

Mechanism of Carbon–Nitrogen Bond Scission on Unsupported Transition Metal Sulfides

Martine Cattenot,* Jean-Louis Portefaix,* Julio Afonso,*¹ Michèle Breyse,*²
Michel Lacroix,* and Guy Perot†

**Institut de Recherches sur la Catalyse, CNRS, 2, avenue Albert Einstein, 69626, Villeurbanne Cedex, France; and †Laboratoire de Catalyse en Chimie Organique, Université de Poitiers, 40, avenue du Recteur Pineau, 86022, Poitiers Cedex, France*

Received June 2, 1997; revised September 1, 1997; accepted September 10, 1997

The reactivity of a series of amines with various structures and different numbers of hydrogen atoms on the carbon atoms in the α and β position, with respect to the nitrogen atom, was examined on four transition metal sulfides, i.e. NbS₃, MoS₂, RuS₂, and Rh₂S₃. It is shown that the reaction mechanism proceeds via an elimination or a nucleophilic substitution the relative importance of which depends on the structure of the substrate to be transformed and on the transition metal sulfides properties. NbS₃ is the most active sulfide of the series for the elimination reaction due to its high acidity, but it is inactive for the nucleophilic substitution. On the other hand, the surface species of Rh₂S₃ can be involved in a nucleophilic substitution but not in an elimination reaction. The other sulfides of the series behave in between. These results clearly demonstrate that the catalysts intervene differently in the HDN mechanism. Moreover, for a given solid the structure of a nitrogen-containing molecule strongly affects the elementary steps of its transformation. Accordingly, a precise mechanistic study of the reactivity of a model molecule at the surface of a sulfide cannot be generalized to the overall HDN process which involves several types of molecules. © 1998 Academic Press

INTRODUCTION

Studies of the periodic trends for transition metal sulfides (TMS) have provided interesting opportunities to obtain insight into the role of the different types of sites. Since the pioneer work of Pecoraro and Chianelli (1) related to the hydrodesulfurization (HDS) of dibenzothiophene, several other studies dealing with HDS, hydrogenation, and hydrodenitrogenation (HDN) reactions were published (2–8). For HDS and hydrogenation, the same trends appear in all the studies involving TMS, either unsupported or supported on carbon. As pointed out recently by Clausen, Topsøe, and Massoth (9) this indicates that the same kind of sites, i.e.

the vacancy sites, are a key factor determining the periodic trends for these reactions. However, for HDN the situation is not so clear-cut. As a matter of fact, several mechanisms have been proposed which involve two types of sites, i.e. vacancies and acid-base sites (10–13). The variation of the concentration of this last type of sites is not clearly related to the position of the element in the periodic table. Another difficulty arises from the fact that the conversion of nitrogen-containing molecules involves hydrogenation and nitrogen–carbon bond cleavage steps, the rates of which are not very different. This means that the nature of the rate-determining step may vary according to the experimental conditions, particularly with the H₂S partial pressure.

Eijsbouts *et al.* (7, 14) studied separately the conversion of quinoline and that of the key intermediates (decahydroquinoline and orthopropylaniline) of this molecule HDN network. They have concluded that TMS catalysed all the reaction steps, namely the hydrogenation of the benzenic ring and of the heterocyclic ring, the ring opening, as well as the nitrogen removal. The first row TMS led to low quinoline conversions to hydrocarbons. When plotted versus the position of the element in the periodic table, a U-shaped curve is observed with a minimum for manganese, iron, and vanadium and cobalt and nickel giving the highest conversions. Among the examined sulfides of the second row elements, molybdenum, ruthenium, rhodium, and palladium, rhodium is the most active and molybdenum the least. A volcano curve is also observed for the third row TMS with a maximum for iridium, the highest activity being observed for these sulfides, compared to the first and second rows. Besides these overall results, differences concerning the ratio of the rates for the decahydroquinoline conversion to hydrocarbons and its formation were observed for the various TMS.

For pyridine conversion, only the second-row TMS supported on carbon were examined by Ledoux *et al.* (8). Ruthenium sulfide was found very active by comparison to the other TMS (six times more active than MoS₂). The results are not very different from those obtained for HDS in the same laboratory (3), but the maximum activities are

¹ Present address: Julio AFONSO, Universidade Federal do Rio de Janeiro, Instituto de Química, Departamento de Química Analítica, Centro de Tecnologia, M. A. Ilha do Fundao, Caixa Postal 69563, CEP 21949-900, Brazil.

