Catalysis Letters Vol. 99, Nos. 3–4, Feburary 2005 (© 2005)
DOI: 10.1007/s10562-005-2110-z

Mechanism of carbon–nitrogen bond scission in the presence of H_2S on Pt Supported catalysts

Martine Cattenot,[1] Elisabeth Peeters,[1] Christophe Geantet,[1,]* Elodie Devers[1] and José Luiz Zotin[2]
[1] *Institut de Recherches sur la Catalyse, 2, avenue Albert Einstein, 69626, Villeurbanne Cedex, France*
[2] *Petrobras S.A.-R and D Center, Cidade Universitaria, Q.D.7, Ilha do Fundao, 21949 900 Rio de Janeiro, R.J., Brazil*

Received 3 October 2004; accepted 9 November 2004

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 was used to evidence the C–N bond scission mechanism in the presence of H_2S on Pt based catalysts (deposited on alumina, zirconia and silica–alumina) and compare it with the mechanism on a NiMoP on alumina sulfide catalyst. The effect of the H_2S partial pressure was also checked. Catalytic activities (amine overall conversion, C_5 hydrocarbon formation, and amine disproportionation) deeply depend on the structure of the N-containing molecule. *Tert*-pentylamine is the most reactive molecule for sulfide catalysts whereas, in the case of *n*-pentylamine, Pt on zirconia was found to be the most efficient for C–N bond breaking. Such properties cannot be related to the acidic properties of the support but to a unique support–metal interaction, since alumina or silica–alumina supported platinum catalysts do not present this behaviour.

KEY WORDS: hydrodenitrogenation; hydrogen disulfide; Pt based catalyst; Zirconia.

1. Introduction

The removal of sulfur and nitrogen by hydrotreating (HDT) is a major industrial process, which must adapt itself to the changes in the demand for different oil products and is also partially ruled by environmental legislation [1]. The most abundant heteroatom is sulfur but, when shifting from light crude to heavier crude or coal derived oils, the nitrogen content in the fuel increases [2]. Presently, hydrodenitrogenation (HDN) processes are performed with sulfide catalysts and devoted to the treatment of gasoils and lube oils to improve their stability, of hydrocracking and FCC feeds to avoid the poisoning of acid sites. However, the processing of high nitrogen content gasoils requires more severe operating conditions (pressure, temperature and space velocity) as compared to sulfur removal. Literature also evidences the inhibiting effect of nitrogen compounds on aromatic saturation, either on sulfide or noble metal catalysts, so that it is mandatory to reach low nitrogen levels for improving significantly cetane number in gasoils [3,4]. For deep HDN, the use of noble metal catalysts, in a two stage process (involving two reactors) or multiple catalyst bed (within a single reactor), could be envisaged [5], similarly to those proposed for deep hydrogenation of aromatics or deep hydrodesulfurization (HDS) [6]. In such an approach, the purpose of the initial step is to reduce the sulfur content of the crude in order to decrease the H_2S partial pressure (below 500 ppm) in the second reactor. Recently, we demonstrated that, under such conditions, noble metal catalysts are more active than conventional sulfide catalysts [7]. HDN on sulfides has been extensively studied and several mechanisms have been proposed, involving two type of sites, i.e., vacancies and acid–base sites [8]. The knowledge of mechanism of C–N bond cleavage on sulfide catalysts was thoroughly improved by studying the reactivity of a series of amines with different structures and different numbers of hydrogen atoms on the carbon atoms in the α and β positions with respect to their nitrogen atom (H_α and H_β, respectively). These amines were previously studied on unsupported transition metal sulfides [9] or Mo or Nb carbides and MoS_2/SiO_2 [10] or phosphides (MoP, WP) on silica [11]. It was shown that the reaction mechanism depended both on the structure of the amine to be converted (steric hindrance around the carbon bearing the NH_2 group and number of hydrogen atoms in the β position) and on the sulfide (or carbide) properties. The C–N bond breaking could proceed via elimination, favoured by the presence of acid sites at the surface of the catalyst, or via a nucleophilic substitution. Homogeneous models attempted also to provide valid reactivity models of the active sites [12]. In the presence of reduced platinum deposited on various supports, we observed in the conversion of 1,2,3,4-tetrahydroquinoline (l,4-THQ) that, whatever the acidity of the support, H_2S inhibits the reaction, whereas it is a promoter with sulfide catalysts [13]. In fact, hydrogenolysis of C–N bond on metals has been mainly studied by Sinfelt [14], but no work was performed on the mechanism of C–N bond cleavage on metals in the actual conditions of HDN, i.e. in the presence of H_2S. Our previous study of 1,4-THQ conversion in the presence of H_2S

