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Mechanism of the C–N-bond breaking in the hydrodenitrogenation of methylcyclohexylamine over sulfided NiMo/γ-Al2O3

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Abstract

The hydrodenitrogenation (HDN) of methylcyclohexylamine was studied over sulfided NiMo/γ-Al_2O_3. 2-Methylcyclohexylamine (MCHA) is an intermediate in the HDN of toluidine that can be detected in addition to the main products, methylcyclohexene (MCHE) and methylcyclohexane (MCH), when a high quantity of cyclohexene (CHE) was added to *o*-toluidine during HDN. The selectivity of MCH in the HDN of MCHA was about 20% at zero conversion. The detection of 2-methylcyclohexanethiol (MCHT) in the HDN of MCHA explains why MCH is observed as a quasi primary product in the HDN of *o*-toluidine. MCH is formed via nucleophilic substitution of the amine group of MCHA, giving MCHT, followed by C–S bond hydrogenolysis. A kinetic investigation at different H_2S partial pressures showed that H_2S increases the rate of nucleophilic substitution, but leaves the rate of the β-Hofmann elimination of ammonia from MCHA unchanged.

Keywords: Hydrodenitrogenation; Mechanism of C–N bond breaking; Toluidine; Methylcyclohexylamine; Nickel-promoted molybdenum sulfide; Nucleophilic substitution

1. Introduction

Hydrodenitrogenation (HDN) reaction networks are usually quite complex because of the large number of reaction steps and different catalytic sites involved [1]. Therefore, model reactants are often used in HDN studies. *o*-Toluidine has many advantages over other nitrogen-containing hydrocarbons as a model reactant in HDN. Due to its molecular structure, all reactions which take place in an industrial HDN process also occur in the HDN network of *o*-toluidine (Fig. 1), such as the hydrogenation of the aromatic ring, C–N bond cleavage and alkene hydrogenation.

In the present work, the HDN of *o*-toluidine and of its first product, 2-methylcyclohexylamine (MCHA), have been studied. A comparison of the HDN of *o*-toluidine and of MCHA allows to compare the cleavage of a $C(sp^2)$–N bond with that of a $C(sp^3)$–N bond. Cleavage of the $C(sp^3)$–N bond of MCHA occurs mainly via β-H elimination to methylcyclohexene (MCHE) [2,3], but a significant fraction of MCHA (10–25%) reacts by direct bond cleavage to methylcyclohexane (MCH). To explain this reaction path from MCHA to MCH, several

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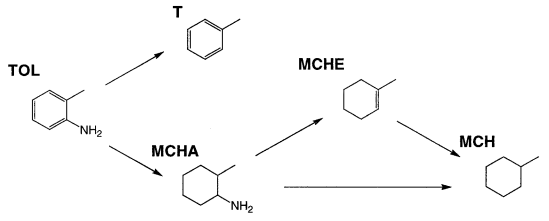

Fig. 1. Network of the HDN of *o*-toluidine.

mechanisms have been proposed. The first explanation was that MCHA reacts very quickly to MCHE, which then is quickly hydrogenated to the final MCH product before being able to diffuse out of the pores [4,5]. This diffusion-limitation mechanism could explain why MCH is observed with non-zero selectivity even at low weight time. Another explanation could be hydrogenolysis. In the HDN of *o*-toluidine and *o*-propylaniline, toluene and propylbenzene are formed as primary products, respectively [5,6]. This points to a direct hydrogenolysis of the $C(sp^2)$–N bond. If this is indeed the case, then it should be even easier to break the $C(sp^3)$–N bond in MCHA. However, no proof for the occurrence of the hydrogenolysis of MCHA could be provided [5].

A third explanation for the direct reaction from MCHA to MCH, which is discussed in the present work, is the nucleophilic substitution of the NH_2 group by SH, followed by hydrogenolysis of the C–S bond. By varying the H_2S pressure and determining its effect on the HDN products, this mechanism has been studied. Several authors have studied the effect of H_2S partial pressure on the HDN of amine compounds [7–11]. It was concluded that the rate of C–N bond cleavage increases significantly in the presence of H_2S, while the rate of hydrogenation decreases slightly. Because of the different influences of H_2S on C–N bond cleavage and hydrogenation, these two reactions are assumed to take place at different catalytic sites [3,7,12,13]. As a consequence, the presence of H_2S may even change the rate-limiting reaction of the HDN [14] and affect its product distribution [9,15]. It has been suggested that H_2S may participate in the HDN reactions by creating new reactive intermediates (e.g. electrophilic H^+ or nucleophilic H_2S) [16,17], new catalytic sites [1,15,18], or by promoting the formation of thiols [19,20].