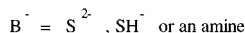
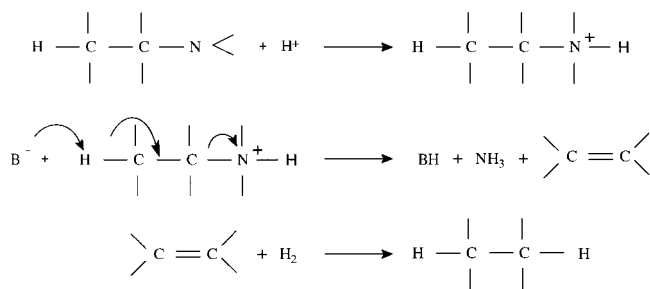
² Present address: Michèle BREYSSE, Laboratoire de Réactivité de Surface, Université P. et M. Curie, Case 178, 4 Place Jussieu, 75252 Paris cedex 05, France.

not observed for the same sulfide, i.e. ruthenium for HDN and rhodium for HDS. From the authors' point of view this difference is not surprising because the high HDS activity is mainly due to a specific structural behavior, whereas the HDN activity is related to the metallic and acidic characters of the sulfides. It might be also argued that the conversion of pyridine involves several steps:

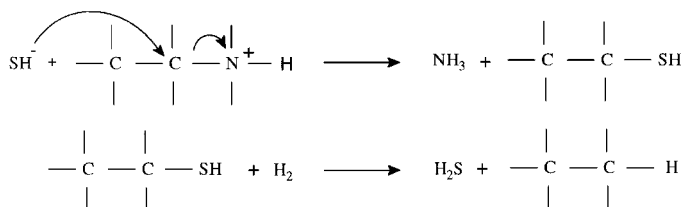


which have not been studied separately. In certain experimental conditions, the hydrogenation step is the slowest and, consequently, similarities with results obtained for the hydrogenation of aromatics are not surprising.

The step corresponding to carbon-nitrogen bond cleavage being the last one, it appeared important to us to examine the properties of TMS in this particular reaction. Unsupported catalysts were chosen for this preliminary study in order to avoid any influence of the support on the catalytic properties (15, 16). Moreover, this allowed the comparison with previous results obtained in our group for dibenzothiophene or thiophene HDS (5) and biphenyl hydrogenation (4). For *n*-pentylamine conversion, the second row TMS were the most active (15). Two maxima were observed, one for rhodium sulfide and the second one for niobium sulfide. To explain this result, it was suggested that two different mechanisms might intervene for the sulfides of the elements of the left or of the right sides of the periodic table. As a matter of fact, the mechanisms most often proposed for HDN (13) consist either in a Hofmann-type elimination (E2) involving a hydrogen atom of the carbon in the β position with respect to the nitrogen atom



or a nucleophilic substitution $\text{S}_{\text{N}}2$ (without any hydrogen atom of the amine molecule involved) leading to the cleavage of the C-N bond.



Laine (17) has offered a different viewpoint and proposed that the C-N bond cleavage mechanism requires metal atoms or ions instead of acid sites and includes metal alkyl or metal alkylidene intermediates; a hydrogen atom in the α position with respect to nitrogen would contribute to the first step of the reaction. However, taken as a whole this mechanism can be considered as a metal-assisted displacement mechanism.

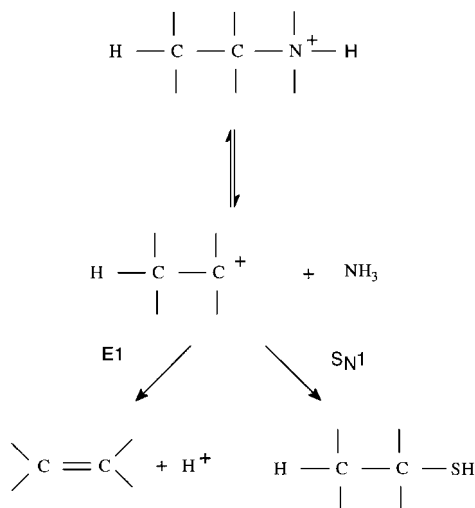
The objective of the present work is to clarify the mechanism of the C-N bond cleavage on four selected transition metal sulfides, i.e. NbS_3 , MoS_2 , RuS_2 , Rh_2S_3 . For this purpose, we utilized the same methodology as reported previously in Refs. (11) and (12); i.e., we studied the reactivity of a series of amines with various structures and different numbers of hydrogen atoms on the carbon atoms in the α and β positions with respect to their nitrogen atom. Depending on the steric hindrance around the carbon bearing the NH_2 group, i.e. on its nature (primary, secondary, or tertiary) and on the number of H atoms in the β position, the expected reactivity of these compounds through the various mechanisms should not be the same. Actually, *n*-pentylamine (with a primary carbon atom and 2 H_{β}), *tert*-pentylamine (with a tertiary carbon atom and 8 H_{β}), and *neo*-pentylamine (with a primary carbon atom and no H_{β}) should exhibit different reactivities (Table 1) with respect to

TABLE 1

Expected Reactivities of Various Nitrogen-Containing Molecules Depending on the HDN Mechanism

