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Iminium cations as intermediates in the hydrodenitrogenation of alkylamines over sulfided NiMo/γ-Al_2O_3

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Abstract

The mechanism of the hydrodenitrogenation of the mixed dialkyl- and trialkylamines C_1–NH–C_6 and C_1–N(C_6)$_2$ was studied over sulfided NiMo/γ-Al_2O_3 at 280 °C and 3 MPa. C_1–NH–C_6 reacted by disproportionation to C_1–N(C_6)$_2$ as well as C_6–N(C_1)$_2$ and by substitution by H_2S to methylamine and hexanethiol as well as hexylamine and methanethiol. C_1–N(C_6)$_2$ reacted by substitution with H_2S to C_1–NH–C_6 and C_6–NH–C_6 and methane- and hexanethiol. The probability of breaking the C_1–N bond was only slightly smaller than of breaking the C_6–N bond in C_1–N(C_6)$_2$. In the reaction of an equimolar mixture of C_5–NH–C_5 and C_1–N(C_6)$_2$ both C_1–N(C_5)$_2$ and C_6–N(C_5)$_2$ were formed. The transfer of the methyl group in these reactions cannot be explained by imine and enamine intermediates, only iminium cation intermediates can explain all the products in the hydrodenitrogenation of monoalkyl-, dialkyl- and trialkylamines.

Keywords: Hydrodenitrogenation; HDN; Disproportionation; Substitution; Mechanism; NiMo/γ-Al_2O_3; Mixed alkylamines; Imine; Iminium ion

1. Introduction

Deep hydrodesulfurization (HDS) technology will be implemented in the coming years to reduce the sulfur level of fuel below 10 ppm, as required by environmental legislation. Nitrogen-containing compounds are harmful in deep HDS, as they inhibit the adsorption of sulfur-containing compounds [1–3] and, therefore, it is important to know how hydrotreating catalysts remove nitrogen-containing molecules.

It is generally accepted that the hydrogenation of the heterocyclic ring is the first step in the HDN of nitrogen-containing aromatic molecules [4]. The mechanism of the second step, the breaking of the aliphatic C–N bond, has been debated for two decades [5–15]. Recent work by Zhao et al. [16–18] showed that it takes place by nucleophilic substitution with H_2S rather than by elimination over sulfided Mo, CoMo, and NiMo catalysts supported on alumina. Product selectivity measurements at short weight time revealed that alkanethiols were the primary products and that the alkenes and alkanes were secondary or even tertiary products. The fast decomposition of the alkanethiols leads to high concentrations of alkenes and alkanes at relatively short contact times and these molecules had therefore in the past been taken for primary products. Moreover, reactions of monoalkyl-, dialkyl- and trialkylamines revealed that the substitution of the amine group results either in an alkanethiol or in a dialkylamine, depending on the concentration of H_2S and alkylamine [16]. Alkanethiol is the main product at higher H_2S partial pressure and dialkylamine at lower partial pressure of H_2S. Monoalkyl- and dialkylamines react by substitution as well as disproportionation to thiols and dialkyl- and trialkylamines, while trialkylamines react only by substitution by H_2S leading to a dialkylamine and alkanethiol. The denitrogenated products, alkenes and alkane, are formed as secondary products from the alkanethiol.

HDN studies on the chiral 2-(*S*)-butylamine demonstrated that the substitution of an amine group to an alkanethiol or a dialkylamine is not a classic organic substitution involving Walden inversion but a multi-step process involving an imine [19]. This multi-step mechanism involves first the dehydrogenation of the amine to an imine. Thereafter, addition of H_2S or another amine molecule to the imine takes place and, after ammonia or amine elimination and hydrogenation, a thiol or a dialkylamine is formed. Imine formation is not possible in trialkylamines. The formation of an imine from an amine requires a hydrogen atom on both N and α-C atoms as in mono- and dialkylamines. However, if the alkyl group of a

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trialkylamine contains a β-hydrogen atom, an enamine can be formed and this would allow reaction with H_2S to a dialkylamine and alkanethiol as well. This would mean that longer alkyl groups, but not methyl groups, could be removed from trialkylamines. To investigate whether imines and enamines play a role as intermediates in the removal of nitrogen atoms from alkylamines, we studied the HDN reactions of the dialkylamine C_1–NH–C_6 and the trialkylamine C_1–N$(C_6)_2$ which both possess a C_1 as well as a C_6 group attached to the N atom.