2. Experimental

The $NiMo/\gamma\text{-}Al_2O_3$ catalyst used in this work contained 8 wt.% Mo and 3 wt.% Ni and was prepared by successive incipient wetness impregnation of $\gamma\text{-}Al_2O_3$ (CONDEA, pore volume 0.5 $cm^3\ g^{-1}$, specific area 230 $m^2\ g^{-1}$) with an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Aldrich), followed by an aqueous solution of $Ni(NO_3)_2\cdot 6H_2O$ (Aldrich). After each impregnation step, the catalyst was dried in air at ambient temperature for 4 h, and then dried in an oven at 393 K for 15 h. The final catalyst was calcined at 773 K for 4 h. The catalyst was crushed and sieved to the desired (230 mesh) particle size to avoid diffusion effects on product distribution and conversion [5].

A sample (0.05 g) of catalyst was diluted with 8 g SiC to achieve plug-flow conditions in the continuous flow fixed-bed reactor. The catalyst was sulfided in situ with a mixture of 10% H_2S in H_2 at 643 K and 1.0 MPa for 4 h. After sulfidation, the pressure was increased to 5.0 MPa, and the liquid reactant (cf. Table 1) was fed to the reactor by means of a high-pressure syringe pump (ISCO 500D). All reactions were performed at 623 K, unless stated otherwise. H_2S was added to keep the chemical properties of the catalyst constant. The H_2S partial pressure was changed by increasing the flow rate of a mixture of H_2S in H_2 and adapting the flow rate of H_2 to maintain the total hydrogen partial pressure in all cases at 4800 kPa. The total pressure varied between 5 and 5.3 MPa. In all reactions, 4 kPa of cyclohexene (CHE) was added to study its hydrogenation. When changing the partial pressure of the reactant, the octane flow was adapted to maintain the partial pressure of hydrogen. The experimental conditions, under which, the results presented in Figs. 3–7 were obtained, are presented in Table 1.

The reaction products were analysed by on-line gas chromatography with a Varian 3800 GC instrument equipped with a 30 m DB-5 fused-silica capillary column (J&W Scientific, 0.32 mm i.d., 0.25 μm film thickness). Detection was made with a flame ionisation detector (FID), as well as with a pulsed flame photometric detector (PFPD), which can detect small amounts of amine and sulfur compounds. Unknown compounds were analyzed by GC-Mass Spectroscopy (MS).

Table 1
Gas phase feed composition for the preformed reactions

Compounds	Partial pressure (kPa)			Function
Figure	Fig. 3a,b,c	Fig. 4a,b	Figs. 5–7	
Hydrogen	4800	4800	4800	Reactant
Octane	169	169	151	Solvent
Heptane	20	20	20	Internal standard
mixture H_2S/H_2	20 to 200	20 to 200	20 and 200	H_2S
Ortho-toluidine	7.0			Reactant
Methylcyclohexylamine		7	25	Reactant
Cyclohexene	4	4	4	Reactant

Weight time was defined as $\tau = w_c/n_{feed}$, where w_c denotes the catalyst weight and n_{feed} denotes the total molar flow fed to the reactor. The weight time (τ) was changed by varying the flow rates of the liquid and the gaseous reactants, while keeping their relative ratios constant.

3. Results and discussion

The HDN of *o*-toluidine (TOL) was carried out at different weight times and the results (Fig. 2a and b) show that the hydrogenation of the aromatic ring is the rate-determining step of the reaction network (see Fig. 1 for the HDN network and abbreviations). Toluene (T) is produced at a constant selectivity of about 5% independent of the conversion of TOL (Fig. 2b). This shows that T is a primary product of the HDN of TOL and that it is produced in parallel to the other products (MCHA, MCHE and MCH). As long as enough TOL is present, T does not react further to MCHE or MCH because of inhibition of the adsorption of T by TOL. MCHE and MCH are the secondary and final product, respectively, and they are present in appreciable quantity in the product mixture. The partial pressure of these products and their selectivities as a function of weight time are given in Fig. 2a and b. These results are extensively discussed in our previous work [5,21]. In the present work, we concentrate on the mechanism of the HDN of MCHA.

