Hydrodenitrogenation of pyridine over activated carbon-supported sulfided Mo and NiMo catalysts. Effects of hydrogen sulfide and oxidation of the support

A. Calafat [a,b], J. Laine [a] and A. López-Agudo [b]

[a] *Lab. Fisicoquímica de Superficies, Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 21827, Caracas 1020A, Venezuela*

[b] *Instituto de Catálisis y Petroleoquímica, Consejo Superior de Investigaciones Científicas, Campus Universidad Autónoma, Cantoblanco, 28049 Madrid, Spain*

Received 17 January 1996; accepted 1 May 1996

The hydrodenitrogenation (HDN) of pyridine over activated carbon-supported Mo and NiMo sulfided catalysts was studied. Without H_2S in the feed the catalysts showed a high conversion of pyridine and of piperidine to C_5 hydrocarbons at the beginning of reaction, followed by a strong deactivation. A large increase in the conversion of pyridine was observed when H_2S was added to the feed at $H_2S/H_2 \geqslant 0.006$. The conversion of piperidine to C_5 hydrocarbons was enhanced by H_2S and it increased as the H_2S pressure increases up to $H_2S/H_2 \geqslant 0.006$. The promotion effect of Ni was operative only when H_2S was present and it increased with the H_2S/H_2 ratio. Without H_2S, the degree of surface oxidation of the support affected the deactivation of the catalysts. When H_2S was added to the feed, the conversion of pyridine was stable and independent of the acid treatment of the support. A more oxidized support enhanced the C–N bond breaking reaction.

Keywords: HDN; carbon-supported catalysts; NiMo catalysts; sulfided catalysts

1. Introduction

Hydrodenitrogenation (HDN) processes convert the various nitrogen compounds contained in petroleum cuts to hydrocarbons and NH_3. Nitrogen removal from petroleum feed-stocks is necessary because, if not removed, it would be an important source of catalyst poisoning when petroleum distillates are processed.

Among the numerous catalytic systems investigated in hydrotreating, the most commonly used are the alumina-supported CoMo and NiMo sulfides [1,2]. Like for hydrodesulfuration (HDS), promising results have recently been obtained in improvement of catalysts for HDN with substitution of alumina support by activated carbon [3–6]. It is well known that, in addition to showing improved coking resistance, carbon-supported Mo and Ni(Co)Mo sulfides are more active HDS and HDN catalysts than the corresponding alumina-supported sulfides. However, one of the main industrial uncertainties for the use of carbon-supported catalysts is their long-term stability.

The data on HDN over carbon-supported catalysts are scarce regarding the effect of H_2S, the promotion effect of Ni (Co) and the effect of the surface properties of the carbon support on the catalyst activity and the product distribution. The effect of H_2S has been extensively studied for alumina-supported catalysts [7–11]. It is well known that H_2S affects very strongly the product distribution in HDN [8,9,11], but there are discrepancies about the effect of the H_2S on the catalyst activity [7,8]. On the other hand, almost all previous data on synergism in HDN concern also alumina-supported catalysts [12–16]. No effect or even a negative one has been reported by some authors for sulfided CoMo and NiMo catalysts [13,15,16]. On carbon-supported systems synergism was not found, the Mo/C catalyst being the most convenient for HDN [6,17]. Finally, there have been several attempts to relate the surface properties of the carbon support with the HDS activity [18–20]. However, to our best knowledge, no previous data are available in the literature in this respect for the HDN reaction.

Within the above scope, the purpose of the present communication is to study the pyridine HDN reaction over carbon-supported Mo and NiMo catalysts, focussing on the effects of H_2S and the surface nature of the support.

2. Experimental

For the present study, a commercial activated carbon (Merck, 917 $m^2\,g^{-1}$, 1 wt% ash) was oxidized by treatment with boiling aqueous HNO_3 solutions at different concentrations (0.0, 1.0 and 6.0 M) for 8 h, followed by extensive washing with distilled water. The texture of the original Merck activated carbon (denoted as M-0) and its derivatives (denoted as M-1 and M-6) were characterized by N_2 adsorption at 77 K using a Micromeritic ASAP 2000 apparatus. Their acidity and the strength of

