

SYNERGISM BETWEEN Ni AND W IN THE Ni-W/C SULFIDE CATALYST IN HYDRODENITROGENATION OF PYRIDINE AND HYDRODESULFURIZATION OF THIOPHENE

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Parallel hydrodenitrogenation (HDN) of pyridine and hydrodesulfurization (HDS) of thiophene was studied over active-carbon-supported Ni, W, and Ni-W sulfide catalysts at 2 MPa and at 280 and 320 °C. Synergism between Ni and W was observed both in HDN and HDS reactions: the activity of the Ni-W catalyst was higher than the sum of the activities of the Ni and W catalysts. However, the synergistic increase in activity was much higher in HDS than in HDN. This led to a characteristic shift in the HDN/HDS selectivity, which was strongly shifted to the HDS side over the Ni-W catalysts as compared with the Ni and W catalysts. HDS was faster than HDN over the Ni-W catalyst, the rate of both reactions being about the same over the Ni catalyst and HDN being faster than HDS over the W catalyst. The selectivity of all the catalysts was shifted to the HDN side with decreasing temperature. The data are a new example for generalisation of the rule that the synergism in activity of bimetallic sulfide Co-Mo, Ni-Mo, and Ni-W catalysts is higher in HDS than in hydrogenation and HDN.

Key words: Hydrodenitrogenation; Hydrodesulfurization; Ni-W sulfide catalyst; Heterogeneous catalysis; Nickel; Tungsten; Hydrogenation.

Various hydrotreatment processes using bimetallic Co-Mo, Ni-Mo, or Ni-W sulfide catalysts are widely used in the production of liquid fuels, lubricating oils and feeds for petrochemistry. A phenomenon of key importance in the hydrotreatment catalysis is the synergistic effect between the two metal sulfides in bimetallic sulfide catalysts: the activity of Co-Mo, Ni-Mo, and Ni-W catalysts is much higher than the sum of activities of their Co, Ni, Mo, and W components. Data and theories of this synergism have been summarized in many reviews, *e.g.* in refs¹⁻⁵.

Most of the relevant literature was devoted to identification of surface sites or phases responsible for synergism and hence the structure of the synergistic catalysts is relatively well understood now. The discussion of this

structure is outside the context of the present contribution. On the other hand, the mechanism of the synergistic effect is much less understood.

An interesting phenomenon related to the mechanism of synergism is that the magnitude of synergism (the ratio of the activity of a bimetallic sulfide system to the sum of activities of the corresponding monometallic sulfide catalysts) is not the same for all reactions involved in hydro-treatment.

For instance, the magnitude of synergism in hydrogenolysis of C-S bonds is always higher than in hydrogenation. As a result, the rate ratio hydrogenolysis of C-S bond/hydrogenation is always much higher over bimetallic synergistic systems Co(Ni)-Mo(W) than over the corresponding monometallic Co, Ni, Mo, and W catalysts. This general rule holds for all combinations Co(Ni)-Mo(W) as indicated by numerous data on the formation of various intermediates in hydrodesulfurization (HDS) and on parallel hydrogenation and HDS (refs⁶⁻⁸).

A second example of unequal magnitude of synergism in various reactions is provided by the fact that the magnitude of synergism seems to be systematically higher in HDS than in HDN. The result is that the rate ratio HDN/HDS (*i.e.* the HDN/HDS selectivity) is much lower over bimetallic synergistic systems than over the corresponding monometallic sulfide catalysts. However, the available literature data are rather limited and all concern Mo-based catalysts only. The HDN/HDS selectivity in a parallel reactions of pyridine and thiophene with a Ni-Mo/C catalyst was much lower than the selectivities of the corresponding Ni/C and Mo/C samples⁹. The HDN/HDS selectivities of Co-Mo/Al₂O₃, Ni-Mo/Al₂O₃, Co-Mo/C, and Ni-Mo/C catalysts were much lower than the selectivities of the corresponding Mo/Al₂O₃ and Mo/C samples. However, data for the corresponding Co/Al₂O₃, Ni/Al₂O₃, Co/C and Ni/C catalysts were not given¹⁰.

