at 10 (■) and 100 (□) kPa H_2S, and 320 °C over sulfided NiMo/Al_2O_3 (DPA = dipentylamine).

of pentanethiol first increased, then reached a maximum, and decreased at shorter weight time. This result was checked by repeating the experiments several times. The selectivity of pentanethiol increased strongly and that of dipentylamine decreased strongly with increasing H_2S pressure over all three catalysts.

The selectivities of the pentenes and pentane as a function of weight time were different over the three catalysts

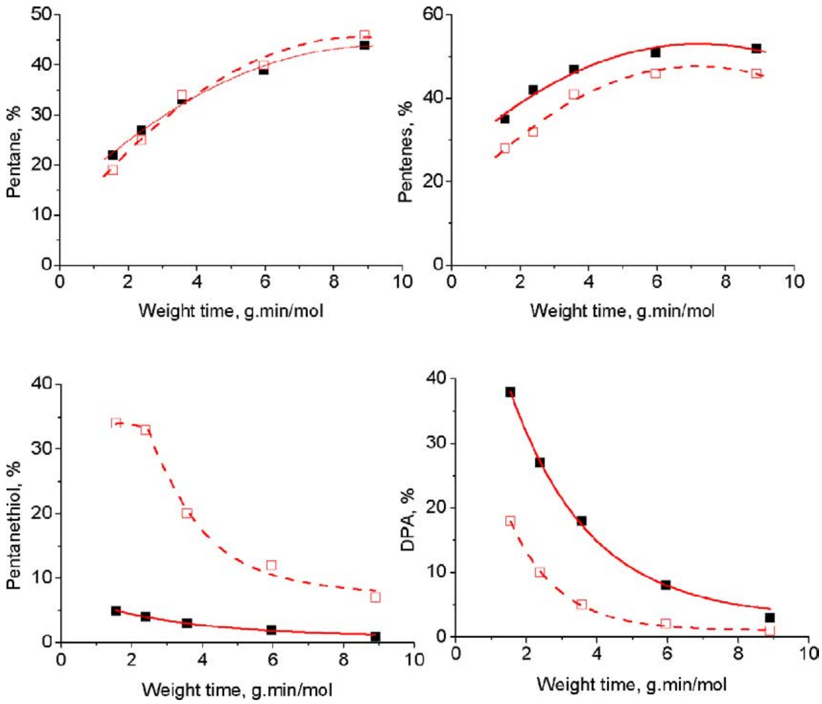


Fig. 4. Product selectivities in the HDN of pentylamine in the presence of hexanethiol at 10 (■) and 100 (□) kPa H_2S, and 320 °C over sulfided $CoMo/Al_2O_3$ (DPA = dipentylamine).

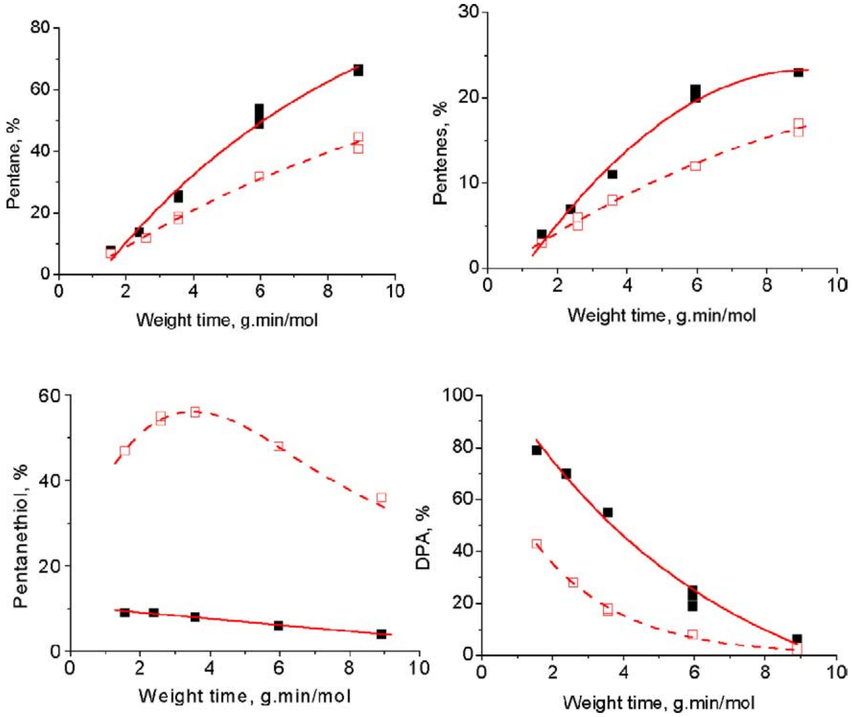


Fig. 5. Product selectivities in the HDN of pentylamine in the presence of hexanethiol at 10 (■) and 100 (□) kPa H_2S, and 320 °C over Mo/Al_2O_3 (DPA = dipentylamine).

(Figs. 3–5). The pentenes and pentane behaved as primary products over $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$, as shown by the fact that the selectivities extrapolate to a nonzero value with decreasing weight time. At the same time the selectivities initially increase with weight time, however, indicating that the pentenes and pentane are secondary or even tertiary products as well. This seemingly confusing conclusion is caused by the complexity of the reaction network, in which products can be formed directly in one step or indirectly in several steps; we will come back to this in the discussion. Over Mo/Al_2O_3, however, the selectivities extrapolate to zero with decreasing weight time, which indicates that, over this catalyst, the hexenes and hexane are secondary (or even tertiary) products only.

The conversion of 5 kPa hexanethiol in the presence of 10 kPa H_2S and 5 kPa pentylamine (simultaneous HDS and HDN) was much higher than that of pentylamine. At $\tau = 1.6$ g min/mol it was 100% at 320 °C (Table 1), while that of pentylamine was only 12% at 320 °C over $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ (Fig. 2). The conversion of hexanethiol decreased when the H_2S pressure was increased from 10 to 100 kPa, most strongly over Mo/Al_2O_3 (Table 1). Nevertheless, for all three catalysts, the conversion of the thiol was complete at 320 °C at short τ. This means that the presence of H_2S during the HDN was actually 5 kPa higher than the indicated 10 or 100 kPa due to H_2S in the feed. The hexenes/hexane ratio, obtained in the HDS of hexanethiol, was similar to the pentanes/pentane ratio obtained in the HDN of pentylamine over all three catalysts (Fig. 6).

