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RESEARCH NOTE

Role of Hydrogenolysis and Nucleophilic Substitution in Hydrodenitrogenation over Sulfided NiMo/γ-Al_2O_3

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The hydrodesulfurization of cyclohexanethiol and 2-methylcyclohexanethiol was studied over a sulfided NiMo/γ-Al_2O_3 catalyst. About two-thirds of the thiols reacted by elimination to (methyl)cyclohexene and one-third by hydrogenolysis of the C–S bond to (methyl)cyclohexane. These values are slightly lower than those for the selectivity to methylcyclohexene and slightly higher than those for the selectivity to methylcyclohexane in the hydrodenitrogenation of 2-methylcyclohexylamine. In aliphatic molecules that contain H atoms in the β position relative to the nitrogen atom, hydrodenitrogenation occurs predominantly (70–80%) by elimination of ammonia. Part of the remaining (20–30%) hydrodenitrogenation takes place by nucleophilic substitution of the amine by H_2S, followed by elimination of H_2S from the resulting thiol and, to a lesser extent, by C–S bond hydrogenolysis; the rest of the remaining hydrodenitrogenation takes place by direct hydrogenolysis of the C–N bond.

Key Words: **hydrodenitrogenation; hydrodesulfurization; hydrogenolysis; nucleophilic substitution; cyclohexanethiol; aniline; cyclohexylamine; sulfide catalyst; NiMo/Al_2O_3.**

INTRODUCTION

Nelson and Levy were the first to publish a general mechanism of hydrodenitrogenation (HDN) of aromatic nitrogen-containing molecules (1). They proposed that the aromaticity of the nitrogen-containing aromatic ring must be broken by hydrogen before C–N bond breaking and removal of the nitrogen atom in the form of ammonia can take place. It was assumed that elimination and nucleophilic substitution are responsible for the C–N bond breaking. In nucleophilic substitution, the NH_2 group is replaced by an SH group through the reaction of the aliphatic amine with H_2S. The resulting alkanethiol then undergoes desulfurization by means of a hydrogenolysis reaction with hydrogen to an alkane and H_2S. These proposals explained the much higher hydrogen consumption in HDN than in hydrodesulfurization (HDS) and the increase in rate as a result of the addition of H_2S (2–5). Portefaix *et al.* (6) and Cattenot *et al.* (7) showed that the aliphatic C–N bond breaking occurs by Hofmann elimination because an increase in the number of hydrogen atoms in the β position with respect to the nitrogen atom in pentylamines and piperidines increased the rate of ammonia removal. Even when there are no hydrogen atoms on the β carbon atom and elimination is not possible, C–N bond breaking is still possible, as shown by Vivier *et al.* for benzylamine (8). They ascribed the C–N bond breaking to nucleophilic substitution and subsequent C–S hydrogenolysis.

In agreement with these findings, we observed that *o*-toluidine reacts mainly by hydrogenation to 2-methylcyclohexylamine and subsequent elimination of ammonia from 2-methylcyclohexylamine to methylcyclohexene (9–11). Part of the 2-methylcyclohexylamine reacted, however, to methylcyclohexane (9). This methylcyclohexane may have been formed by nucleophilic substitution of 2-methylcyclohexylamine to 2-methylcyclohexanethiol and subsequent hydrogenolysis to methylcyclohexane (10, 11). Methylcyclohexane may also form, however, through direct hydrogenolysis of the C–N bond of 2-methylcyclohexylamine. The possibility of C(sp^3)–N bond breaking by hydrogenolysis is suggested by the observation that, in the HDN of aniline (12, 13), *o*-toluidine (9–11), 2-propylaniline (14), and naphthylamine (15), part of the reactant reacted directly to benzene, toluene, propylbenzene, and naphthalene, respectively. This indicates that C(sp^2)–N bond breaking is possible on metal sulfide catalysts. If this is the case, then C(sp^3)–N bond breaking should also be possible because a C(sp^3)–N bond is weaker than a C(sp^2)–N bond.

To determine whether nucleophilic substitution or hydrogenolysis is responsible for the C(sp^3)–N bond breaking, we studied the HDS of cyclohexanethiol over sulfided NiMo/γ-Al_2O_3. Cyclohexanethiol was chosen as a model compound because it is commercially available and it is

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the product of the nucleophilic substitution of the NH_2 group by the SH group in cyclohexylamine. Thus, cyclohexanethiol can be used to perform reactions and obtain information about the importance of the nucleophilic substitution in the HDN mechanism. To ensure that methyl substitution does not lead to a drastic change in the reactivity of cyclohexanethiol, we synthesized a small amount of 2-methylcyclohexanethiol and compared its HDS with that of cyclohexanethiol. NiMo/γ-Al_2O_3 was chosen as the catalyst because the same catalyst was used in our study of the stereochemistry of elimination of ammonia from cyclohexylamine (16). Furthermore, the elimination and nucleophilic substitution reactions are about equally fast over sulfided Mo/γ-Al_2O_3 as over sulfided NiMo/γ-Al_2O_3 (9).