Table 1
Characterization of the activated carbon treated with HNO_3

Support	Treatment HNO_3 solution	S_{BET} ($m^2 g^{-1}$)	Acidity (meq n-$C_4H_9NH_2$ (0.1 N) g^{-1})	Acid strength E_0 [a] (mV)
M-0	non-treated	917	1.7	−55 (w)
M-1	1 M	812	2.1	203 (vs)
M-6	6 M	710	3.6	200 (vs)

[a] Initial electrode potential; w = weak, vs = very strong.

the acid sites were measured by titrating a suspension of the activated carbon in acetonitrile with 0.1 N n-butylamine using a CRISON-Microph 2001 pH meter. The corresponding data are shown in table 1, where a decrease in surface area and a considerable increase in the number of acid sites and acid strength of the activated carbon surface is observed as the concentration of the acid solutions increases.

The resulting supports were used to prepare the supported Mo and NiMo catalysts by incipient wetness impregnation using ammonium heptamolybdate and/or nickel nitrate solution. Molybdenum was first impregnated for the bimetallic catalysts. The nominal compositions of the catalysts were 10 wt% MoO_3 for the Mo/C catalysts, and 3 wt% NiO and 10 wt% MoO_3 for the NiMo/C samples.

The pyridine HDN activity was measured using a stainless steel fixed-bed type reactor connected to a flow system at 30 bar and 350°C. Catalyst samples (0.20 g) were sulfided in situ by a mixture of H_2S/H_2 (1/10) for 2 h at 400°C. A solution of 7 wt% of pyridine in cyclohexane was introduced into the reaction system by means of a liquid pump at a rate of 12 ml min^{-1}. When necessary, CS_2 was added to the liquid reactant to generate H_2S in the reaction system (molar H_2S/H_2 ratio between 0.001 and 0.028). The reaction products were collected at the end of the reactor and analyzed by gas chromatography. Conversions measured every 30 min were used to calculate the pyridine conversion per mole of metal, expressed in moles of pyridine converted per mole Me (Me = Mo or Mo + Ni) per second. When necessary (see below), the activity was normalized by the surface area of the support and, therefore, expressed in moles of pyridine converted per square nanometer of support surface area per atom of Me per second.

3. Results and discussion

3.1. HDN of pyridine

Fig. 1 shows the results of the HDN of pyridine without H_2S in the feed for Mo and NiMo catalysts supported on activated carbon (M-0) as a function of reaction time. These catalysts show a high conversion of pyridine at 60 min of reaction (time when the first product sample is taken), followed by a strong deactivation. It is also seen that the decrease in the hydrogenation of pyridine is parallel with an increase of the piperidine to C_5 ratio (Pip/C_5), indicating that the ability of the catalysts for the denitrogenation reaction (conversion of piperidine to C_5 hydrocarbons) is relatively more inhibited than the hydrogenation of pyridine during the reaction. The decrease in the production of C_5 hydrocarbons could be related with the desulfuration of the catalysts during reaction, which could not be resulfided by the reactant as in the HDS reaction. This desulfuration eliminates Brønsted acid sites for the C–N bond cleavage [7], affecting the denitrogenation capacity of the catalysts. By contrast, it could be expected that desulfuration of the catalyst might not affect the hydrogenation of pyridine, since this reaction takes place over the sulfur vacancies [7] generated during the reaction. However, the conversion of pyridine clearly decreases with reaction time (fig. 1). The inhibition of the conversion of pyridine observed could also be explained as due to catalyst desulfuration if it is assumed, as it has been done before [8], that the hydrogen necessary for the hydrogenation