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*To whom correspondence should be addressed.
E-mail: geantet@catalyse.cnrs.fr

demonstrated that reaction pathways are similar on NiMo and Pt based catalysts [7], but the mechanism involved in C–N bond breaking on sulfide catalysts cannot be transposed to the metallic ones. Furthermore, Pt on zirconia was found to be the most efficient catalyst as compared to Pt on alumina or silica–alumina [15].

In the present work, the reactivities of substituted amines over Pt based catalysts were determined in order to understand the nature of the C–N bond breaking mechanism, the role of H_2S and the support effect.

2. Experimental

2.1. Catalysts

The catalysts utilized in this work were prepared according to the procedures described elsewhere [7]. Platinum was deposited on alumina (Condea), silica–alumina (Condea, 40% of SiO_2 so-called SiA140) or zirconia (prepared by aqueous precipitation of zirconium oxychloride) by incipient wetness impregnation using chloroplatinatic acid as the metal precursor. Samples were calcined at 773 K for 1 h and then reduced under hydrogen at 583 K for 6 h. The NiMoP commercial catalyst was sulfided under a mixture of H_2/H_2S (15%) flowing gas at 673 K for 4 h. The dispersion of Pt based catalysts was obtained from H_2 chemisorption technique and the dispersion of the sulfide catalysts (length and stacking) from the statistical analysis of TEM pictures (JEM 2010 microscope). Table 1 summarizes the textural properties and the active phase dispersion of the catalysts.

Table 1
Characteristics of the sulfide reference and Pt based catalysts

Catalyst	$NiMoP/Al_2O_3$	Pt/ Al_2O_3	Pt/ZrO_2	Pt/SiO_2 $-Al_2O_3$
Specific surface area (m^2/g)	165	180	100	374
Active phase loading	4 wt% NiO, 20 wt% MoO_3, 3 wt% P	1 wt%		
1.3 wt%	1 wt%			
Active phase dispersion*	–	0.6	0.6	0.7

*Determined from H_2 chemisorption for Pt based catalysts, from TEM for the sulfide catalyst:average length: 3 nm, average stacking: 2

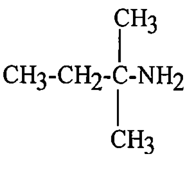
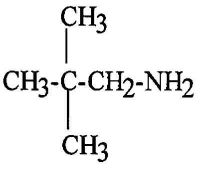
2.2. Catalytic activities

All the experiments were carried out in catalytic microreactors operated in the dynamic mode in the gas phase. Liquid reactants were introduced by means of a gas saturator.

HDN of 1,4-THQ was performed at 623 K with 0.1 g of catalyst. The reactants were composed of hydrogen (3000 kPa), hydrogen sulfide (0.3 kPa, corresponding to 100 ppm) and 1,4-THQ (4 kPa). These conditions were chosen to prevent thermodynamic equilibrium of dehydrogenation of 1,4-THQ to displace too much the reaction toward quinoline (Q) and 5,6,7,8-tetrahydroquinoline (5,8-THQ) formation [16]. However, the 5,8-THQ and Q formed were considered as unconverted reactant for the purpose of conversion calculation. Rate constants were calculated according to a pseudo-first order kinetic. Supports alone did not have any activity.

The substituted amines were the same as in reference [9], namely neo-pentylamine ($2H_\alpha$ and no H_β) *n*-pentylamine ($2H_\alpha$ and $2H_\beta$) and *tert*-pentylamine (no $H_\alpha$and 8 H_β). Their transformation was carried out in the vapour phase at atmospheric pressure similarly to [9]. 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 20% (except for *tert*-pentylamine conversion on NiMoP, which reached 46%). The other experimental conditions were the following ones: amine partial pressure 0.329 kPa (standard conditions), total reactant flow ~2.2 mL/s, catalyst weight 0.025/0.080 g. The H_2S concentation was varied from 83 to 333 vol ppm (instead of 0.4%, 0.395 kPa, for [9]). Table 2 presents the reactants used in this study. The conversion of amines is a complex reaction leading to several products. Reactants and products were analyzed before and after the reactor by on-line gas chromatog-

Table 2
N containing molecules used as reactants

Reactant	H in α position	H in β position
n-pentylamine	2	2
$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}NH_2$		
Tert-pentylamine	0	8
 $CH_3\text{-}CH_2\text{-}C(CH_3)_2\text{-}NH_2$		
neo-pentylamine	2	0
 $CH_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}NH_2$		

raphy. 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 C5 hydrocarbons as well as the heaviest products within 40 min. The mass balance is higher than 95%. Overall amine conversion and product distribution were determined after a period of at least 15 h on stream, which was enough for reaching stable conversions.