Table 1
Conversions (%) of hexanethiol, 2-pentanethiol, and 2-methyl-2-butanethiol in the presence of pentylamine, 2-hexylamine, and hexylamine respectively at 270 and 320 °C and at 10 and 100 kPa H_2S at $\tau = 1.6$ g min/mol over $NiMo/Al_2O_3$, $CoMo/Al_2O_3$, and Mo/Al_2O_3

	Hexanethiol 320 °C		2-Pentanethiol 320 °C		2-Methyl-2-butanethiol 270 °C	
H_2S (kPa)	10	100	10	100	10	100
NiMo	100	90	100	89	76	32
CoMo	100	79	99	83	77	26
Mo	88	24	98	59	65	22

3.2. Simultaneous reaction of 2-hexylamine and 2-pentanethiol

The conversion of 2-hexylamine was higher than that of pentylamine over NiMo and CoMo and increased weakly

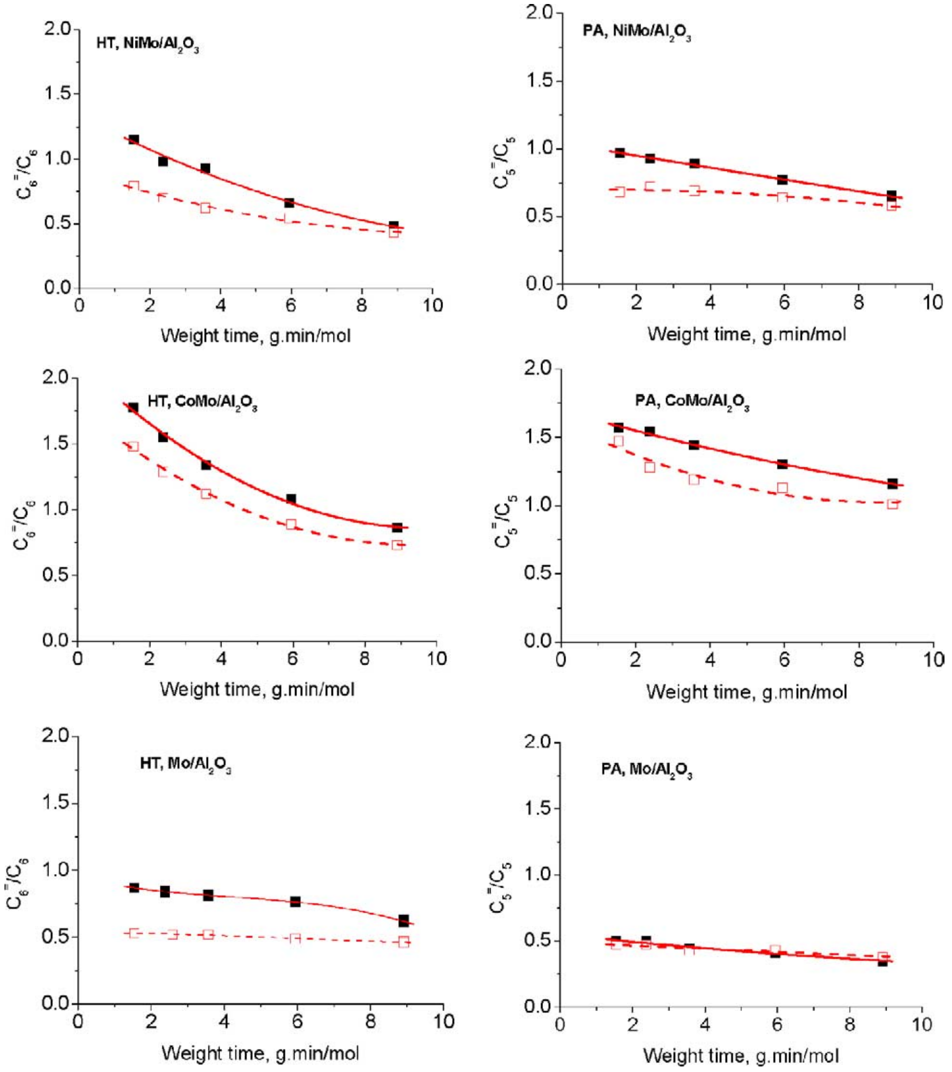


Fig. 6. Hexenes/hexane ratio in the HDS of hexanethiol (HT) and pentenes/pentane ratio in the HDN of pentylamine (PA) at 10 (■) and 100 (□) kPa H_2S, and 320 °C over sulfided $NiMo/Al_2O_3$, $CoMo/Al_2O_3$, and Mo/Al_2O_3 (DPA = dipentylamine).

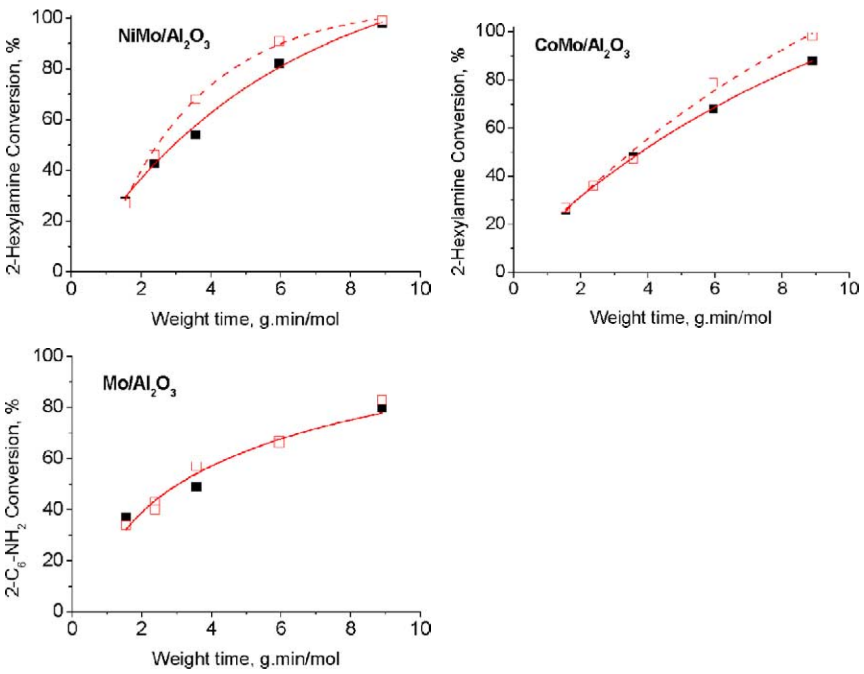


Fig. 7. Conversion of 2-hexylamine in the presence of 2-pentanethiol at 10 (■) and 100 (□) kPa H_2S and at 320 °C over sulfided NiMo/Al_2O_3, CoMo/Al_2O_3, and Mo/Al_2O_3.