The MCHA selectivity increases with decreasing weight time (Fig. 2b), indicating that it is a primary product in the HDN of TOL. However, MCHA reacts so quickly that it can only be observed in trace amounts. This difficulty in detecting MCHA is analogous to that of the propylcyclohexylamine intermediate in the HDN of quinoline, in which HDN follows the sequence quinoline–decahydroquino-

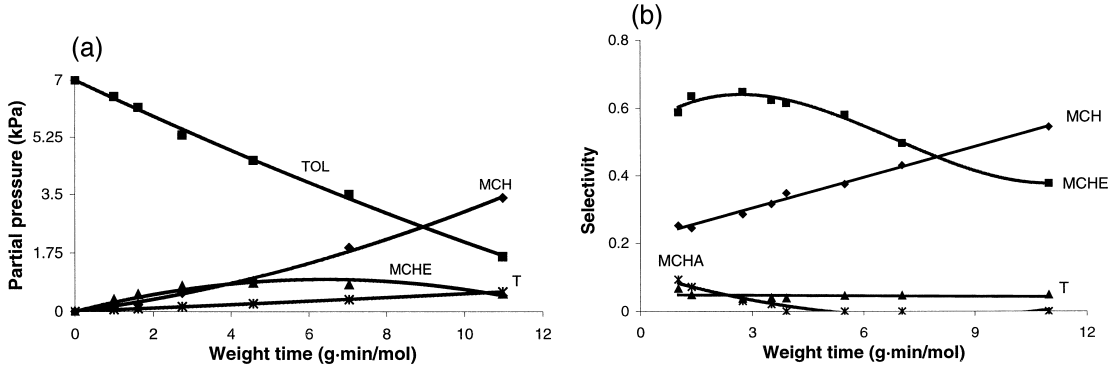

Fig. 2. (a) Product distribution of TOL reaction with NiMo catalyst at 390°C. (b) Product selectivities in the HDN of *o*-toluidine.

line–propylcyclohexylamine–hydrocarbons [1,4]. When the HDN of MCHA itself is performed, it is observed that MCHA reacts in parallel reactions to MCHE and to MCH, because the selectivities of these two products are constant at low conversion [5]. At higher MCHA conversions, MCHE can react further to MCH by hydrogenation of its double bond. MCHA reacts to MCHE via β-H elimination [22]. In earlier work [5,21], we also showed that a direct pathway from MCHA to MCH seems to exist, as demonstrated by a non-zero selectivity of MCH at low weight time (Fig. 2b). This apparent direct pathway is partly due to diffusion limitation when the catalyst particle size is large. For small catalyst particles, as used in the present work, there is no diffusion limitation and the MCH selectivity at zero weight time is still unequal to zero, indicating that a direct chemical pathway from MCHA to MCH exists. A logical explanation for this direct $C(sp^3)$–N bond cleavage would be hydrogenolysis, that is a concerted reaction of the C–N fragment and hydrogen at the catalyst surface, leading to a hydrocarbon and NH_3. The $NiMo/\gamma\text{-}Al_2O_3$ catalyst is able to break the $C(sp^2)$–N bond of *o*-toluidine and form toluene (Fig. 2a). Therefore, this catalyst should be able to break the weaker $C(sp^3)$–N bond of MCHA in the same way. To see if hydrogenolysis is responsible for the direct bond cleavage of the C–N bond of MCHA, the HDN of TOL and MCHA was studied at different H_2S partial pressures.