Reactant	Mechanism of C-N bond cleavage—expected reactivity			
	$\text{S}_{\text{N}}1$	$\text{S}_{\text{N}}2$	E1	E2
<i>n</i> -pentylamine $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$	Very low	High	Very low	Medium-high
<i>tert</i> -pentylamine $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{-CH}_2\text{-C-NH}_2 \\ \\ \text{CH}_3 \end{array}$	High	Very low	Very high	High
<i>neo</i> -pentylamine $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{-C-CH}_2\text{-NH}_2 \\ \\ \text{CH}_3 \end{array}$	Very low	Very low	None	None

the mechanisms considered above, i.e. E2 and S_N2. Besides these already proposed mechanisms, Table 1 includes the E1 and S_N1 mechanisms which could be also considered. They differ from the others mainly because the transition state is formed by dissociation of the C–N bond leading to a carbocation as shown:



This monomolecular step is the rate-limiting one, while its transformation by elimination or nucleophilic substitution is generally fast. According to these mechanisms it is expected that the reactivity of *tert*-pentylamine will be higher than those of the other isomers because the intermediate is a tertiary carbocation. By contrast, if the S_N2 mechanism prevails the reactivity of the substrates will depend on the steric hindrance of the C_α carbon; i.e., the most reactive molecule would be the *n*-pentylamine, while the presence of three substituents or one *tert*-butyl group would decrease the reactivity of the *tert*- and *neo*-pentylamine, respectively. The E-type mechanisms could not occur with the *neo*-pentylamine, whereas the reactivity of the *tert*-pentylamine would be very high.

At the surface of sulfide catalysts it is known that acidic sites such as coordinatively unsaturated ions, H⁺ from SH groups or basic centers like S²⁻ or SH⁻ may coexist in the experimental conditions required for hydrotreating reactions (18) and the relative concentration of these species should depend on the nature of the TMS. Consequently, it could be expected that the relative importance of the elimination or substitution mechanisms varies according to the acid–base properties of the solids. In order to compare the acidic character of our samples with their HDN properties, we also studied their catalytic performances for the conversion of 2,2,4-trimethylpentane (isooctane). This reaction is less demanding in terms of acidity strength than the conversion of other alkanes such as 2,4-dimethylpentane, 2-methylpentane, and especially *n*-hexane. It requires only Brønsted acid sites of medium strength (19). Moreover, it was shown recently for ruthenium sulfide clus-

ters dispersed in a series of zeolites that this model reaction gives information on the acidity of the solids similar to that obtained by IR spectroscopy (20).

EXPERIMENTAL

Catalysts

The unsupported catalysts utilized in this work were prepared according to the procedures described elsewhere (4, 15, 16). Ruthenium sulfide catalyst (RuS₂) was prepared by precipitation at room temperature from an aqueous solution of RuCl₃ by pure H₂S and by further sulfidation in an H₂S flow at 673 K for 2 h (4, 15). Molybdenum sulfide (MoS₂) was obtained by decomposition of ammonium tetrathiomolybdate (4, 15). The niobium sulfide (NbS₃) sample prepared by combination of the elements has a rather low surface area (2–3 m² g⁻¹). An intercalation–desintercalation treatment with buthyl-lithium allowed the preparation of a higher surface area sample (11–20 m² g⁻¹) (21). Rhodium sulfide (Rh₂S₃) was prepared by mixing two methanolic solutions of RhCl₃ and Na₂S (16). The obtained precipitate was thoroughly washed in order to remove NaCl and was then sulfided at 673 K in a H₂–H₂S atmosphere for 2 h. Several batches of each catalyst were prepared in order to use only fresh samples for catalytic measurements. This procedure prevents the solids from air oxidation which may influence their acid–base properties.

As was shown previously, the surface area of transition metal sulfides decreased during the catalytic test. The surface areas of the various TMS were consequently determined after reaction, according to the procedure already described (4).

Catalytic Activities

The HDN reactions were carried out in the vapour phase at atmospheric pressure, using a dynamic flow microreactor. Since the reactivity of the different amines varies in a wide range, the activities were measured at 523 K with different amounts of catalyst or feed flow rates in order to keep the conversion below 40% with the most active (per gram) catalyst, i.e. RuS₂. The other experimental conditions were

- amine partial pressure, 0.329 kPa
- H₂S partial pressure, 0.395 kPa
- total reactant flow, ~2.2 ml/s
- catalyst weight, 0.025–0.080 g.

The reactants and products were analyzed before and after the reactor by on-line gas chromatography. The conversion of amines is a complex reaction leading to several products. For instance, the HDN of *n*-pentylamine gives C₅ hydrocarbons (1 pentene, 2 *cis*- and *trans*-pentenes, pentane), pentanethiol, dipentylamine, and valeronitrile is formed by dehydrogenation. The column used, a WCOT fused silica CP-Sil-5 CB (length = 50 m, internal diameter =

0.32 mm, film thickness = 5 μm), allows the separation of all the C_5 hydrocarbons, as well as the heaviest products within 40 min. The mass balance is higher than 90%. The reported activities were all measured after 18 h on-stream when steady states were achieved. The results given below are expressed per square meter of catalyst since it was shown in a preliminary study that the rate is proportional to the surface area of the sample (15, 16).

