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MECHANISM OF CARBON–NITROGEN BOND CLEAVAGE DURING AMYLAMINE HYDRODENITROGENATION OVER A SULPHIDED NiMo/Al_2O_3 CATALYST

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By comparison of the hydrodenitrogenation rate of amylamine with those of neopentylamine and tert-amylamine over a conventional catalyst, it was evidenced that the hydrogen atoms of the carbon in the β position with respect to the nitrogen atom participate in the C–N bond cleavage. A detailed mechanism including the interaction with the catalyst is proposed for this reaction.

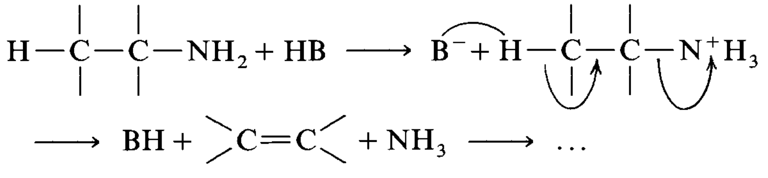
Keywords: Amylamine hydrodenitrogenation, C–N bond cleavage mechanism, hydrotreating catalysts.

Hydrodenitrogenation (HDN) is the catalytic process by which nitrogen is removed as NH_3 from petroleum feedstocks. Owing to the evolution of both economic and environmental constraints, the conventional catalysts constituted of promoted molybdenum or tungsten sulphide supported on alumina give less satisfactory results and a new generation of catalysts having higher performances is to be developed. For that purpose, the knowledge of the detailed mechanism operative in the C–N bond cleavage during amines conversion would be very useful. Therefore, by studying the relations between the structure and the reactivity of three isomeric primary amines, we have aimed at providing a comprehensive hypothesis of that mechanism.

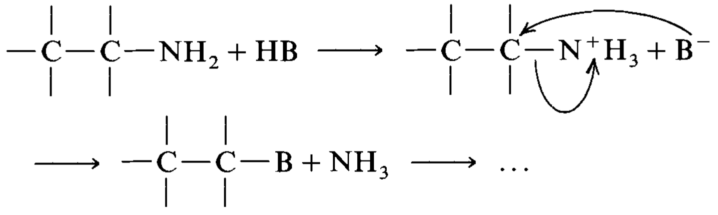
A few years ago, two main mechanisms were proposed respectively by Nelson and Levy [1] and by Laine [2], in order to explain hydrodenitrogenation reactions and to account for most of the experimental observations.

Nelson and Levy, drawing and analogy with the amine removal reaction in organic chemistry, have suggested that nitrogen elimination during hydrotreating processes proceeds with the classical Hofmann degradation mechanism; the initial step of the reaction is either a β-elimination (involving a hydrogen atom of the carbon in the β position with respect to the nitrogen atom) or a displacement (without any hydrogen atom of the amine molecule involved); the acido-basic properties of the catalyst would participate in both reactions.

β-elimination:



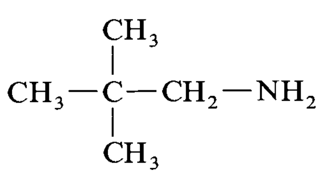
displacement:



C—N bond cleavage according to Nelson and Levy [1]

Laine has offered a different viewpoint and proposed that the C–N bond cleavage mechanism requires metal atoms or ions instead of acidic sites and includes metal alkyl or metal alkylidene intermediates; a hydrogen atom of the carbon atom in the α position with respect to the nitrogen atom would contribute to the first step of the reaction.

This is the reason why we compared the rate of hydrodenitrogenation of a simple primary amine, amylamine, with those of two isomeric amines varying by their numbers of hydrogen atoms on the carbon atoms in the α and β positions with respect to the nitrogen atom, namely neopentylamine (with 2 H on C_α and none on C_β when amylamine has 2 H on C_α and 2 on C_β) and tert-amylamine (with no H on C_α and 8 on C_β).

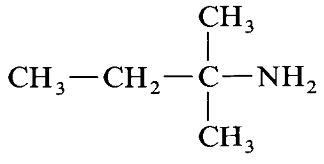


$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-NH_2$$

neopentylamine

$CH_3-CH_2-CH_2-CH_2-CH_2-NH_2$

amylamine



$$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-NH_2$$

tert-amylamine

As far as hydrodenitrogenation processes are, most of the time, operated in the presence of sulfur containing molecules which could intervene in the reaction mechanism, we performed some experiments with hydrogen sulfide added to the reactants mixture and others without.