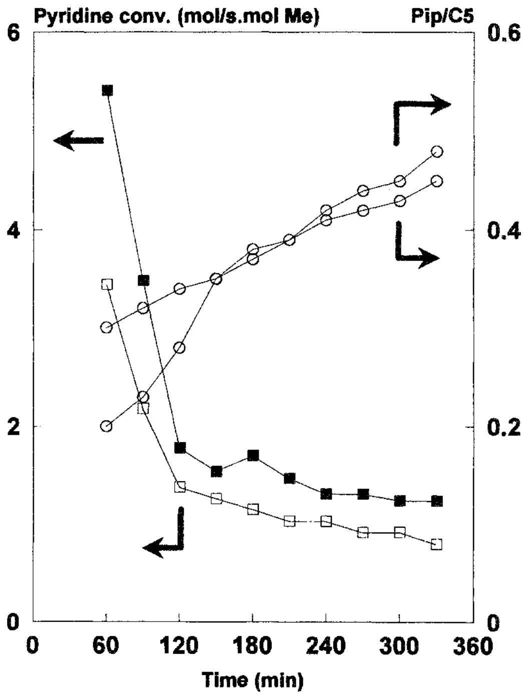

Fig. 1. Pyridine conversion and piperidine to C_5 molar ratio (Pip/C_5) versus reaction time for the HDN reaction over carbon-supported Mo (empty symbols) and NiMo (filled symbols) catalysts. Reaction conditions: support: M-0; $P = 30$ bar; $T = 350°C$; $W/F_{Pyr} = 13$ g mol^{-1} h^{-1}.

reaction does not adsorb on the same site where the nitrogen compound does. It has been reported that hydrogen may be dissociatively bound to SH groups [1,10] which serve as hydrogen donors while they impart Brønsted acidity to the catalyst surface for the C–N bond breaking reaction [21]. Thus, catalysts desulfuration would also affect the surface concentration of sites for hydrogen activation, rendering the hydrogenation of pyridine less favorable.

The higher pyridine conversion of the NiMo catalyst compared to the Mo (fig. 1) shows that the promotion effect of Ni on Mo/C catalyst in the HDN of pyridine, when H_2S is not added with the reactants, occurs significantly only at the beginning of the reaction. Furthermore, it is clear that at the first hour of reaction Ni promotes the conversion of piperidine to C_5 hydrocarbons, indicated by a lower Pip/C_5 ratio. As the reaction continues, this ratio becomes similar to those observed for the unpromoted Mo catalyst. Therefore, Ni does promote the hydrogenation of pyridine to piperidine at any stage of the reaction, but thereafter the conversion of piperidine to C_5 hydrocarbons is almost blocked.

The nonexistence of Ni promotion on Mo for the HDN reaction, without H_2S in the feed, has been noticed before for NiMo/Al_2O_3 catalysts [11]. In the present carbon supported catalysts, it could be assigned to variations in the sulfuration degree of the catalyst. If the synergistic phase for HDN is the same NiMoS pseudophase identified for the HDS reaction, the desulfuration of the catalysts will affect the concentration of this phase on the surface and, therefore, the promoting effect of Ni on the C–N bond cleavage capability of the Mo catalyst. This is reflected in the present NiMo catalyst by a sharp increase of the Pip/C_5 ratio as the reaction, and therefore the desulfuration of the surface, takes place (fig. 1).

3.2. Influence of H_2S

Fig. 2 shows the variation of the pyridine conversion of the carbon (M-0) supported Mo and NiMo catalysts with reaction time at different concentrations of H_2S in the reaction feed. The effect of H_2S concentration on pyridine conversion is shown in fig. 3. As it was mentioned above, the catalysts show a high conversion of pyridine at the beginning of the reaction, when H_2S is not present in the feed, followed by a strong deactivation due to desulfuration of the catalysts. For both the Mo and NiMo catalysts, low concentrations of H_2S in the feed (H_2S/H_2 between 0.001 and 0.002) do not affect the total conversion of pyridine. This result is not consistent with those commonly observed in the literature [1,7,11] where a slight reduction in the hydrogenation rates in the presence of H_2S was observed and assigned to the transformation of sulfur anion vacancies (hydrogenation sites) into acid (C–N bond breaking) sites on the catalyst surface. However, the data in