2. Experimental

The NiMo/γ-Al_2O_3 catalyst used in the reactions of the alkylamines contained 8 wt% Mo and 3 wt% Ni and was prepared by a two-step pore-volume impregnation of γ-Al_2O_3; the details of the catalyst preparation have been reported before [16]. The catalyst was sulfided in situ in a continuous-flow fixed bed reactor with a mixture of 10% H_2S in H_2 at 370 °C and 1 MPa for 4 h. After sulfidation, the pressure was increased to 3 MPa and the liquid reactant was fed to the reactor by means of a high-pressure syringe pump (ISCO 500D). The feed consisted of 5 kPa amine, 10 kPa H_2S, 185 kPa octane (solvent), 20 kPa heptane (internal standard for GC analysis), and 2.78 MPa H_2. The experiments were carried out at 280 °C. To study the influence of weight time (the ratio between the catalyst weight and the total molar flow fed to the reactor) on product distribution, the weight time was changed by varying the flow rates of the liquid and the gaseous reactants with respect to the amine, while keeping their ratio constant. The reaction products were analyzed by off-line gas chromatography with a flame ionization detector (FID) and a pulsed flame photometric detector (PFPD). Mass spectrometry was used to identify the reaction products [16]. All products and reactants could be analyzed and quantified, with the exception of the C_1 products C_1–SH and C_1–NH_2. They could be detected but not quantified because their volatility was too high compared with the other products and a combined on-line and off-line analysis did not result in a good mass balance. After each series of HDN experiments, the original feed was re-entered to verify whether the activity of the catalyst had remained constant. Before the initiation of a new experiment, the whole reactor was cleaned by purging with only the solvent (octane) and a H_2S/H_2 gas mixture for 12 h at the reaction temperature. The samples were tested for the absence of any impurity in the reactor by GC-MS.

Similar to Zhao et al. [16–18], we will use the selectivities of the products in the HDN reaction of the alkylamines as a function of weight time to determine the reaction mechanism. Selectivities make it easy to distinguish between primary and higher order products, because primary products have a non-zero selectivity at $\tau = 0$, while secondary or tertiary products have a zero selectivity. Also, the selectivity of primary products decreases with τ while that of secondary and tertiary products increases with τ. The selectivity S_i of a product i was defined as $S_i\ (\%) = 100N_iP_i(\Sigma N_iP_i)$, with P_i being the number of molecules converted to product i and N_i the number of carbon atoms in product molecule i. In a bimolecular reaction involving pentyl- and hexylamines, selectivities based on the C_5-group as well as the C_6-group were calculated. With this selectivity definition, the mass balance of the C atoms is preserved. For instance, in the reaction

$$2C_5{-}NH{-}C_6 \rightarrow C_5{-}N(C_6)_2 + C_5{-}NH_2$$

the C_5 selectivity of C_5–N$(C_6)_2$ is 50%, while the C_6 selectivity is 100%. In a reaction of dialkylamine with a trialkylamine, for example

$$C_5{-}NH{-}C_5 + C_1{-}N(C_6)_2 \rightarrow C_6{-}N(C_5)_2 + C_1{-}NH{-}C_6$$

the C_6 selectivity of C_6–N$(C_5)_2$ is 50% and that of C_1–NH–C_6 is 50%. The C_5 selectivity of C_6–N$(C_5)_2$ is 100% while that of C_1–NH–C_6 is 0%. The conversion was determined from the amount of unreacted reactant.

3. Results

3.1. HDN of C_6–NH–C_6

Dihexylamine (5 kPa) reacted fast over sulfided NiMo/γ-Al_2O_3; at 280 °C and 3 MPa, in the presence of 10 kPa H_2S, the conversion was 87% at 9.5 g min/mol (Fig. 1). The main products of the reaction were trihexylamine, hexylamine, hexanethiol, hexane and hexenes. The selectivities of trihexylamine, hexylamine and hexanethiol were non-zero at $\tau = 0$ g min/mol, meaning that these molecules are primary products (Fig. 1). Trihexylamine and hexylamine can form as primary products by disproportionation of dihexylamine

$$2C_6{-}NH{-}C_6 \rightarrow (C_6)_3N + C_6{-}NH_2 \quad (1)$$

The fast decrease of the trihexylamine selectivity with τ must be due to the reaction

$$H_2S + (C_6)_3N \rightarrow C_6{-}NH{-}C_6 + C_6{-}SH \quad (2)$$

which is known to be fast over sulfided NiMo/γ-Al_2O_3 [16]. The primary character of hexanethiol is due to the reaction

$$H_2S + C_6{-}NH{-}C_6 \rightarrow C_6{-}SH + C_6{-}NH_2 \quad (3)$$

Eqs. (1) and (3) both produce hexylamine as a primary product. The increase in hexylamine selectivity with increasing weight time (Fig. 1) may indicate that Eq. (1) dominates at low τ (selectivity 25%) and Eq. (3) at high τ (selectivity 50%).

All three hexenes and hexane behaved as secondary products, as their selectivities extrapolated to zero at $\tau = 0$ g min/mol and increased with increasing weight time. Hexene can form from hexanethiol by the elimination reaction

$$C_6{-}SH \rightarrow C_6{}^{=} + H_2S \quad (4)$$

The selectivity of 1-hexene is initially higher than that of 2-hexene and 3-hexene and goes through a maximum (Fig. 1), indicating that 1-hexene is the product of hexanethiol and that 2-hexene and 3-hexene are formed by subsequent isomerization from 1-hexene. Hexane can form as a secondary product by the hydrogenolysis of hexanethiol

$$C_6{-}SH + H_2 \rightarrow C_6 + H_2S \quad (5)$$