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Hydrodenitrogenation of 2-methylpyridine and its intermediates 2-methylpiperidine and tetrahydro-methylpyridine over sulfided NiMo/γ-Al_2O_3

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Abstract

The reaction network and mechanism of the hydrodenitrogenation (HDN) of 2-methylpyridine and 2-methylpiperidine were studied at 280–340 °C and 1–3 MPa in the absence and presence of H_2S over sulfided NiMo/γ-Al_2O_3. By the addition of 2-ethylpiperidine to the HDN of 2-methylpyridine and of 2-ethylpyridine to the HDN of 2-methylpiperidine, the mutual inhibiting effects of 2-methylpyridine and 2-methylpiperidine could be determined. 2-Ethylpyridine hardly affected the HDN of 2-methylpiperidine, but 2-ethylpiperidine strongly retarded the hydrogenation of 2-methylpyridine and promoted its denitrogenation at low partial pressure and inhibited it at high partial pressure. Substantial amounts of 2,3,4,5-tetrahydro-6-methylpyridine were detected in the HDN reactions; thus, its HDN was studied. This imine intermediate reacted very rapidly to 2-methylpiperidine by hydrogenation. 2-Methylpiperidine reacted to 1-hexylamine and even more strongly to 2-hexylamine. The final hydrocarbon products were 1-hexene, 2-hexene, and hexane. Based on these results and on previous HDN studies of dialkylamines, we propose that 2-methylpyridine first reacts by hydrogenation to 2-methylpiperidine and that both react to the imines 2,3,4,5-tetrahydro-2-methylpyridine and 2,3,4,5-tetrahydro-6-methylpyridine. Breaking of the first C–N bond and ring opening of the imines occurs as a result of the addition of H_2S, elimination, and hydrogenation, forming amino-hexanethiols. The amino-hexanethiols react by hydrogenolysis to hexylamines, and the second C–N bond is broken by hexylimine formation, H_2S addition, and NH_3 elimination.

Keywords: Hydrodenitrogenation; 2-Methylpiperidine; 2-Methylpyridine; 2,3,4,5-Tetrahydro-6-methylpyridine; Inhibition; Sulfided NiMo/γ-Al_2O_3

1. Introduction

The removal of sulfur and nitrogen from fuels by hydrotreatment is an increasingly important area of research because of ever more-stringent environmental regulations. The sulfur level in gasoline and diesel fuel must be reduced from the present maximum of 50 to 10 ppm in 2010, and even lower limits can be expected in the future. Deep hydrodesulfurization (HDS) technology is needed to attain this low sulfur level. Nitrogen-containing compounds strongly inhibit the HDS of sulfur-containing compounds through competitive adsorption, especially in deep HDS [1–3]. In addition, reducing the content of nitrogen-containing compounds has a positive effect on the stability of fuels and decreases NO_x emissions. Therefore, hydrodenitrogenation (HDN) is becoming more important and has been attracting more attention in recent years [4,5].

A considerable number of studies have led to a better understanding of the mechanism of HDN. It is generally accepted that the first step in the HDN of nitrogen-containing aromatic molecules is hydrogenation of the heterocyclic ring, and that C–N bond cleavage occurs thereafter [4–9]. This can be explained in part by the fact that the aromatic C=N bond is stronger than the aliphatic C–N bond. The mechanisms of C–N bond scission and nitrogen removal were first proposed by Nelson and Levy [6], who suggested that removal of the nitrogen atom from an alkylamine occurs by nucleophilic substitution or Hofmann β-H elimination. Evidence for both mechanisms has been provided [10–13] and the molecule, the catalyst, and the reaction conditions all have been found to influence the mechanism [12].

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Recently, Zhao et al. [14–16] found that C–N bond breaking of an alkylamine, in which the nitrogen atom is linked to a primary or secondary carbon atom, occurs exclusively by nucleophilic substitution by H_2S to form an alkanethiol and NH_3. Subsequent work showed that the substitution does not occur by a classic S_N2 substitution, but rather by a sequence of reactions in which the amine first dehydrogenates to an intermediate imine [17,18], followed by addition of H_2S to the imine, and, after ammonia elimination and hydrogenation, formation of a thiol.

Pyridine, as the smallest nitrogen-containing heterocyclic molecule, was once considered the simplest probe molecule for studying HDN. In recent years, 2-methylpyridine and 2-methylpiperidine have proven to be better probe molecules than pyridine and piperidine, respectively [19,20]. This is because the introduction of a methyl group on the α carbon atom of piperidine strongly suppresses the disproportionation to *N*-pentylpiperidine and NH_3, which is severe in the HDN of piperidine [7,21], so that it hardly interferes with the other reactions occurring during HDN. The mechanisms of the HDN of 2-methylpyridine and 2-methylpiperidine were studied by several groups. Portefaix et al. [10] suggested that the HDN of 2-methylpiperidine occurs by elimination, through a nucleophilic attack on β-hydrogen atoms. Egorova et al. suggested that the ring opening of piperidine and nitrogen removal occur by elimination as well as by nucleophilic substitution of the amino group by a sulfhydryl group, followed by elimination of H_2S or hydrogenolysis of the C–S bond [19]. Oyama and Lee [20] deduced that the preferred pathway of HDN of unhindered piperidine and 2-methylpiperidine is an S_N2-type substitution reaction involving nucleophilic attack on an open α carbon atom by a surface sulfur atom and formation of a piperidinium ion intermediate. Both Egorova et al. [19] and Oyama and Lee [20] reported substantial amounts of the imine 2,3,4,5-tetrahydro-6-methylpyridine at short weight time; this imine was considered the intermediate of hydrogenation and dehydrogenation.

To gain further insight into the HDN mechanism, we investigated the HDN of 2-methylpyridine and 2-methylpiperidine at 280–340 °C and 1–3 MPa in the absence and presence of H_2S. We also used 2,3,4,5-tetrahydro-6-methylpyridine, the reaction intermediate of the HDN network, as a reactant. By adding 2-ethylpiperidine to the HDN of 2-methylpyridine and of 2-ethylpyridine to the HDN of 2-methylpiperidine, we hoped to determine the mutual inhibitive adsorption effects of 2-methylpyridine and 2-methylpiperidine. We also studied the effects of H_2S, pressure, and NH_3.

2. Experimental

The NiMo/γ-Al_2O_3 catalyst used in this work contained 8 wt% Mo and 3 wt% Ni and was prepared by successive incipient wetness impregnation of γ-Al_2O_3 (Condea; pore volume, 0.5 cm^3/g; specific surface area, 230 m^2/g). The catalyst was crushed and sieved to a 230-mesh (<0.063 mm) particle size. Further details of the catalyst preparation have been given previously [19].

The catalytic reactions were carried out in continuous mode in a fixed-bed inconel reactor heated in an oven and filled with 0.05 g of catalyst, diluted with 8 g SiC to achieve plug-flow conditions. The catalyst was sulfided in situ with a mixture of 10% H_2S in H_2 (25 ml/min) at 400 °C and 1.0 MPa for 4 h. After sulfidation, the pressure was increased to reaction pressure, the temperature was decreased to reaction temperature, and the liquid reactant was fed to the reactor by means of an ISCO 500D syringe pump. The experiments in which the weight time was varied were carried out at 340 °C. Experiments at a fixed weight time of 5.0 g min/mol were carried out at 280–340 °C. In most of the experiments, the gas-phase feed was composed of 140 kPa decane (as solvent for the nitrogen-containing compounds), 20 kPa heptane (as GC reference for the nitrogen-containing compounds), 2.5–10 kPa amine reactant, 0 or 20 kPa H_2S, and 2.8 MPa H_2 (3.0 MPa total pressure). Some experiments were performed at 0.8 MPa H_2 (1.0 MPa total pressure). The reaction products were analyzed off-line by gas chromatography with a Varian 3800 gas chromatograph equipped with a PTA-5 fused silica capillary column. Detection was performed with a flame ionization detector. Mass spectrometry was used to identify the reaction products. The analysis was performed with an Agilent 6890 gas chromatograph equipped with a HP-5MS capillary column and an Agilent 5973 mass selective detector. Weight time was defined as the ratio of the catalyst weight to the molar flow to the reactor (1 g min/mol = 1.1×10^{-2} g h/L at 340 °C and 3.0 MPa). The weight time was changed by varying the flow rates of the liquid and the gaseous reactants while keeping their ratio constant.