EXPERIMENTAL

Cyclohexanethiol was obtained from Fluka; a mixture of *cis*- and *trans*-2-methylcyclohexanethiol (MCHT) was prepared by the free radical addition of thiolacetic acid to 1-methylcyclohexene followed by hydrolysis of the formed thiol acetates, as reported by Bordwell and Hewett (17). This procedure provides an excellent synthetic route to pure thiols since yields are high and the reaction proceeds exclusively by anti-Markovnikov addition. In short, thiolacetic acid (Aldrich, 96%) was slowly added to 1-methylcyclohexene (Aldrich, 97%) while irradiating with a 150-W lamp. The 2-methylcyclohexylthiol acetate was distilled under vacuum and then hydrolyzed by refluxing for 1 h in a solution of KOH in aqueous alcohol. After neutralization with glacial acetic acid and separation of the aqueous and nonaqueous phases, the aqueous phase was extracted three times with *n*-hexane. These extracts and the nonaqueous phase were combined and dried over magnesium sulfate. After the hexane evaporated, the product was distilled under vacuum. The final purity of the mixture of *cis* and *trans* isomers was 97%, and the ratio *cis*-to *trans*-MCHT was 81 : 16.

The preparation of the NiMo/γ-Al_2O_3 catalyst, which contained 8 wt% Mo and 3 wt% Ni, has been described elsewhere (10). In short, it was prepared by incipient wetness impregnation, dried at 120°C for 15 h, and calcined at 500°C for 4 h. The resulting catalyst was crushed and sieved to a particle size of 230 mesh to avoid diffusion effects on product distribution and conversion (9). The catalyst was then diluted with SiC and loaded into a continuous-flow fixed-bed reactor. *In situ* sulfidation was carried out with 10% H_2S in H_2 at 370°C and 1 MPa for 4 h. Thereafter, the pressure was increased to 5 MPa and the liquid feed of cyclohexanethiol (CHT, Fluka) or MCHT, octane (solvent), and heptane (internal standard) was fed to the reactor by a high-pressure syringe pump. A mixture of 10% H_2S in H_2 was added to keep the H_2S partial pressure constant at 20 kPa in all the experiments (unless indicated otherwise). In the event of a change in the partial pressure of the reactant, the octane flow was adapted to keep the partial pressures of hydrogen, heptane, and hydrogen sulfide constant. The HDS reactions of CHT were performed between 250 and 375°C at CHT partial pressures of 10, 15, and 50 kPa as well as with 15 kPa CHT in the presence of 25 kPa methylcyclohexylamine (MCHA). The HDS reaction of 15 kPa MCHT in the presence of 25 kPa cyclohexylamine (CHA) was performed only at 250°C. The mass balances for the HDS reactions were generally better than 90%; only in the case of the reaction of MCHT together with CHA did we experience plugging of the reactor and the mass balance for CHA was only 80%. The mass balance for MCHT was, however, almost 100%. The HDN of 25 kPa CHA was performed between 250 and 375° C in the same way as the HDS of CHT. Samples were collected at the reactor outlet using an automated valve maintained at 300°C and reactor pressure. The reaction products were injected from the valve into a gas chromatograph equipped with a 30-m DB-5 fused silica capillary column (0.32-mm i.d. and 0.25-μm film thickness) and a flame ionization as well as a pulsed flame photometric detector.

RESULTS

Reactions of CHT with 20 kPa H_2S were performed at 10, 15, and 50 kPa of CHT and at 250, 300, 325, 350, and 375°C; the only products detected were cyclohexene (CHE) and cyclohexane (CH). Because of the high reactivity of CHT, its conversion was 100% at and above 325°C, even at the lowest weight time. Consequently, the CHE and CH selectivities were influenced by the subsequent conversion of CHE to CH. Even at 250°C, the conversion of CHE to CH was not sufficiently slow to enable the measurement of the real selectivity of CHT to CH. To inhibit the conversion of CHE to CH (11), 25 kPa MCHA was added during the reaction of 15 kPa CHT. MCHA was used because it influences elimination and direct C(sp^3)–N bond breaking in the same way (11). In the presence of MCHA, the CHE and CH selectivities were only slightly dependent on CHT conversion; the real selectivities of CHE and CH during the CHT reaction were determined by extrapolation of the CH selectivities to zero weight time. Thus, the initial selectivities for the direct transformation of CHT to CH in the presence of 20 kPa H_2S were 15, 25, and 30% at 250, 325, and 350°C, respectively (Fig. 1). At 350°C and at the higher H_2S partial pressure of 200 kPa, 35% CHT reacted to CH.