The acidity of the catalysts was evaluated by hydrocracking of 2,2,4-trimethylpentane (isooctane) [17,9]. The reaction was carried out at 523 K at atmospheric pressure, with an isooctane partial pressure of 1.7 kPa, a hydrogen flow rate of 0.67 mL/s and a catalyst weight 0.05–0.75 g. No deactivation was observed during the experiments.

3. Results and discussion

The figure 1 illustrates the unique properties of Pt/ZrO_2 catalysts on the conversion of 1,4-THQ in the presence of 100 ppm of H_2S. HDN products correspond to propylcyclohexene, propylbenzene and propylcyclohexane. The first step of this reaction is the hydrogenation of the aromatic ring of 1,4-THQ to form decahydroquinoline (DHQ), followed by C, N carbon scissions giving propylcyclohexilamine (PCHA) and hydrocarbons. *o*-Propylaniline (OPA) and heavy products are produced in minor amounts. Quinoline and 5,8-THQ are also formed and are considered in equilibrium with 1,4-THQ in the reaction conditions. Under such a low concentration of H_2S, Pt on zirconia is about 10-times more active than the conventional NiMoP sulfide catalyst. The following range of activity is observed Pt/ZrO2 > Pt/silica–alumina > NiMoP/alumina sulfide > Pt/alumina.

The overall rate constants of the substituted amine transformation are presented in table 3, as well as the conversion (% in brackets) for a concentration of 333 ppm of H_2S. In fact, since disproportionation reaction is often observed, it is better to examine the rate of production of each product (given in table 4). Only C_5 hydrocarbons and diamines are observed. As compared to unsupported sulfide catalysts, on which traces of thiols were observed in the presence of 0.4% H_2S [9], the presence of such products was never evidenced, probably because of the low amount of H_2S added. Figure 2 allows the comparison of the rate of formation of C5 hydrocarbon on all the catalysts and supports.

3.1. Support contribution

It has to be noticed first that, among the supports, only silica–alumina (SiAl40) is active (see figure 1). Since neopentylamine does not react and only *tert*-pentylamine is converted, it can be assumed that the reaction occurs through an elimination mechanism (El) on this support.

The high conversion of *tert*-pentylamine (indicating that the dissociation of the C–N bond leading to a carbocation is the rate-limiting step [9]) can be related to the Brönsted acidity. Then, the acidic properties of the silica–alumina support were determined from the hydrocracking of isooctane, which is sensitive to Brönsted acidity [17] (see figure 3). It evidences the strong acidity of the silica–alumina as compared to the two other supports.

On the contrary, this support is poorly active for *n*-pentylamine conversion, which suggests that the stability of the tertiary carbocation in *tert*-pentylamine is more important than the number of H_β. C_5 products are mainly composed of pentenes, in agreement with an E1 elimination mechanism.

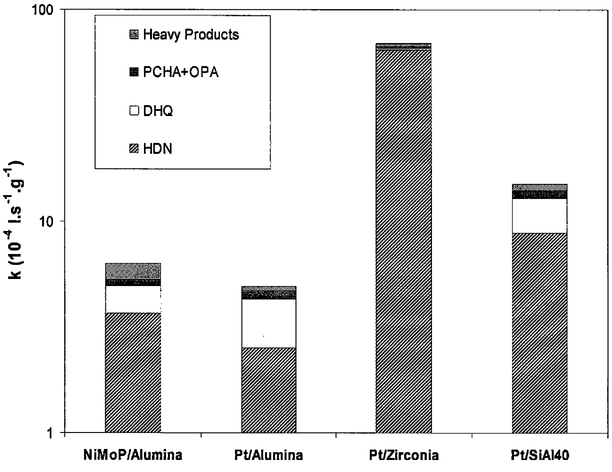


Figure 1. Rate constants and product distribution obtained in the conversion of 1,4-DHQ at 623 K in the presence of 100 ppm of H_2S on various Pt supported catalysts and sulfide NiMoP on alumina referencecatalyst. DHQ = decahydroquinoline, OPA = orthopropylaniline, PCHA = propylcyclohexylamine.