The purpose of the present work is to find out whether the higher magnitude of synergism in HDS than in HDN observed for Mo-based systems is also exhibited by the W-based catalysts. No relevant literature data on the subject (*i.e.*, HDN and HDS data for all three catalysts Ni, W, and Ni-W under the same conditions) are available.

The above mentioned rules on the relative magnitude of synergism in various hydrotreatment reactions hold independently of the type of catalyst support⁶⁻¹⁰. From this point of view, any support is in principle suitable for the purpose of the present work. However, the use of alumina, a conventional support, is disadvantageous. The Ni/Al₂O₃ catalyst is known to possess a very low activity as compared with activities of W/Al₂O₃ and

Ni-W/Al₂O₃ and this makes a comparison of all three catalysts at the same temperature rather difficult. A carbon support was selected in the present work because the activity of the Ni/C catalyst is not so different from the activities of the W/C and Ni-W/C samples. An another argument for using carbon support is that tungsten is very difficult to sulfide when supported on alumina (*i.e.* ref.¹¹), but not on carbon. The model reactions were HDS of thiophene and HDN of pyridine.

EXPERIMENTAL

Catalysts

The active carbon used was a commercial product (GA-05, Slovenské Lučobné závody, Hnúšťa, Slovakia) with a BET surface area of 1 100 m² g⁻¹, a pore volume 0.75 cm³ g⁻¹, and a micropore volume of 0.35 cm³ g⁻¹. It was crushed and sieved to the particle size fraction 0.16–0.32 mm, purified successively by refluxing several times with water, ethanol, and butanol, heating with dimethyl sulfoxide at 100 °C, washing several times with cold water, refluxing several times with water and dried in a vacuum rotary evaporator before impregnation.

The W/C, Ni/C, and Ni-W/C catalysts contained 21.5 wt.% WO₃, 7 wt.% NiO, and 21.5 wt.% WO₃ and 3 wt.% NiO (based on the weight of the catalyst), respectively. Their molar composition was 0.93 mmol WO₃, 0.93 mmol NiO, and 0.93 mmol WO₃ and 0.4 mmol NiO per gram of catalyst, respectively. The content of NiO in the monometallic Ni/C was higher than in the bimetallic Ni-W/C catalyst for activity reasons: the conversions achievable with the 3 wt.% NiO/C catalyst were limited by the catalyst bed volume available in the reactor used. It was established in the low conversion region that the activity of the Ni/C catalyst was proportional to the NiO loading. The measurement with 7 wt.% NiO/C catalyst allowed to obtain data in a broader range of conversions. It was assumed that the HDN/HDS selectivity of the Ni/C catalyst is essentially independent of loading. (This assumption is supported by our unpublished results that selectivity in the hydrotreatment over monometallic sulfide catalysts is insensitive to loading.)

The W/C, Ni/C, and Ni-W/C catalysts were prepared by conventional impregnation with ammonium paratungstate, nickel nitrate, and successive impregnation with ammonium paratungstate and nickel nitrate, respectively. The catalysts were dried in a rotary vacuum evaporator at 100 °C and were not calcined. They were presulfided *in situ* as described below.

Apparatus

Data were obtained in a tubular flow reactor (stainless steel, i.d. 2 or 4 mm, depending on catalyst charge) with a fixed catalyst bed and with all reactants in the gas phase. Catalyst charge, *W*, was varied in the range 0.01–1 g; the feed rates, *F_p*, of hydrogen, thiophene (TH), and pyridine (PY) were 400, 0.09, and 0.08 mmol h⁻¹, respectively. The feed was generated in a simple evaporator (not bubble saturator) where stream of hydrogen passed over a liquid mixture of TH and PY. Composition at the inlet and outlet of the reactor was analysed using an on line gas chromatograph (122 °C, glass column, 2.5 m, 3 mm i.d., packed with 60/80

mesh Carbowax 20 M/0.8% KOH, Supelco). The products of the TH reaction were C_4 hydrocarbons (C4); other carbon-containing products were negligible. The products of the PY reaction were C_5 hydrocarbons (C5), piperidine (PI), and pentylamine (PA). The amount of PA was always much lower than that of PI. These intermediate saturated amines (PI and PA) are together named SA. Pentylpiperidine, which was found as an intermediate during the reaction of pyridine in the absence of sulfur in the feed¹² was not found in our case. Products H_2S and NH_3 were not analyzed.