With the limited amount of MCHT that was synthesized (10 g), we could perform only a few experiments at 250°C and 15 kPa MCHT. The addition of 25 kPa CHA slowed down the conversion of methylcyclohexene (MCHE, resulting from the ammonia elimination from MCHT) to methylcyclohexane (MCH); thus, it was possible to measure the

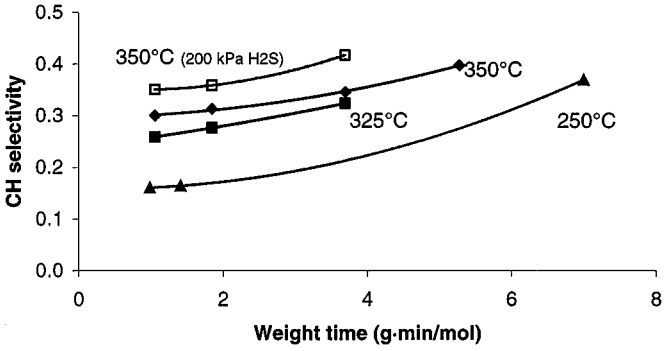

FIG. 1. Cyclohexane (CH) selectivity in the HDS of cyclohexanethiol at 250, 325, and 350°C in the presence of 25 kPa 2-methylcyclohexylamine and 20 kPa (solid symbols) and 200 kPa (open symbols) H_2S.

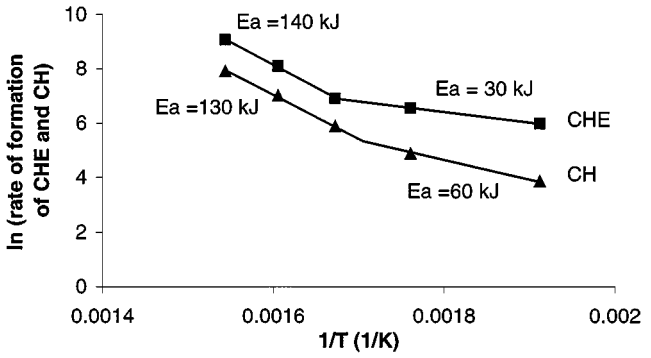

FIG. 3. Arrhenius plots for the rates of formation of cyclohexene (CHE) and cyclohexane (CH) in the HDN of 20 kPa cyclohexylamine in the presence of 20 kPa H_2S.

true MCHE and MCH selectivities. The results (Fig. 2) show that *cis*-MCHT reacts fast and partly to *trans*-MCHT. The selectivities of the products MCHE-1, MCHE-3, and MCH were 50, 30, and 20%, respectively.

The HDN of CHA was studied to compare the rates of formation of the CHE and CH products with those obtained in the HDS of CHT. The rates were obtained from data measured at 250, 295, 325, 350, and 395°C and were extrapolated to zero space time; they are presented in the form of Arrhenius plots in Fig. 3.

DISCUSSION

As explained in the Introduction, the aim of this study was to determine the roles of nucleophilic substitution and hydrogenolysis in the HDN of aniline-like molecules and their intermediates. The HDN of CHA can be described by three reactions: (A) the elimination of NH_3, leading to cyclohexene (CHE), (B) the nucleophilic substitution of the NH_2 group by H_2S, leading to CHT, and the subsequent reaction of the formed CHT via hydrogenolysis to cyclohexane (CH) or via elimination to CHE, and (C) the direct hydrogenolysis of CHA to CH (compare Fig. 4 for the equivalent scheme of reactions for MCHA). To study the role of nucleophilic substitution and hydrogenolysis, we investigated the HDS of CHT. The main product was CHE, in agreement with a former study, which demonstrated that ethene is the main elimination product in the HDS of ethanethiol (18). The selectivity to the minor product CH was 15 to 35%, as was the case for the minor product ethane in the HDS of ethanethiol (18). The rate of hydrogenolysis of ethanethiol to ethane (18) was equal to that of methanethiol to methane (19).