The HDN of 7 kPa TOL in the presence of 4 kPa (CHE) was performed at H_2S partial pressures of 20, 50, 100 and 200 kPa. The results show that with increasing H_2S partial pressure, the TOL conversion decreases (Fig. 3a). Hydrogenation is known to be inhibited by H_2S [9,15]. Also, the hydrogenation of CHE present in the reaction mixture to cyclohexane (CH) decreased with increasing H_2S partial pressure (Fig. 3b). The plot of the partial pressure of the toluene product as a function of weight time shows that less T is formed at higher H_2S concentration (Fig. 3c). Thus, H_2S not only inhibits the hydrogena-

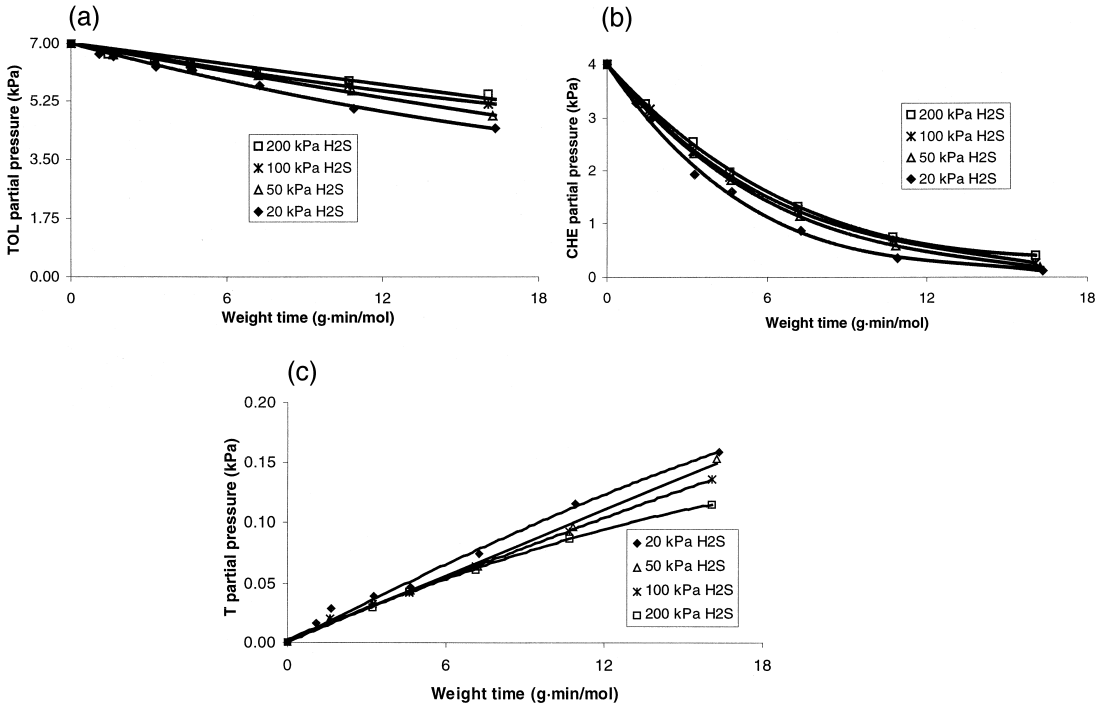

Fig. 3. Combined HDN of 7 kPa TOL and hydrogenation of 4 kPa CHE at different partial pressure of H_2S (20, 50, 100 and 200 kPa). (a) Partial pressure of TOL. (b) Partial pressure of CHE. (c) Partial pressure of T.

tion of TOL (Fig. 3a), but also, its C(sp^2)–N bond cleavage (Fig. 3c).

The HDN of 7 kPa MCHA in the presence of 4 kPa CHE at different H_2S partial pressures shows that the MCHA conversion increases with increasing H_2S partial pressure (Fig. 4a). The product distribution of MCH and MCHE is influenced by the subsequent hydrogenation of MCHE to MCH. To independently study the hydrogenation of olefins, 4 kPa CHE was added to the reaction feed. The hydrogenation of the double bond of CHE in the presence of MCHA shows that the conversion of CHE increases with increasing H_2S partial pressure (Fig. 4b). At first glance, this result seems surprising because it is well known that H_2S decreases the hydrogenation activity of sulfide catalysts [9,15], as shown above in the hydrogenation of TOL (Fig. 3a) and CHE (Fig. 3b). The explanation is that MCHA inhibits the adsorption of CHE very strongly [21]. The hydrogenation is therefore suppressed at low weight time, when the MCHA concentration is high. Once the MCHA concentration is substantially decreased by HDN, the CHE hydrogenation begins to accelerate. This explains the bending point in the curve of CHE vs. weight time (Fig. 4b). Since TOL adsorbs much weaker than MCHA, TOL inhibits the hydrogenation of CHE less and the curve of CHE vs. weight time does not show a bending point in the presence of TOL (Fig. 3b). In the presence of H_2S, MCHA reacts faster (Fig. 4a). As a consequence, there is less MCHA to inhibit the hydrogenation of CHE and this allows CHE to react faster in the presence of H_2S (Fig. 4b).