2-Methylpiperidine (Acros), 2-methylpyridine (Fluka), 2-ethylpiperidine (Aldrich), 2-ethylpyridine (Acros), and 1-butylamine (Aldrich) were all used as purchased in the HDN tests. 2,3,4,5-Tetrahydro-6-methylpyridine was synthesized as described previously [22] and purified by distillation.

3. Results

3.1. HDN of MPi

The HDN of 2.5, 5, and 10 kPa 2-methylpiperidine (MPi) was carried out as a function of weight time at 340 °C and 1.0, as well as 3.0 MPa in the absence and presence of 20 kPa H_2S over the sulfided NiMo/γ-Al_2O_3 catalyst. Typical reaction profiles and product selectivities in the HDN of 5.0 kPa MPi in the absence and presence of 20 kPa H_2S are presented in Figs. 1 and 2, respectively.

No products with mass greater than that of the reactant (e.g., disproportionation or condensation products) were detected. Seven products were observed: 2-methylpyridine (MPy); 2,3,4,5-tetrahydro-6-methylpyridine (TH-6MPy); 1-hexylamine; 2-hexylamine; 1-hexene; 2-hexene; and hexane. The most abundant products were MPy, 1-hexene, 2-hexene, and hexane (with the latter three designated C6 products), indicating that two reactions occurred in the HDN of MPi: dehydrogenation of MPi and nitrogen removal from MPi. TH-6MPy, 1-hexylamine, and 2-hexylamine were observed in small amounts. Their yields passed through a low maximum, indicating that their rates of

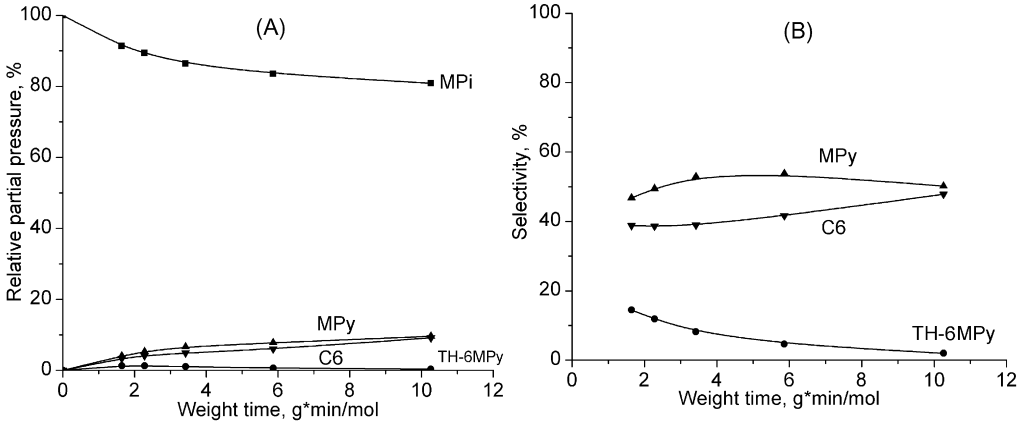


Fig. 1. Relative partial pressures (A) and selectivities (B) of the products of the HDN of 5 kPa MPi as a function of weight time at 340 °C, 3.0 MPa, and 0 kPa H_2S.

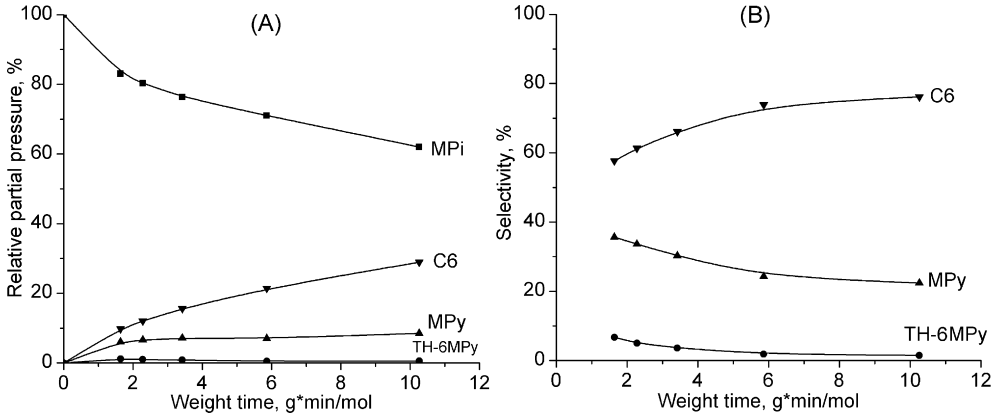


Fig. 2. Relative partial pressures (A) and selectivities (B) of the products of the HDN of 5 kPa MPi as a function of weight time at 340 °C, 3.0 MPa, and 20 kPa H_2S.

further reaction were much greater than their rates of formation. The yield of 2-hexylamine was much higher than that of 1-hexylamine. This is consistent with the results of Egorova et al. [19] and Oyama and Lee [20], although the reaction conditions were different, suggesting that the bond between the N atom and the methylene group can be more easily broken than the bond between the N atom and the $CH(CH_3)$ group. The denitrogenated C6 products showed continuously increasing yields and were the final products of the HDN network.

The selectivities of TH-6MPy, 1-hexylamine, and 2-hexylamine extrapolated to nonzero values at weight time zero, suggesting that they were primary products. Their decrease with increasing weight time indicates that they reacted further and thus were reaction intermediates. The selectivity of MPy showed a different trend in the absence of H_2S than in the presence of H_2S. In the absence of H_2S, the MPy selectivity went through a maximum, and at low weight time, it decreased with decreasing weight time (Fig. 1). In the presence of H_2S, MPy selectivity increased continuously with decreasing weight time, and MPy yield first increased until $\tau = 3$ g min/mol and then leveled off with increasing weight time (Fig. 2). Thus, at 3.0 MPa and 20 kPa H_2S, MPy behaved purely as a primary product.

Also in the reaction of 5 kPa MPi at the lower pressure of 1.0 MPa (Fig. 3), TH-6MPy, 1-hexylamine, and 2-hexylamine behaved as primary products. Higher selectivities of TH-6MPy were observed than at 3.0 MPa. The selectivities of MPy and C6 decreased with decreasing weight time, suggesting that these were secondary products. If the MPy selectivity could be extrapolated to a nonzero value at weight time zero, then MPy might be considered a primary product as well.

The results of the HDN of different partial pressures of MPi at 340 °C and 1.0 and 3.0 MPa in the absence and presence of 20 kPa H_2S and at a weight time of 10.4 g min/mol are summarized in Table 1. At 1.0 MPa, the increased partial pressure of MPi decreased the conversion of MPi and the yield and selectivity of both MPy and C6, but increased the yield and selectivity of TH-6MPy. The conversion of MPi decreased by about 60%, and the yield of TH-6MPy increased by a factor of 2.5–3 when the MPi partial pressure was increased from 2.5 to 10 kPa. At 3.0 MPa, a 50% decrease in the conversion of MPi was observed when its partial pressure was increased from 2.5 to 10.0 kPa. The increase in partial pressure of MPi hardly changed the selectivity of MPy, slightly decreased the selectivity of the C6 products, and increased the (small) selectivity of TH-6MPy.