The isooctane hydrocracking was carried out at 548 K at atmospheric pressure (isooctane partial pressure, 2.2 kPa; H_2S partial pressure, 2.5 kPa) using a total flow rate of 0.67 ml/s and a catalyst weight in the range of 0.05–0.1 g.

RESULTS

Amine Conversion

The overall rates of the amine conversion are represented in Fig. 1. For *n*-pentylamine, the results obtained at 523 K are in good agreement with those obtained previously at 548 K with a U-shaped variation of the activity with the position of the element in the periodic table (15). NbS_3 is the most active of the series and RuS_2 is the least active. With the other nitrogen containing molecules, the results are totally different. For example, NbS_3 is still the most active of the series for the *tert*-pentylamine conversion, but this sulfide is inactive for the conversion of *neo*-pentylamine, while for this last reaction, MoS_2 appears to be the most efficient catalyst.

The overall rates of the reactions and those of the formation of the various products are given in Table 2. With *tert*-pentylamine the only products observed were pentenes. With *n*-pentylamine the products were different, depending on the TMS of the series. On NbS_3 pentenes were the major ones and only a very small amount of pentanethiol was

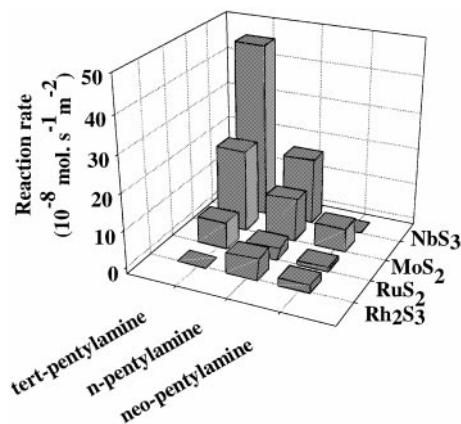


FIG. 1. Overall conversion rates at 523 K of *tert*-pentylamine, *n*-pentylamine, and *neo*-pentylamine on NbS_3 , MoS_2 , RuS_2 , and Rh_2S_3 .

observed with a significant amount of the dipentylamine. In the presence of MoS_2 pentenes were negligible, the major product being the dipentylamine. On RuS_2 and Rh_2S_3 the thiol formation was more significant than that of the dipentylamine. It should be mentioned that the formation of thiols by the addition of H_2S to pentenes was not observed under the present experimental conditions. Similar results were obtained with *neo*-pentylamine (except with NbS_3), although the overall reactivity was much lower.

For a better understanding of the properties of NbS_3 , MoS_2 , and Rh_2S_3 a more complete study of the changes of the product distribution versus conversion of *n*-pentylamine was carried out at 548 K. At this temperature, it was expected that the rate of transformation of the intermediates would be greater, which would permit getting additional information on the reaction scheme. The total conversion was varied by changing the contact time, the reaction temperature being maintained constant. The

TABLE 2

Amine Conversion Rates for Nb, Mo, Ru, and Rh Sulfides

Reactant	Rates	NbS_3	MoS_2	RuS_2	Rh_2S_3
<i>n</i> -pentylamine $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$	V_{tot}	18 (5.3)	11.2 (10)	3.4 (38)	5.6 (52)
	V_{C_5}	8.4	0	0.4	0
	V_{diamine}	4.6	4.8	0.5	1.4
	V_{thiol}	0.3	1.6	2	2.8
<i>tert</i> -pentylamine $\text{CH}_3\text{-CH}_2\text{-C(CH}_3)_2\text{-NH}_2$	V_{tot}	47 (5.3)	22.3 (13)	7.2 (66)	0 (51)
	V_{C_5}	47	22.3	7.2	0
	V_{diamine}	0	0	0	0
	V_{thiol}	0	0	0	0
<i>neo</i> -pentylamine $\text{CH}_3\text{-C(CH}_3)_2\text{-CH}_2\text{-NH}_2$	V_{tot}	~0 (5.3)	6.4 (12)	1.1 (48)	2.2 (51)
	V_{C_5}	0	0	0	0
	V_{diamine}	0	2.9	0.25	0.5
	V_{thiol}	~0	0.6	0.6	1.2

Note. (Rates are in $10^{-8} \text{ mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$). BET areas determined after test are given in brackets.