Procedure

Catalysts were presulfided *in situ* at atmospheric pressure with a H_2S/H_2 mixture (1 : 10) at 400 °C for 2 h. Feed rates F_i were the same in all experiments and space time W/F was changed by variation of the catalyst charge W . The run at each space time value was performed with a fresh catalyst charge.

The composition of the reaction mixture was expressed in mole fractions, a_i ; $a_{TH} = n_{TH}/n_{TH}^0$, $a_{PY} = n_{PY}/n_{PY}^0$, $a_{SA} = n_{SA}/n_{PY}^0$, and $a_{C5} = n_{C5}/n_{PY}^0$, where n_i^0 and n_i are the initial and final number of moles, respectively. The mole fractions are related to the conversions: $x_{TH} = 1 - a_{TH}$, $x_{PY} = 1 - a_{PY}$, $x_{SA} = a_{SA}$, and $x_{C5} = a_{C5}$, where x_{TH} is the conversion of TH, x_{PY} is the overall conversion of PY, x_{SA} is the conversion of PY to SA, and x_{C5} is the conversion of PY to C5.

RESULTS AND DISCUSSION

Kinetics

The result of the measurement was the dependence of the reaction mixture composition a_i on space time W/F (a_{TH} on W/F_{TH} and a_{PY} , a_{SA} , and a_{C5} on W/F_{PY}) at two temperatures for each catalyst. The data obtained at 320 °C are shown in Fig. 1. The features of the data obtained at 280 °C were similar to those at 320 °C but the activity of the catalysts was clearly lower and it was necessary to use higher space times W/F to cover the whole range of mole fractions (conversions).

The kinetic curves $a_i = f(W/F)$ were correlated by simple formal kinetics with the aim to evaluate conversion-independent activity and selectivity parameters (the change in the hydrogen partial pressure in the course of the reaction was neglected because hydrogen was fed in large excess). It was not the purpose of the present work to study the detailed kinetics of the reactions.

The reaction of thiophene followed a simple pseudo first-order equation:

$$a_{TH} = \exp(-k_{TH} * W/F_{TH}), \quad (1)$$

where k_{TH} is the rate constant ($\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$). The reaction of pyridine was correlated by a simplified reaction scheme of two consecutive pseudo first-order rate equations:



(for codes PY, SA, and C5, see Experimental). Integration of the corresponding rate equations gives the dependence of mole fractions on space time:

