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Hydrodenitrogenation Activity and Selectivity of Well-Dispersed Transition Metal Sulfides of the Second Row on Activated Carbon

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The study of the second row of transition metal sulfided catalysts well-dispersed on activated carbon and of a conventional NiMo/alumina sulfided catalyst shows that these sulfides can be classified into three families following their pyridine hydrodenitrogenation activity: the very poor catalysts (order 1) such as NiMo, Zr, Ag, and Nb; the active catalysts (order 10) such as Mo, Rh, and Pd; and the very active catalyst Ru. The selectivity of products differs greatly from one catalyst to another: the higher the concentration in saturated C_5 hydrocarbons, the higher the activity; the higher the concentration in cracked hydrocarbons (C_4, C_3, C_2, and C_1) the lower the activity. In addition, there is no simple correlation between the concentrations of the different intermediate amines (piperidine and pentylamines mainly) and activity, which excludes any simple kinetical explanation.

INTRODUCTION

In a preceding work (*1*), we found an influence of the sulfide structures on the hydrodesulfurization (HDS) activity of carbon-supported catalysts. All transition metals in the first, second, and third rows have been studied; among them the maximum activity was found on Rh sulfide. If the second row is selected as an example, whatever the temperature of reaction between 227 to 350°C, Rh sulfide is always 1000 times more active than Zr or Ag sulfides, the two weakest catalysts. After that, Nb sulfide is 10 times more active than Ag sulfide, and Mo, Ru, and Pd sulfides 100 times less active than Rh sulfide, with a slight advantage for Ru sulfide, the second best catalyst in this row. To explain such a range of activity, a combination of an electronic effect (Harris and Chianelli theory (*2*)) and a geometric effect (existence of a natural overstoichiometric pseudo-stable or stable phase) was proposed.

It was very exciting to test these catalysts for the hydrodenitrogenation reaction (HDN) in order to check whether the same sort of effects as those found for the HDS could be observed for the HDN of an aromatic compound. The same idea was probably at the origin of the results published by Prins *et al.* (*3, 13*). They found a similar trend for HDN and HDS on carbon-supported metal sulfides. However, the two reactions were made under different conditions, flow or batch, and thus could lead to very different conclusions. In addition the very high conversion for some of their tests prevents any clear estimation of the intrinsic activity which allows a correct comparison between the sulfides.

The HDN activity and selectivity for pyridine, of the second row of transition metals sulfides highly dispersed on an activated carbon support, are the object of this article.

EXPERIMENTAL

The best experimental conditions that we found to achieve this goal are described in this section.

(*1*) *Choice of the Test Molecule*

Pyridine has been selected for two main

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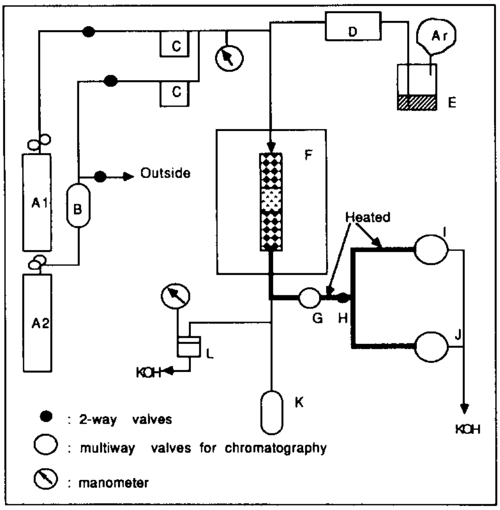

FIG. 1. Scheme of the high-pressure micropilot. A1, H_2/H_2S 2 vol% ultrahigh purity, 250 bar; A2, H_2 ultrahigh purity, 250 bar; B, purifier (CuO + zeolites) + regenerator oven; C, flow regulator + flow meter (Brooks electronic); D, high-pressure liquid injector (range 0.5 μl/min to 10 cc/min) (Gilson); E, distillated pyridine kept under argon; F, tubular reactor in an oven; the catalyst is placed between two layers of silica balls and silica wool and the temperature is regulated at 0.5°C on 21 cm; G, adjustable microleak (Micromitte); H, high-pressure cap; I, J, chromatographs; K, removable condenser; L, pressure regulator (Grove).

reasons: first because the number of reaction products is sufficiently low to allow us to perform the total analysis, characterizing each product, by the use of gas-phase chromatography, and second because the different mechanisms and their relation with active sites responsible for the pyridine HDN have previously been characterized by our group (*4–9*).

(*a*) *Analysis of products*. The reaction apparatus is described in the next section and the schematic design is shown in Fig. 1. Two gas-phase chromatographs are directly connected to the outlet of the flow reactor by means of an adjustable microleak which allows depressurization without condensation of the heaviest products. In addition, in order to avoid further condensation, all stainless-steel pipes are heated to 150–200°C up to the different injectors.