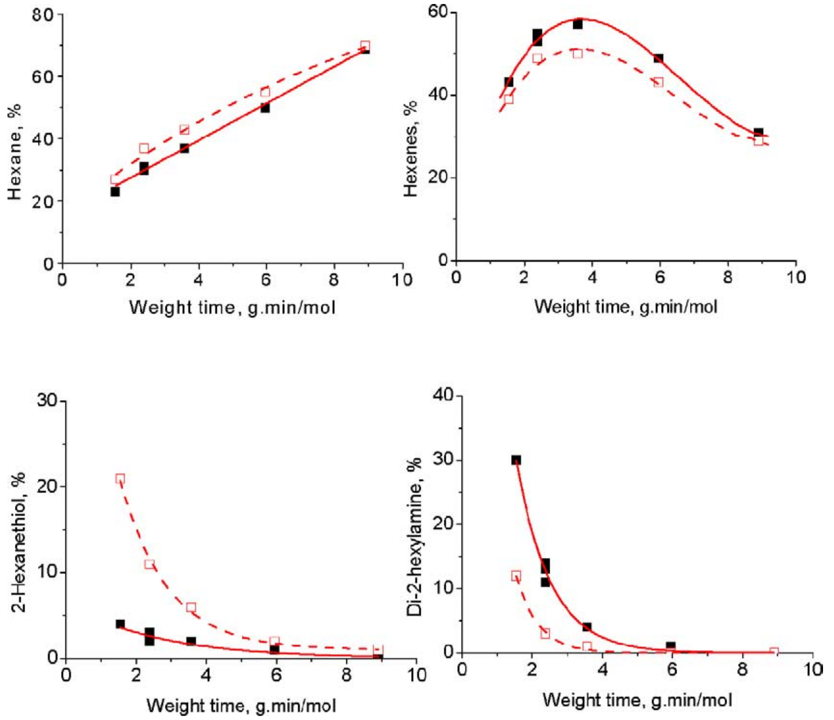


Fig. 8. Product selectivities in the HDN of 2-hexylamine in the presence of 2-pentanethiol at 10 (■) and 100 (□) kPa H_2S and at 320 °C over sulfided NiMo/Al_2O_3.

with increasing H_2S pressure (cf. Figs. 2 and 7). The main products were 2-hexanethiol, di-(2-hexyl)amine, hexenes (i.e., the sum of the three hexene isomers), and hexane. As for pentylamine, the selectivities for disproportionation and substitution increased in the order NiMo < CoMo < Mo, and those for hexane and hexenes decreased in the same order (Figs. 8–10). The selectivities of 2-hexanethiol and di-(2-hexyl)amine increased with decreasing weight time (Figs. 8–

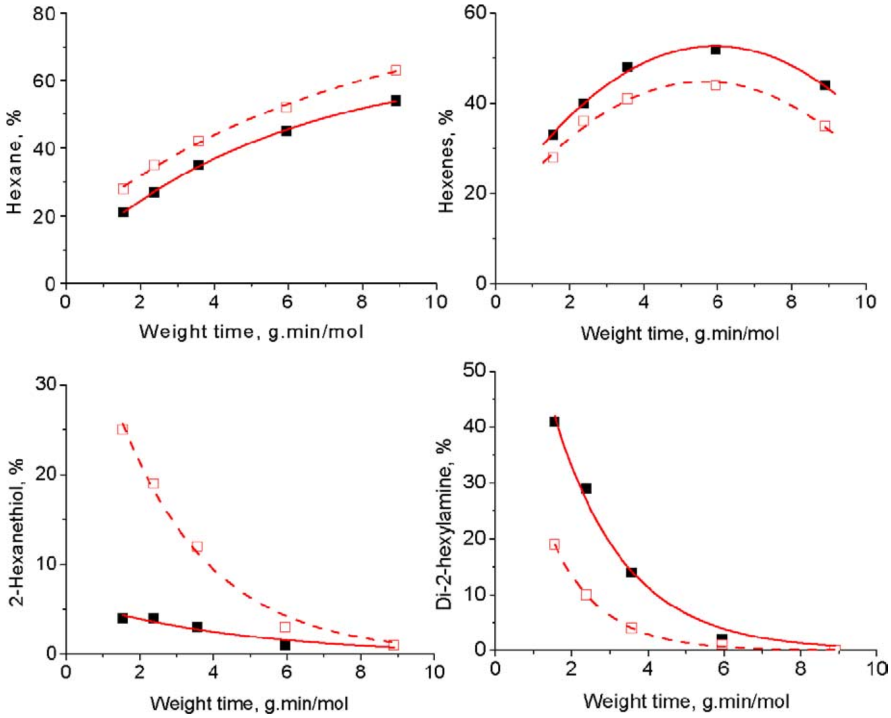


Fig. 9. Product selectivities in the HDN of 2-hexylamine in the presence of 2-pentanethiol at 10 (■) and 100 (□) kPa H_2S and at 320 °C over sulfided $CoMo/Al_2O_3$.