If the reaction of MCHE to MCH could be suppressed, the selectivity of the direct C(sp^3)–N bond cleavage from MCHA to MCH could be measured directly, without having to account for the subsequent MCHE to MCH reaction. We therefore investigated the effect of the MCHA pressure on the rate of reaction of CHE to CH, assuming that it would have the same effect on the MCHE to MCH reaction. At high partial pressure of MCHA (25 kPa), the inhibition of the conversion of CHE by MCHA turned out to be so high that the concentration of CHE only slightly decreased with weight time below $\tau = 5$ g min/mol (Fig. 5). This corresponds roughly to an MCHA conversion of 40%. This made it possible to study the selectivity of MCH as a function of the H_2S partial pressure without other influences. Therefore, we performed a reaction at 25 kPa MCHA in the presence of 4 kPa CHE, where CHE is used to obtain information about the hydrogenation of MCHE. Fig. 6 shows the selectivity of MCH at 20 and 200 kPa H_2S. The MCH selectivity increases with increasing H_2S partial pressure, indicating that the formation of MCH from MCHA is catalyzed by H_2S.

The comparison between the formation of MCH in the HDN of MCHA and that of T in the HDN of TOL at different H_2S partial pressures shows that H_2S has a different effect on the reactions of TOL to T and MCHA to MCH. The reaction of TOL to T is inhibited by H_2S (Fig. 3c), while the reaction of MCHA to MCHE and MCH is accelerated by H_2S (Fig. 4a), and the selectivity to MCH is increased (Fig. 6). Thus, the reaction of MCHA to MCH is

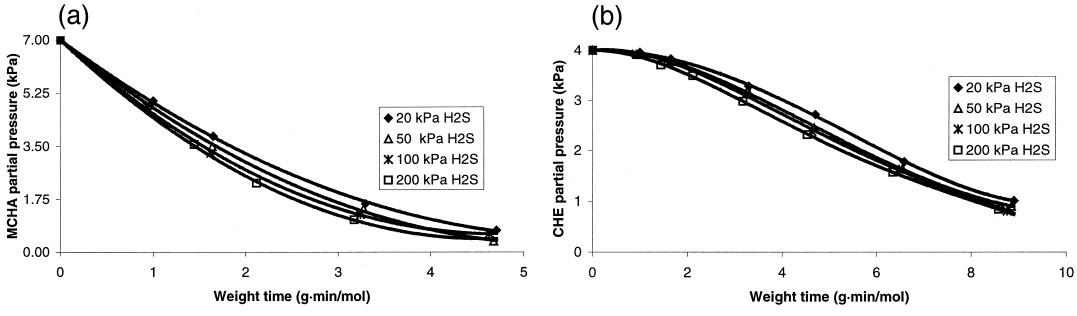

Fig. 4. Combined HDN of 7 kPa MCHA and hydrogenation of 4 kPa CHE at different partial pressure of H_2S (20, 50, 100 and 200 kPa). (a) Partial pressure of MCHA. (b) Partial pressure of CHE.

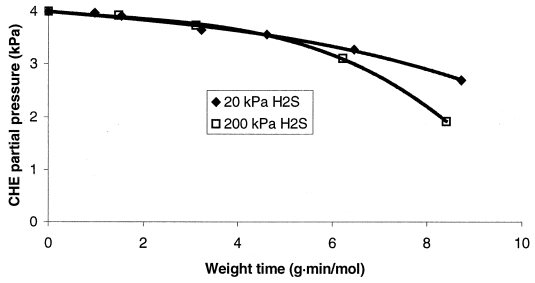

Fig. 5. Hydrogenation of 4 kPa CHE in the presence of 25 kPa MCHA at 20 and 200 kPa H_2S.