The first column ($\frac{1}{8}$-in.) is packed with Carbowax 20000 supported on Chromosorb 5% KOH. This column is used to separate all the products containing a nitrogen atom(s) and some of the heaviest hydrocarbons. Typical products measured with this column contain pyridine, dihydropyridine, tetrahydropyridine, piperidine, α-picoline, *n*-C_5 amines (mainly *n*-pentane and *n*-pentene amines), cyclo- and *n*-C_5 hydrocarbons; the other amines (other picolines, the lutidines, C_{10} amines, C_4, C_3, C_2, C_1 amines) were never observed in the studied reactions.

The second column ($\frac{1}{8}$ in.) is packed with SE30 silicon phase supported on firebrick. This column allows the very precise measurement of most of the hydrocarbons from C_1 to C_7. Only the different linear C_5 (pentene-1, pentane, pentene-2-*trans* and *cis*) are not separated correctly. In order to obtain the relative contribution of these C_5, a third column, capillary coated with a thick film of OV101 (silicon), is also used. A sample of the gas mixture is syringed out of the flow through a special high-pressure cap and injected directly into the capillary unit.

A combination of these three chromatographic analyses permits measurement of the relative molecular amount of each of the reaction products. By assuming, at very low conversion (see below), a first-order reaction rate, the specific rate of reaction can be evaluated and by combining this rate and the weight of catalyst (where the metal content has been measured by atomic absorption) one can deduce the nominal turnover rate (expressed in h^{-1}). As for the HDS study (see (*1*)), one must assume that, because of the very low metal content, all the metal atoms are accessible and are a potential active site.

The only products which are not analyzed in our system are NH_3 and ammonium sulfide.

(*b*) *Reaction mechanisms*. Two families of mechanisms have been characterized by the analysis of products of the pyridine HDN (*7*, *8*).

The classical Hoffmann elimination leads to ($C_5 + NH_3$), ($C_3 + C_2 + NH_3$), and ($5C_2 + 2NH_3$) (through $C_5 + C_5 \rightarrow C_{10} \rightarrow 5C_2$). In the following, $5C_2$ will be reported as $\frac{5}{2}C_2$ in C_5 equivalent. For more details of this mechanism, schemes are reported in (*4*, *7*).

The Hoffmann elimination applied to the pyridine requires three main properties from the catalyst:

—acidic protons to perform the quaternization of the nitrogen atom,

—a metallic or pseudo-metallic site which allows the saturation of the β-carbon atom by hydrogenation of at least two double bonds,

— a conjugated basic site to extract a proton on the saturated sp^3 β-carbon.

When the metallic or pseudo-metallic character of the catalyst is weak, cyclic C_5 and $5C_2$ cracking are favored over n-C_5 and $C_3 + C_2$ cracking; obviously the percentage of saturated C_5 in the C_5 fraction also depends upon this metallic character. Generally a perfect correlation is observed between cyclic C_5 and saturated C_5; the higher the concentration of saturated C_5, the lower the concentration of cyclic C_5.

The second mechanism responsible for HDN is a metallic cracking equivalent to the metallic cracking of hydrocarbons observed in the reforming reaction. This mechanism leads to ($C_4 + C_1 + NH_3$), ($C_3 + 2C_1 + NH_3$), or even ($5C_1 + NH_3$). Under certain conditions, it can also give C_4, C_3, C_2, and C_1 amines.

It has been shown (*8*) that the relative amounts of these different products depend directly on the size of the metallic site (or ensemble). On very small ensembles (monoatomic for instance) only small amounts of $C_4 + C_1$ are observed. $C_3 + 2C_1$ and $5C_1$ are found only on sufficiently large ensembles of metallic or pseudo-metallic atoms. Pseudo-metallic atoms are generally oxided metal at a very low degree of oxidation (Mo^{2+} for instance) or sulfided metal, when this sulfide has a metallic electronic structure (band of conduction). These pseudo-metallic catalysts generally have an ensemble of only a very small size and can perform only $C_4 + C_1$ cracking and obviously hydrogenation of double bond.

Finally, it is important to emphasize that these mechanisms have been characterized at normal H_2 pressure. There is no reason to believe that their nature is modified by higher H_2 pressures, because they depend only on the nature of the active site which is independent of the H_2 pressure; only the relative contribution of these different mechanisms will depend on H_2 pressure either because of kinetical parameters or because of a higher reduction state of the surface. In this study, these mechanisms are assumed to be true across the periodical table.