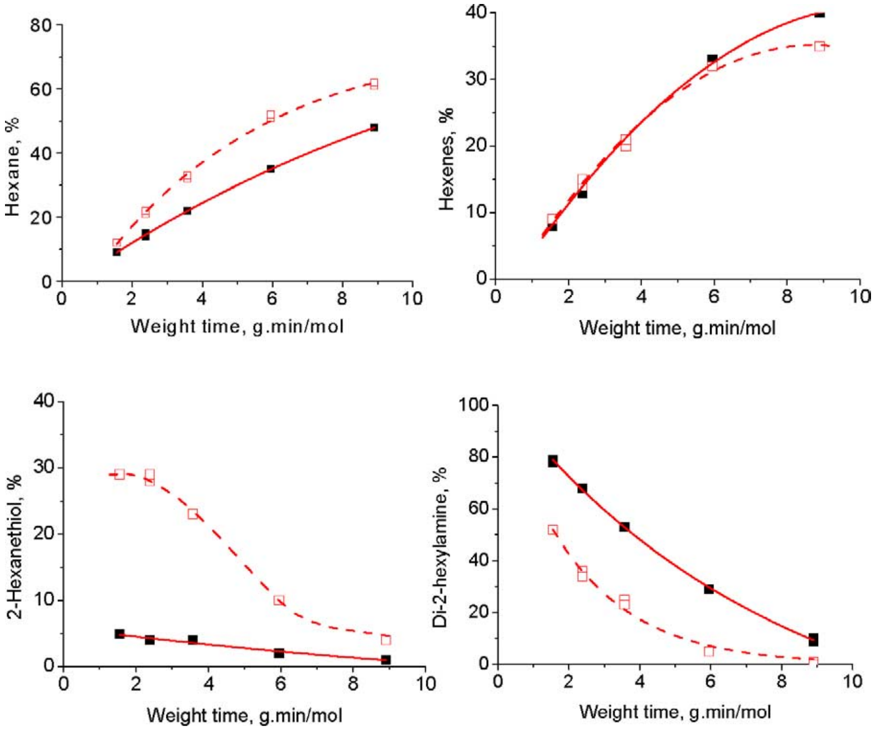


Fig. 10. Product selectivities in the HDN of 2-hexylamine in the presence of 2-pentanethiol at 10 (■) and 100 (□) kPa H_2S and at 320 °C over sulfided Mo/Al_2O_3.

10), which shows that they are primary products. The selectivity of di-(2-hexyl)amine decreased with increasing H_2S pressure, whereas the reverse was true for the selectivity of 2-hexanethiol.

The selectivities of the hexenes and hexane as a function of weight time were different over the three catalysts (Figs. 8–10). Hexenes and hexane behave as primary products over $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$, because the se-

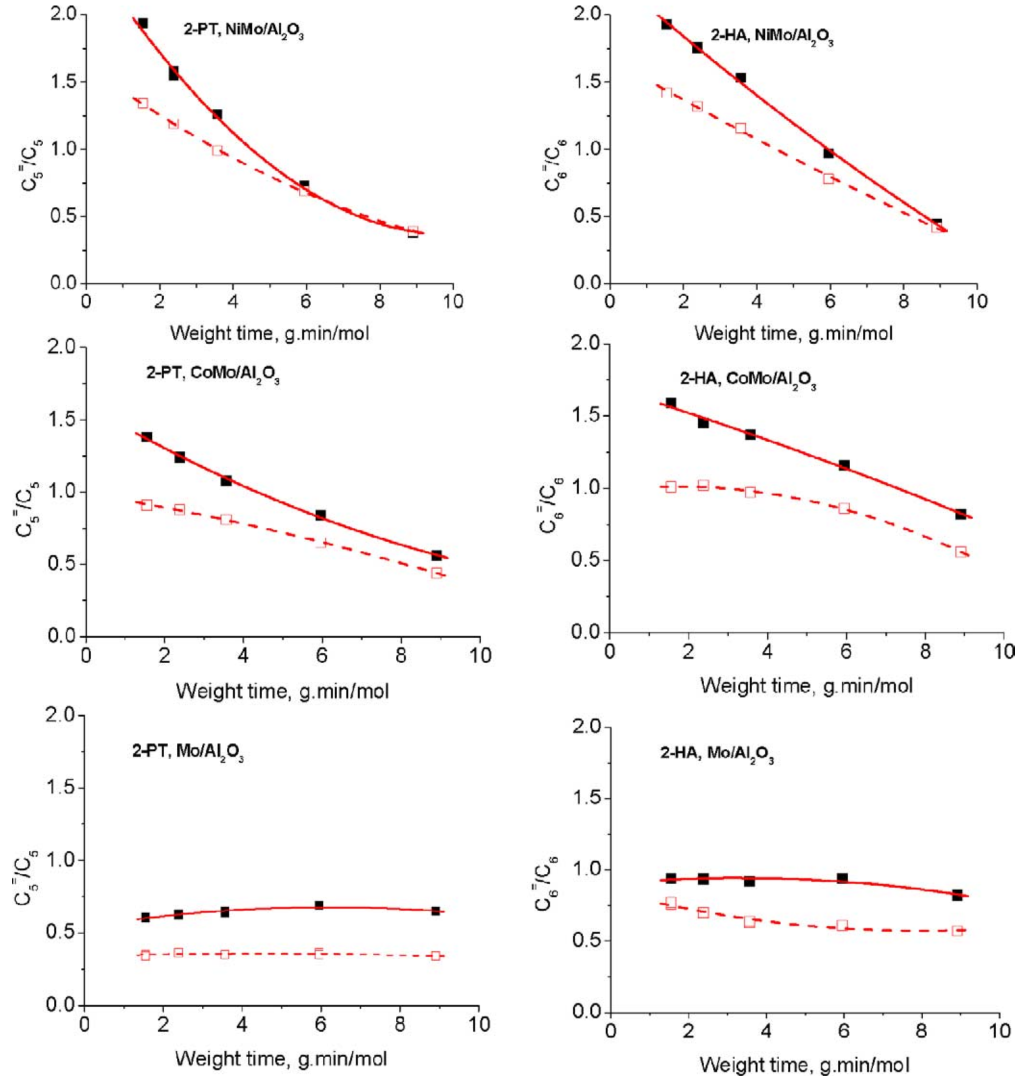


Fig. 11. Pentenes/pentane ratio in the HDS of 2-pentanethiol (2-PT) and hexenes/hexane ratio in the HDN 2-hexylamine (2-HA) at 10 (■) and 100 (□) kPa H_2S and at 320 °C over sulfided $NiMo/Al_2O_3$, $CoMo/Al_2O_3$, and Mo/Al_2O_3.

lectivities extrapolate to nonzero values with decreasing weight time and as secondary products, because the selectivities increase initially with increasing weight time. Over Mo/Al_2O_3, however, the selectivities extrapolate to zero with decreasing weight time, which indicates that hexenes and hexane are secondary or tertiary products only.