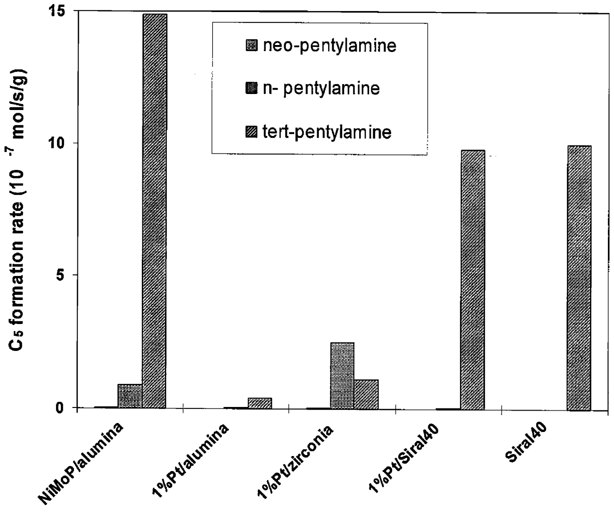


Figure 2. Rate of formation of C_5 products in the conversion of various pentylamines on the Pt supported catalysts and a sulfide catalyst in the presence of H_2S.

Table 3
Total rates of tranformation of the various amines at different H_2S concentrations

Reactant	H_2S conc. (ppm)	Total rate (10^{-7} mol s^{-1} g^{-1})[conversion %]				
		NiMoP/Al_2O_3	Pt/Al_2O_3	Pt/ZrO_2	Pt/SiA140	SiA140
neo-pentylamine	83	3.1	3.4	8.4	15.7	0
166	2.7	3.1	8.2	14.8	0	
333	2.4 [9]	2.6 [10]	7.2 [16]	12.8 [21]	0	
n-pentylamine	83	4.1	5.0	14.1	14.0	0.1
166	3.8	4.4	11.3	12.9	0.1	
333	3.5 [15]	3.5 [14]	9.8 [22]	11.5 [22]	0.1 [0.04]	
Tert-pentylamine	83	15.0	ε	0.9	9.8	10.0
166	14.0	ε	0.8	8.9	9.1	
333	12.7 [46]	ε	0.7 [2]	7.8 [14]	8.2 [16]	

ε-traces

3.2. *Activity of the sulfided NiMoP on alumina*

If we only consider the rates of formation of C_5 hydrocarbons (figure 2), the general trend observed for the 3 molecules (*tert*-pentylamine > *n*-pentylamine > neo-pentylamine) on unsuported MoS_2 [9] and MoS_2 on SiO_2 [10] is also obtained on our NiMoP catalyst. Such a behaviour was attributed to mechanisms involving basic nucleophilic species and/or Brönsted acid sites, i.e., SN_1, E_1 or E_2 mechanisms (see mechanisms proposed in ref [9]).

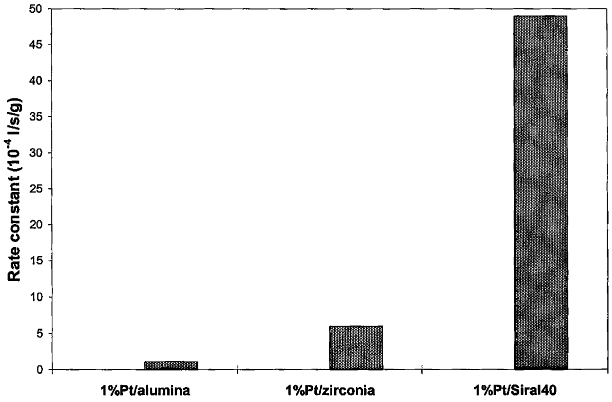


Figure 3. Isooctane hydrocraking properties of Pt based catalysts.