The selectivity to CH increased with increasing temperature (Fig. 1), showing that the C–S bond hydrogenolysis has a higher activation energy than the elimination of H_2S. Moreover, the CH selectivity increased with increasing H_2S partial pressure. This observation may explain why an increase in the partial pressure of H_2S increased the formation of MCHT in the HDN of MCHA (10, 11). Assuming that MCHT can easily react via hydrogenolysis to MCH, it was suggested that the formation of MCH from MCHA occurs via nucleophilic substitution of the NH_2 group by an SH group, followed by hydrogenolysis of the intermediate MCHT to MCH.

We want to compare the CH selectivities of 30 and 35%, obtained in the HDS of CHT in the presence of MCHA

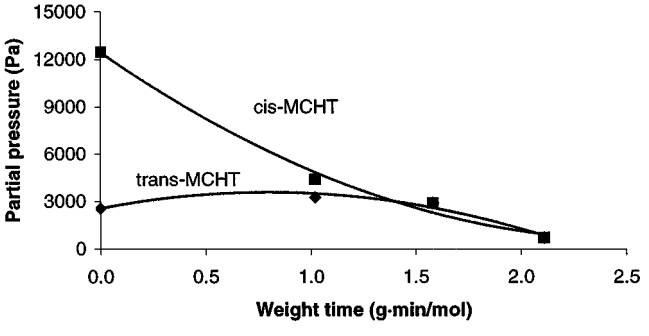

FIG. 2. Conversion of *cis*- and *trans*-2-methylcyclohexanethiol (MCHT) in the presence of 25 kPa cyclohexylamine and 20 kPa H_2S at 250°C.

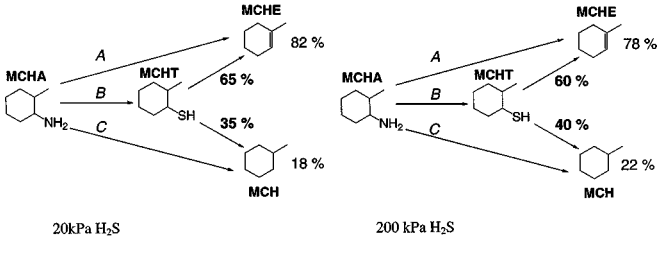

FIG. 4. Selectivities for elimination (A), nucleophilic substitution (B), and hydrogenolysis (C) in the HDN of 2-methylcyclohexylamine (MCHA) and the observed selectivities of methylcyclohexene (MCHE) and methylcyclohexane (MCH) in the HDN of 2-methylcyclohexylamine (normal figures) and in the HDS of 2-methylcyclohexanethiol (MCHT) (bold figures) in the presence of 20 kPa (left-hand side) and 200 kPa (right-hand side) H_2S.

TABLE 1

Five Cases of Selectivities of Elimination, Substitution, and Hydrogenolysis of Methylcyclohexylamine at 350°C and 20 kPa H_2S

Case	A Elimination (%)	B Substitution (%)	C Hydrogenolysis (%)
1	49	51	0
2	60	34	6
3	71	17	12
4	76	9	15
5	82	0	18

and 20 or 200 kPa H_2S, respectively (Fig. 1), with those obtained in the HDN of MCHA (10). To do so, we assume that the MCH selectivity obtained in the MCHT reaction at 350°C is 5% larger than that of CH in the reaction of CHT, as observed at 250°C. These adapted selectivities are used in the network of MCHA (Fig. 4) to explain the MCH selectivities of 18 and 22% and the MCHE selectivities of 82 and 78% for the reaction of MCHA at 350°C and 20 and 200 kPa H_2S, respectively (10).

Since the selectivity for hydrogenolysis of MCHT to MCH does not differ dramatically from the selectivity for the formation of MCH in the HDN of MCHA, it is not possible to determine the contributions of nucleophilic substitution and hydrogenolysis unequivocally. Nevertheless, the following discussion enables us to draw some qualitative conclusions. Table 1 lists five possibilities for the rates of the three different pathways (elimination (A), nucleophilic substitution (B), and hydrogenolysis (C)) in the presence of 20 kPa H_2S. The MCH selectivities are equal to $0.35B + C$ (in %) and were calculated on the basis of the observed MCH selectivity of 18% in the HDN of MCHA and of 35% for the reaction of MCHT to MCH (Fig. 4). Table 1 also lists the extreme cases in which neither hydrogenolysis nor nucleophilic substitution occurs.