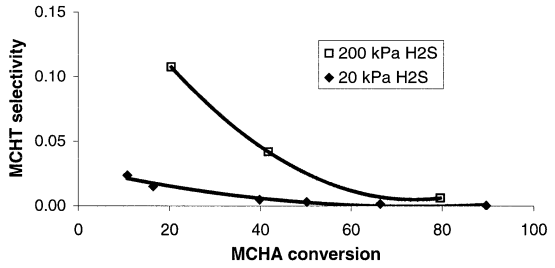

Fig. 7. Formation of MCHT in the HDN of 25 kPa MCHA in the presence of 4 kPa CHE at 20 and 200 kPa H_2S.

catalyzed by H_2S. This means that the reaction from MCHA to MCH does not follow the same mechanism as the reaction from TOL to T. If TOL reacts to T by hydrogenolysis, then MCHA apparently does not react to MCH by hydrogenolysis.

An alternative mechanism for the direct reaction of MCHA to MCH is that MCHA reacts via nucleophilic substitution of NH_2 by SH followed by C−S bond hydrogenolysis. During the HDN of 25 kPa MCHA in the presence of 4 kPa CHE and 20 or 200 kPa H_2S, two new compounds were detected. These new compounds were analyzed by GC-MS. They had the same MS spectrum and were determined to be *cis*- and *trans*-2-methylcyclohexanethiol (MCHT). MCHT is the expected intermediate product from the nucleophilic substitution of the NH_2 group of MCHA by H_2S. The MCHT selectivity (Fig. 7) strongly increased with decreasing MCHA conversion, which shows that MCHT is a primary product in the HDN of MCHA. At 20 kPa H_2S partial pressure, the maximum observed partial pressure of MCHT was about 60 Pa, but at 200 kPa H_2S, it was 600 Pa, thus, unequivocally allowing its analysis with GC and GC-MS. Nucleophilic substitution, followed by C−S bond hydrogenolysis, explains the reaction of MCHA to MCH (Fig. 8). MCHA adsorbs on the surface close to a Brønsted acid SH^- group, which can substitute for the NH_2 group. The resulting MCHT intermediate reacts to MCH via C−S hydrogenolysis, which is a quick reaction [22,23]. Černý [19] and Černý and Trka [20] already demonstrated that the substitution of an amine by a sulfhydryl group takes place at high H_2S pressure. SH^- and S^{2-} sites are present on the catalyst surface, and increasing the H_2S partial pressure increases the SH species on the catalyst surface and, therefore, the rate of nucleophilic substitution.

MCHT can also be formed by addition of H_2S to MCHE, that is formed via elimination of MCHA. To study this addition, CHE hydrogenation was performed alone at several H_2S partial pressures. The results showed that the thermodynamic equilibrium is never achieved. The detected cyclohexanethiol partial pressure was only about 5% of the possible partial pressure at equilibrium. Another CHE hydrogenation was performed in the presence of H_2S and MCHA under the same conditions as before, and the amount of cyclohexanethiol detected was three times less. The presence of a strong base, like MCHA,

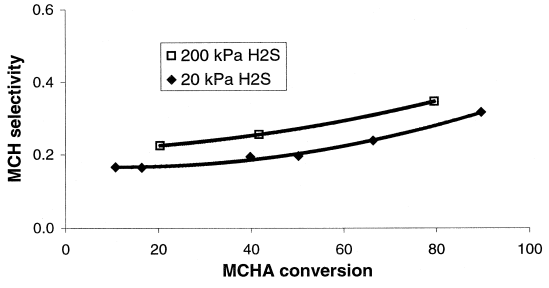

Fig. 6. MCH selectivity at different H_2S partial pressures.

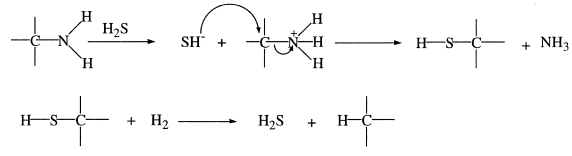

Fig. 8. Nucleophilic substitution of NH_2 by SH followed by C−S hydrogenolysis.

inhibits this addition. Therefore, the high amount of MCHT detected in the HDN of MCHA cannot be explained by the addition of H_2S to MCHE. Moreover, the MCHT partial pressure is increasing with decreasing weight time, in contrast to the partial pressure of MCHE that decreases with decreasing weight time. So, the observed MCHT is not formed by the addition of H_2S to MCHE, but by the substitution of amine group of MCHA by H_2S.