$$a_{\text{PY}} = \exp(-k_{\text{PY}} * W/F_{\text{PY}}), \quad (4)$$

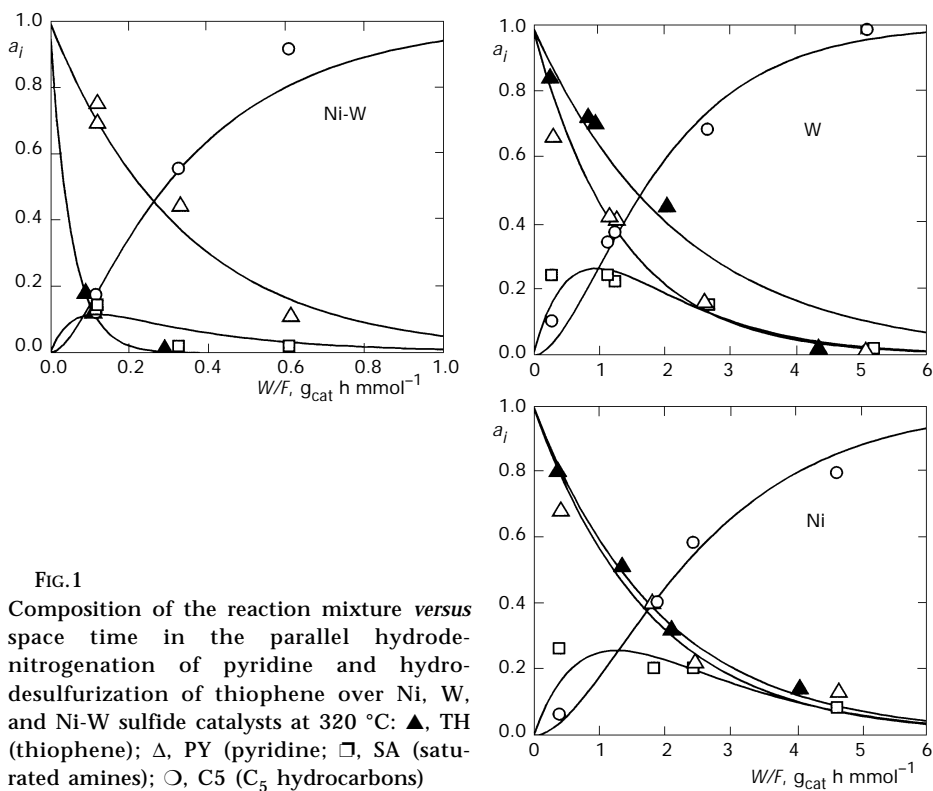


FIG. 1

Composition of the reaction mixture *versus* space time in the parallel hydrogenation of pyridine and hydrodesulfurization of thiophene over Ni, W, and Ni-W sulfide catalysts at 320 °C: \blacktriangle , TH (thiophene); \triangle , PY (pyridine); \square , SA (saturated amines); \circ , C5 (C_5 hydrocarbons)

$$a_{SA} = (k_{PY}/(k_{C5} - k_{PY})) * ((\exp(-k_{PY} * W/F_{PY})) - (\exp(-k_{C5} * W/F_{PY}))), \quad (5)$$

$$a_{C5} = 1 - ((k_{C5}/(k_{C5} - k_{PY})) * \exp(-k_{PY} * W/F_{PY})) + \\ + ((k_{PY}/(k_{C5} - k_{PY})) * \exp(-k_{C5} * W/F_{PY})), \quad (6)$$

where k_{PY} and k_{C5} are the rate constants ($\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$), corresponding to steps (2) and (3), respectively.

The constants k_{TH} , k_{PY} , and k_{C5} were obtained by non-linear regression of the experimental data by Eqs (1) and (4)–(6); they are summarized in Table I. The curves calculated using these equations and rate constants are shown in Fig. 1 for 320 °C. The quality of the fit of data at 280 °C was similar.

Magnitude of Synergism

The purpose of the present work was to compare the magnitude of synergism in HDS and HDN. A possibility of doing that is to use kinetic constants from Table I. The magnitude of synergism is defined as the ratio of

TABLE I
Kinetic constants ($\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$) in parallel hydrodenitrogenation of pyridine and hydrodesulfurization of thiophene

Catalyst	HDS		HDN	
	k_{TH}	k_{PY}	k_{C5}	A_{HDN}
280 °C				
Ni/C	0.1	0.4	0.3	0.2
W/C	0.1	0.5	0.4	0.3
Ni-W/C	3.5	1.4	2.3	1.0
320 °C				
Ni/C	0.5	0.6	1.1	0.5
W/C	0.5	0.8	1.4	0.6
Ni-W/C	19.1	3.0	17.9	3.4

activity of the bimetallic catalyst to the sum of activities of the corresponding monometallic catalysts. This ratio equals unity if no synergism occurs being higher than unity in the case of positive synergism.