(*2*) *Apparatus*

A schematic design of the high-pressure micropilot is shown in Fig. 1. All pipes and equipment are stainless-steel 1200 bar proof, except the inside of the reactor which is made of a tube of copper welded inside a bigger stainless-steel tube. The gas flows are regulated at 0.1 N cc/min, the liquid feed at 1% of the selected flow, and the temperature of the oven at 0.5°C on the full range (room temperature to 600°C).

All the outlet gases are passed through a KOH water solution in order to destroy H_2S and dissolve most of the amines.

(*3*) *Operating Conditions*

The best operating conditions were selected by varying the following parameters independently on a classical $NiMo/Al_2O_3$ catalyst: mass of catalyst, temperature of reaction, gas flow rate, liquid feed flow rate, H_2S/H_2 ratio, and total reaction pressure. The *in situ* presulfidation step was chosen to reproduce the same results as those obtained for the HDS tests (*1*). The same batches of catalysts were also used.

Presulfiding step. The total volume ($\cong$60 cm^3) of the pilot is flashed with pure H_2 at atmospheric pressure and at room temperature for 15 min; then the gas is replaced by the mixture H_2S/H_2 (2%) at normal pressure, with a flow rate of 150 N cc/min. The temperature is raised to 450°C in ½ h, left 2 h, and then cooled in 1 h to room temperature. The flow is then strongly increased to 600 N cc/min; at the same time pyridine is introduced at 0.5 μl/min liquid, the adjustable leak is closed, and the temperature is raised to 340°C in 10 min, a pressure of 60 bar and a temperature of 340°C are reached.

Reaction step. The gas flow is then regulated at 100 N cc/min with 0.5% (or 5000 ppm) of H_2S; the pyridine flow at 1 μl/min and the adjustable leak are opened in order to admit 90 N cc/min. Because of the volume of the pilot between the reactor and the different chromatographs, each variation of pyridine flow is observed only by chromatography after 35 min; a perfect stationary flow is obtained, after 1½ h. Under these conditions, the pyridine partial pressure is 82.5 Torr. The pilot can run for weeks without intervention.

In order to keep the conversion sufficiently low to work in a differential system, the mass of the catalyst is used as variable parameter. Under these conditions all the catalysts were studied in a strictly equivalent situation of flow, temperature, and pressure. It was ensured that the system was differential and without diffusion phenomena. By variation of the gas flow and the mass of catalyst, strictly reproducible measures were found.

(*4*) *Catalysts*

An inactive ultrapure carbon (activated charcoal Fluka, ≈1100 m^2/g) was used as support for two reasons:

—one can expect a low HDN activity of such a support where the acidic functions of the usual alumina support are not as strong, although some weak activity was found for the HDN of piperidine which does not require a hydrogenating step;

—a high dispersion of the metallic sulfides has generally been found on this support as long as the metal concentration is kept below 1 wt%. The number of metal atoms per gram of catalyst is reported in each activity table.

A solution of a nitrate or an acetylacetonate salt of the studied metal was stirred in the presence of the support (0.2–0.5 mm) for 4 h at 100°C until the solvent (water or ethanol) had totally evaporated. Then the impregnated catalyst was dried at 120°C in air for 12 h. A complete description of these preparations was published in (*1*).

RESULTS

In Tables 1a–1d the different measures made on Zr, Nb, Mo, Ru, Rh, Pd, and Ag/C catalysts as a function of time are reported. After tests, we found that deactivation was very slow after 20 h and for many days; for this reason we stopped the reaction after 25 h. In Table 1c the measures made on a reference catalyst, $NiMo/Al_2O_3$ HR346 from Procatalyse, are reported.

The most striking results are shown in the different figures. The turnover numbers, the only way to compare the activities of the different catalysts, as a function of time are reported in Fig. 2.

The catalysts can be separated into three families according to their activity measured in molecule of pyridine transformed per atom of metal per hour (unit = h^{-1}). Ruthenium sulfide is a very active and stable catalyst (t.o. ≅ 16 h^{-1}). A second family contains Mo, Rh, and Pd sulfides. The principal characteristic of this family is a fairly high activity at the beginning of the reaction followed by a strong deactivation and a stable and important activity (t.o. ≅ 2.5–3.5 h^{-1}). The third family contains weak catalysts, Nb, Ag, Zr, and $NiMo/Al_2O_3$ sulfides. The characteristic of these catalysts is a strong deactivation at the beginning of the reaction, followed by a slight reactivation, followed by a steady and continuous deactivation. After a run of one day the activity lies between 0.3 and 0.7 h^{-1}. In conclusion, two orders of magnitude separate the most active from the least active catalyst for the

TABLE 1a

Pyridine HDN under 60 Bar (0.5% H_2S) on Zr/C (1.13%) and Nb/C (0.43%), Presulfided