In the absence of H_2S and with 5 kPa MPi in the feed, the yields of MPy and TH-6MPy decreased and the yield of C6 products increased when the H_2 pressure was increased from

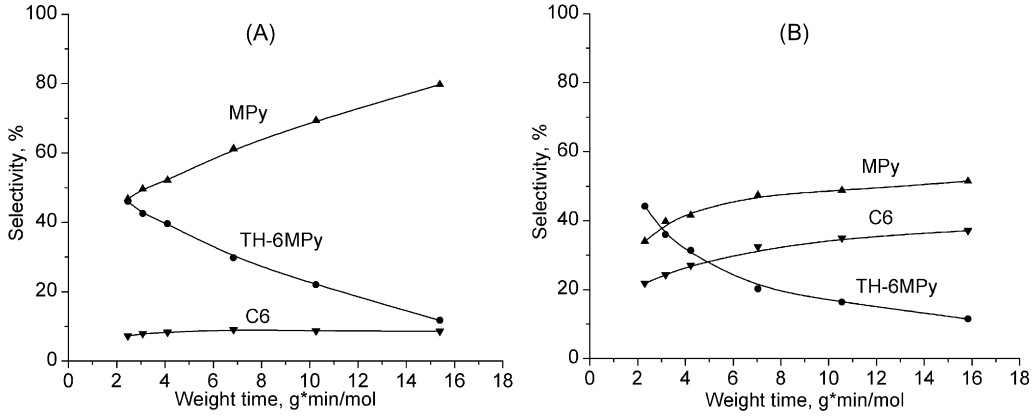


Fig. 3. Selectivities of the products of the HDN of 5 kPa MPi as a function of weight time at 340 °C and 1.0 MPa, in the absence (A) and presence (B) of 20 kPa H_2S.

Table 1
HDN of MPi over NiMo/γ-Al_2O_3 at 340 °C and $\tau = 10.4$ g min/mol, and at different total pressures, H_2S partial pressures, and MPi partial pressures

P_{total} (MPa)	P_{H_2S} (kPa)	P_{MPi} (kPa)	Conversion (%)	Yield (selectivity) (%)		
				MPy	C6	TH-6MPy
1.0	0	2.5	34	27 (79)	5 (15)	2.0 (6)
		5.0	22	15 (69)	2 (9)	4.8 (22)
		10.0	14	7 (50)	1 (6)	6.1 (44)
	20	2.5	35	15 (43)	18 (51)	2.2 (6)
		5.0	28	14 (49)	10 (35)	4.6 (16)
		10.0	16	6 (35)	5 (33)	5.2 (32)
3.0	0	2.5	25	13 (51)	12 (48)	0.2 (0.8)
		5.0	19	10 (50)	9 (48)	0.4 (2)
		10.0	12	6 (50)	4 (45)	0.6 (5)
	20	2.5	54	12 (23)	42 (77)	0.3 (0.6)
		5.0	38	9 (22)	29 (76)	0.6 (1.6)
		10.0	28	6 (22)	21 (75)	0.8 (3)

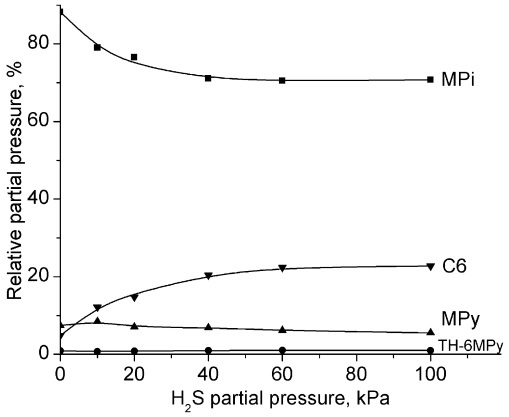


Fig. 4. Effect of H_2S partial pressure on the HDN of 5 kPa MPi at 340 °C, 3.0 MPa, and $\tau = 5.0$ g min/mol.

0.8 to 2.8 MPa. Because the sum of the yields of MPy (15–10%) and TH-6MPy (4.8–0.4%) decreased more than the yield of the C6 products increased (2–9%), the MPi conversion decreased slightly. In the presence of 20 kPa H_2S, an increase of the H_2 pressure from 0.8 to 2.8 MPa led to a stronger increase of the yield of C6 products (10–29%) than the decrease of the yields of MPy (14–9%) and TH-6MPy (4.6–0.6%). As a result, the MPi conversion increased. These results indicate that the denitrogenation of MPi was improved with increasing hydrogen partial pressure, whereas the dehydrogenation of MPi was inhibited.

In all cases, the introduction of 20 kPa H_2S greatly enhanced the yield of C6 products and slightly reduced the MPy yield (Figs. 1 and 2 and Table 1). To further study the effect of H_2S, we performed the HDN of MPi at a fixed weight time of 5.0 g min/mol, 340 °C, and 3.0 MPa total pressure, while increasing the H_2S partial pressure from 0 to 100 kPa (Fig. 4). The conversion of MPi and yield of C6 products increased from 0 to 40 kPa and remained constant at higher H_2S pressure. The yield of MPy increased from 0 to 10 kPa H_2S and decreased at higher H_2S pressure. The occurrence of an optimum H_2S concentration for the dehydrogenation of MPi may be due to the fact that at high concentration, H_2S adsorbed on the active sites and poisoned the hydrogenation/dehydrogenation reaction, whereas at very low H_2S concentration, the catalyst surface reconstructed, and the number of hydrogenation/dehydrogenation sites decreased [3]. However, the changes in MPy yield were small, and the changes in conversion were due mainly to C6 formation. Therefore, it can be concluded that at 340 °C, H_2S had a slightly negative effect on the dehydrogenation of MPi and a positive influence on the denitrogenation of MPi.

We studied the effect of reaction temperature on the HDN of MPi by carrying out an experiment at a fixed weight time of 5.0 g min/mol at 3.0 MPa total pressure in the presence of 20 kPa H_2S. As shown in Fig. 5, when the reaction temperature was increased from 280 to 340 °C, the conversion of MPi and the yields of both MPy and C6 increased, the selectivity of MPy decreased, and the selectivity of C6 increased; the conversion of MPi was 8% at 280 °C and 22% at 340 °C.

3.2. HDN of MPy

Reaction profiles and product selectivities in the HDN of 5.0 kPa MPy at 340 °C and 3.0 MPa in the absence and presence of 20 kPa H_2S are presented in Figs. 6 and 7, respectively. The most abundant products were MPi and C6, indicating that hydrogenation of MPy and removal of nitrogen from MPi were

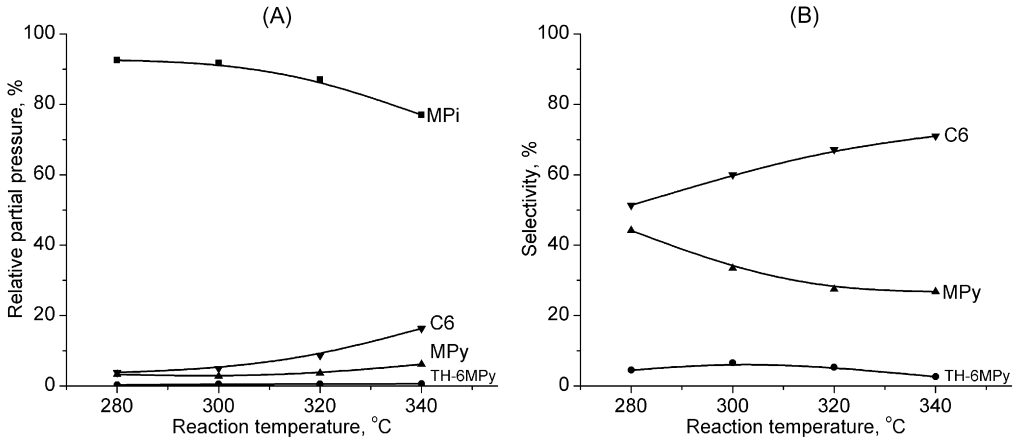


Fig. 5. Relative partial pressures (A) and selectivities (B) of the products of the HDN of 5 kPa MPi at 3.0 MPa, $\tau = 5.0$ g min/mol, and 20 kPa H_2S at different temperatures.

