HDN of 1–4 tetrahydroquinoline over MoN_xO_y and NbN_xO_y: effect of transition metal, solvent and ammonia

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Oxynitrides of early transition metals are bifunctional catalysts active in hydrodenitrogenation (HDN). The strength of the hydrogenating function and the acidic properties of molybdenum and niobium oxynitrides were investigated, as well as the inhibiting effect of ammonia and the effect of solvent (cyclohexane or tetradecane) on HDN of 1,2,3,4-tetrahydroquinoline (1–4 THQ). Even under high hydrogen pressure (4.5 MPa) the reaction was found to be able to proceed without hydrogenation of the aromatic cycle of 1–4 THQ before C–N bond scission, which is not the case over sulfided NiMo supported catalysts in HDN. Experiments in presence of ammonia permitted to support a bifunctional dual site concept.

Keywords: molybdenum and niobium oxynitrides, surface acidity, solvent, ammonia

1. Introduction

Catalytic hydrodenitrogenation (HDN) is a process of nitrogen removal from hydrocarbon feedstocks. Organic nitrogen is most commonly removed under high pressure of hydrogen (5–15 MPa) at 600–670 K. The most well known catalysts for HDN are sulfided NiMo or NiW supported on alumina. These catalysts are efficient, but generally require, in agreement with bond energy calculations, hydrogenation of aromatic rings prior to hydrogenolysis of carbon(sp^3)–nitrogen bonds. The hydrogen consumption during hydrogenation steps is, at least, as high as for the desired denitrogenation one.

As feeds also present sulfur-containing compounds, design of bifunctional catalysts (metallic and acidic sites), stable at low H_2S pressure, with a strong hydrogenating function necessary for high HDN conversion, remains one of the recent challenges in hydrotreating [1,2].

The works by Schlatter et al. [3], Sayag [2] and Lee et al. [4] have shown that molybdenum nitrides might offer an interesting alternative to already existing HDN catalysts. Both molybdenum and niobium nitrides were studied in this work. They can be considered as resulting from the insertion of nitrogen atoms into the cubic lattice of the early transition metals [1]. They present the face-centered cubic (*fcc*) lattice of NaCl-like structure.

Why nitrides or carbides catalyze hydrogenation reactions characteristic of precious metals, can be firstly explained qualitatively. The introduction of N or C atoms into the lattice of an early transition metal leads to an increase of its lattice parameter a_0. Simultaneously, according to the quantum-mechanical theory, the width of the d-band of the transition metal decreases as $1/a_0^5$. Hence the d-electron density of the transition metal after carburization or nitridation becomes higher at the Fermi level, and properties of, say, Mo_2N or Mo_2C shift towards those of metals on the right of the Periodic Table, that is, towards precious metals. Special features such as *interchangeability* between surface nitrogen, carbon and oxygen make these materials interesting for reforming and hydrotreating reactions such as HDN and HDS. Nevertheless, if nitrogen and carbon bring the transition metal a metallic behaviour, the higher is the oxygen content, the lower are both the carbon or nitrogen contents and, consequently, the metallic behaviour of the material as its tendency is to go back to the oxide structure and properties.

In the case of molybdenum compounds, Gouin et al. [5] have shown that these structures are non-stoichiometric ones, vacancies being considered in the metal sub-lattice of the NaCl-like structure. Furthermore, chemical analysis of Mo nitrides have shown that stoichiometry can be near from 0.8 Mo atom for 1 N atom. These Mo compounds clearly lack molybdenum atoms, but preserve the X-ray diffraction pattern of the *fcc* γ-Mo_2N. The same conclusions can be drawn for niobium nitride as it will be seen hereafter. A review of these structures has been made by Oyama [6].