Catalysts	Zr/C *m* = 0.1413 g				Nb/C *m* = 0.1009 g			
Nb of atoms/g	74.6×10^{18}				28.2×10^{18}			
Time (min)	140	250	360	1500	150	255	480	1330
Conversion (%)	0.72	0.49	0.62	0.66	0.97	0.84	1.08	0.47
r. (10^{-10} mole/g · s)	104.7	71.6	90.5	96.5	198.2	171.7	220.5	96.2
t.o. (h^{-1})	0.30	0.21	0.26	0.28	1.52	1.32	1.70	0.74
Pyr (%)	98.8	95.4	95.8	95.3	94.3	92.8	94.2	96.2
Pip	0.8	0.8	0.7	2.4	1.3	3.8	2.8	2.2
n-C_5 amines	0.4	3.9	3.5	1.9	4.3	3.5	3.0	1.5
α-Pic	—	—	—	0.6	—	—	—	—
Hydrocarbon (%)								
C_5	61.3	65.5	65.8	65.9	58.7	65.1	71.8	70.0
$C_4 + C_1$	2.5	2.8	7.2	0.5	1.2	1.3	1.5	0
$C_3 + C_2$	14.3	14.6	11.9	11.2	18.0	15.1	14.3	12.2
$C_3 + 2C_1$	—	—	—	—	—	—	—	—
$\frac{5}{2}C_2$	21.8	19.2	15.1	12.9	22.1	18.5	12.3	17.8
$5C_1$	—	—	—	9.5	—	—	—	—
C_6–C_1	—	—	—	—	—	—	—	—
C_5 sat./ΣC_5	37.6	53.7	57.1	58.0	62.3	60.2	58.4	76.3
C_5 cycl./ΣC_5	61.3	35.5	32.5	33.2	38.9	36.0	42.1	20.8
Σ cracking	38.6	34.5	34.2	34.1	41.3	34.9	28.2	30.0

TABLE 1b

Pyridine HDN under 60 Bar (0.5% H_2S) on Mo/C (0.79%) and Ru/C (0.36%), Presulfided

Catalysts	Mo/C *m* = 0.0680 g				Ru/C *m* = 0.0110 g		
Nb of atoms/g	49.6×10^{18}				21.7×10^{18}		
Time (min)	120	240	400	1100	130	240	1320
Conversion (%)	3.31	2.59	2.11	2.02	0.85	0.86	0.84
r. (10^{-10} mole/g · s)	979.2	773.2	630.5	606.7	1582.6	1605.3	1570.3
t.o. (h^{-1})	4.28	3.38	2.76	2.65	15.81	16.04	15.69
Pyr (%)	93.2	93.0	95.6	95.5	97.0	96.3	96.4
Pip	1.6	2.2	1.8	3.9	1.0	1.8	2.7
n-C_5 amines	5.2	3.6	2.5	0.5	2.0	1.9	0.9
α-Pic	—	—	—	—	—	—	—
Hydrocarbon (%)							
C_5	71.5	74.9	78.7	75.8	79.8	88.0	87.7
$C_4 + C_1$	2.5	1.9	1.6	2.0	0.9	0.5	0.5
$C_3 + C_2$	19.6	17.8	14.5	17.5	12.2	8.4	6.2
$C_3 + 2C_1$	—	—	—	—	—	—	—
$\frac{5}{2}C_2$	6.4	5.5	5.2	4.4	5.5	3.1	3.5
$5C_1$	—	—	—	—	—	—	—
C_6–C_1	—	—	—	0.4	1.7	—	2.1
C_5 sat./ΣC_5	72.1	77.1	71.8	73.3	73.3	85.7	85.8
C_5 cycl./ΣC_5	15.9	6.3	13.3	15.1	14.6	4.0	6.3
Σ cracking	28.5	25.1	21.3	23.8	18.5	12.0	10.2

TABLE 1c

Pyridine HDN under 60 Bar (0.5% H_2S) on Rh/C (0.77%) and Pd/C (0.87%) Presulfided