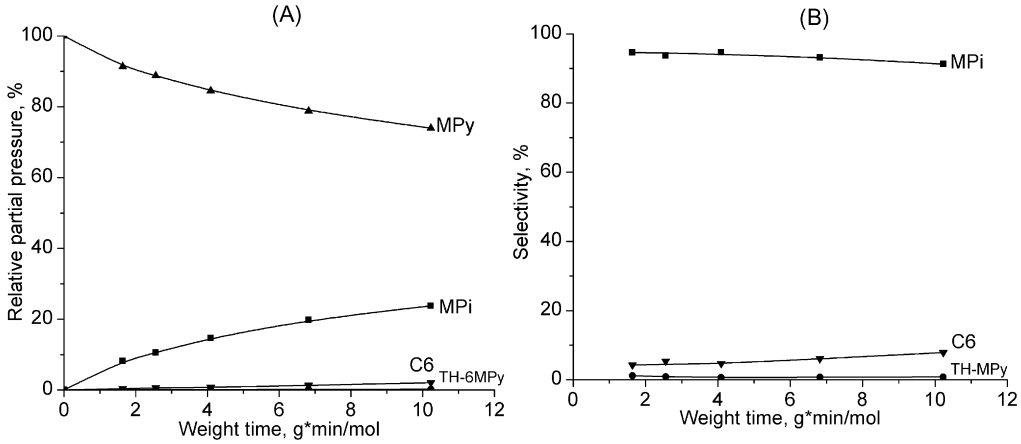


Fig. 6. Relative partial pressures (A) and selectivities (B) of the products of the HDN of 5 kPa MPy as a function of weight time at 340 °C, 3.0 MPa, and 0 kPa H_2S.

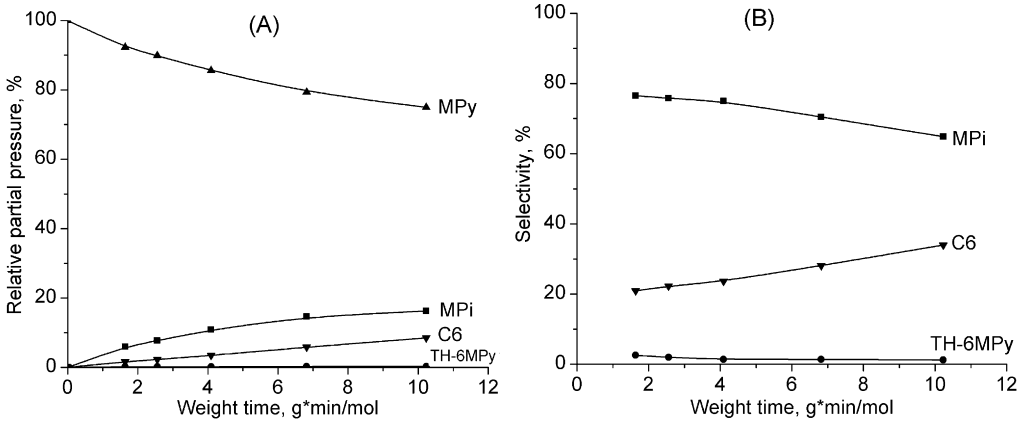


Fig. 7. Relative partial pressures (A) and selectivities (B) of the products of the HDN of 5 kPa MPy as a function of weight time at 340 °C, 3.0 MPa, and 20 kPa H_2S.

the main reactions. TH-6MPy, 1-hexylamine, and 2-hexylamine were observed in very small amounts. The product selectivities show that MPi and TH-6MPy were primary products.

The conversion of MPy at $\tau = 10.3$ g min/mol decreased when the MPy partial pressure was increased from 2.5 to 10.0 kPa (Table 2). At the same time, the yields of MPi and the C6 products decreased, but the MPi selectivity increased and the C6 product selectivity decreased. This indicates that the decreased conversion of MPy and decreased formation of C6 products were not proportional, probably due to inhibition by the hydrogenation product MPi. Although the (relative) yield of MPi decreased with increasing partial pressure of MPy, its

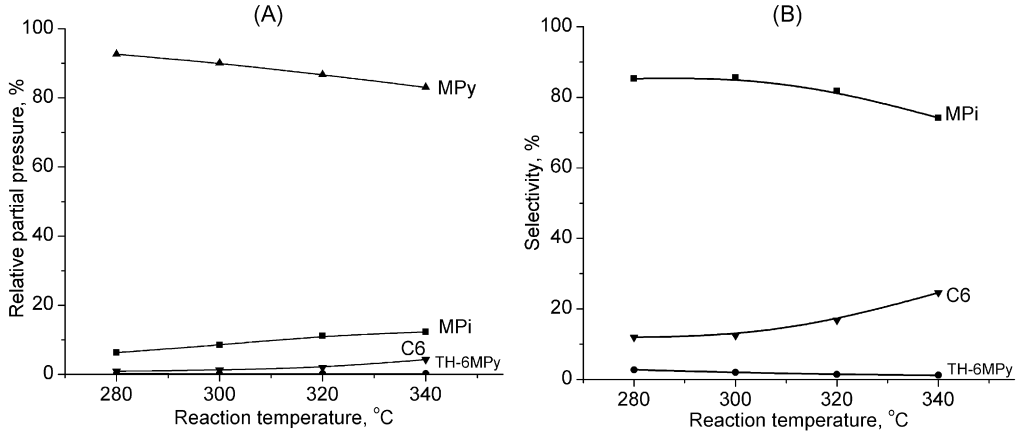


Fig. 8. Relative partial pressures (A) and selectivities (B) of the products of the HDN of 5 kPa MPy at 3.0 MPa, $\tau = 5.0$ g min/mol, and 20 kPa H_2S at different temperatures.

Table 2
HDN of MPy over NiMo/γ-Al_2O_3 at 3.0 MPa, 340 °C and $\tau = 10.3$ g min/mol, and at different H_2S partial pressures and MPi partial pressures

P_{H_2S} (kPa)	P_{MPy} (kPa)	Conversion (%)	Yield (selectivity) (%)		
			MPi	C6	TH-6MPy
0	2.5	37	32 (86)	5 (13)	0.3 (0.8)
	5.0	25	24 (95)	2 (8)	0.2 (0.8)
	10.0	22	20 (90)	2 (9)	0.2 (0.9)
20	2.5	36	21 (57)	15 (42)	0.2 (0.6)
	5.0	25	16 (65)	9 (34)	0.3 (1.2)
	10.0	20	15 (74)	5 (25)	0.2 (1.0)

partial pressure increased, and thus increased inhibition of denitrogenation occurred. As a result, the yield of C6 products decreased more rapidly.

Figs. 6 and 7 and Table 2 show that at each MPy partial pressure, the conversion of MPy decreased only slightly when the H_2S pressure was increased from 0 to 20 kPa, whereas the MPi yield decreased and the C6 yield increased. MPy is first hydrogenated to MPi and MPi is subsequently denitrogenated. Thus, the conversion of MPy depends only on its hydrogenation, whereas the yield of MPi depends on the hydrogenation of MPy, as well as on the denitrogenation of MPi. The lower yield of MPi in the presence of H_2S must be due to the enhancement of its denitrogenation, because the conversion of MPy hardly changed. Thus, at 340 °C, H_2S had a slightly negative effect on the hydrogenation of MPy and a positive influence on the denitrogenation of MPi.

The effect of reaction temperature on the HDN of MPy was studied at a fixed weight time of 5.0 g min/mol, at 3.0 MPa total pressure, in the presence of 20 kPa H_2S. With increasing reaction temperature from 280 to 340 °C, the conversion of MPy and the yields of both MPi and C6 increased, whereas the selectivity of MPi decreased and the selectivity of C6 increased (Fig. 8).

3.3. HDN of TH-6MPy

The foregoing results demonstrate that the imine TH-6MPy is an intermediate and primary product in the HDN of MPi, as well as in the HDN of MPy. To further investigate the mechanism of the HDN of MPi, the intermediate TH-6MPy was synthesized and its HDN reaction was studied. The results of the HDN of 5.0 kPa TH-6MPy at 340 °C and 3.0 MPa showed that TH-6MPy was converted almost completely, even at the lowest weight time. The main product was the hydrogenated product MPi, with a yield (selectivity) of 86% at a weight time of 1.6 g min/mol and of 71% at 10.3 g min/mol. In addition, the dehydrogenated product MPy and denitrogenated product C6 were observed. We tried to suppress the conversion of TH-6MPy to see whether other primary products could be observed.