results are shown in Figs. 2, 3, and 4. The overall reaction scheme

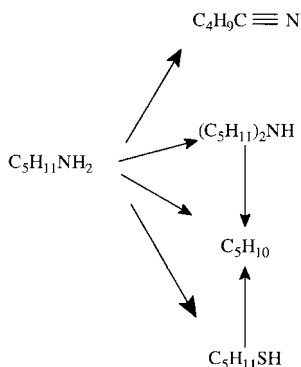


Figure 2 shows that on NbS_3 , pentenes and dipentylamine are primary products. Actually a large fraction of the hydrocarbons seems to be formed directly from *n*-pentylamine. However, at high conversion a certain amount is also formed by decomposition of dipentylamine. On MoS_2 (Fig. 3), two more primary products are formed: valerionitrile by dehydrogenation of *n*-pentylamine and the thiol. The shape of the curve representing the pentenes indicates that they are mainly secondary products coming from dipentylamine. However, a fraction of them results also from the desulfurization of the thiol. On Rh_2S_3 , the same products are formed, but their distribution is different. The main intermediate for the formation of the C5-hydrocarbons (which are clearly secondary products) is the thiol (Fig. 4).

Hydrocracking of Isooctane

The hydrocracking of isooctane was used by Bourdillon *et al.* (19) as a measure of the catalyst acidity. The conver-

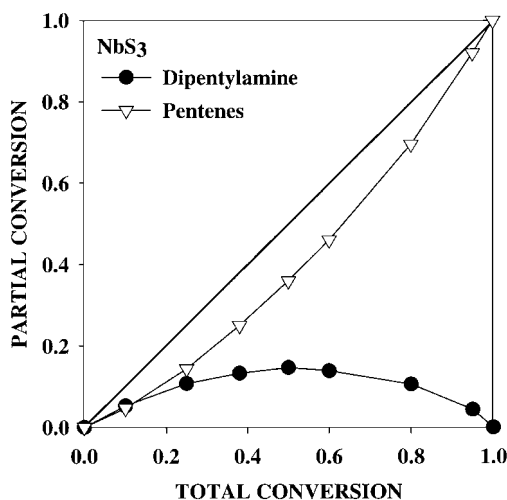


FIG. 2. *n*-pentylamine conversion over NbS_3 at 548 K: partial conversion into dipentylamine, and pentenes as a function of the total *n*-pentylamine conversion.

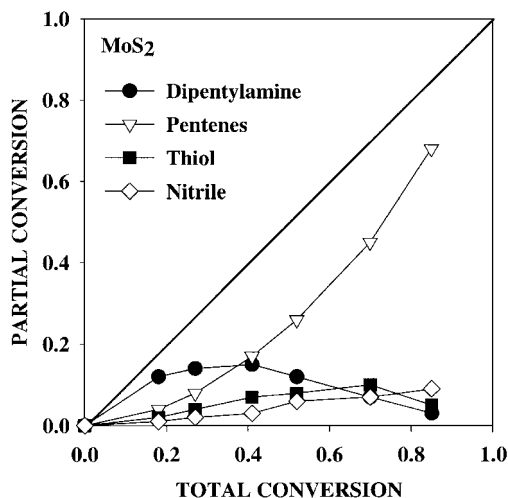
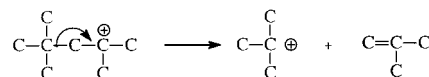


FIG. 3. *n*-pentylamine conversion over MoS_2 at 548 K: partial conversion into dipentylamine, pentenes, thiol and nitrile as a function of the total *n*-pentylamine conversion.

sion of this molecule implies a tertiary carbocation as the intermediate which transformation gives mainly isobutane and isobutene according to



The data reported in Fig. 5 show that the activity continuously decreases from NbS_3 to Rh_2S_3 . It is worth mentioning that these results are in full agreement with those obtained in biphenyl and toluene conversions (16). The sulfides of the elements in the middle of the periodic table present almost no activity for these reactions. The opposite situation is observed for the elements of the left part of the table

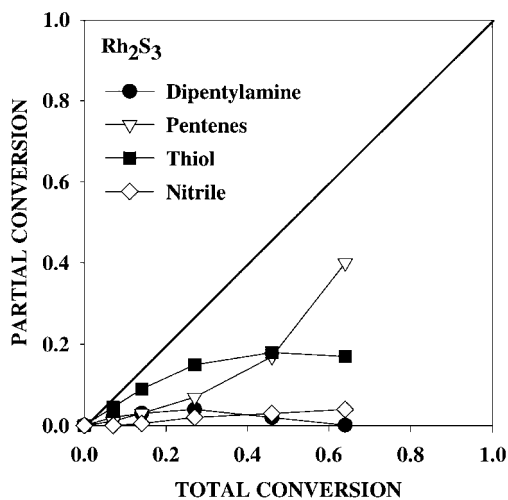


FIG. 4. *n*-pentylamine conversion over Rh_2S_3 at 548 K: partial conversion into dipentylamine, pentenes, thiol and nitrile as a function of the total *n*-pentylamine conversion.