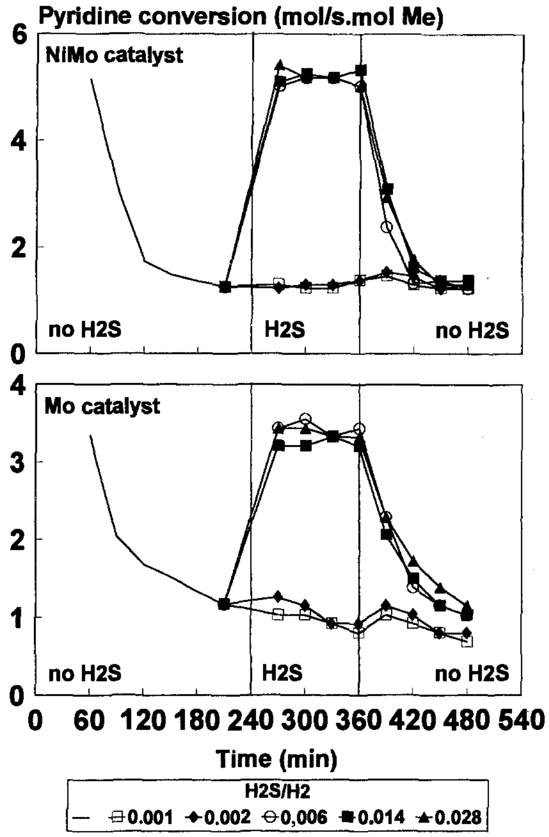

Fig. 2. Variation of the pyridine conversion of the carbon-supported Mo and NiMo catalysts with reaction time at different concentrations of H_2S in the reaction feed. Reaction conditions as in fig. 1.

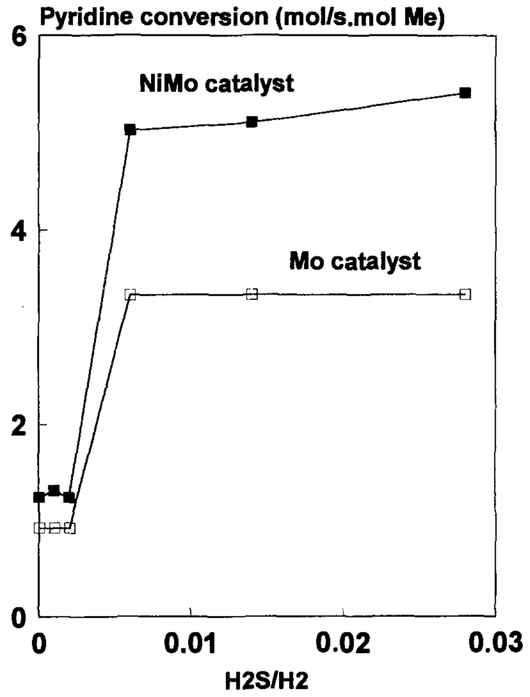

Fig. 3. Effect of the H_2S/H_2 ratio on the pyridine conversion over carbon-supported Mo and NiMo catalysts. Reaction conditions as in fig. 1.

figs. 2 and 3 agree with the results of Hanlon [8], who showed that the hydrogenation of pyridine to piperidine over a commercial NiMo/Al_2O_3 catalyst was unaffected by the partial pressure of H_2S. Also, van Gestel et al. [10,22] reported that in the HDN of 2,6-dimethylaniline over CoMo/Al_2O_3 and NiMo/Al_2O_3 the catalysts maintain high activities at high H_2S levels in the feed, indicating that the model compound still interacts with the surface of the catalysts, on sites different from sulfur vacancies.

A strong effect on the conversion of pyridine is observed at a H_2S/H_2 ratio of 0.006 (figs. 2 and 3). The conversion of pyridine rapidly increases and reaches the initial value obtained for the reaction when H_2S is not present in the feed (fig. 2). This conversion is stable until the addition of H_2S is stopped, and a strong deactivation of the catalysts is again observed. Higher H_2S/H_2 ratios do not affect the conversion of pyridine. It seems to be clear that the increased conversion of pyridine at a certain H_2S/H_2 ratio could be related to resulfuration of the catalyst surface. As we mentioned above, a certain degree of sulfuration of the catalyst is necessary for high conversion of pyridine, since sulfur sites could serve as hydrogen donors for the hydrogenation reaction. In the present case, the constant activity observed at H_2S/H_2 higher than 0.006 suggests that this ratio is sufficient to accomplish totally the resulfuration of the catalyst surface.

Fig. 4 shows the variation of the Pip/C_5 ratio for the carbon (M-0) supported Mo and NiMo catalysts with reaction time at different concentrations of H_2S in the reaction feed. The effect of H_2S concentration on the Pip/C_5 ratio is shown in fig. 5. Due to desulfuration of the catalysts, the Pip/C_5 increases with reaction time when H_2S is not present in the feed. As the H_2S pressure increases up to a H_2S/H_2 ratio equal to 0.006, the Pip/C_5 ratio decreases. At higher ratios, the conversion of piperidine to C_5 is constant. This result is consistent with those reported by others [8,9,11]. Hanlon [8] suggested that a surface acidic species, □–S, play an active role in the C–N bond breaking reaction. This species, proposed to be of the form NiMoS in the bimetallic catalysts, is formed from an equilibrium reaction between H_2S, H_2 and the catalyst surface,