Fig. 9 shows the reaction profiles of the HDN of 5.0 kPa TH-6MPy with 10 kPa 2-ethylpiperidine at 340 °C and 3.0 MPa, in the presence and absence of 20 kPa H_2S. The main product was MPi and MPy and C6 were also observed, but even with the inhibition of 10 kPa 2-ethylpiperidine, the conversion of TH-6MPy was still higher than 98%. Therefore, the HDN of TH-6MPy was carried out at lower temperature (280 °C) and lower H_2 pressure (0.8 MPa) in the presence of abundant 2-ethylpiperidine (20 kPa) to inhibit the hydrogenation of TH-6MPy. Furthermore, less active Mo/γ-Al_2O_3 was used as the catalyst instead of NiMo/γ-Al_2O_3. Nevertheless, even under these inhibiting conditions, the lowest conversion of TH-6MPy was still about 90%, and the main product was always MPi. This proves that the hydrogenation of TH-6MPy to MPi was extremely fast. Other primary products of the HDN of TH-6MPy were not observed.

3.4. Mutual influences of MPi and MPy

The mutual effects of MPi and MPy on their HDN reactions were investigated by the HDN of one compound in the presence of the other. However, because the two compounds are products of each other, we used 2-ethylpyridine (EPy) and 2-ethylpiperidine (EPi) as reactants. EPy had only a weak influence on the HDN of MPi. In the absence of H_2S, no changes were observed (Fig. 10A), whereas in the presence of H_2S small changes occurred (Fig. 10B). The yield of MPy increased slightly and did not level off as in the absence of EPy.

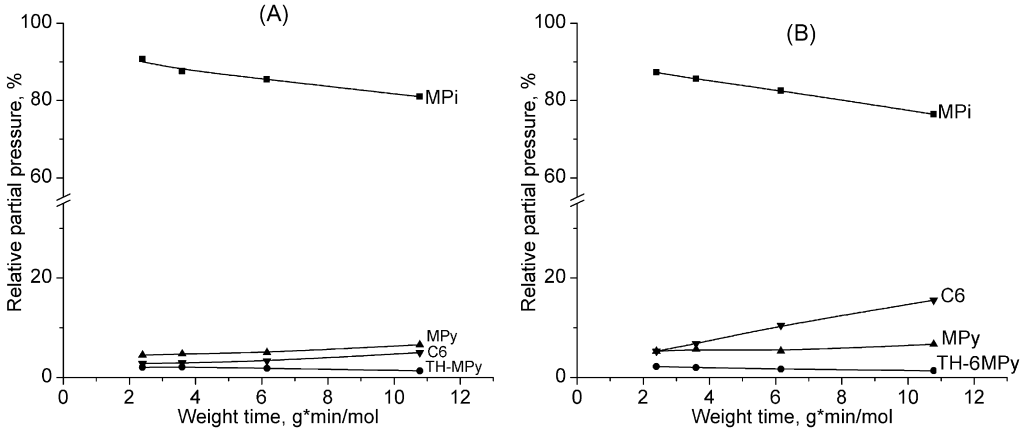


Fig. 9. Relative partial pressure of the products of the HDN of 5 kPa TH-6MPy with 10 kPa EPi as a function of weight time at 340 °C and 3.0 MPa, in the absence (A) and presence (B) of 20 kPa H_2S.

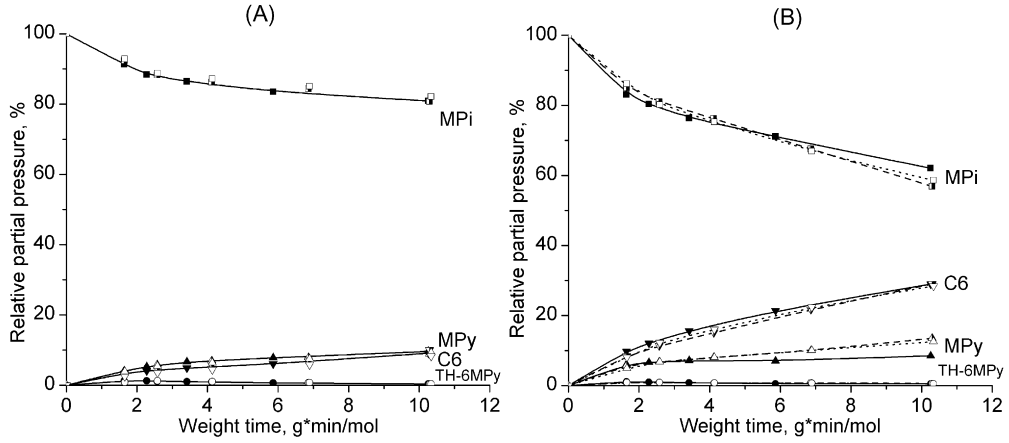


Fig. 10. HDN of 5.0 kPa MPi with 0 kPa (drawn lines, solid symbols), 1 kPa (dashed lines, half-open symbols) and 2 kPa (dotted lines, open symbols) EPy at 340 °C and 3.0 MPa, in the absence (A) and presence (B) of 20 kPa H_2S.

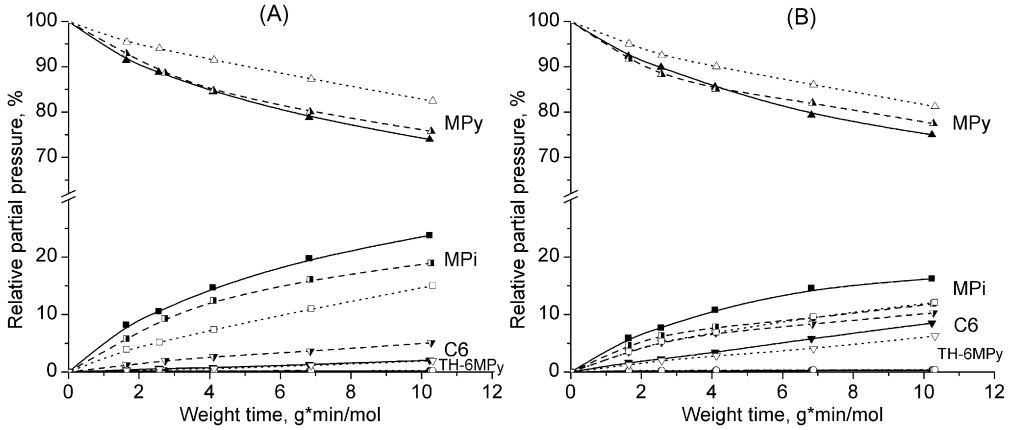


Fig. 11. HDN of 5.0 kPa MPy with 0 kPa (drawn lines, solid symbols), 1 kPa (dashed lines, half-open symbols) and 2 kPa (dotted lines, open symbols) EPi at 340 °C and 3.0 MPa, in the absence (A) and presence (B) of 20 kPa H_2S.