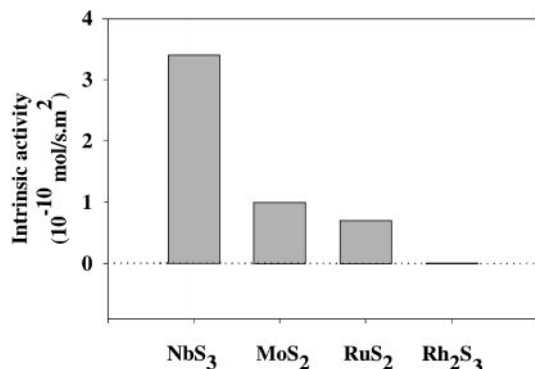


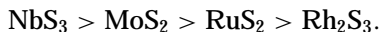
FIG. 5. Isooctane conversion on NbS₃, MoS₂, RuS₂, Rh₂S₃.

where the highest cracking activity is observed for niobium sulfide.

DISCUSSION

Isooctane Conversion and Acidity of the Catalyst

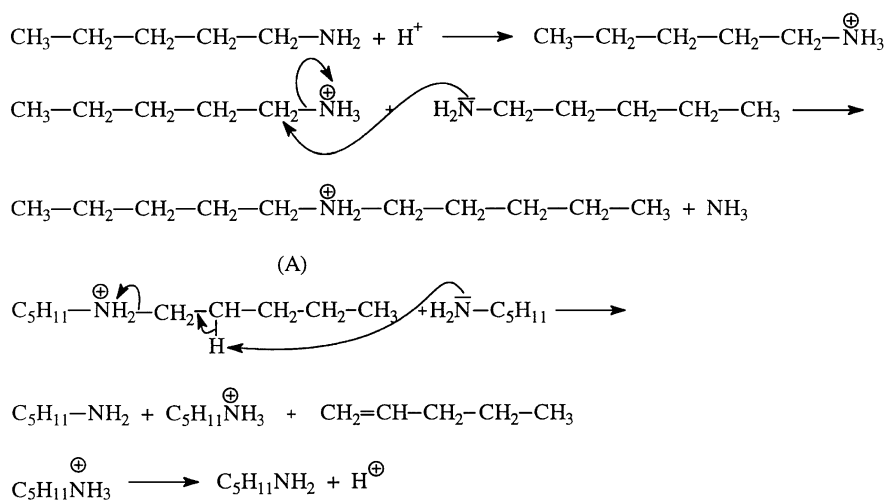
Assuming that the activity in isooctane conversion is related to the Brønsted acidity of the solid (19), it can be concluded that the latter varies in the following order:



Product Distribution and Reaction Mechanisms

The product distribution obtained with *n*-pentylamine shows that two mechanisms are involved with all the catalysts:

(a) The elimination mechanism which in the case of *n*-pentylamine takes place either directly from the reactant or from di-*n*-pentylamine which itself comes from a disproportionation reaction (a S_N2 reaction) as:



This is particularly clear with NbS₃. The reaction is supposedly cocatalyzed by acid sites.

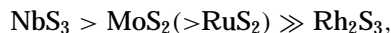
(b) The displacement mechanism involving a thiol as intermediate, which can occur either with *n*-pentylamine as shown above in the cleavage of the C-N bond (in the Introduction) or from the equivalent protonated di-*n*-pentylamine with SH⁻ as the nucleophile. At 548 K both mechanisms coexist on MoS₂ and Rh₂S₃, but the displacement mechanism is prevailing on Rh₂S₃.

Amine Reactivity—Comparison of the Various Catalysts

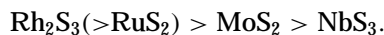
As shown in Fig. 1 and Table 2, the reactivity sequence is in accordance with the predictions of Table 1. Whatever the catalysts, *neo*-pentylamine is less reactive than the other amines. On the other hand, *tert*-pentylamine is more reactive than the others with all the catalysts, except Rh₂S₃. In the presence of this catalyst, *tert*-pentylamine does not react and *n*-pentylamine is the most reactive. This can be interpreted (Table 1) by assuming that on this catalyst the reaction occurs exclusively through a S_N2 mechanism, in agreement with the diagram in Fig. 4, where the thiol is the most important product of the conversion of *n*-pentylamine. With the other catalysts, there is obviously a coexistence of both elimination and substitution reactions (at least for *n*-pentylamine decomposition) as shown by the presence of the thiol intermediate which indicates that a substitution mechanism is involved. Its contribution is all the more significant as the acidity of the catalyst (as estimated from isooctane cracking) is lower. On the other hand, the contribution of the elimination mechanism, as well as the total acidity, increases with the increasing acidity. For instance, elimination is the main reaction path for both *n*-pentylamine and *tert*-pentylamine conversion on NbS₃ which is the most acidic catalyst. The elimination can occur directly from the primary amine as is probably the case with *tert*-pentylamine, or from the

secondary amine resulting from a disproportionation reaction in the case of *n*-pentylamine, as can be deduced from the product distribution (see the foregoing discussion and Figs. 2–4). However, on all catalysts, *tert*-pentylamine seems to react only through an elimination and leads exclusively to C₅ hydrocarbons. In fact *tert*-pentylamine can be very reactive through S_N1 or E1 mechanisms, as well as through a E2 mechanism, which are not sensitive to steric hindrance, but not through a S_N2 mechanism which is very sensitive to it.