Catalysts	Rh/C m = 0.0200 g				Pd/C m = 0.0644 g			
Nb of atoms/g	45.4×10^{18}				49.3×10^{18}			
Time (min)	100	180	255	1285	140	260	470	1360
Conversion (%)	1.35	0.99	0.78	0.52	15.13	3.23	2.63	2.51
r. (10^{-10} mole/g · s)	1384.2	1017.1	802.3	536.0	4478.1	1018.8	834.7	796.5
t.o. (h^{-1})	6.6	4.8	3.8	2.5	20.1	4.4	3.6	3.5
Pyr (%)	97.9	97.3	93.4	96.0	91.6	87.7	92.6	92.8
Pip	0.4	0.6	5.2	3.5	1.1	3.1	2.4	2.5
n-C_5 amines	1.7	1.8	1.2	0.5	7.3	9.2	5.0	4.6
α-Pic	0.05	0.3	0.2	—	—	—	—	—
Hydrocarbons (%)								
C_5	76.3	77.4	79.6	88.4	16.0	55.8	55.6	72.2
$C_4 + C_1$	3.3	2.1	2.1	ε	0.7	1.6	1.6	0.5
$C_3 + C_2$	16.0	14.3	13.6	7.4	18.4	26.6	33.1	19.0
$C_3 + 2C_1$	—	—	—	—	63.7	—	—	—
$\frac{5}{2}C_2$	0.4	2.9	1.3	0.9	—	13.2	8.2	8.3
$5C_1$	—	—	—	—	—	—	—	—
C_6–C_1	4.1	3.3	3.4	3.2	1.2	2.7	1.5	—
C_5 sat./ΣC_5	63.5	53.6	56.3	68.3	39.4	49.6	57.3	68.0
C_5 cycl./ΣC_5	10.9	19.5	13.4	5.4	52.4	23.3	22.7	30.4
Σ cracking	19.6	19.3	17.0	8.4	82.8	41.5	42.9	27.8

TABLE 1d

Pyridine HDN under 60 Bar (0.5% H_2S) on Ag/C (0.72%) and NiMo/Al_2O_3 Procatalyse HR346, Presulfided

Catalysts	Ag/C m = 0.1948 g					NiMo/Al_2O_3 HR346 m = 0.0700 g				
Nb of atoms/g	40.2×10^{18}					508.6×10^{18} Mo. at./g				
Time (min)	140	240	370	490	1350	100	170	240	320	1260
Conversion (%)	5.89	1.30	2.06	1.67	0.80	6.01	3.27	3.93	3.79	2.16
r. (10^{-10} mole/g · s)	606.3	137.2	217.0	176.4	84.4	1719.6	949.1	1138.4	1097.4	632.6
t.o. (h^{-1})	3.2	0.7	1.1	0.9	0.4	0.7	0.4	0.4	0.4	0.2
Pyr (%)	95.7	94.2	92.2	92.4	94.3	79.1	85.3	83.7	81.8	92.5
Pip	0.5	1.3	2.9	3.0	3.1	18.9	9.8	13.6	15.6	7.2
n-C_5 amines	3.7	4.5	4.9	4.5	2.5	0.8	0.4	0.7	0.7	0.1
α-Pic	—	—	—	—	—	1.2	4.6	2.0	1.9	0.3
Hydrocarbons (%)										
C_5	12.7	60.7	59.6	65.2	72.3	90.6	75.3	88.3	89.5	86.0
$C_4 + C_1$	0.4	2.3	0.8	1.2	0.9	0.2	ε	ε	ε	0.8
$C_3 + C_2$	2.5	17.3	14.2	13.3	11.4	7.1	2.0	2.5	2.7	9.4
$C_3 + 2C_1$	—	—	—	—	—	—	—	—	—	—
$\frac{5}{2}C_2$	84.4	19.8	25.8	20.3	15.4	1.5	0.7	0.8	0.4	3.7
$5C_1$	—	—	—	—	—	0.6	22.0	8.3	7.4	—
C_6–C_1	—	—	—	—	—	—	—	—	—	—
C_5 sat./ΣC_5	40.1	61.1	65.5	69.6	64.9	77.3	72.3	75.0	77.8	62.4
C_5 cycl./ΣC_5	55.8	35.6	31.8	20.9	26.6	18.4	11.2	9.5	7.9	23.0
Σ cracking	87.3	39.3	40.8	34.8	27.7	9.4	24.7	11.7	10.5	14.0