The conversion of 2-pentanethiol in the simultaneous reaction with 2-hexylamine in the presence of 10 kPa H_2S was much larger than that of the corresponding amine. It was almost 100% at $\tau = 1.6$ g min/mol at 320 °C (Table 1), whereas that of the corresponding amine was 30% (Fig. 7). The conversion of hexanethiol decreased when the H_2S pressure was increased from 10 to 100 kPa, most strongly over Mo/Al_2O_3. The pentenes/pentane ratio in the HDS of 2-pentanethiol was the same as the hexenes/hexane ratio in the HDN of 2-hexylamine over $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ (Fig. 11). The ratio originating from 2-pentanethiol was slightly lower than that from 2-hexylamine over Mo/Al_2O_3.

3.3. 2-Methyl-2-butylamine and 2-methyl-2-butanethiol

The HDN of 2-methyl-2-butylamine was fast; the conversion was already 17% at 270 °C and 10 kPa H_2S at low weight time (1.6 g min/mol) and reached 75% at $\tau = 8.9$ g min/mol over $NiMo/Al_2O_3$ (Fig. 12). The conversions over $CoMo/Al_2O_3$ and Mo/Al_2O_3 were even higher than those over $NiMo/Al_2O_3$. In all cases, the main products were 2-methyl-2-butene, 2-methyl-1-butene, and 2-methylbutane (not shown). The methylbutenes were primary products and methylbutane was a secondary product.

The conversion of 2-methyl-2-butanethiol at 270 °C in the presence of 10 kPa H_2S and 5 kPa hexylamine was much larger than that of the equivalent amine. It was already 76% at $\tau = 1.6$ g min/mol over $NiMo/Al_2O_3$

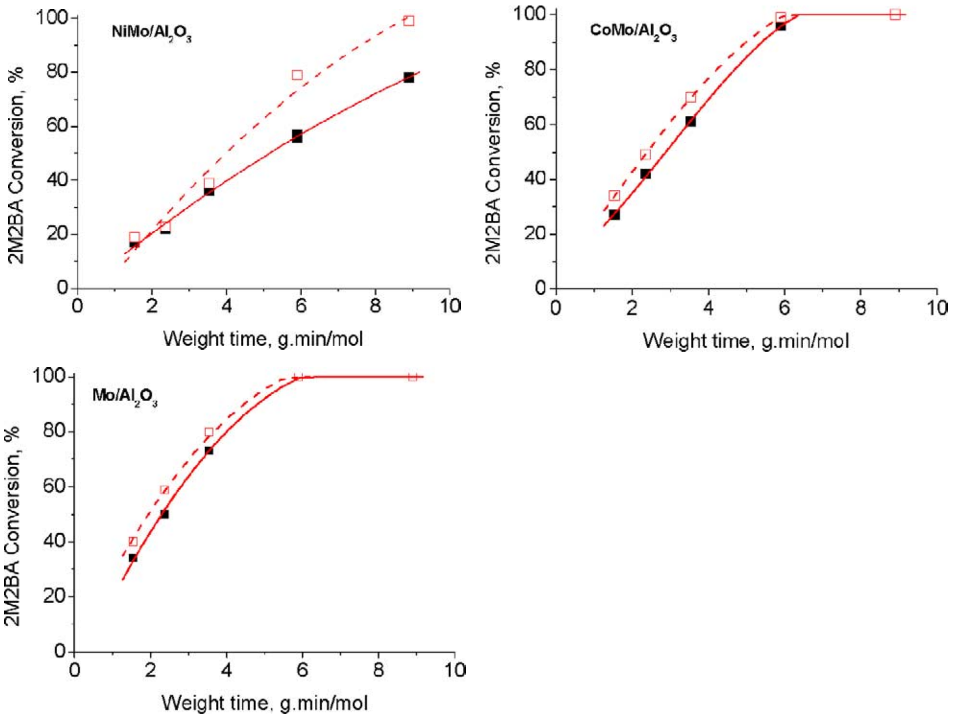


Fig. 12. Conversion of 2-methyl-2-butylamine (2M2BA) at 270 °C and at 10 (■) and 100 (□) kPa H_2S over sulfided NiMo/Al_2O_3, CoMo/Al_2O_3, and Mo/Al_2O_3.

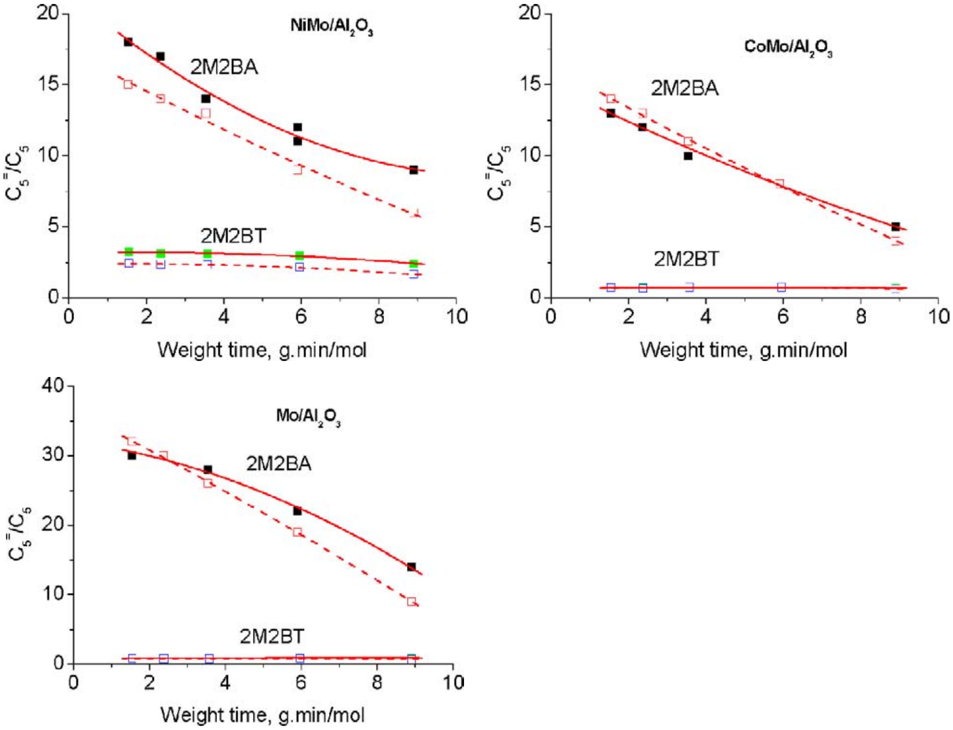


Fig. 13. Methylbutenes/methylbutane ratio in the HDN of 2-methyl-2-butylamine (2M2BA) and HDS of 2-methyl-2-butanethiol (2M2BT) in the presence of hexylamine at 270 °C and at 10 (■) and 100 (□) kPa H_2S over sulfided NiMo/Al_2O_3, CoMo/Al_2O_3, and Mo/Al_2O_3.