Hence, it can be concluded that the activity sequence for the elimination mechanism is



while for the substitution (displacement) reaction with a thiol as intermediate for denitrogenation, the activity sequence is the reverse:



We must, however, consider that the formation of di-*n*-pentylamine (which actually is supposed to occur through a displacement reaction between two molecules of *n*-pentylamine) is a special case as it can be favoured considerably (compared to the displacement reaction leading to the thiol) by the high concentration of the nucleophile (the amine itself) compared to SH⁻. If we except this, the activity sequences are perfectly in accordance with the reactivity sequences of the amines on the various catalysts (and with the predictions of Table 1). These are the following:

- (i) on NbS₃, *tert*-pentylamine (E1 and/or E2) > *n*-pentylamine (E2 and S_N2) \gg neopentylamine (no reactivity);
- (ii) on MoS₂ and RuS₂, *tert*-pentylamine (E1 and/or E2) > *n*-pentylamine (S_N2 and E2 from di-*n*-pentylamine) > neopentylamine (S_N2);
- (iii) and on Rh₂S₃, *n*-pentylamine (S_N2) > neopentylamine (S_N2) \gg *tert*-pentylamine (no reactivity).

The activity and reactivity sequences can be explained on the basis of the reaction mechanisms. In the E₁ mechanism, the rate-limiting step is the departure of the amine group which is favoured by acid cocatalysis. The nucleophile or base has no influence on the kinetics. In E₂ or S_N2 mechanisms both the departure of the leaving groups (also acid-cocatalyzed) and the attack of the base or nucleophile are involved in the rate-limiting step. NbS₃ is the more active in both cases where E1 (*tert*-pentylamine) or E2 (*n*-pentylamine) can occur because of its high acidity. It is not active at all in the case (neopentylamine) where only the S_N2 reaction can take place, probably because the surface SH groups are weaker as nucleophiles than on the other catalysts.

Relation with the Transition Metal Sulfide Properties

The first step of the HDN mechanism requires the chemisorption of the amine to be transformed independently of its structure. Such interaction might occur either on Lewis acid sites or Brønsted ones. By contrast the second step which involves the C–N bond breaking is dependent on the nature of the reactant and, as described above, can be either an elimination or a nucleophilic substitution mechanism. On TMS surfaces several species are present, the concentration of which is related to the nature of the catalyst and also to the experimental conditions used to determine their catalytic properties. These species are (i) anionic vacancies formed by sulfur removal, (ii) SH groups created either by hydrogen or by H₂S heterolytic adsorption, and (iii) bridged S²⁻ and S₂²⁻ anions. As anionic vacancies are sulfur-deficient sites they possess an electron withdrawing character able to coordinate nitrogen-containing molecules via the lone pair of electrons present on the nitrogen atom. The role of SH groups is probably more complicated because the protonic character of the hydrogen atom may depend on the metal–sulfur bond strength. For instance, a strong metal–sulfur bond would weaken the S–H bond, leading to a larger H⁺ acidity. On the contrary, for weakly bonded metal–sulfur the S–H bond strength would be reinforced and the SH groups may intervene rather as a nucleophilic moiety.

Experimental data related to the reducibility of the TMS have shown that this parameter increased from the left to the right side of the periodic table (22). Theoretical calculations using a bond energy model have shown that the metal–sulfur bond strength varies in a large extent depending on the position of the element in the periodic table (23). The weakest sulfur bond energy was observed for noble metal sulfides such as Ru, Os, Ir, and Rh metal sulfides and, consequently, the highest calculated sulfur bond energies correspond to Nb, Ta, Mn, Ti, and Zr sulfides. These results agree fairly well with the experimental HDS activity, supporting the assumption that the HDS takes place on coordinatively unsaturated sites. From these calculations it could be also predicted that the SH groups' properties might differ, depending on the nature of the sulfide under investigation; i.e., the nucleophilic character of the SH groups is expected to increase from the sulfides of the elements of the left side of the periodic table to the noble metal sulfides, while the Brønsted character followed an opposite trend.