3.3. *Influence of H_2S on the HDN mechanism*

The kinetic orders with respect to H_2S (tables 5 and 6) show that H_2S accelerates the C_5 hydrocarbon formation on the sulfided NiMoP catalyst in the conversion of *n*-pentylamine, in agreement with HDN studies carried out on sulfide catalysts [13,18,19]. H_2S promoting effect for C_5 formation is observed on *n*-pentylamine, evidencing the nucleophilic substitution involving SH^- (and H in α position) as proposed in [9,13] and not on *tert*-pentylamine. In that case, a β elimination (Hoffman type) with only H_β, H_2S has an inhibiting effect as an adsorption competitor.

On the noble metal supported catalysts, H_2S has an inhibiting effect, whatever the molecule and the catalyst, as observed by Peeters [20] in the conversion of 1,4-THQ. Therefore, on these catalysts, H_2S does not intervene in the mechanism, but only acts as an inhibitor of HDN.

Table 4
Rates of formation of the products under various concentrations of H_2S for the Pt based catalysts and the reference sulfide catalyst

Reactant	H_2S conc. (ppm)	Rate (10^{-7} mol s^{-1} g^{-1})									
		NiMoP/Al_2O_3		Pt/Al_2O_3		Pt/ZrO_2		Pt/SiA140		SiA140	
		C_5	Diamine	C_5	Diamine	C_5	Diamine	C_5	Diamine	C_5	Diamine
neo-pentylamine	83	ε	1.4	0	1.7	ε	4.1	0	7.8	0	0
166	ε	1.3	0	1.6	ε	4.0	0	7.4			
333	ε	1.1	0	1.3	ε	3.6	ε	6.1			
n- pentylamine	83	0.9	1.7	ε	2.5	2.5	5.8	ε	7.0	0	0.05
166	1.1	1.4	ε	2.2	1.6	4.9	ε	6.5			
333	1.8	0.9	ε	1.7	1.3	4.2	ε	5.8			
Tert- pentylamme	83	15.0	0	ε	ε	0.9	0	9.8	0	10	0
166	14.0	0	ε	ε	0.8	0	8.6	0	9.1	0	
333	12.7	0	ε	ε	0.7	0	7.8	0	8.2	0	

ε–traces

Table 5
Kinetic order with respect to H_2S for NiMo on alumina catalyst

Reactant	Kinetic order with respect to H_2S		
	Reactant disparition	C_5 production	Disproportionation
neo-pentylamine	−0.19	–	−0.19
n-pentylannne	−0.09	+0.31	−0.29
Tert-pentylamine	0.13	−0.13	–

Table 6
Kinetic order with respect to H_2S for Pt supported catalysts

Reactant	Kinetic order with respect to H_2S			
	Pt/Al_2O_3	Pt/ZrO_2	Pt/SiAl40	SiAl40
neo-pentylamine	−0.19 (Diamine)	−0.10 (Diamine)	−0.15 (Diamine)	inactive
n-pentylamine	−0.26 (Diamine)	−0.26 (C_5:−0.50) (Diamine:−0.22)	−0.15 (Diamine)	inactive
Tert-pentylamine	–	−0.15	−0.15 (C_5)	−0.15 (C_5)

3.4. *Reactivity of Pt supported catalysts*

Pt on silica–alumina was found active for *tert*-pentylamine conversion, but these properties are only due to the support and not to the presence of platinum.

It can be noticed that for neo-pentylamine, whatever the catalyst used (sulfide or metal), disproportionation is the main reaction, only traces of C_5 products being observed. Pt on silica–alumina is the most active but, in that case, it cannot be attributed to the support alone. However, diamine formation and acidic properties correspond to the same scale of activity: Pt/silica–alumina > Pt/zirconia > Pt/alumina. Both acidic properties and presence of H_α (as well as in *n*-pentylamine) favour the attack of a second molecule of amine, the resulting condensed molecule being stabilized by the presence of activated H_2 on the surface of the metal.

The conversion of *n*-pentylamine (see table 4) evidences the unique properties of Pt on zirconia. As noticed above, the condensation of the amine is the main reaction, but C_5 products are also observed. For a similar conversion, Pt on zirconia provides both products, whereas Pt on silica–alumina only allows disproportionation reaction. As compared to sulfide catalysts, Pt on zirconia is three to four times more active for HDN products. But this effect is specific to the combination between Pt and zirconia.

From their experiments, Cattenot *et al.* [9] distinguished two kinds of transition metal sulfides sensitive to the nature of the amine: one corresponding to an acidic character (NbS_3, MoS_2) with a reactivity range analogous to the supported sulfide catalysts, and another corresponding to highly reducible sulfides such as Rh_2S_3. This latter sulfide does not provide C_5 products but mainly thiols and condensed *n*-pentylamine, suggesting that S_N2 is the main mechanism.