The HDS activity is well characterized by the rate constant k_{TH} . The magnitude of synergism in HDS, MS_{HDS} , is thus defined by the ratio

$$MS_{\text{HDS}} = k_{\text{TH,Ni-W}} / ((3/7) * k_{\text{TH,Ni}} + k_{\text{TH,W}}), \quad (7)$$

where $k_{\text{TH},j}$ is the HDS activity for the catalyst j . The content of NiO in the Ni-W/C catalyst was lower than in the Ni/C catalyst and this is why the value of $k_{\text{TH,Ni}}$ was multiplied by 3/7 in Eq. (7) (see Experimental).

The definition of the HDN activity is not so straightforward. The overall reaction of pyridine to C_5 hydrocarbons and ammonia consists of two steps (Eqs (2) and (3)) and neither k_{PY} nor k_{C_5} alone defines the activity. The overall conversion of PY to HDN products depends on both these constants in a rather complex manner described by Eq. (6). However, the HDN activity of a catalyst, A_{HDN} , can be defined as the reciprocal value of W/F_{PY} at which $a_{\text{C}_5} = 0.5$. The dimension of A_{HDN} is the same as that of the rate constants, i.e. $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$. The values of A_{HDN} were obtained from the curves $a_{\text{C}_5} = f(W/F_{\text{PY}})$ calculated using the constants k_{PY} and k_{C_5} , and are presented in Table I. The magnitude of synergism in HDN, MS_{HDN} , is defined by the ratio

$$MS_{\text{HDN}} = A_{\text{HDN,Ni-W}} / ((3/7) * A_{\text{HDN,Ni}} + A_{\text{HDN,W}}), \quad (8)$$

where $A_{\text{HDN},j}$ is the HDN activity for the catalyst j ; $A_{\text{HDN,Ni}}$ was corrected for the content of NiO by multiplying by 3/7.

The magnitudes of synergism were evaluated for HDS and HDN at temperatures 280 and 320 °C using the constants in Table I; the results are summarized in Table II. It can be seen that the magnitude of synergism is much higher in HDS than in HDN.

Synergistic Shift in HDN/HDS Selectivity

Another possibility of comparing the magnitude of synergism in HDS and HDN is a comparison of the HDN/HDS selectivities of the catalysts. The selectivities at 280 and 320 °C are evaluated graphically in the conversion

versus conversion graphs in Figs 2 and 3, respectively. The curves shown were calculated using the constants given in Table I. In the case of a similar magnitude of synergism in HDN and HDS, the selectivity of the bimetallic sulfide Ni-W catalyst should be intermediate between the selectivities of the Ni and W sulfides. However, the data in Figs 2 and 3 show that the selectivity of the Ni-W catalyst is strongly shifted to the HDS side compared with the Ni and W catalysts. This indicates that the magnitude of synergism is much higher in HDS than in HDN.

The data of the present work were obtained under model conditions which differ from the conditions of the industrial hydrotreatment mainly in three points: the simple low molecular weight model compounds were used and the feed did not contain any hydrocarbons and hydrogen sulfide.

TABLE II
Magnitude of synergism^a between Ni and W in the Ni-W/C sulfide catalyst

Temperature, °C	HDS	HDN
280	28	3
320	28	4

^a For definitions see Eqs (7) and (8).