The third species (S²⁻ or S₂²⁻) may act as basic centers and, consequently, they are probably involved in the abstraction of a hydrogen atom present in a β position. The amount of such species should be higher on poorly reducible solids like NbS₃ than on a highly reducible catalyst such as Rh₂S₃. Such properties of the solid explain why on NbS₃ the reactivity of the various amines can be interpreted in terms of an elimination mechanism. Conversely, the weak Rh–S bond may account for the nucleophilic substitution

mechanism observed on Rh₂S₃. The other sulfides of the series behave intermediary between these two opposite situations.

CONCLUSION

This work allows us to conclude that the reaction mechanism for C–N bond cleavage greatly depends on the structure of the N-containing molecule. This explains why with compounds like quinoline, tetrahydroquinoline, or ortho-propylaniline the reaction occurs mainly through the elimination mechanism, while with compounds like isoquinoline or benzylamines a displacement reaction is favoured (24).

The nature and the concentration of the species present at the surface of transition metal sulfides are related to the reactivity of these solids in the presence of a highly reducing medium. Reducible solids such as Ru or Rh sulfides exhibit a low Brønsted acidity while more stable chalcogenides like NbS₃ and MoS₂ display more acidic sites. The nature of the surface species favours one of the possible mechanisms. Consequently, the study of the reactivity of a model molecule at the surface of one transition metal sulfide cannot be generalized to other catalysts and more complex HDN processes involving several types of molecules.

REFERENCES

1. Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **67**, 430 (1981).
2. Vissers, J. P. R., Groot, C. K., van Oers, E. M., de Beer, V. H. J., and Prins, R., *Bull. Soc. Chim. Belg.* **93**, 813 (1984).
3. Ledoux, M. J., Michaux, O., Agostini, G., and Panissod, P., *J. Catal.* **102**, 275 (1986).
4. Lacroix, M., Boutarfa, N., Guillard, C., Vrinat, M., and Breyse, M., *J. Catal.* **120**, 473 (1989).
5. Lacroix, M., Marrakchi, M., Calais, C., and Breyse, M., in "Heterogeneous Catalysis and Fine Chemicals II" (M. Guisnet, J. Barrault, C. Bouchoule, D. Duprez, G. Pérot, R. Maurel, and C. Montassier, Eds.), p. 277. Elsevier, Amsterdam, 1991.
6. Sudhakar, C., Eijbouts, S., de Beer, V. H. J., and Prins, R., *Bull. Soc. Chim. Belg.* **96**, 885 (1987).
7. Eijbouts, S., de Beer, V. H. J., and Prins, R., *J. Catal.* **109**, 217 (1988).
8. Ledoux, M., and Djellouli, B., *J. Catal.* **115**, 580 (1989).
9. Topsøe, H., Clausen, B. S., and Massoth, F. E., in "Hydrotreating Catalysis, Science and Technology" (J. R. Anderson and M. Boudart, Eds.), p. 225. Springer-Verlag, Berlin/Heidelberg, 1996.
10. Nelson, N., and Levy, R. B., *J. Catal.* **58**, 485 (1979).
11. Portefaix, J. L., Cattenot, M., Guerriche, M., and Breyse, M., *Catal. Lett.* **9**, 127 (1991).
12. Portefaix, J. L., Cattenot, M., Guerriche, M., Thivolle-Cazat, J., and Breyse, M., *Catal. Today* **10**, 473 (1991).
13. Perot, G., *Catal. Today* **10**, 447 (1991).
14. Eijbouts, S., Sudhakar, C., de Beer, V. H. J., and Prins, R., *J. Catal.* **127**, 605 (1991).
15. Afonso, J., Portefaix, J. L., Lacroix, M., and Breyse, M., in "Proc. 12th Iberoamerican Symp. Catal., 1990," Vol. 2, p. 570.
16. Afonso, J., thesis, University of Lyon, 1990.
17. Laine, R. M., *Catal. Rev.-Sci. Eng.* **25**, 459 (1983).
18. Kasztelan, S., in "Hydrotreating Technology for Pollution Control" (M. L. Occelli and R. Chianelli, Eds.), p. 29. Dekker, New York, 1996.
19. Bourdillon, G., Gueguen, C., and Guisnet, M., *Appl. Catal.* **61**, 123 (1990).
20. Breyse, M., Cattenot, M., Kougonas, V., Lavalley, J. C., Mauge, F., Portefaix, J. L., and Zotin, J. L., *J. Catal.* **168**, 143 (1997).
21. Danot, M., Afonso, J., Portefaix, J. L., and Breyse, M., *Catal. Today* **10**, 629 (1991).
22. Scheffer, B., Dekker, N. J. J., Mangnus, P. J., and Moulijn, J. A., *J. Catal.* **121**, 31 (1990).
23. Nørskov, J. K., Clausen, B. S., and Topsøe, H., *Catal. Lett.* **13**, 1 (1992).
24. Vivier, L., Dominguez, V., Pérot, G., and Kasztelan, S., *J. Mol. Cat.* **67**, 267 (1991).