Oxygen can be incorporated into the lattice of the nitrides during the passivation step following their preparation. This step is necessary to avoid their bulk reoxidation due to the pyrophoricity of these materials when contacting air [1,7]. As they contain oxygen, these solids are called *oxynitrides* [1] and are written as MoN_xO_y or NbN_xO_y. They still preserve the *fcc* crystal structure of γ-Mo_2N and δ-NbN, respectively. After passivation, the materials need to suffer a reduction step to remove oxygen. Surface studies of passivated molybdenum oxynitrides have been already published in a previous paper [8]. Chemical composition

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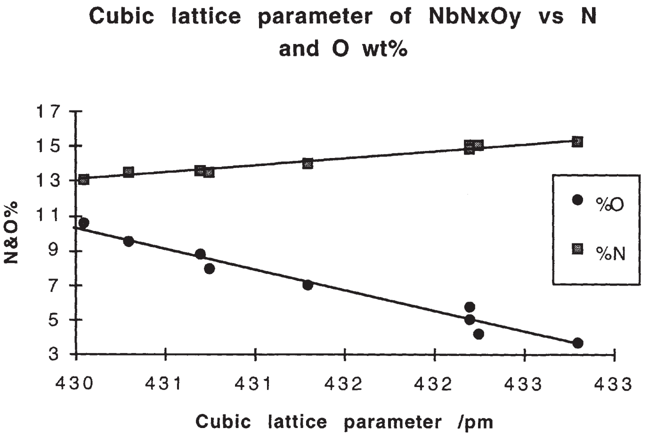


Figure 1. Weight percentages in oxygen and nitrogen (chemical analysis) versus cubic lattice parameter a_0 of oxynitrides as measured from XRD patterns. For a stoichiometric *fcc* NbN (13.1 wt% N), $a_0 = 439.2$ pm [1].

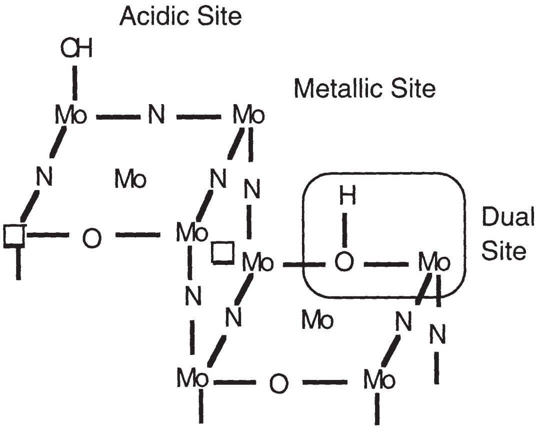


Figure 2. Acidic site (OH group), metallic site (Mo) and dual site model for MoN_xO_y.

of non-stoichiometric bulk oxynitrides can be determined from the value of the cubic lattice parameter a_0, as shown in figure 1 in the case of niobium oxynitrides. It shows the evolution of the cubic lattice parameter a_0 of the *fcc* δ-NbN structure versus the percentages in weight of N and O atoms inserted in the lattice of the nitride. The percentages in oxygen and nitrogen were determined by chemical analysis of materials, and the lattice parameter from XRD patterns. The same kind of relationship can be established for molybdenum compounds. The non-stoichiometry of these oxynitrides can be evidenced by the chemical composition, which shows that materials are quite deficient in Nb relatively to the stoichiometric NbN. The same trend is observed for Mo oxynitrides.

In the present study the following mean chemical compositions were found: $MoN_{0.7}O_{0.7}$ and $NbN_{0.91}O_{0.98}$ for Mo and Nb compounds, respectively. After reaction, the X-ray diffraction patterns of the catalysts remain that of γ-Mo_2N and δ-NbN, but during catalytic runs the surface of the oxynitride can be chemically modified, as previously shown for molybdenum oxynitride [7]. Then the turnover rates remain the best way for *in situ* characterization of different catalysts. Once demonstrated the metallic or acidic properties of materials, discussion can be made in terms of mol% transformed.

Table 1

Bifunctional activity of MoN_xO_y and NbN_wO_z in both isomerization, dehydrogenation and cracking of cyclohexane (flow reactor, cyclohexane at 8.5 bar, hydrogen at 41.4 bar at 663 K).

	Catalyst	v_t[a] (s^{-1})	Reference
Isomerization	NbN_wO_z	2.8×10^{-3}	8
	MoN_xO_y	3.1×10^{-4}	2
Cracking	NbN_wO_z	5.7×10^{-4}	8
	MoN_xO_y	2.8×10^{-4}	2
Dehydrogenation	NbN_wO_z	3.0×10^{-5}	8
	MoN_xO_y	1.3×10^{-3}	2

[a] Turnover rates (v_t), based on site densities (metallic or acidic sites), estimated as 20% of the theoretical number of metal atoms exposed, were calculated according to the specific surface area of materials for a stoichiometric *fcc* lattice [7]. Assumption of dual sites is made for the acid sites in the case of isomerization and cracking.