The effect of EPi on the HDN of MPy was much stronger than that of EPy on the HDN of MPi. The conversion of MPy decreased slightly in the presence of 1 kPa EPi and by about 30% at 2 kPa EPi (Fig. 11). Thus, EPi strongly inhibited the hydrogenation of MPy. The effect of EPi on the dinitrogenation was peculiar. The yield of C6 products increased at 1 kPa EPi and decreased slightly at 2 kPa EPi. This result is similar to findings reported by Egorova and Prins that the DDS of dibenzothiophene was promoted at low partial pressure of MPi and inhibited at high partial pressure of MPi [23]. Their ex-

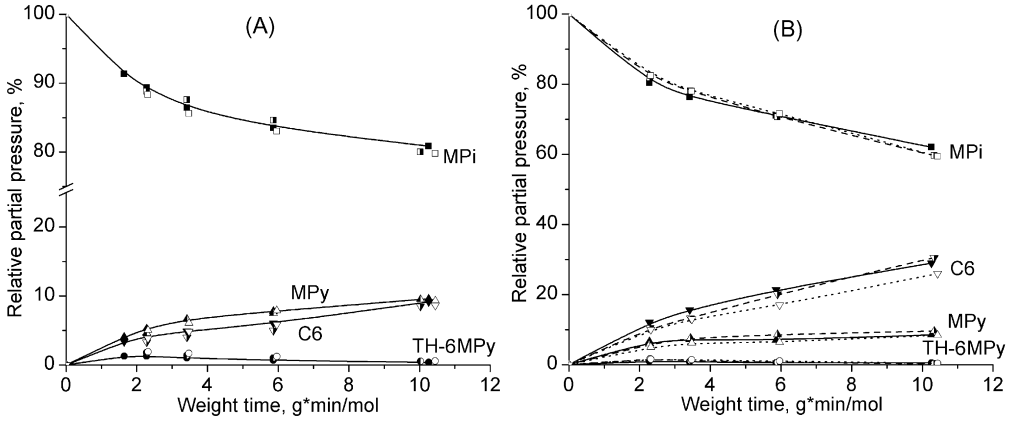


Fig. 12. HDN of 5.0 kPa MPi with 0 kPa (drawn lines, solid symbols), 1 kPa (dashed lines, half-open symbols) and 2 kPa (dotted lines, open symbols) *n*-butylamine at 340 °C and 3.0 MPa, in the absence (A) and presence (B) of 20 kPa H_2S.

planation for this was that the enhanced DDS at low partial pressure of MPi is due to a transformation of hydrogenation sites into desulfurization sites, due to one-point adsorption of MPi on a hydrogenation site. In our case, EPi might be adsorbed in a one-point manner on a hydrogenation site, consisting of a metal atom not covered by a sulfur atom, leaving the neighboring metal atom free. This metal atom is not available for the hydrogenation of MPy, which needs at least two free neighboring sites, but remains available for the one-point adsorption of MPi and thus for the denitrogenation of MPi. In this way, an active hydrogenation site can be transformed into a denitrogenation site at low partial pressure of EPi. At high partial pressure of EPi, EPi blocks all metal atoms, thereby also decreasing the denitrogenation of MPy. Thus, EPy hardly affects the HDN of MPi, but EPi strongly inhibits the hydrogenation of MPy, promotes denitrogenation at low partial pressure, and slightly inhibits denitrogenation at high partial pressure.

3.5. Effect of NH_3 on the HDN of MPi

NH_3 is the by-product of HDN, with a yield equal to that of C6. Thus, the NH_3 partial pressure in the product is substantial and might influence the HDN of MPi. Under our reaction conditions, the HDN of an alkylamine is fast [14], and thus a partial pressure of NH_3 can be created by introducing an alkylamine into the feed as NH_3 source. We added 2.0 and 5.0 kPa 1-butylamine to the feed and studied the HDN of MPi at 340 °C and 3.0 MPa total pressure in the absence and presence of 20 kPa H_2S. The conversion of 1-butylamine varied from 60 to 90% for 2.0 kPa 1-butylamine and from 55 to 80% for 5.0 kPa 1-butylamine when the weight time was increased from 2.3 to 10.4 g min/mol. In the absence of H_2S, 1-butylamine did not influence the HDN of MPi (Fig. 12A). In the presence of H_2S (Fig. 12B), the conversion of MPi and the yield of MPy hardly changed, whereas the yield of C6 products decreased slightly in the presence of 5.0 kPa 1-butylamine. The decreased C6 yield was due mainly to the increased yields of 1- and 2-hexylamine. This demonstrates that the HDN of 1- and 2-hexylamine was slightly inhibited by the competitive adsorption of NH_3 or 1-butylamine.

4. Discussion

4.1. Reaction network and mechanism of the HDN of MPi and MPy

Under our conditions, MPi was the major product in the HDN of MPy, and MPy was the major product in the HDN of MPi over the sulfided NiMo/γ-Al_2O_3 catalyst. The conversions of the hydrogenation of MPy and dehydrogenation of MPi were lower than expected on the basis of thermodynamics. For instance, if we take the equilibrium constant for the methylpyridine–methylpiperidine equilibrium to be equal to that for the pyridine–piperidine equilibrium [24], then the MPi/MPy ratio at 340 °C and 2.8 MPa H_2 should be 6.9, whereas in the HDN of MPy, it was between 0.19 and 0.51 (Table 2). This demonstrates that the reaction of MPy to MPi was still far from equilibrium and thus relatively slow. At 0.8 MPa H_2 and 340 °C, the MPi/MPy ratio should be 0.16, but the observed ratio in the HDN of MPi was much higher, between 2.4 and 14.0, and increasing with increasing MPi starting pressure (Table 1). Thus, the reaction of MPi to MPy also was far from equilibrium. The observed MPi/MPy ratios were closer to the equilibrium value when the yield of C6 products was substantial in the HDN of MPi at 340 °C and 2.8 MPa H_2. At 0 kPa H_2S, the ratio increased from 5.8 to 14.7, and at 20 kPa H_2S, it increased from 3.8 to 12.0 when the MPi pressure was increased from 2.5 to 10 kPa. At 10 kPa MPi, the MPi/MPy ratio was above the equilibrium value because equilibrium had not yet been reached. At 2.5 kPa MPi, the MPi/MPy ratio was below the equilibrium value, because MPi also reacted irreversibly to C6.

The primary products in the HDN of MPy were MPi and TH-6MPy, demonstrating that MPy underwent only hydrogenation. In the HDN of MPi, the primary products were TH-6MPy, MPy, and the two hexylamines, indicating that MPi underwent both dehydrogenation and denitrogenation. A small amount of TH-6MPy was observed in the HDN of MPi and MPy, and its yield passed through a maximum, demonstrating that TH-6MPy is an intermediate product. The denitrogenated hydrocarbons 1-hexene, 2-hexene, and hexane (C6 products) are final prod-

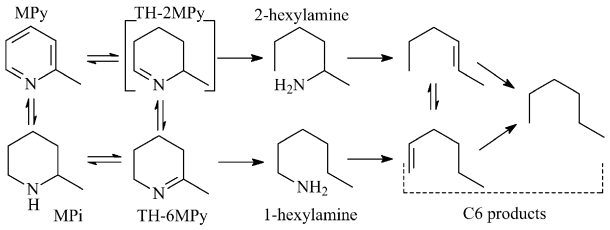
ucts of the HDN reaction, because the C6 yield and selectivity increased continuously as a function of weight time. The two aliphatic amines, 1- and 2-hexylamine, were observed in small amounts, and their yields passed through a maximum. Thus, they are intermediates of the denitrogenation reaction, that is, products of the ring-opening of MPi. Although they behave as primary products, with selectivities that do not go to zero at low conversion of MPi, 1- and 2-hexylamine actually should be secondary or tertiary products rather than primary products, because if the ring opening of MPi occurred by nucleophilic substitution by H_2S, then aminohexanethiols would be primary products. If the ring opening occurred by elimination, then hexenylamines would be primary products. Apparently, 1- and 2-hexylamine behave as primary products because the actual primary products, the parent compounds of 1- and 2-hexylamine, react rapidly to the two amines. If all of the surface-adsorbed intermediates involved reacted faster than they desorbed, then the intermediates would be hardly observed in the gas phase, and the alkylamines would appear to be primary products. The results of Zhao et al. [14–16] indicate that 1- and 2-hexylamine react by substitution of the NH_2 group by SH to form a hexanethiol, and that the resulting hexanethiols react to hexene and hexane, which are the final products of the HDN of MPi and MPy. Because the cleavage of the second C–N bond is fast, 1- and 2-hexylamine were observed in small amounts only.