(Table 1), whereas the conversion of the corresponding amine was only 17% (Fig. 12). The conversion of 2-methyl-2-butanethiol decreased strongly with increasing H_2S pressure. The methylbutenes/methylbutane ratio in the HDS of 2-methyl-2-butanethiol in the presence of hexylamine was very different from the ratio in the HDN of 2-methyl-2-butylamine under the same conditions over all three catalysts (Fig. 13).

4. Discussion

4.1. Pentylamine

The conversion of pentylamine at 320 °C was similar over $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ (Fig. 2) but it was higher over Mo/Al_2O_3. It decreased more strongly over Mo/Al_2O_3 with increasing H_2S pressure from 10 to 100 kPa H_2S. These results may seem to contradict other reports that $NiMo/Al_2O_3$ is a better HDN catalyst than $CoMo/Al_2O_3$ and much better than Mo/Al_2O_3 [23–25]. However, these publications are mainly concerned with the HDN of aromatic N-containing molecules, for which hydrogenation and not the final N-removal step is rate-determining. Indeed, the position of the maximum in the selectivity of the pentenes at lower τ for NiMo (Fig. 3) than for CoMo (Fig. 4) and Mo (Fig. 5) indicates that hydrogenation is fastest for the NiMo catalyst and slowest for the Mo catalyst. Furthermore, the product selectivities in the HDN of pentylamine must be considered in detail. The selectivity for dipentylamine, formed by the disproportionation reaction of pentylamine, was 20% over $NiMo/Al_2O_3$ (Fig. 3), 40% over $CoMo/Al_2O_3$ (Fig. 4), and 80% over Mo/Al_2O_3 (Fig. 5) at $\tau = 1.6$ g min/mol, 320 °C, and 10 kPa H_2S. Thus, the higher conversion over Mo/Al_2O_3 is due mainly to the greater disproportionation of pentylamine to dipentylamine. We will put forward an explanation for the higher activity of Mo/Al_2O_3 in Section 4.3.

Hexanethiol converted very fast at 320 °C (Table 1). The conversion was already 100% at $\tau = 1.6$ g min/mol over both $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ at 10 kPa H_2S. At 100 kPa H_2S, $NiMo/Al_2O_3$ performs slightly better than $CoMo/Al_2O_3$ in the HDS of hexanethiol, but the two catalysts are more or less the same in the HDN of alkylamines as well as in the HDS of alkanethiols. The HDS of hexanethiol is slower over Mo/Al_2O_3, however, and decreased strongly when the H_2S pressure was increased from 10 to 100 kPa. We ascribe the lower thiol conversion over Mo/Al_2O_3 to the much lower number of sulfur vacancies on MoS_2 than on Co or Ni-promoted MoS_2 [19,20] and the decreased conversion with increasing H_2S pressure to the filling of these vacancies by H_2S.

Pentanethiol was a primary product in the HDN of pentylamine over all three catalysts, as shown by the fact that the selectivity extrapolated to a nonzero value at time zero (Figs. 3–5). At 100 kPa H_2S, the selectivity for pentanethiol increased with decreasing weight time over $NiMo/Al_2O_3$, seemed to reach a maximum at short weight time over $CoMo/Al_2O_3$ (Fig. 4), and clearly reached a maximum with decreasing weight time over Mo/Al_2O_3 (Fig. 5). This was checked by repeating the experiments several times. Pentanethiol can form in two ways: 1) substitution of pentylamine with H_2S,

$$C_5H_{11}NH_2 + H_2S \rightarrow C_5H_{11}SH + NH_3, \tag{1}$$

and 2) substitution of dipentylamine with H_2S,

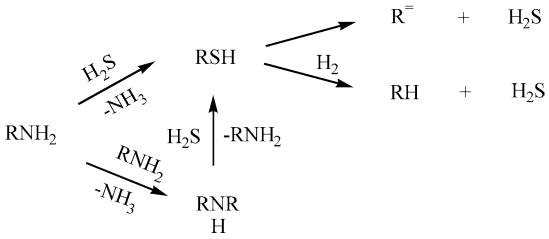
$$C_5H_{11}NH_2 + C_5H_{11}NH_2 \rightarrow C_5H_{11}NHC_5H_{11} + NH_3, \tag{2}$$

$$C_5H_{11}NHC_5H_{11} + H_2S \rightarrow C_5H_{11}SH + C_5H_{11}NH_2. \tag{3}$$

Pentanethiol is a primary product in Eq. (1) and a secondary product in Eqs. (2) and (3). This shows that the selectivity of pentanethiol is not zero at $\tau = 0$ (Eq. (1)) and that it increases with increasing weight time at 100 kPa H_2S (Eqs. (2) and (3)). At higher weight time, the pentanethiol selectivity decreases because of the reaction of the thiol to an alkene by elimination and to an alkane by hydrogenolysis. The initial increase in the pentanethiol selectivity with increasing weight time at 100 kPa H_2S proves that dipentylamine, formed by disproportionation of pentylamine, reacts fast with H_2S to form pentanethiol and pentylamine over Mo/Al_2O_3. Over $NiMo/Al_2O_3$, dipentylamine reacts faster with H_2S to form pentylamine and pentanethiol than does pentylamine to form pentanethiol [9]. For $NiMo/Al_2O_3$, the decomposition of the formed pentanethiol is very fast, whereas for Mo/Al_2O_3 it is slower (Table 1). This shows that maximum thiol selectivity for $NiMo/Al_2O_3$ is not reached above $\tau = 1.6$ g min/mol (the lowest weight time that could be obtained), whereas for Mo/Al_2O_3 there is a clear maximum. For $CoMo/Al_2O_3$, with an intermediate rate of thiol decomposition (Table 1), there seems to be a maximum (Fig. 4).