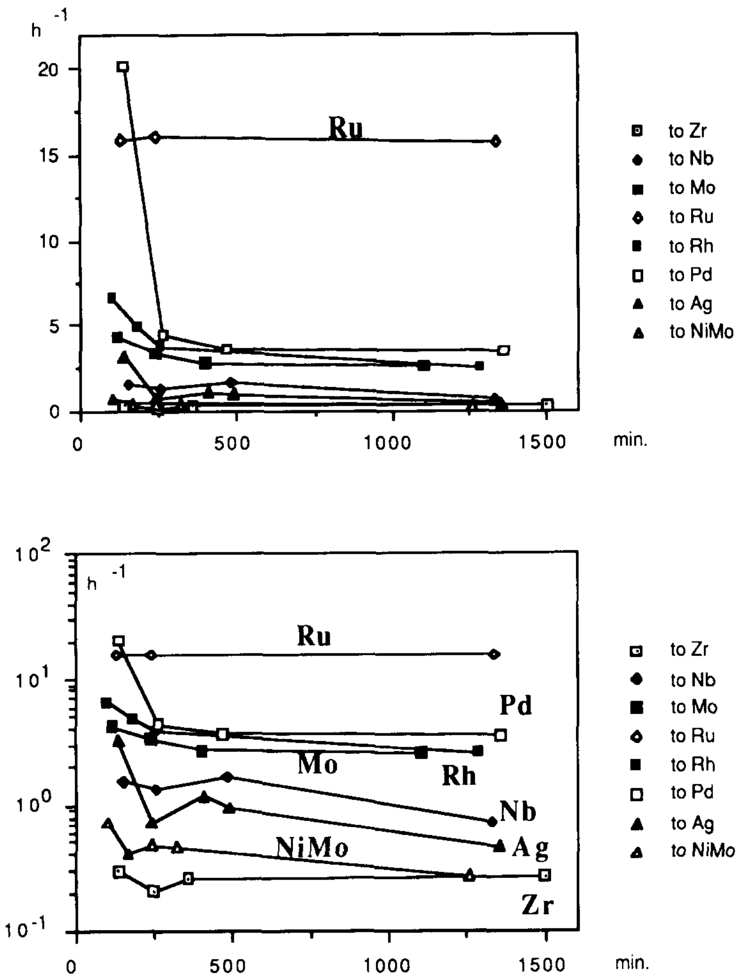

FIG. 2. Turnover numbers versus time.

HDN reaction while, for the same row, four orders of magnitude were observed for HDS. In addition, the best HDS catalyst was Rh sulfide, followed two orders below by, respectively, Ru, Pd, and Mo, three orders below by Nb and Zr, and four orders below by Ag sulfide. The NiMo catalyst was then equivalent in activity to the second catalyst, Ru sulfide.

DISCUSSION

If these results are in themselves important, it is interesting to try to understand them. The best approach is probably to make a detailed analysis of the selectivity in products which is permitted by our choice of experiment.

(i) It is interesting to note that, according to the mechanisms which have been detailed above, the Hoffmann elimination is almost exclusively responsible for the HDN reaction on this series of catalysts because the products obtained by metallic-type cracking (C_4 + C_1, C_3 + $2C_1$, and $5C_1$) are negligible. However three remarks must be made:

—C_4 + C_1, the products obtained by metallic cracking on small ensembles according to our preceding works (*8*), are always present at low concentrations, show-

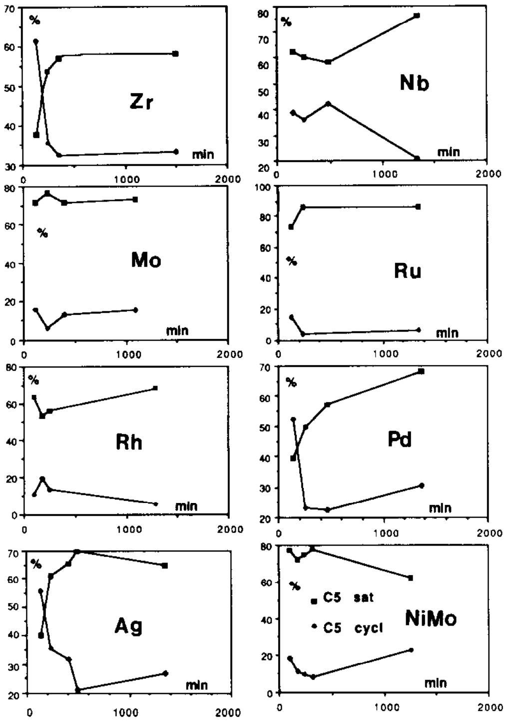

FIG. 3. Evolution of the saturated and cyclic C_5 hydrocarbons.

ing that at least small ensembles with metallic character are present on the surface of the catalysts. These ensembles are also responsible for the hydrogenation steps which are necessary for the Hoffmann elimination.

—The very strong activity of the Pd sulfide at the beginning of the reaction (higher than Ru sulfide), 20.19 h^{-1}, is due to a very selective metallic mechanism giving 63.7% of $C_3 + 2C_1$. Because of the absence of the other products given by the classical metallic cracking ($5C_1$ but especially $C_4 + C_1$), we believe that this transient state is probably due to selective cracking of the C_5 hydrocarbons by an unknown mechanism and for an unknown reason, probably a transient state of the surface. The C_5 products represent only 16.0% of the hydrocarbon C_5 equivalent distribution, which is totally exceptional for this kind of reaction.

—The NiMo/Al_2O_3 catalyst gives, before a total poisoning of this function after 21 h, a significant amount of $5C_1$, a product of an extensive metallic cracking, characteristic of the nickel metal (*8*). This is another argument in favor of the presence of Ni metal on the surface of NiMo sulfided catalysts, a question which has already been raised in preceding works (*9, 10*). This point and its consequences for explaining the better HDN activity of NiMo than that of CoMo will be published elsewhere.