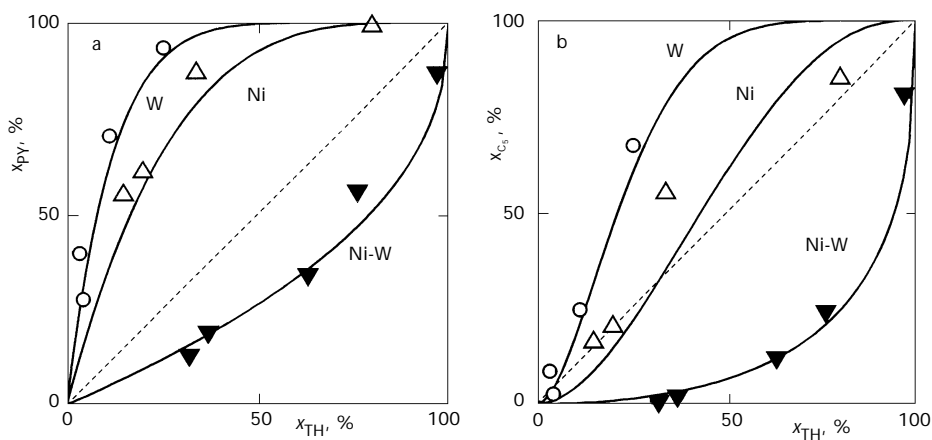


FIG. 2

Selectivity in the parallel reactions of pyridine and thiophene over Ni, W, and Ni-W sulfide catalyst at 280 °C: a overall conversion of pyridine versus hydrodesulfurization conversion; b conversion of pyridine to C_5 hydrocarbons versus hydrodesulfurization conversion

The most important of these points is probably the very low partial pressure of hydrogen sulfide in our experiments (it was produced only by HDS of TH). It is well known that the effect of hydrogen sulfide on various hydrotreatment reactions is different. Hydrodesulfurization is mostly strongly inhibited by hydrogen sulfide. Hydrodenitrogenation is influenced less, the effect of hydrogen sulfide being mildly positive or negative, depending on the partial pressure of hydrogen sulfide. It is expected that the addition of hydrogen sulfide to the feed should shift the selectivity HDN/HDS to the HDN side under our reaction conditions. However, it is believed that this effect should be rather similar for all the catalysts studied and that the different magnitude of synergism in HDN and HDS (Table II) and the synergistic shift in selectivity (Figs 2 and 3) are qualitatively independent of the partial pressure of hydrogen sulfide.

Importance of Results for Theory of Hydrotreatment

The results of the present work are a new contribution to the generalization of the phenomenon of a different magnitude of synergism in various hydrotreatment reactions (comparison of synergism in HDN and HDS over Ni, W, and Ni-W catalysts under the same conditions has not been reported in literature). However, interpretation of this phenomenon remains difficult. The difference of HDS from hydrogenation and HDN is that the reac-

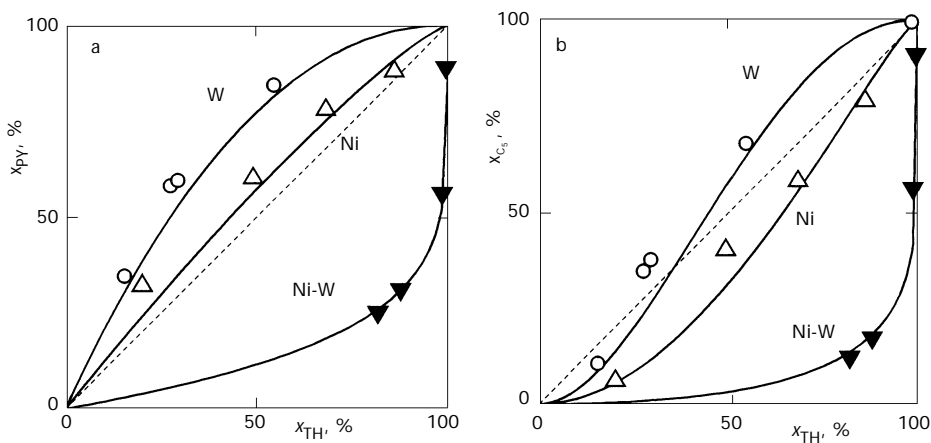


FIG. 3

Selectivity in the parallel reactions of pyridine and thiophene over Ni, W, and Ni-W sulfide catalyst at 320 °C: a overall conversion of pyridine versus hydrodesulfurization conversion; b conversion of pyridine to C_5 hydrocarbons versus hydrodesulfurization conversion

tion product, H_2S , interacts deeply with the catalyst. Sulfur is contained not only in the HDS reactants and products but also in the sulfide catalyst. The outstanding position of the C-S bond hydrogenolysis among other hydrotreatment reactions as regards the magnitude of synergism seems to indicate that the mechanism of synergism might be associated with the way in which sulfur species are transferred through the catalytic cycle. A more detailed discussion of this possibility is beyond the scope of experimental data obtained in the present paper.