The determinations of the reaction rates were performed using a dynamic flow reactor working at low conversion and medium high pressure. The experimental conditions were the following ones:

hydrogen pressure = $20 \cdot 10^5$ Pa
reactant pressure = $266 \cdot 10^2$ Pa
hydrogen sulphide pressure = 0 or $333 \cdot 10^2$ Pa
reaction temperature = 523 K
reactants flow = $250 \cdot 10^{-8}$ $m^3 \cdot s^{-1}$
catalyst weight = $150 \cdot 10^{-6}$ kg.

The reactant mixtures were analysed before and after the reaction by on-line chromatography with a FID detector.

The catalyst employed was a commercial NiMo/Al_2O_3 purchased from Procatalyse (referenced as HR346) and containing 14.0 wt% MoO_3 and 3.0 wt% NiO in the oxidic state, sulphided before the experiments at 673 K for 4 hours under a 15% H_2S–85% H_2 mixture.

Under the experimental conditions used, the only reaction products observed in the presence of hydrogen sulphide were those, denoted HDN products, resulting from a C–N bond cleavage (for instance pentane and pentane when starting from amylamine). Without H_2S in the feed, the rate of formation of these products was smaller and some heavier products resulting from a reaction between two molecules of amines were also observed. In both conditions, the rate of formation of the HDN products (fig. 1) is almost equal to zero when no hydrogen atoms are present on the carbon atom in the β position with respect to the nitrogen atom, and satisfactorily follows the increase of the number of these hydrogen atoms.

This result suggests that the removal of such a hydrogen atom on the β carbon is a key step of the C–N bond cleavage, and confirms that, as proposed by Nelson and Levy but never experimentally evidenced, a β-elimination Hofmann mechanism is responsible for this reaction. But the way Nelson and Levy wrote the reaction is not satisfactory insofar as no role is clearly attributed to the catalytic site. Therefore, we tried to write, in the case of amylamine hydrodenitrogenation, a mechanism which accounts for experimental observations and involves a catalytic site. There is still a debate in the literature concerning the exact nature of the active site of the mixed NiMo catalysts [3]. The objective of this paper is not to take part in this controversy, so we have chosen to write the mechanism with a catalytic site constituted by a hexacoordinated molybdenum

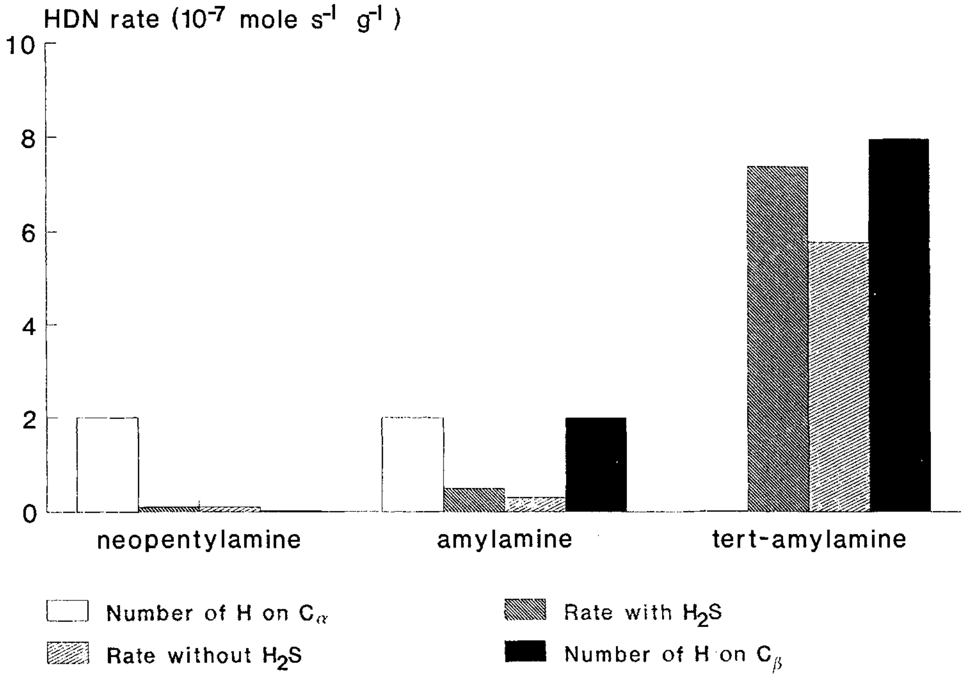


Fig. 1. Relations between the numbers of hydrogen atoms on the α and β carbon atoms and the rate of formation of HDN products.

atom. Furthermore, this is supported by the fact that for the C–N bond cleavage reaction, no promoting effect of nickel, or only a small one, is observed [4].