Case 1, in which hydrogenolysis does not take place, would lead to the conclusion that the substitution pathway contributes 51% to the HDN of MCHA. This result differs from the results of a stereochemical investigation of the HDN of *cis*- and *trans*-2-MCHA (16). In that study, elimination was shown to be much faster for the *cis* diastereomers than for the *trans* diastereomers of several cyclohexylamines because they allow for an anti-geometric relationship in the chair conformation between the amino group and a hydrogen atom in the β position. If substitution were to account for 51% of the total rate of the cyclohexylamines, then a substantial contribution of Walden inversion would follow at the α-carbon atom when MCHA reacts to MCHT by nucleophilic substitution (20). That means that *cis*-2-MCHA, which was found to react much faster than *trans*-2-MCHA, would be transformed into *trans*-2-MCHT. *Trans*-MCHT should not result in the formation of MCHE-1 at low temperature because it must react via *syn* elimination, which is known to be more difficult than *anti* elimination. Figure 2 indeed shows that *trans*-2-MCHT reacts very slowly at 250°C. However, *cis*-2-MCHA reacts fast to MCHE-1 (16). Therefore, substitution of the NH_2 group by an SH group cannot be dominant in MCHA, and the cases (Table 1) in which the substitution is relatively low ($\leq$34%) seem most likely. As Table 1 shows, this also means that a direct contribution of 6 to 18% C(sp^3)–N bond breaking (via hydrogenolysis) must occur.

Case 5, in which nucleophilic substitution does not occur, is not possible either, as proven by the detection of MCHT and the increasing MCH selectivity with increasing H_2S partial pressure (10). H_2S also increases the CH selectivity in the HDS of CHT (Fig. 1). Consequently, C(sp^3)–N bond breaking of methylcyclohexylamine must (at least partially) take place via nucleophilic substitution of MCHT followed by hydrogenolysis to MCH.

The above discussion shows that neither nucleophilic substitution nor hydrogenolysis dominates. A possibility for the HDN of MCHA at 350°C in the presence of 20 kPa H_2S may thus be 71% elimination, 17% nucleophilic substitution, and 12% hydrogenolysis. In the presence of 200 kPa H_2S these values may be 60, 30, and 10%, respectively.

The HDN of CHA showed that also in the reaction of this molecule elimination to CHE dominated over the reaction to CH; 80% of CHA reacted to CHE and 20% to CH at 325°C. The Arrhenius plots of the rates of formation of CHE and CH in the HDN of CHA show two temperature regions for each product (Fig. 3). Between 250 and 325°C, the activation energy for CH formation (60 ± 10 kJ) is higher than that of CHE (30 ± 10 kJ), leading to an increase in CH selectivity with increasing temperature. Above 325°C, the activation energies for the rates of formation of CHE and CH are about the same (140 ± 10 and 130 ± 10 kJ, respectively). The changes in the activation energy of CHE and CH clearly indicates that two mechanisms are operating in both molecules during the HDN of CHA. This supports the network presented in Fig. 4, which shows that MCHE can be formed by the direct elimination of MCHA and by substitution to MCHT followed by elimination. MCH can also be formed by two reactions, through direct hydrogenolysis of MCHA and through substitution to MCHT followed by C–S hydrogenolysis.

The way in which hydrogenolysis of the aliphatic C–N bond takes place is not yet clear. Hydrogenolysis of a C–S bond is an accepted phenomenon, although in this case, too, the mechanistic aspects have not been studied in depth. It is unlikely that the C–S or C–N bond is broken as in the hydrogenolysis of hydrocarbons on metals. During the latter hydrogenolysis, the C–C bond is assumed to be parallel to two metal surface atoms and the breaking of the C–C bond and the formation of two *M*–C bonds are assumed to take place in a concerted reaction. However, neither

the greater metal–metal distance in metal sulfides than in metals nor the intermediate sulfur atoms favor a similar hydrogenolysis reaction on the surface of a metal sulfide. The mechanism proposed for C–S bond breaking in thiols on a $Mo_2Co_2S_3$ cluster (21) is a more likely hydrogenolysis mechanism on metal sulfides. During this process, the S–*R* group is η_3-bonded to three metal atoms (perpendicular instead of parallel to the surface), and the H atom binds to a neighboring sulfur atom. The strong bonding of the sulfur atom in the S*R* group to the metal atoms weakens the S–C bond, causing it to break and, thus, enabling the *R*H molecule to form. A similar mechanism, in which an N–*R* group is η_3-bonded to three metal atoms, may explain the hydrogenolysis of the C–N bond.

APPENDIX: ABBREVIATIONS

CH	Cyclohexane
CHA	Cyclohexylamine
CHE	Cyclohexene
CHT	Cyclohexanethiol
MCH	Methylcyclohexane
MCHA	2-Methylcyclohexylamine
MCHE	Methylcyclohexene
MCHT	2-Methylcyclohexanethiol

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