Pentene and pentane behaved not only as primary, but also as secondary products over $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ (Figs. 3 and 4), and they behaved as secondary products only over Mo/Al_2O_3. However, the pentenes/pentane ratio in the simultaneous reaction of pentylamine and hexanethiol was very similar to the hexenes/hexane ratio over all three catalysts (Fig. 6). This demonstrates that the alkenes and alkane are determined by the thiol, which is an intermediate between alkylamine and hydrocarbons. Thus, substitution is the predominant reaction in the HDN of pentylamine over all three catalysts. Pentenes and pentane behave as primary products because of the very fast decomposition of the intermediate pentanethiol (Table 1). Only when this decomposition is slowed down, as over Mo/Al_2O_3 (Table 1), is the formation of the pentenes and pentane clearly not primary. The fact that their selectivities seem to extrapolate to zero for $\tau > 0$ (Fig. 5) suggests that the pentenes and pentane might primarily be tertiary products (cf. curve D in Fig. 1B with the pentenes and pentane selectivities in Fig. 5, both at low τ). They would then form from dipentylamine (Scheme 3).

Figures 6 and 11 show that the alkene/alkane branching ratio decreases with increasing H_2S pressure, meaning that the elimination of the alkanethiol to the alkene is more suppressed by H_2S than is the hydrogenolysis to the alkane. It is not clear why this is the case. Our DFT calculations show that in both reactions a vacancy on the edge surface of MoS_2 is needed for the adsorption of the thiol as well as a sulfur atom on a neighboring site [26]. In the elimination reaction this sulfur atom is needed for the elimination of the β-H



Scheme 3. Reaction network for the removal of nitrogen from alkylamines with the amine group attached to a primary or secondary carbon atom.

atom from the alkyl group. In the hydrogenolysis reaction this sulfur atom facilitates the splitting of the S–H bond of the thiol, and the resulting hydrogen atom on the neighboring sulfur atom facilitates the splitting of the C–S bond of the thiolate and the concerted hydrogenation of the alkyl group. These arguments show that there is no simple answer to why the alkene/alkane branching ratio in the reaction of an alkanethiol decreases with increasing H_2S pressure.

4.2. 2-Hexylamine

The reaction rate of 2-hexylamine was faster than that of pentylamine over NiMo/Al_2O_3 and CoMo/Al_2O_3 because of the weaker C–N bond of the alkylamine with the NH_2 group attached to a secondary carbon atom [10]. The conversion of 2-hexylamine increases slightly with increasing H_2S pressure, whereas that of pentylamine decreases with increasing H_2S pressure. The influence of H_2S is at least twofold. On the one hand, it has a positive influence as a reaction partner in the nucleophilic substitution of the alkylamine to an alkanethiol. On the other, it adsorbs on the catalyst surface and hinders the reaction, as shown by the negative influence on the disproportionation of the alkylamines to dialkylamines and on the reaction of alkanethiols (Table 1). The much stronger effect of H_2S on the Mo/Al_2O_3 catalyst (Fig. 2), which shows the highest selectivity for dipentylamine (Fig. 5), suggests that the inhibition of the disproportionation explains the negative influence of H_2S on the HDN of pentylamine. For 2-hexylamine the increased acidity of the catalyst surface due to H_2S adsorption and dissociation [12–14,27] may also play a role. The ionic character of the C–N bond in the secondary carbon atoms may be increased by a higher proton concentration at the catalyst surface.

As for pentylamine, the selectivity for the dialkylamine (di-(2-hexyl)amine in this case) is much higher over Mo/Al_2O_3 than it is over NiMo/Al_2O_3 and CoMo/Al_2O_3 (Figs. 8–10). With increasing weight time, the selectivity of di-(2-hexyl)amine decreased much more strongly over the Ni(Co)-promoted catalysts than over Mo/Al_2O_3. It shows that disproportionation takes place easily over Mo/Al_2O_3, but that the dialkylamine disproportionation product reacts more slowly over Mo/Al_2O_3 than it does over NiMo/Al_2O_3 and CoMo/Al_2O_3. The selectivity for hexane, the final product in the HDN of 2-hexylamine, always increased with increasing weight time over all three catalysts. On the other hand, the selectivity of the hexenes first increased with increasing weight time and later decreased over NiMo/Al_2O_3 and CoMo/Al_2O_3. This must be due to the high HDN conversion and, thus, the decreased inhibition of the hydrogenation of the hexenes by the amines at higher weight time. The hexenes/hexane ratio in the simultaneous reaction of 2-hexylamine and 2-pentanethiol was very similar to the pentenes/pentane ratio due to 2-pentanethiol over all three catalysts (Fig. 11). This demonstrates that the hexenes are mainly produced from 2-hexanethiol, formed by substitution of H_2S in the HDN of 2-hexylamine over all three catalysts. The substitution of 2-hexylamine with H_2S can be a direct substitution (Eq. (1)) or an indirect substitution after the disproportionation reaction of 2-hexylamine (Eqs. (2) and (3)). The indication that a maximum is reached in the 2-hexanethiol selectivity at short τ for Mo/Al_2O_3 (Fig. 10) suggests that, at least for this catalyst, both routes play a role. Because of the secondary carbon atom in 2-hexylamine and 2-hexanethiol, these molecules react faster than pentylamine and pentanethiol, respectively. As a consequence, maxima due to formation of intermediates shift to shorter τ for reactants with the secondary carbon atoms. This explains why only the maximum for 2-hexanethiol is unclear (Fig. 10) and why the maxima for the alkenes are at shorter τ in the HDN of 2-hexylamine than in the HDN of pentylamine (cf. Figs. 8–10 with Figs. 3–5).