As a consequence of the passivation step, acidic sites appear at the surface of these materials.

The concept of "*dual sites*" [1] linked to the proximity of acidic and metallic sites has been proposed for bulk nitrides or carbides, as shown in figure 2, where metallic and acidic sites are side by side. As for precious metal-supported catalysts, the following functions can be envisaged for each kind of sites:

Metalic site

- (De)hydrogenation
- Hydrogenolysis

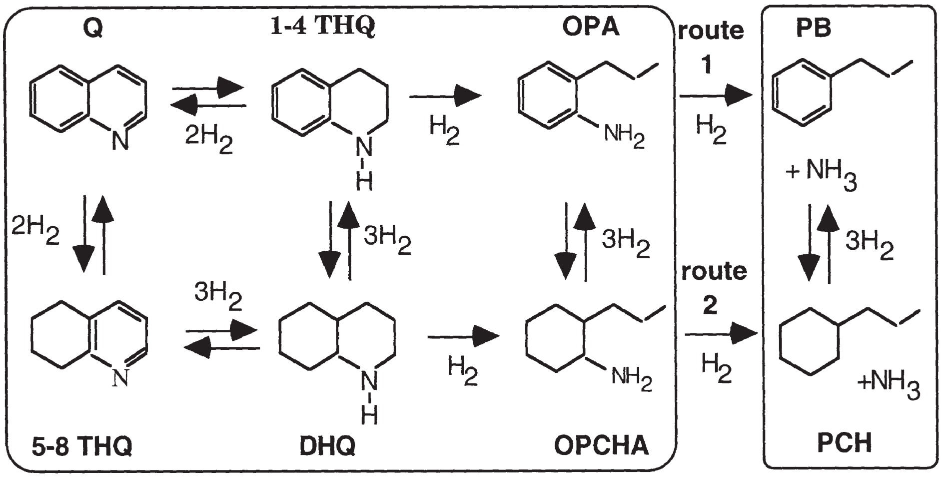
Acid site

- Isomerization
- Cracking

Table 1 shows that nitrides, as well as precious metals supported over an acidic support, are active in isomerization reaction. Table 1 first reports the *turnover rate* for the bifunctional isomerization of cyclohexane to methylcyclopentane over two different acidic materials: MoN_xO_y (not too much acidic) and NbN_wO_z (much more acidic). According to the strength of the acidic sites, global turnover rates of *cracking* of cyclohexane to light hydrocarbons are quite different. *Dehydrogenation* data are also reported, as it became clear that MoN_xO_y has quite a higher hydrogenating function than NbN_wO_z. Furthermore, NbN_wO_z has a higher *isomerization* and cracking activity than MoN_xO_y.

It has been reported [3] that Mo_2N has HDN activity similar to that of sulfided $NiMo/Al_2O_3$ commercial catalysts, but exhibits much higher selectivity towards the formation of aromatic products than sulfided NiMo supported catalysts.

Hydrodenitrogenation of 1,2,3,4-tetrahydroquinoline (1–4 THQ) over molybdenum and niobium oxynitrides was



Q : Quinoline 1-4 THQ : 1,2,3,4-Tetrahydroquinoline
DHQ : decahydroquinoline 5-8 THQ : 5,6,7,8-Tetrahydroquinoline
OPA : orthopropylaniline OPCHA : orthopropylcyclohexylamine
PB : Propylbenzene PCH : Propylcyclohexane

Figure 3. Reaction pathways for HDN of quinoline over Mo_2N according to Schlatter et al. [3].

selected in the present work as a molecular probe reaction to emphasize the surface properties of this kind of materials. Schlatter et al. [3] have proposed a reaction network for HDN of quinoline over Mo_2N (figure 3), which will be considered in this paper. Two routes can be considered. Route 1, without saturation of the aromatic ring of 1–4 THQ or orthopropylaniline (OPA), leads to propylbenzene (PB). Route 2 goes through decahydroquinoline (DHQ), leads to propylcyclohexane (PCH) and is more hydrogen consuming than route 1. Lee et al. [4] have shown that route 1 is efficient and the main one for HDN of quinoline at *atmospheric* pressure. Route 1 can be connected to route 2 via OPA hydrogenation to orthopropylcyclohexylamine (OPCHA).