$$H_2S + \square \rightleftharpoons \square{-}S + H_2$$

Notice that the NiMoS pseudophase, the possible synergistic structure in HDN as well as in HDS, is favored by high pressures of H_2S. This is consistent as compared the denitrogenation abilities of NiMo and Mo catalysts reported in fig. 5. It could be observed that the promotion effect of Ni continues to be operative only when H_2S is present and it increases with the H_2S/H_2 ratio (figs. 4 and 5). As mentioned before, when H_2S is not present in the catalytic system, desulfuration of the NiMo catalysts affects the concentration of this phase on the surface and Ni promotion is no longer observed.

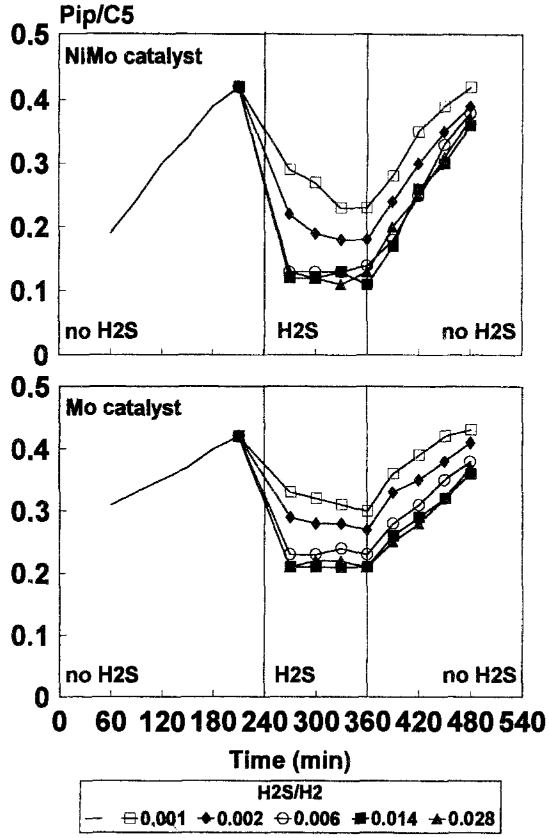

Fig. 4. Variation of the Pip/C_5 ratio of the carbon-supported Mo and NiMo catalysts with reaction time at different concentrations of H_2S in the reaction feed. Reaction conditions as in fig. 1.

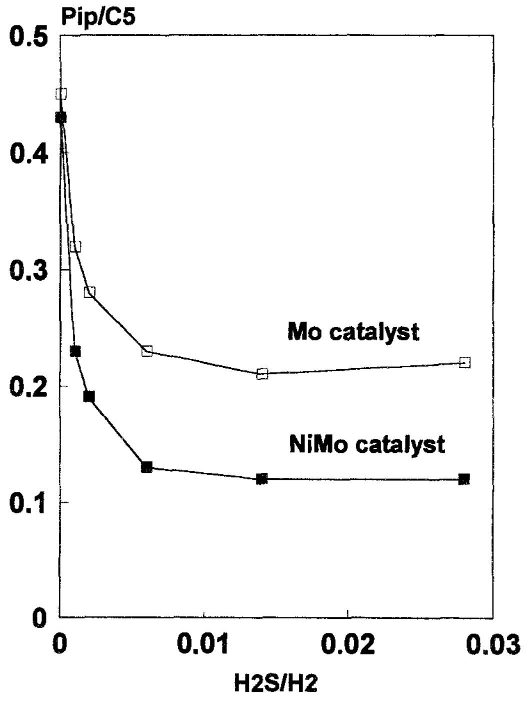

Fig. 5. Effect of the H_2S/H_2 ratio on the Pip/C_5 ratio for carbon supported Mo and NiMo catalysts. Reaction conditions as in fig. 1.

3.3. Effect of surface oxidation of the carbon support

Fig. 6 shows the effect of surface oxidation of the carbon support on the HDN of pyridine in the absence and presence of H_2S in the feed, for NiMo catalysts. For all the carbon supports studied, the conversion of pyridine is almost the same at the beginning of the reaction (fig. 6A). As it was shown above, a deactivation of the catalysts is observed as the reaction continues. This deactivation is more pronounced when the activated carbon support has been oxidized by HNO_3. On the other hand, the Pip/C_5 ratio is lower for the acid-treated supports than for the untreated activated carbon at any stage of the reaction (fig. 6B), indicating that the acidity of the activated carbon surface favors the C–N bond breaking reaction.