Depending on the conditions in the HDN of MPi, MPy behaved as a secondary or a primary product. At low pressure, MPy behaved as a secondary product, indicating that MPy was formed mainly from MPi via an intermediate. MPi first dehydrogenated to TH-MPy, which could undergo desorption, C–N bond cleavage (see below), or further dehydrogenation. Because of the existence of a double bond, TH-MPy is flatter than MPi, and its dehydrogenation is easier than that of MPi on the (de)hydrogenation site. Thus, MPy was formed mainly by a two-step dehydrogenation of MPi via TH-MPy and behaved as a secondary product. At high pressure and in the absence of H_2S, MPy acted as a secondary product as well as primary product, and in the presence of H_2S, it acted as a primary product. H_2S promoted denitrogenation, and thus TH-MPy reacted mainly by denitrogenation. The yield of MPy via TH-MPy was low, and MPy was formed mainly by direct dehydrogenation. Thus MPy behaved as a primary product, and its yield was low.

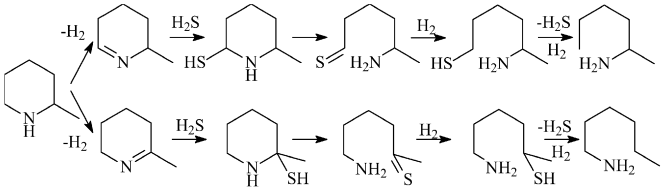
The primary products in the HDN of MPy were MPi and TH-MPy. Whereas the yield and selectivity of TH-MPy were always very low, even at the lowest weight time, the yield and selectivity of MPi were high. An explanation for this is that the hydrogenation of MPy to MPi occurs through the TH-MPy intermediate. If the desorption of the TH-MPy intermediate from the catalyst surface is slow and the reaction of TH-MPy to MPi is fast, then the concentration of TH-MPy in the gas phase will be low and a direct MPy to MPi reaction will appear to exist. Because MPy does not adsorb strongly (cf. Section 3.4), it does not drive TH-MPy off the catalyst surface, and the flat π-bonded MPy molecule can be easily hydrogenated all the way to MPi. In addition to a catalytic reaction, TH-MPy also can be formed by a thermal reaction. Egorova et al. [19] reported that the TH-6MPy yield increased by increasing the temperature from 300 to 350 °C in the HDN of MPi in a reactor without catalyst. This can explain why we always observed TH-6MPy, even at the highest weight time, even though its denitrogenation and (de)hydrogenation are fast.

Several mechanisms have been proposed for the denitrogenation of piperidine and MPi. Nelson and Levy [6] suggested that removal of the nitrogen atom occurs by nucleophilic substitution or Hofmann β-H elimination from an alkylamine. Laine [25] proposed that the C–N bond cleavage of piperidine occurs on metal sites rather than on acidic sites and involves a metal alkyl or metal alkylidene intermediate. Hadjiloizou et al. [26] proposed two mechanisms for piperidine ring opening—an E2 elimination reaction and an S_N2 substitution reaction—with the formation of the various products supposedly involving Lewis and/or Brønsted acid sites as well as basic sites. Portefaix et al. suggested that the HDN of 2-methylpiperidine occurs by elimination, through a nucleophilic attack on a β-hydrogen atom [10]. Egorova et al. suggested that the ring opening of piperidine occurs by elimination [19]. Oyama and Lee proposed that the HDN of MPi is an S_N2-type substitution reaction with a piperidinium ion intermediate [20]. More recent results [14–18] indicate that the C–N bond breaking of the alkylamine occurs exclusively by nucleophilic substitution by H_2S, and that the substitution is not a classic organic substitution but rather a multistep mechanism starting with dehydrogenation of the amine to an imine. Thereafter, addition of H_2S to the imine occurs, and, after ammonia elimination and hydrogenation, a thiol is formed.

On the basis of our experimental results and the proven HDN mechanism for dialkylamines [14], we propose the reaction network of the HDN of MPi and MPy as presented in Schemes 1 and 2. MPy first hydrogenates to MPi, which then reacts to the imines TH-2MPy and TH-6MPy. Ring opening of the imines leads to 1- and 2-hexylamine. The two amines are denitrogenated to hexene and hexane. Hydrogenation and dehydrogenation of the imines also leads to MPi and MPy, respectively.



Scheme 1. Reaction network of the HDN of MPi and MPy.



Scheme 2. Mechanism of the denitrogenation of MPi: substitution of MPi to amino-hexanethiols through imine intermediates, then desulfurization of the thiols to hexylamines.

This reaction network is quite different from that proposed in earlier studies [5,7,27–29], in which an MPy-MPi (or pyridine-piperidine) equilibrium and a direct reaction of MPi (or piperidine) by ring opening to an alkylamine are assumed, without a TH-MPy intermediate. In the schemes proposed by Egorova et al. [19] and Oyama and Lee [20], TH-MPy is considered a hydrogenation intermediate between MPy and MPi, but not an intermediate in denitrogenation. In our case, however, TH-MPy is considered both a hydrogenation and a denitrogenation intermediate.

In accordance with the results obtained for alkylamines [14–16], the ring opening of MPi is proposed to occur as shown in Scheme 2. The imines of MPi, 2,3,4,5-tetrahydro-2-methylpyridine (TH-2MPy), and 2,3,4,5-tetrahydro-6-methylpyridine (TH-6MPy), are formed by dehydrogenation of MPi. Adding H_2S to the imines gives the thio-methylpiperidines. These compounds are unstable, because of the electron density push toward the carbon atom connected to the N and S atoms. Consequently, either the C–S bond is broken (giving back the imine and H_2S), or the C–N bond is broken by elimination, and amino-thiohexanones are formed. Hydrogenation of the thioketones gives amino-hexanethiols, which react to 1- and 2-hexylamine by hydrogenolysis. Thereafter, 1- and 2-hexylamine repeat the scheme (i.e., imine formation, H_2S addition, NH_3 elimination, hydrogenation) to remove the nitrogen atom. The reaction of the imines to amino-hexanethiols might not be a simple addition of H_2S, but rather a reaction with sulfur atoms at the catalyst surface. The TH-MPy intermediates then form alicyclic thiolates, which react to adsorbed amino-thioketones (Scheme 3):

$$C_6H_{11}N + 2HS^* + S^* \rightarrow H_2N\text{–}C_5H_{10}\text{–}CH{=}S^* + 2S^*. \quad (1)$$

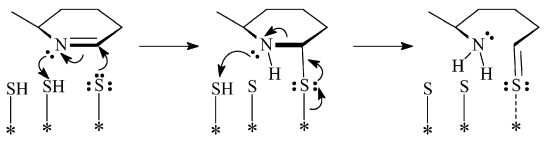
The adsorbed amino-thioketone reacts to an amino-hexanethiolate, which reacts further to hexylamine:

$$H_2N\text{–}C_5H_{10}\text{–}CH{=}S^* + 2HS^* \rightarrow H_2N\text{–}C_6H_{13} + 3S^*. \quad (2)$$

The sulfhydryl group (HS*) can be generated by adsorption and dissociation of H_2S molecules and also can be regenerated by adsorption and dissociation of H_2molecules:

$$2H_2 + 4S^* \rightarrow 4HS^*. \quad (3)$$

This leaves the question of why we observe only hexylamines but no aminohexenes. The HDS of an alkanethiol always gives a mixture of an alkane by hydrogenolysis and an alkene by elimination [14,16]. The absence of aminohexenes might be due to rapid hydrogenation, because the amino group aids their adsorption on the catalyst surface. Thus, different from the low conversion of hexene to hexane in the presence of amines [16], an aminohexene may be hydrogenated under our conditions and not be observed; for instance, the final product in Scheme 3, the amino-thioketone, might undergo hydrogenation and subsequent hydrogenolysis before desorbing from the catalyst surface.



Scheme 3. Reaction of TH-2MPy via an amino-alkylthiolate to an adsorbed thioketone at the catalyst surface.