In the present work, the reaction was conducted in a batch reactor (autoclave) under high hydrogen pressure (5 MPa) with or without ammonia (0.1 MPa). The first objective was to check the product distribution during HDN of 1–4 THQ in these high hydrogen pressure conditions according to the two main reaction routes presented in figure 3. It also led us to study the role of ammonia on the inhibition of the surface active sites, in respect to the “dual site” concept [1].

As niobium leads to a more acidic material than molybdenum [1], it was chosen as a second transition metal to evidence the influence of the ratio between the hydrogenating function and the acidic one. The bifunctionality of Mo and Nb oxynitrides will be compared.

Finally, as 1–4 THQ is diluted in a solvent, the choice of the solvent can modify significantly the activity and selectivity of catalysts, as it has been emphasized by Ishihara et al. [9], and this paper will describe data related to the use of tetradecane and cyclohexane as solvents. The origin of by-products such as indane and methyl indane in the presence of cyclohexane will therefore be evidenced.

2. Experimental

2.1. Catalyst preparation

MoN_xO_y was prepared following the procedure of Volpe and Boudart [10]. Molybdenum oxide (MoO_3, Janssen Chimica) was placed in a quartz reactor and nitrided in flowing NH_3. The temperature of nitridation was increased from 290 to 630 K with a heating rate of 18 $K\,min^{-1}$, then from 630 to 730 K with a heating rate of 0.6 $K\,min^{-1}$, and afterwards to 970 K at 1.8 $K\,min^{-1}$. The material was finally held at 970 K for 3 h. After cooling to room temperature the catalyst was passivated in a mixture of 1 vol% O_2 in He for 1 h. X-ray diffraction patterns of the sample showed the characteristic lines of Mo_2N. The specific surface area (BET method) was typically in excess of 130 m^2/g.

NbN_xO_y was prepared from Nb_2O_5 (Prolabo) in a quartz reactor by nitriding with pure ammonia. The temperature was increased from 290 to 900 K with a heating rate of 2.5 $K\,min^{-1}$, and the material was held at that temperature for 12 h. After cooling to room temperature the catalyst was passivated in the same way as for MoN_xO_y. The specific surface area of NbN_xO_y was 53 $m^2\,g^{-1}$. X-ray diffraction showed patterns characteristic of NbN.

2.2. Chemical analysis

Elemental analysis of solids, before and after reaction, were obtained from the Service Central d’Analyse du Centre National de la Recherche Scientifique (Vernaison, France). Oxygen and nitrogen amounts were determined by a combustion method and analyses of the effluent gases. Molybdenum and niobium analyses were performed by plasma emission spectroscopy.

2.3. Catalytic device

The reactions were performed in a 250 cm^3 batch autoclave. A volume of 30 cm^3 of 1 wt% 1–4 tetrahydroquinoline (THQ) in cyclohexane (or 1 wt% 1–4 THQ in tetradecane) was introduced in the autoclave together with 2 wt% of catalyst (related to the total weight of reaction mixture). The reactor was flushed by nitrogen, then filled up with hydrogen to 2 MPa at room temperature (RT). In the case of experiments with ammonia, after flushing the autoclave with nitrogen, ammonia was introduced up to 0.1 MPa (RT) into the reactor, and then hydrogen was admitted up to 2 MPa (RT).

The reactor was heated to 670 K at 5 $K\,min^{-1}$ and held at 670 K for 1 h. The total pressure in the autoclave at that final temperature was 4.5 MPa.

Samples were analysed on a Hewlett-Packard gas chromatograph 5890, combined with a HP 5971A mass selective detector equipped with a capillary column (25 m, "ultra-2" cross-linked 5% phenyl methyl silicone), and on a Hewlett-Packard gas chromatograph 5890 series II, equipped with the same column.

3. Results and discussion

3.1. Blank run over cyclohexane (CH) and total conversion of 1–4 THQ in CH without added ammonia: comparison between MoN_xO_y and NbN_xO_y

Table 2 reports the main data on blank runs (cyclohexane alone in the presence of molybdenum or niobium oxynitride), total conversion of 1–4 THQ over both catalysts, and distribution of intermediates and products of HDN reaction (mol%) for HDN of 1–4 THQ.