However, the characteristic shift in hydrogenation/HDS or HDN/HDS selectivities to the HDS side accompanying synergism in activity might be useful for the theory of synergism also from another point of view. For the catalyst of a given composition, the selectivity is an easily measurable, useful indication of the extent of contact or degree of co-operation of the two transition metal sulfides in the synergistic pair. The selectivity of the catalyst with the best contact or co-operation of both components is in an extreme position at the HDS side. Any slight damage of this optimum contact or co-operation (at the same overall composition) is indicated by a shift of hydrogenation/HDS or HDN/HDS selectivities to the hydrogenation or the HDN side, respectively. Catalytic activity of industrial Co-Mo, Ni-Mo, and Ni-W sulfide catalysts decreases during time on stream and during oxidative regeneration (for a recent discussion and references, see *e.g.* refs^{4,5}). Among various causes of the deactivation, selectivity is expected to be much more sensitive to segregation of active components (decreasing the degree of utilization of the components for synergism) or to decomposition of active synergistic phases than to surface coking and support texture sintering. In a conventional approach, segregation of active components or decomposition of active synergistic phases is studied by various spectroscopic techniques^{4,5}. It is suggested that measurements of HDS/hydrogenation or HDN/HDS selectivities, such as shown in Figs 2 and 3, might be a convenient alternative way of getting additional information.

Remarks on the HDN/HDS Selectivity

It is worth mentioning two points concerning the HDN/HDS selectivity not directly associated with the main purpose of the present work.

a) Over conventional industrial Co-Mo, Ni-Mo, and Ni-W catalysts, HDN is always more difficult than HDS (refs¹³⁻¹⁵). It is sometimes concluded that this relative reactivity is generally valid for all sulfide catalysts. However, it has recently been shown that HDN is faster than HDS over some unconventional sulfide catalysts: HDN of pyridine and HDS of thiophene over Pt/C

and Ir/C sulfide catalysts¹⁶ and Ni/C, and Mo/C sulfide catalysts⁹, hydrotreatment of light catalytic cycle oil over unsupported Fe-W and Fe-Mo sulfides¹⁷, and in hydrotreatment of coal-derived naphtha over Ir/Al₂O₃ and Pt/Al₂O₃ sulfide catalysts¹⁸. It can be seen in Figs 2 and 3 that also W/C catalysts rank among catalysts where HDN can be faster than HDS.

b) It seems that the activation energy of HDN is always lower than that of HDS. This leads to a decrease in the HDN/HDS selectivity with increasing temperature. This was observed for Ni/C (ref.⁹), Mo/C and Ni-Mo/Al₂O₃ (ref.¹⁹), Ni-MoAl₂O₃ and unsupported Fe-Mo (ref.¹⁷), and Co-Mo/Al₂O₃-SiO₂ (ref.²⁰) sulfide catalysts and over a Mo₂N catalyst²¹. A comparison of selectivities shown in Figs 2 and 3 for 280 and 320 °C, respectively, indicates that this rule also holds for W/C and Ni-W/C sulfide catalysts (the data for the Ni/C catalyst in Figs 2 and 3 confirm our previous results with another Ni/C catalyst⁹).

CONCLUSIONS

The magnitude of the synergistic effect resulting from a combination of Ni and W in a Ni-W sulfide catalyst is higher in the HDS of thiophene than in the HDN of pyridine. As a result, the HDN/HDS selectivity of the Ni-catalyst is strongly shifted to the HDS side compared with the Ni and W catalysts. HDN of pyridine is more difficult than HDS of thiophene over the Ni-W catalysts but it is easier than HDS over the W catalyst. The HDN/HDS selectivity is shifted to the HDN side by decreasing temperature. It is suggested that the HDN/HDS selectivity measurements can be useful to indicate if a decomposition of active synergistic structures has occurred during the catalyst life and regeneration; decomposition of the synergistic structure should be accompanied by a shift of the selectivity to the HDN side.

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