4.3. 2-Methyl-2-butylamine

Pentylamine and 2-hexylamine showed weak conversion below 300 °C, whereas the conversion of 2-methyl-2-butylamine was already very high at 270 °C. Hydrocarbons and a trace of thiol (not shown) formed in the HDN of 2-methyl-2-butylamine, in accordance with our former results for NiMo/Al_2O_3 [10]. Methylbutenes were primary products, and the methylbutenes/methylbutane branching ratio in the HDN of 2-methyl-2-butylamine was about 5 times higher than that obtained in the HDS of 2-methyl-2-butanethiol in the presence of hexylamine over NiMo/Al_2O_3, 20 times higher over CoMo/Al_2O_3, and 30 times higher over Mo/Al_2O_3 at $\tau = 1.6$ g min/mol, 270 °C, and 10 kPa H_2S (Fig. 13). The branching ratio in the HDS of the thiol with the SH group attached to a tertiary carbon atom (Fig. 13) was similar to that of thiols with the SH group attached to a primary (Fig. 6) or secondary (Fig. 11) carbon atom. The branching ratio in the HDN of the amine group attached to a tertiary carbon atom was different, however. Therefore, 2-methyl-2-butanethiol cannot be the intermediate in the HDN of 2-methyl-2-butylamine.

Furthermore, the very small amount of thiol formed shows that the amine with the NH_2 group attached to a tertiary carbon atom does not react or hardly reacts by substitution with H_2S to the corresponding thiol. In that case the concentration of 2-methyl-2-butanethiol would be much higher. The conversion of 2-methyl-2-butanethiol in the presence of an amine is lower at 270 °C than that of hexanethiol and

2-pentanethiol at 320 °C (Table 1). Nevertheless, the thiol selectivities in the HDN of pentylamine (Figs. 3–5) and 2-hexylamine (Figs. 8–10) were high and that of 2-methyl-2-butylamine was very low. Thus, 2-methyl-2-butylamine does not react by substitution with H_2S to a thiol or by substitution with another amine molecule to a dialkylamine, since this disproportionation product was not observed over any of the catalysts. This may be due to steric hindrance at the α-carbon atom. Because the main primary products in the HDN of 2-methyl-2-butylamine are alkenes, we conclude that this HDN mechanism takes place by elimination. The weak effect of H_2S and the tertiary carbon atom suggest that the elimination is of the E1 type over all three catalysts, as discussed in detail for $NiMo/Al_2O_3$ [10].

2-Methyl-2-butylamine reacted fastest over Mo/Al_2O_3 and slowest over $NiMo/Al_2O_3$ (Fig. 12). This HDN reaction is probably catalyzed by acid sites, which may be Lewis acid sites, consisting of a sulfur vacancy on a molybdenum, cobalt, and nickel atom, or Brønsted acid sites, consisting of H atoms on the sulfur atoms (protons of SH^- groups). The activity order shows that sulfided Mo/Al_2O_3 is more acidic than $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$. In an ionic model, this might be ascribed to the higher charge of Mo^{4+} compared with Co^{2+} or Ni^{2+} (Lewis sites) or to the weaker bonding of H^+ to S^{2-} that is bonded to Mo^{4+} than to Co^{2+} or Ni^{2+} (Brønsted site).

The conversion of 2-methyl-2-butylamine increased when the H_2S pressure was increased from 10 to 100 kPa. This cannot be due to competition of H_2S with the amine for the adsorption sites on the catalyst surface. Since nucleophilic substitution hardly occurred for 2-methyl-2-butylamine, this does not explain the positive influence of H_2S either. On the other hand, H_2S introduces protons to the catalyst surface and thus increases the acidity of the catalyst. While it is impossible to turn a primary carbon atom into a carbenium ion, the tertiary carbon atom of 2-methyl-2-butylamine can easily form a carbenium ion after protonation by H_2S and the splitting off of NH_3. With increasing H_2S pressure, the conversion of 2-methyl-2-butylamine thus increases over all three catalysts. This means that Brønsted acid sites, not Lewis acid sites, are responsible for the elimination of NH_3 from the amine with an NH_2 group attached to a tertiary carbon atom. It also explains why Mo/Al_2O_3, the catalyst with the lowest number of sulfur vacancies, has the highest activity.

Mo/Al_2O_3 has the highest activity not only in the HDN of 2-methyl-2-butylamine, but also in the HDN of pentylamine (Fig. 2). The latter reactivity is due to the disproportionation to dipentylamine and the substitution to pentanethiol. The major product is dipentylamine, suggesting that the disproportionation is also acid-catalyzed and that the order of the three catalysts is the same for the HDN of 2-methyl-2-butylamine and of pentylamine.

The conclusion that MoS_2 is more acidic than Co–MoS_2 and Ni–MoS_2 catalysts is in agreement with DFT calculations of the heat of adsorption of NH_3 on Lewis and Brønsted acid sites on the surface of promoted and unpromoted M–MoS_2 systems [20]. Travert et al. found that the heat of adsorption on metal sites, which were not fully coordinated by sulfur atoms (CUS, Lewis sites), was stronger for Mo than for Co and Ni and decreased with increasing sulfur coordination. The heat of adsorption on Brønsted SH groups was stronger for SH groups attached to Mo atoms, as is expected because a stronger metal–sulfur bond will induce a higher protonic character of the SH group. The IR investigation of Petit et al. showed that H_2S adsorption leads to an increase in the number of Brønsted acid sites and a decrease in the number of Lewis acid sites on sulfided Mo/Al_2O_3 and $CoMo/Al_2O_3$ [12].

5. Conclusion

The results of the HDN of alkylamines over $CoMo/Al_2O_3$ and Mo/Al_2O_3 support our previous studies over $NiMo/Al_2O_3$ [9,10]. The alkylamine with the amine group attached to a primary or secondary carbon atom reacts by substitution of the NH_2 group by SH or an amine to form an alkanethiol or a dialkylamine, respectively, over all three catalysts. The alkanethiol forms an alkene and an alkane. Only tertiary alkylamines react directly to hydrocarbons by means of an E1 mechanism over all three catalysts. An E2 mechanism seldom occurs in the HDN of alkylamines over our catalysts. The fact that Mo/Al_2O_3, the catalyst with the smallest number of sulfur vacancies, has the highest HDN activity and that H_2S has a positive influence on the HDN of the alkylamines with an NH_2 group attached to a tertiary carbon atom suggests that alkylamines react on Brønsted acid sites. The HDS of alkanethiols, on the other hand, requires vacancies because Mo/Al_2O_3 has the lowest HDS activity and H_2S has a strong negative effect on all three alkanethiols, even with the SH group attached to a tertiary carbon atom.

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