Products are divided in two groups: the first one corresponds to N-containing intermediates – orthopropylaniline (OPA), orthoethylaniline (OEA), methylaniline (MA) and aniline (A) – and the second group to products obtained after HDN – propylbenzene, ethylbenzene, benzene and propylcyclohexane.

The blank experiments mainly showed the formation of indane and methylindane. These two by-products issued from the solvent were observed in all experiments over MoN_xO_y and NbN_xO_y catalysts and were not considered in the general balance of the products of HDN of 1–4 THQ.

Table 2 shows that MoN_xO_y presents a global conversion of 1–4 THQ (N-containing intermediates + products of HDN) about 4 times higher than NbN_xO_y (24.1% for 5.7%). It can be partially explained by a higher specific surface area of the former catalyst (130 $m^2\,g^{-1}$) compared to that of NbN_xO_y (53 $m^2\,g^{-1}$). But the main reason can be linked to a stronger hydrogenating function of MoN_xO_y relative to NbN_xO_y [1] as will be confirmed later.

Figure 4 shows how the reactions of hydrogenolysis and/or dealkylation can lead to 63.8 mol% of the products issued from the transformation of 1–4 THQ over MoN_xO_y. These results are in agreement with Abe and Bell data observed at atmospheric pressure over Mo_2N [11]. In the case of NbN_xO_y, there is no OPA and the main intermediate products of HDN are OEA, MA and A. This can be due to the higher acidity of this material leading to a cracking of the lateral chain.

Table 2
Total conversion and distribution of reaction products and intermediates formed at 670 K in standard conditions (1–4 THQ in cyclohexane).

	MoN_xO_y	NbN_xO_y
Total conversion (%)		
Blank run (cyclohexane)	2.8	2.8
1–4 THQ global conversion	24.1	5.7
Product distribution[a] (mol%)		
N-containing compounds		
Orthopropylaniline	27.4	0.1
Orthoethylaniline	10.4	5.8
Methylaniline + aniline	26.0	71.5
Total	63.8	77.4
HDN products		
Route 1 (figure 2)		
Propylbenzene	9.8	6.2
Ethylbenzene	9.0	13.8
Toluene	10.4	0.0
Benzene	0.0	0.0
Total	29.2	20.0
Route 2 (figure 2)		
Propylcyclohexane	6.9	2.7
Total HDN products	36.1	22.7

[a] Product distribution (mol%) calculated for 100 mol of compounds issued from 1–4 THQ converted to N-containing intermediates and products of HDN.

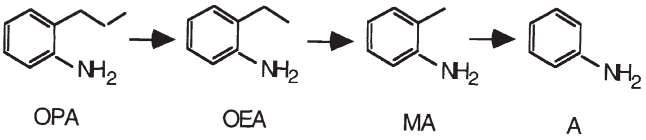


Figure 4. Successive hydrogenolysis of the lateral chain and/or dealkylation leading to N-containing intermediates.

Similarly to OPA in figure 4, PB can lead to ethylbenzene (EB), toluene (T) and benzene (B). Only PB, EB and T were observed over MoN_xO_y, whereas no T nor B were detected over niobium oxynitride.

Propylcyclohexane was observed over both catalysts, MoN_xO_y being more hydrogenating (6.96 mol%) than NbN_xO_y (2.7 mol%). Finally, even taking into account the difference in specific surface areas between Mo and Nb oxynitrides, MoN_xO_y seems to be more hydrogenating and, therefore, more active than NbN_xO_y in HDN of 1–4 THQ.

3.2. Comparison between routes 1 and 2 (figure 3) over MoN_xO_y and NbN_xO_y

Sayag has shown [2] that hydrogenation of propylbenzene alone in cyclohexane over MoN_xO_y at 670 K under 5 MPa hydrogen pressure was total, but that introduction of

Table 3
Ratio between routes 1 and 2 during HDN of 1–4 THQ over MoN_xO_y and NbN_xO_y.

	MoN_xO_y	NbN_xO_y
Propylbenzene (PB) (mol%)	9.8	6.2
Propylcyclohexane (PCH) (mol%)	7	2.7
Ratio PB/PCH = ratio route 1/route 2	1.4	2.3

OPA into the feed completely inhibited the reaction. This result showed the competitive adsorption of OPA and PB on the dual site, OPA being quite stronger adsorbed than PB. It can be assumed that OPA adsorbed on the acidic Brønsted group of the dual site, sterically inhibiting the adsorption of PB on the metallic site. Kim [12] for the same reaction, in the same experimental conditions, found that NbN_xO_y was unable to hydrogenate PB in solution in cyclohexane, evidencing the lower hydrogenating function of this catalyst.