Kinetic measurements were performed to find out how the H_2S partial pressure influences the reaction from MCHA to MCH. We assume that the HDN of MCHA takes place at one catalytic site and follows a Langmuir–Hinshelwood mechanism and that the adsorption of the hydrocarbons (MCH, MCHE, and the solvent) can be ignored [21]. These assumptions lead to Eq. (1), where τ is the weight time, p_{MCHA} is the partial pressure of MCHA, $p_{MCHA,0}$ is the initial partial pressure of MCHA, K is the adsorption constant of MCHA, and k_1 and k_2 are the rate constants for substitution and elimination, respectively:

$$\frac{dp_{MCHA}}{d\tau} = -\frac{(k_1 + k_2)\cdot K \cdot p_{MCHA}}{1 + K \cdot p_{MCHA,0}} \quad (1)$$

$$S_{MCH} \cong \frac{k_1}{k_1 + k_2} \quad (2)$$

Eq. (1) is valid at small weight time when the conversion of MCHA is small. From the initial rates of disappearance of MCHA (Fig. 9) at two initial concentrations (7 and 25 kPa) and two H_2S partial pressures (20 and 200 kPa) and the MCH selectivities presented in Fig. 6, it is possible to calculate the rate constants k_1 and k_2 and the adsorption constant K at 20 and 200 kPa H_2S. The values obtained (Table 2) show that the substitution rate constant k_1 increases (50%) with increasing H_2S partial pressure, while the elimination rate constant k_2 increases only slightly (5%) and the adsorption constant K of MCHA does not change significantly with H_2S pressure. This means that the substitution pathway is manly responsible for the increase of conversion of MCHA with increasing H_2S pressure, but that elimination remains the main reaction for converting MCHA (80% of the conversion).

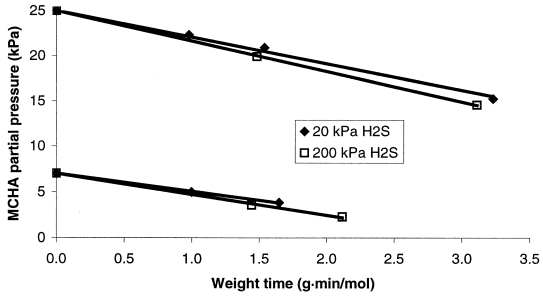

Fig. 9. HDN of 7 and 25 kPa MCHA at 20 and 200 kPa H_2S.

Table 2
Kinetic parameters for substitution (k_1), elimination (k_2) and adsorption (K) of MCHA

Parameter	H_2S	
	20 kPa	200 kPa
k_1 (kPa mol/g min)	0.6	1.0
k_2 (kPa mol/g min)	3.0	3.2
K (kPa^{-1})	0.16	1.17

The acidity of the catalyst increases with increasing H_2S partial pressure, because the dissociation of H_2S converts a surface vacancy and a sulfur anion to two sulfhydryl (SH^-) groups. The decrease of sulfur vacancies leads to a decrease of the hydrogenation pathway and the C(sp^2)–N bond cleavage, as shown before. The increase of sulfhydryl groups can help the substitution pathway (C(sp^3)–N bond cleavage) significantly [18]. This pathway is often called hydrogenolysis [8,15], even though it was shown to occur via an elimination or substitution reaction [16]. At the same time, the formed Brønsted acid can help the β-H elimination (k_2) that is acid-catalyzed.

4. Conclusions

In the hydrogenation of *o*-toluidine and *o*-methylcyclohexylamine, MCH is formed with a selectivity that suggests that it is a primary product. The apparent direct cleavage of the C–N bond in the methylcyclohexylamine reaction does not proceed via hydrogenolysis, like in the pathway from *o*-toluidine to toluene, but via nucleophilic substitution of NH_2 by SH, followed by C–S hydrogenolysis. The detection of methylcyclohexanethiol, the expected intermediate product after substitution of NH_2 by SH, proved the mechanism.

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