Our results (lack of thiols, only condensation observed) suggest that the mechanisms proposed for sulfide (or carbide) catalyts are not relevant for Pt poisoned by H_2S and underligne the specific properties of Pt on zirconia.

On noble metal based catalysts in the absence of H_2S, two main mechanisms were proposed. According to Laine [21], C-N hydrogenolysis is initiated by insertion of the catalyst into the α-C–H bond to form a σ-complexed or α, β adsorbed intermediate, i.e., one metallic site is involved. Later, various homogeneous models were proposed for HDN catalysis [22,23,24] and several examples of metal-mediated C–N scissions were reported. η^2 (N–C) coordination modes for pyridine and quinoline transition metal complexes were proposed to be the most active mode for a subsequent nucleophilic attack. But ultimate denitrogenation apparently requires the cooperation of two metal centers [23].

According to Sinfelt [25], hydrogenolysis of methylamine proceeds via a mechanism analogous to that described for C–C bond scission i.e. a hydrogen deficient intermediate formed upon chemisorption. This mechanism can be transposed to *n*-pentylamine as following:

$$CH_3{-}(CH_2)_3{-}CH_2{-}NH_2 \leftrightarrow CH_3{-}(CH_2)_3{-}CH_x{-}NH_y(\text{ads}) + (4\text{-}x\text{-}y)H(\text{ads})$$

$$CH_3{-}(CH_2)_3{-}CH_x{-}NH_y(\text{ads}) + \text{vacant site} \rightarrow CH_3{-}(CH_2)_3{-}CH_x(\text{ads}) + NH_y(\text{ads})$$

Scission of C–N bond produces two hydrogen deficient surface fragments which further yields to ammonia and denitrogenated molecule. Two neighboring sites are then required. From the differences observed on the three amines, it can be proposed that this mechanism is the most probable. Steric hindrance may explain the poor activity for hydrogenolysis of the two other molecules. The presence of both H_α and H_β may also play a role on the specific sites of Pt on zirconia catalysts. But the origin of this specific selectivity for C–N bond breaking remains unclear.

Concerning the disproportionation reaction S_N2, the following mechanism was proposed [25]:

$$CH_3{-}(CH_2)_3{-}CH_x(\text{ads}) + CH_3{-}(CH_2)_3{-}CH_x{-}NH_y(\text{ads}) \rightarrow (C_5H_{11})_2NH$$

The resulting dialkylamine may undergo elimination as proposed in [9].

In the absence of H_2S, disporportionation reaction predominates on platinum, whereas only hydrogenolysis is observed on rhodium [25].

From these considerations, we can conclude that the HDN mechanism on Pt in the presence of H_2S is similar to the one proposed on metals without H_2S and different than those proposed on sulfides or carbides. A metal assisted displacement mechanism is highly probable, with the intervention of $H\alpha$ (high reactivity of neo-pentylamine). However, this mechanism is sensitive to support effect which may modify the electronic properties of small particles of Pt providing more selective catalysts for C5 production.

4. Conclusion

The present study reveals that Pt based catalysts behave differently than conventional sulfide (or carbides or phophides) catalysts in the conversion of a series of amines. The mechanism proposed by Sinfelt can explain such differences, assuming that 2 sites are required for the adsorption of the nitrogen molecule. It suggests a metal assisted displacement mechanism, with intervention of $H\alpha$ (high reactivity of neo-pentylamine). Elimination mechanisms seems not to be possible on the reduced platinum catalysts, since H_β species do not intervene (*tert*-pentylamine is inactive). H_2S on Pt catalysts always acts as an inhibitor of the HDN sites and exclude SN_2 mechanism.

As already observed for the conversion of 1,4-THQ [15], Pt/ZrO_2 presents a unique behaviour with a strong activity and high selectivity in HDN products. This effect is confirmed in the conversion of *n*-pentylamine. C–N bond hydrogenolysis is strongly favoured on this system for this molecule. It illustrates again the fact that HDN activity (C_5 production) drastically depends on the nature of the reactant and the nature of the active phase. Furthermore, in the case of noble metal based catalysts, the nature of the support contributes to a large extent to the enhancement of the HDN catalytic properties.

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