As a conclusion, it can be deduced from these two previous data on PB hydrogenation over both catalysts that hydrogenation of PB to PCH is prohibited in the condition of HDN. Therefore, the ratio PB/PCH gives the ratio between routes 1 and 2 in both cases.

Once more, it appears from tables 2 and 3 that (i) MoN_xO_y is more hydrogenating than NbN_xO_y, and (ii) correlatively, MoN_xO_y is more active in HDN of 1–4 THQ than NbN_xO_y.

Furthermore, Lee et al. [4] have detected decahydroquinoline (DHQ) in the products of reaction. This is not the case in the present work, even under high hydrogen pressure. Let us note that DHQ was one of the intermediates proposed by Schulz et al. [13] over sulfided $NiMo/Al_2O_3$ and NiW/Al_2O_3 catalysts. This lighted the main difference between nitrides and sulfides in HDN reactions, even at high hydrogen pressure: nitrides follow routes 1 and 2, whereas sulfides mainly follow route 2.

3.3. Dual sites: effect of ammonia on HDN conversion and distribution of products

Table 4 reports data on the effect of ammonia on HDN reactions. For both catalysts, ammonia inhibits conversion of 1–4 THQ. The strongest inhibition effect is observed over MoN_xO_y (24.1% without ammonia against 15.5% in the presence of NH_3), whereas it is less pronounced for NbN_xO_y whose 1–4 THQ global conversion is quite lower in both cases (5.7% without ammonia against 4.3% only in the presence of ammonia) related to MoN_xO_y. Lower conversions can be considered as due to the adsorption of ammonia on the Brønsted site of dual sites, sterically inhibiting the metallic site, as in the case of inhibition of PB hydrogenation by OPA over MoN_xO_y[2].

The inhibiting effect of ammonia towards N-containing intermediates is drastic. Ammonia obliges OPA to desorb from MoN_xO_y and, consequently, there is a higher concentration of OPA in the gas phase and a lower conversion to final HDN products: 34.6 mol% OPA in presence of ammonia against 27.4 without NH_3; 26.2 mol% total HDN products in presence of ammonia against 36.1 without NH_3. The C–N bond scission proceeds on dual sites and, due to the competitive effect and blocking of active sites by ammonia, the C–N bond rupture is prohibited and larger amounts of aniline and methylaniline are observed.

Table 4
Effect of ammonia on total conversions and distribution of reaction products and intermediates formed at 670 K: standard conditions (1–4 THQ in cyclohexane) + NH_3 (0.1 MPa).

	MoN_xO_y	NbN_xO_y
Total conversion (%)		
Blank run (cyclohexane)	2.8	2.8
1–4 THQ global conversion	15.5	4.3
Product distribution[a] (mol%)		
N-containing compounds		
Orthopropylaniline	34.6	0.0
Orthoethylaniline + methylaniline + aniline	39.1	76.9
Total	73.7	76.9
HDN products		
Route 1 (figure 2)		
Propylbenzene	6.2	4.8
Ethylbenzene + toluene	15.7	17.0
Benzene	0.0	0.0
Total	21.9	21.8
Route 2 (figure 2)		
Propylcyclohexane	4.3	1.2
Total HDN products	26.2	23.0

[a] Product distribution (mol%) calculated for 100 mol of compounds issued from 1–4 THQ converted to N-containing intermediates and products of HDN.

This phenomenon is not so marked over the acidic and weak hydrogenating NbN_xO_y, with 76.9 mol% of (OEA + MA + A) against 77.3 mol% without ammonia and 23.0 mol% HDN products against 22.7. For these two last values, it seems that NbN_xO_y is more efficient in HDN, but, in fact, product distribution (mol%) is calculated for 100 mol of compounds issued from 1–4 THQ converted to products of HDN and these two values have to be corrected by the 1–4 THQ global conversion to compare them in term of concentration.

3.4. Effect of solvent on total conversion and product distribution of hydrodenitrogenation of 1–4 THQ

The nature of solvent can affect catalytic activity and selectivity in hydrotreating reactions, as reported by Ishihara and Kabe [9].