As suggested by TPR results over the same sulfided catalysts [22], a more reactive sulfided phase toward hydrogen would indicate a higher desulfuration rate of the catalyst during reaction. As it has been suggested above, excessive desulfuration seems to be responsible for the decrease in the conversion of pyridine, which explains that on a more reactive sulfided phase the deactivation of the catalysts is more pronounced than on that obtained over a non-treated support. These observations fit quite well with the results presented in fig. 6A, when H_2S is absent. Notice that when H_2S is added to the feed and the catalysts are probably completely sulfided, the conversion of pyridine is, however, stable and almost independent of the acid treatment of the activated carbon.

However, if the desulfuration rate of the catalyst is favored over the treated activated carbons, it might be expected that over these supports, as the reaction continues, the Pip/C_5 ratio would become higher than that obtained for the untreated support, since the acidic sulfur sites which are needed for the C–N bond breaking reaction are easily removed. This is not the case over the present NiMo catalysts since the Pip/C_5 ratio is lower (fig. 6B). Although a deactivation of the catalysts is observed due to desulfuration, the denitrogenation reaction is still favored for the acid-treated activated carbons, suggesting that a more oxidized support increases the acid strength of the catalyst upon sulfuration and, therefore, the intrinsic activity of those sites where the reaction takes place. Consistent with this, when H_2S ($H_2S/H_2 = 0.006$) is present, the Pip/C_5 ratio decreases due to resulfuration and formation of acid sites associated with the MoS phase which favors the C–N bond cleavage reaction, but the effect due to oxidation of the support is still observed. This latter effect suggests, therefore, that the acidic sites associated to the support may also participate in the denitrogenation reaction.

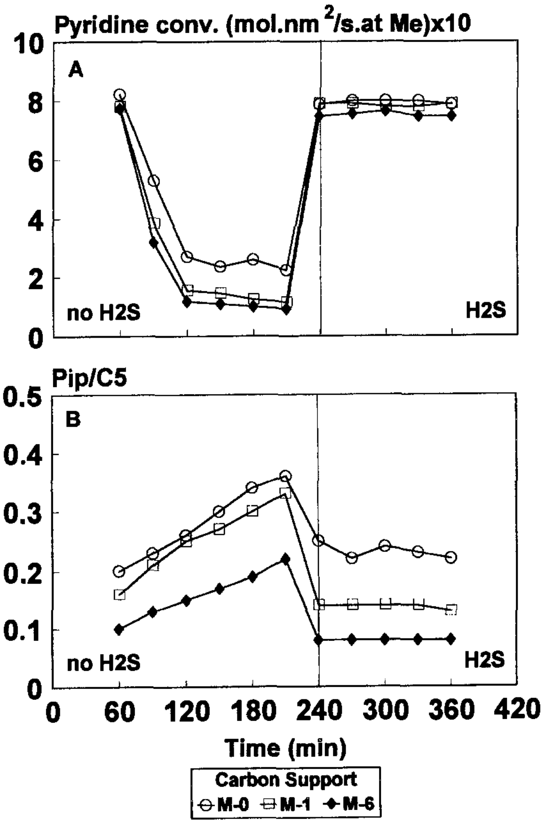

Fig. 6. Effect of the acid treatment of the carbon support on (A) pyridine conversion and (B) Pip/C_5 ratio for NiMo catalysts, in the absence and presence of H_2S ($H_2S/H_2 = 0.006$) in the reaction feed.

4. Conclusions

The present Mo and NiMo catalysts showed a high conversion of pyridine, as well as a high conversion of piperidine to C_5 hydrocarbons at the beginning of reaction, followed by a strong deactivation. The decrease in both hydrogenation and hydrogenolysis reactions is related to the desulfuration of the catalysts, which could not be resulfided by the feed.

The desulfuration of the catalysts also affects the promotion effect of Ni on the C–N bond breaking capability of the NiMo catalyst, which is only observed at the beginning of the reaction. As the reaction continues, the Pip/C_5 ratio for the NiMo catalyst is similar to that observed for the unpromoted Mo catalyst.