Much more 2-hexylamine than 1-hexylamine was observed, meaning that the methyl group had a negative effect on the cleavage of the C–N bond, due to steric hindrance of the methyl group on adsorption of MPi in the dehydrogenation to TH-MPy and subsequent addition of H_2S. Apparently most MPi molecules react via TH-2MPy and not via TH-6MPy. Nevertheless, TH-2MPy was never observed in our reactions. This might be due to the fact that TH-2MPy has a higher energy than TH-6MPy, because the methyl group stabilizes the double bond. In analogy with the stereoselective hydrogenation of ethyl-(Z)-α-acetamidocinnamate [30], in which the minor diastereoisomeric catalyst-substrate adduct was more reactive than the major one and thus determined the chirality of the product, we believe that the TH-2MPy isomer with the higher energy reacts faster than the TH-6MPy isomer with the lower energy. The TH-6MPy isomer, with the methyl group directly linked to the double bond, is energetically more stable but also is less reactive, because the double bond is more hidden. As long as a rapid equilibrium exists between the TH-2MPy and TH-6MPy isomers, the faster reaction rate of TH-2MPy will compensate for the higher concentration of TH-6MPy.

4.2. Inhibition effects on the HDN of MPi and MPy

The hydrogenation of MPy and dehydrogenation of MPi are always major reactions; that is, a large amount of MPy is present in the HDN of MPi, and, similarly, a large amount of MPi is present in the HDN of MPy. These products might effect the reaction of the reactant through competitive adsorption. Therefore, we investigated the mutual effects of MPi and MPy on their HDN reactions by performing the HDN reaction of one compound in the presence of the other. Because the two compounds are products of each other, we used 2-ethylpyridine (EPy) and 2-ethylpiperidine (EPi) as the simultaneous reactants. The results of the HDN of 5 kPa MPi in the presence of 1 and 2 kPa EPy show that EPy hardly affects the C–N bond cleavage of MPi and the dehydrogenation of MPi. Moreover, the selectivities of the MPy and C6 products in the HDN of MPi were independent of the partial pressure of MPi, indicating that the MPy product had no effect on the HDN of MPi.

In contrast to the slight effect of EPy on MPi, EPi exhibited a clear effect on the HDN of MPy. The conversion of MPy decreased with increasing partial pressure of EPi, indicating that EPi strongly retarded the hydrogenation of MPy. The effect of EPi on the C–N bond cleavage was less simple; it demonstrated a promoting effect at low EPi partial pressure and an inhibiting effect at high partial pressure. The selectivity of the C6 products in the HDN of MPy decreased with increasing partial pressure of MPy (Table 2), indicating an inhibiting effect of MPi (cf. Section 3.2). Thus, EPi inhibited the denitrogenation of MPy by competitive adsorption. The enhanced denitrogenation at low partial pressure of EPi might be caused by a transformation of the hydrogenation sites into denitrogena-

tion sites by one-point adsorption of EPi on a hydrogenation site. The stronger inhibition of MPi (EPi) compared with that of MPy (EPy) is reasonable, because aliphatic nitrogen-containing compounds are more basic than aromatic nitrogen-containing compounds and thus adsorb and inhibit more strongly. Hanlon [7] reported relative adsorption constants of piperidine, pyridine, and ammonia of 12:6:1.

Ammonia is a final product of the HDN of MPi, along with hexene and hexane. Its content is equal to that of the C6 products and thus is substantial. The results of adding 1-butylamine to the MPi feed proved, however, that ammonia had no effect on the dehydrogenation and first C–N bond cleavage of MPi. This is in accordance with the much smaller adsorption constant of ammonia compared with that of amines [7]. The slightly decreased yield of C6 products and increased yield of 1- and 2-hexylamine should be due to inhibition by the competitive adsorption of 1-butylamine, not by ammonia.

Our results (Table 1) show that with increasing total pressure (i.e., higher hydrogen partial pressure), the denitrogenation of MPi was improved, whereas the dehydrogenation of MPi was inhibited. The inhibited dehydrogenation of MPi is understandable, because dehydrogenation is favored by a low hydrogen pressure. Because the first step in the denitrogenation reaction of MPi is dehydrogenation, which is suppressed by higher hydrogen pressure, the positive influence of hydrogen must be due to a secondary effect—probably the number of vacancies on the catalyst surface, which is dependent on the H_2S/H_2 ratio and, at constant H_2S pressure, increases with H_2 pressure.

Some studies have reported that H_2S has a dual effect on the HDN reactions of pyridine, indole, and quinoline [31–33]. It slightly inhibits hydrogenation and dehydrogenation but markedly promotes C–N bond cleavage. Our results are in accordance with these findings. In the HDN of MPi, the conversion of MPi increased with the addition of H_2S due to a slightly decreased yield of MPy and a markedly increased yield of C6. In the HDN of MPy, the conversion of MPy decreased slightly due to inhibited hydrogenation by H_2S and an increased yield of C6. Two reactions—hydrogenation–dehydrogenation and C–N bond cleavage—take part in the HDN of MPi and MPy. This suggests the presence of two active sites: those responsible for the hydrogenation–dehydrogenation and those promoting C–N bond breaking. H_2S has a different effect on the two reactions and active sites. As a reaction partner, it has a positive influence on the substitution; it adsorbs on the catalyst surface and covers the vacancies or hinders the reaction. The fact that in all cases, H_2S increases the denitrogenation rate suggests that it does not adsorb on the C–N cleavage sites or has a weaker absorption than MPi on those sites. The slight decrease in the rates of hydrogenation and dehydrogenation at higher pressure of H_2S (>10 kPa) suggests that H_2S adsorbs on the (de)hydrogenation sites, which are commonly considered to be sulfur vacancies. Because its adsorption is not much stronger than that of MPi or MPy, its inhibitory effect by competitive adsorption is not strong. Moreover, a slight increase in the dehydrogenation of MPi was observed when the H_2S partial pressure was increased from 0 to 20 kPa, in good agreement with the results of Egorova and Prins [3]. This might be due to the fact that at very low H_2S concentration or without H_2S, the catalyst surface reconstructs, and the number of (de)hydrogenation sites decreases.

Our findings on the HDN of MPi and MPy at different temperatures clearly show that both the hydrogenation/dehydrogenation activity and denitrogenation activity of the HDN increased with increasing reaction temperature. The C6 selectivity also increased in the HDN of both MPi and MPy, indicating higher temperature sensitivity for denitrogenation compared with (de)hydrogenation. This finding is similar to that reported by Bunch et al. [33] and demonstrates that the denitrogenation reaction has a higher activation energy than the (de)hydrogenation reactions and thus is more sensitive to temperature. Moreover, the fact that the hydrogenation and dehydrogenation activities all increased with increasing temperature demonstrates that the system was still in the kinetic regime and not under thermodynamic control.

5. Conclusions

To study the reaction network and mechanism of the HDN of MPi and MPy, we investigated the HDN of these two molecules, as well as of TH-6MPy, the reaction intermediate of the HDN network. Based on our experimental results and the proven HDN mechanism for dialkylamines, we propose that the HDN of MPi and MPy occurs via the TH-MPy intermediate, which is considered to be a hydrogenation intermediate as well as a denitrogenation intermediate. TH-MPy is formed by dehydrogenation of MPi and hydrogenation of MPy. Addition of H_2S to the TH-MPy imine gives thio-methylpiperidines, followed by cleavage of the C–N bond by elimination and formation of amino-thiohexanones. Hydrogenation of the thioketones gives amino-hexanethiols, which react to 1- and 2-hexylamine by hydrogenolysis. Subsequently, 1- and 2-hexylamine react further to remove the nitrogen atom. Furthermore, a surface reaction mechanism of the imines to amino-hexanethiols involving alicyclic thiolates and adsorbed amino-thioketone intermediates is deduced.

We also studied the HDN inhibitory effects of MPi and MPy. We found that EPy hardly affects the HDN of MPi, but EPi strongly retards the hydrogenation of MPy and promotes denitrogenation at low partial pressure and inhibits it at high partial pressure. H_2S inhibits (de)hydrogenation slightly. Both H_2S and H_2 promote denitrogenation strongly. NH_3 hardly affects the HDN of MPi.

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