Table 5 reports total conversions and distributions of products for HDN of 1–4 THQ in tetradecane over both catalysts. Blank runs lead to solvent conversions still less significant with tetradecane than with cyclohexane (only 0.2% conversion compared to 2.8% for cyclohexane, and no possibility for cyclic by-products). Total conversion

Table 5
Total conversions and distribution of reaction products and intermediates formed at 670 K in standard conditions (1–4 THQ in tetradecane).

	MoN_xO_y	NbN_xO_y
Total conversion (%)		
Blank run (cyclohexane)	0.2	0.2
1–4 THQ global conversion	18.1	3.8
Product distribution[a] (mol%)		
N-containing compounds		
Orthopropylaniline	46.8	0.0
Orthoethylaniline	12.0	12.2
Methylaniline + aniline	12.1	73.8
Total	70.9	86.0
HDN products		
Route 1 (figure 2)		
Propylbenzene	8.4	14.0
Ethylbenzene	3.0	0.0
Toluene	2.8	0.0
Benzene	4.8	0.0
Total	19.0	14.0
Route 2 (figure 2)		
Propylcyclohexane	10.0	0.0
Total HDN products	29.0	14.0

[a] Product distribution (mol%) calculated for 100 mol of compounds issued from 1–4 THQ converted to N-containing intermediates and products of HDN.

of 1–4 THQ is lower for both catalysts (24.1% in cyclohexane against 18.1% in tetradecane for MoN_xO_y, and 5.7% against 3.8% for NbN_xO_y) clearly evidencing the global effect of solvent.

The nature and mol% of compounds in the product distribution of N-containing intermediates is drastically modified. For MoN_xO_y, table 5 reports 70.9 mol% of total amount of N-containing compounds instead of 63.8 mol% in the presence of cyclohexane, and a larger amount of OPA is observed (46.8 mol% instead of 27.4 mol%). The difference remains less drastic for NbN_xO_y: no OPA is detected, whereas aniline remains the major intermediate (73.8 mol%) as in the presence of cyclohexane (71.5 mol%). Nevertheless, the total amount of N-containing compounds is now 86.0 mol% with tetradecane, compared to 77.4 mol% in the presence of cyclohexane.

The lack of PCH over NbN_xO_y shows that the reaction follows exclusively route 1 (figure 3). In contrast, the presence of PCH in the products obtained over MoN_xO_y permits to calculate a ratio route 1/route 2 $= 0.8$. These data are quite different from those observed in the presence of cyclohexane, demonstrating the importance of the solvent for comparing two catalysts in HDN reactions. An inhibiting effect of the solvent can be considered to explain these differences, tetradecane (long chain) being more inhibiting than cyclohexane. Nevertheless, MoN_xO_y still remains more hydrogenating than NbN_xO_y.

NbN_xO_y being quite more acidic than MoN_xO_y, OPA strongly adsorbs on the acidic sites of NbN_xO_y leading to a drastic cracking of its lateral alkyl chain. OPA probably occupies the dual sites and completely inhibits route 2 over NbN_xO_y. Then no PCH can form.

4. Conclusion

MoN_xO_y and NbN_xO_y enable C–N hydrogenolysis of the saturated heterocycle of 1–4 tetrahydroquinoline. This reaction can occur with saturation of 1–4 THQ to DHQ (figure 3, route 2) or without prior saturation of the aromatic ring (figure 3, route 1), even under high hydrogen pressure (5 MPa).

Sayag has shown [2] that hydrogenation of PB to PCH cannot occur during HDN reaction. Therefore, the ratio PB/PCH leads to the evaluation of the ratio route 1/route 2. For MoN_xO_y this ratio is lower than for NbN_xO_y. It means that molybdenum oxynitride is more hydrogenating than niobium oxynitride and, consequently, MoN_xO_y appears to be more active in HDN of 1–4 THQ than NbN_xO_y.

Addition of ammonia in the feed leads to an inhibition of the acidic function of both catalysts, simultaneously with a steric inhibition of the hydrogenating one. The competitive adsorption of ammonia with reaction intermediates such as OPA leads to a lower HDN conversion over both catalysts, and this data supports the concept of dual site.

Comparison of data over both catalysts using two different solvents shows that differences in activity and selectivity can be observed. The origin of this effect still remains to be discussed.

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