High concentrations of H_2S in the feed enhance the conversion of pyridine and of the piperidine to C_5 hydrocarbons. The promotion effect of Ni continues to be operative only when H_2S is present and it increases with the H_2S/H_2 ratio.

Even if the conversion of pyridine for all the NiMo catalysts studied is the same at the beginning of the reaction, surface oxidation of the carbon support affects the deactivation of the catalysts that follows, being more pronounced when the activated carbon has been treated with HNO_3. When H_2S is added to the feed, the conversion of pyridine is stable and independent of the acid treatment of the activated carbon.

A more oxidized support increases the acid strength of the catalyst upon sulfuration and, therefore, the intrinsic activity of those sites where the denitrogenation reaction takes place. This effect is observed despite the presence or not of H_2S in the feed, suggesting that the acidic sites associated to the support may also participate in the denitrogenation reaction.

Acknowledgement

This research was partially supported by the Proyecto CE93-0012 DGICYT (Spain). Financial support from the Venezuelan Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT) and The Gran Mariscal de Ayacucho Foundation (Fundayacucho) for a grant to AC is gratefully acknowledged.

References

[1] G.C. Hadjiloizou, J.B. Butt and J.S. Dranoff, Ind. Eng. Chem. Res. 31 (1992) 2503.
[2] M.J. Girgis and B.C. Gates, Ind. Eng. Chem. Res. 30 (1991) 2021.
[3] C.K. Groot, V.H.J. de Beer, R. Prins, M. Stolarski and W.S. Niedzwiedz, Ing. Eng. Chem. Prod. Res. Dev. 25 (1986) 522.
[4] Z. Vit and M. Zdrazil, J. Catal. 119 (1989) 1.
[5] E. Hillerova, Z. Vit, M. Zdrazil, S.A. Shkuropat, E.N. Bogdanets and A.N. Startsev, Appl. Catal. 67 (1991) 231.
[6] Z. Vit, Catal. Lett. 13 (1992) 131.
[7] S.H. Yang and C.N. Satterfield, Ind. Eng. Chem. Proc. Des. Dev. 23 (1984) 20.
[8] R.T. Hanlon, Energy Fuels 1 (1987) 424.
[9] L. Vivier, P. D'Arujo, S. Kasztelan and G. Pérot, Bull. Soc. Chim. Belg. 100 (1991) 807.
[10] J. van Gestel, J. Leglise and J.C. Duchet, Appl. Catal. 92 (1992) 143.
[11] M. Jian, J.L. Rico Cerda and R. Prins, Bull. Soc. Chim. Belg. 104 (1995) 225.
[12] W. Ripperger and W. Saum, J. Less Common Met. 54 (1977) 353.
[13] M.J. Ledoux, G. Agostini, R. Benazouz and O. Michaux, Bull. Soc. Chim. Belg. 93 (1984) 635.
[14] R.E. Tischer, N.K. Narain, G.J. Stiegel and D.L. Cillo, Prepr. Am. Chem. Soc. Div. Petrol. Chem. 30 (1985) 459.
[15] S. Mendioroz, J.M. Palacios, J.L.G. Fierro and A. Lopez Agudo, Bull. Soc. Chim. Belg. 96 (1987) 891.
[16] M.M.R. de Agudelo and A. Morales, in: *Proc. 9th Int. Congr. on Catalysis*, Vol. 1, eds. M.J. Phillips and M. Ternan (The Chemical Institute of Canada, Ottawa, 1988) p. 42.
[17] J. Sobczak, Z. Vit and M. Zdrazil, Appl. Catal. 45 (1988) L23.
[18] J.M. Solar, C.A. Leon y Leon, K. Osseo-Asare and L.R. Radovic, Carbon 28 (1990) 369.
[19] J.M. Solar, F.J. Derbyshire, V.H.J. de Beer and L.R. Radovic, J. Catal. 129 (1991) 330.
[20] A. Calafat, J. Laine and A. Lopez Agudo, Proc. 14th North Am. Meet. Catal. Soc., Poster Session A, Utah 1995, p. 144.
[21] S.H. Yang and C.N. Satterfield, J. Catal 81 (1983) 168.
[22] A. Calafat, J. Laine, A. López-Agudo and J.M. Palacios, submitted.