The mechanism proposed is given on fig. 2. It is generally admitted that the surface of a transition metal sulphide catalyst includes metal atoms surrounded by S^{2-} or SH^- groups and sulphur vacancies, whose numbers depend on the composition of the gas phase and the temperature. The first step of the mechanism of the carbon–nitrogen bond cleavage is the coordination by the nitrogen free electron pair of an amylamine molecule by a molybdenum atom having a coordination nonsaturation. The following step involves activation of a hydrogen atom attached to the β carbon. This activation takes place on the β carbon because of geometric considerations or because of the weakening of the corresponding C–H bond (this weakening could result from the coordination of the amylamine molecule with the molybdenum atom, which is an acido-basic type interaction). In fig. 2, the activation of the hydrogen atom is attributed to a S^{2-} group. Alternatively, a SH^- entity or an adjacent Mo site may be involved in C–H activation. Presumably, the concerned hydrogen atom becomes attached to the bridged sulphur atom and the electron pair shared between this atom and the molybdenum atom is responsible for the formation of a hydrosulphide. The anionic charge developed on the β carbon leads to the formation of a carbon-

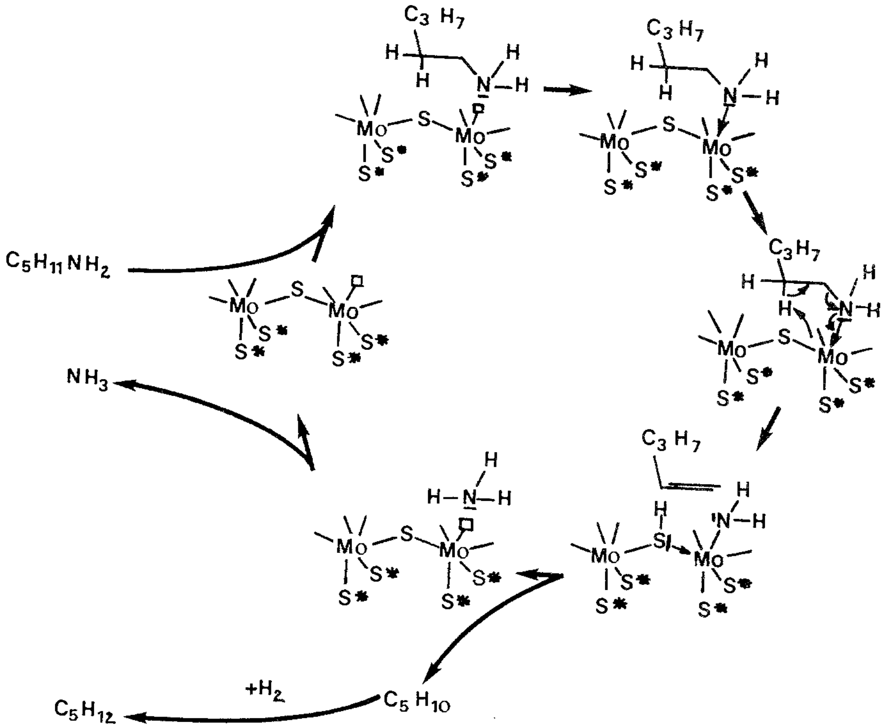


Fig. 2. Mechanism proposed for C–N bond cleavage reaction during hydrodenitrogenation of amylamine over a sulfided NiMo/Al_2O_3 catalyst (S* represents a sulphur atom of the bulk of the catalyst).

carbon double bond, the C–N bond is cleaved, and the electron pair of this bond plays a part in the formation of a σ C–Mo bond. The result of such a concerted process is the formation of an unsaturated hydrocarbon, pentene, of a NH_2 species bounded to the molybdenum atom and of a hydrosulphide entity bridging two molybdenum atoms. The unsaturated hydrocarbon can react with hydrogen from the gas phase and give pentane, the final product of the amylamine hydrodenitrogenation. The NH_2 species could finally undergo a protonation, either from the hydrosulphide entity or from a hydrogen atom attached to the molybdenum, leading to ammonia desorption and setting free the catalytic site.

One can imagine that the condensation products are also formed by a nucleophilic reaction but with an other amylamine molecule as nucleophilic reactant instead of sulphided entities.

Work is now in progress in order to get information about the mechanism of formation of these condensation products, and to determine the validity of the mechanism proposed with amines having more complex a structure, such as for instance those including a heteroring.

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