In addition to the hydrocarbons' distribution, which corresponds exactly to that expected from a Hoffmann elimination mechanism detailed above, the perfect correlation between saturated C_5 hydrocarbons and cyclic C_5 hydrocarbons for all the studied catalysts is a second strong argument in favor of this mechanism. In Fig. 3, it can be observed that when "saturated C_5" increases, "cyclic C_5" always decreases and vice versa. Two exceptions are

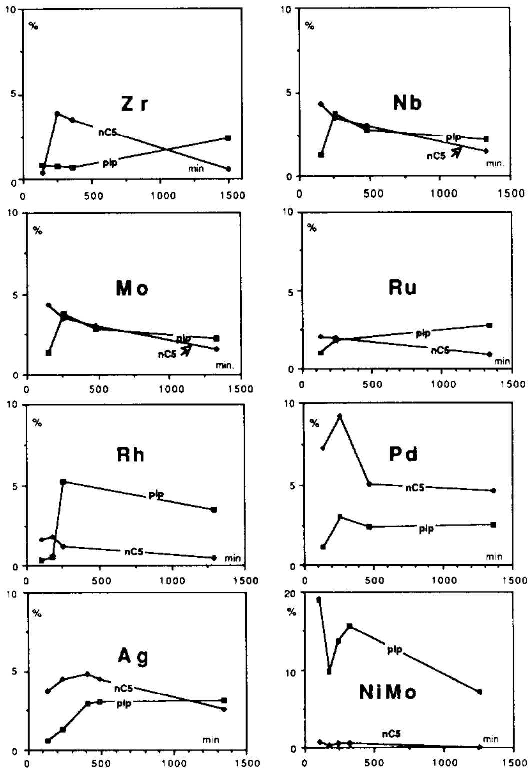

FIG. 4. Amine concentrations versus time.

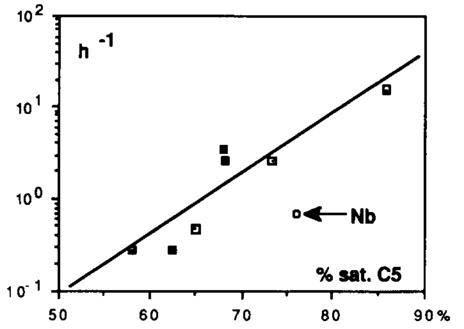

FIG. 5. Activity (h^{-1}) versus saturated C_5 hydrocarbon products.

the first measurements made on Nb and on NiMo, probably because the flow was not sufficiently stabilized.

(ii) Many authors have explained the HDN activity of different catalysts by using kinetical and thermodynamical arguments and principally by taking into account the concentrations of the different intermediate amines (α-picoline (as well as C_6 hydrocarbons) is a secondary product which holds no interest to this study). Figure 4 features three main facts showing that there is no correlation between activity and intermediate amine concentrations.

—Most of the catalysts, except NiMo, present about the same relative concentration of piperidine (≅3%) after 20 h of stabilization while the activities vary in two orders of magnitude. Piperidine also includes dihydro- and tetrahydropyridine.

—On the contrary, n-C_5 amine relative concentrations vary from 0.5 to 4.6% without any correlation with the activity.

—While the activity generally decreases regularly, the concentrations of the different amines pass through maxima. Even when the variation of activity is very small (Mo) or nil (Ru), important variations of the amine concentrations are observed.

With the exception of the NiMo catalyst, where the activity follows the piperidine concentration, the general trend over time on the other catalysts is an increase in or at least a stabilization of the piperidine concentration and a decrease of the n-C_5 amine concentration. The steady state in terms of amine concentrations is probably the result of a very complex equilibrium between the intervention of the gas phase (H_2S and thermodynamic constant) and the intervention of the support (a blank experiment on pure carbon with pyridine gives no activity and with piperidine a small formation of olefinic C_5 and C_{10} hydrocarbons due to acidic sites on the surface on the activated carbon (*5*, *6*)).

(iii) The only good correlations found between activity and selectivity are shown in Figs. 5 and 6.

Figure 5 shows that the higher the concentration of saturated products (n-pentane and cyclopentane) in the C_5 hydrocarbon fraction, the higher the HDN activity. The catalysts were compared after a run of 1500 min. This relation does not mean that the best catalysts (Ru, Pd, Rh, etc.) have a high activity in the hydrogenation of aromatic nitrogen compounds (here pyridine), but that they are efficient for the hydrogenation of unsaturated hydrocarbons. This ability has already been clearly reported by Boutarfa *et al.* (*11*) for bulk ruthenium sulfide. But, unfortunately, in this work, Ru was only compared to first and second row transition metal sulfides.

Thus, it seems that the consequence of this hydrogenation ability is the "cleaning" of the catalyst surface of unsaturated prod-

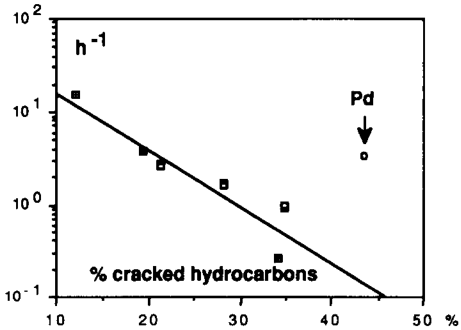

FIG. 6. Activity (h^{-1}) versus concentration of cracked hydrocarbon products.

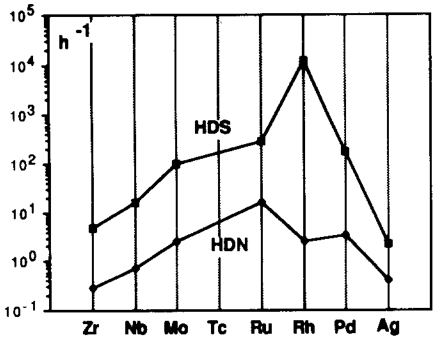

FIG. 7. Comparison of HDS and HDN activities at 350°C, 1 bar, and 340°C, 60 bar, respectively.

ucts which would be in competition for adsorption with the pyridine on potential hydrogenating sites.

Only niobium sulfide is outside this correlation with the second position for hydrogenation and a medium position for its activity (between the active group and the very low activity group). To explain this peculiar behavior, one can speculate that niobium sulfide (no indication of the structure or the stoichiometry of the present phase is available at this stage) possesses specific hydrogenating sites for unsaturated hydrocarbons which are not available for pyridine. Thus, there is no correlation between hydrogenation of hydrocarbons and HDN activity. It is very interesting to note that Vrinat *et al.* (*12*) have clearly shown that bulk niobium sulfide is a very good catalyst for the hydrogenation of biphenyl, toluene, and cyclohexene. The presence of specific sites (S_2^- pair) on NbS_3 was proposed to explain this high activity.

Figure 6 shows that the higher the relative amount (in equivalent C_5) of cracked hydrocarbons in the products, the lower the activity. This correlation was established for the catalysts after a run of 400 min because the poisoning is too severe after 1500 min for some of the sulfides and the correlation is less evident.

Most of these cracked products are given by the Hoffmann-type mechanism, $C_3 + C_2$ and $\frac{5}{2}C_2$. On some catalysts (Rh, Zr, Mo), the metallic-type mechanism of cracking, $C_4 + C_1$ on a small ensemble, is relatively important.

Thus it seems that the presence of these cracked molecules is the source of a significant poisoning of the surface, which would explain the poor HDN activity when the formation of cracked molecules is favored by the nature of the catalyst.

Palladium sulfide is an exception which confirms the rule. Pd sulfide is the best catalyst at the beginning of the run, much higher than even Ru sulfide. This activity is mainly due to a specific metallic-type cracking leading to 63.5% of $C_3 + 2C_1$, the total cracking amounting to 82.8%. It was then easy to predict, following the rule, that such a high cracking ability would lead to a strong and rapid deactivation; this deactivation was, of course, observed.

The next step is to find a structural or electronic explanation of these different behaviors, as done for HDS (*1*, *2*). Figure 7 shows a comparison of the HDS and HDN activities for the second row of the transition metal sulfides.

The trend is not very different, but the large difference in the position of the maximum excludes any similar conclusions. This difference is not surprising because the high HDS activity was mainly due to a specific structural behavior where, to be active, the sulfide ought to present sulfur vacancies leading to a gas–solid reaction where the solid catalyst was more than a catalyst, but itself a reactant. For a nitrogen atom, this type of reaction on a sulfide is not possible (a nitrogen atom cannot substitute a sulfur atom in the bulk) and one must rely only on the metallic and the acidic characters of the sulfides. The complete study of the first and third rows of transition metals (in progress) will probably answer this question.

Comparison with results published by Eijsbouts *et al.* (*13*) shows a great difference; first on the maximum position (Ru in our study, Rh in their study) and second on the scale of activity, for instance, between

Mo and Ru, they found a factor ≈1.6 where we found ≈6. If one excludes temporarily the effect of the high conversion on the measurement of the activity, this discrepancy can result from the choice of the test molecule (quinoline or pyridine) and from the fact that Eijsbouts *et al.* did not measure the cracked molecules which amounted to one-fifth or one-quarter of the reaction products.

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