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Hydrotreating on mixed vanadium–nickel sulphides
A study of the synergetic effect

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Abstract

The preparations of pure and mixed vanadium–nickel sulphides were carried out by the homogeneous precipitation method (under inert atmosphere). Thiophene HDS, pyridine HDN, toluene hydrogenation and vanadyl porphyrin HDP, were carried out as catalytic tests. The catalysts were also characterized by XPS, TPR, BET surface area and XRD. These solids, after sulphidation procedure, exhibit a synergetic effect, the importance of which depends on the hydrotreating reaction. The product distributions obtained in the thiophene hydrodesulphurization and the pyridine hydrodenitrogenation and the activity observed for toluene hydrogenation suggest that the synergy is mainly related to the hydrogenation step. The cause of this synergy could tentatively be assigned to an electronic transfer between the two metallic components in the mixed sulphides. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrotreating; Synergetic effect; Vanadium–nickel sulphides

1. Introduction

Pure transition metal sulphides (TMS), and more particularly those of the second and third row of the periodic table, are well known for its good hydrodesulphurization (HDS) activity [1–3]. Pecoraro and Chianelli [1] showed that bulk Re, Ru, Os, Rh, Ir, Pd or Pt sulphides are promising for HDS of dibenzothiophene. Similar observations were obtained with carbon supported TMS catalysts [2,3]. Unfortunately, except in case of exceptional selectivity, the most active metals (i.e. Ru, Rh, and Os) are too expensive for a possible industrial development. Therefore, we used TMS, which are usually regarded as less performing but also less expensive (like V). However, vanadium sulphide has, on its own, certain hydrotreating activity: its HDS activity is similar to that of nickel sulphide and higher than iron sulphide [1]. Vanadium sulphide has been used for the hydrotreatment of heavy feedstocks as bulk or supported catalyst [4,5]. Concerning the hydrodemetallation (HDM) process, V supported on silica or alumina is very efficient [6,7] and Bonné et al. [6] showed that it is even better than CoMo/Al_2O_3. In a previous investigation [7], we found that Ni in Ni–MoS_2/alumina catalysts can be, at least partly, exchanged by V coming from vanadyl porphyrin. However, to improve the activity of these vanadium sulphides, we prepared some new mixed TMS. Indeed, it is known that binary systems can show interesting synergetic effect. As an example, the uses of binary sulphides obtained by combination of V and another TM in hydrotreating reactions was

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investigated by Guillard et al. [8]. It was found that V–M (M=Co, Ni or Mo) mixed sulphides exhibit good performance in hydrogenolysis, and a synergetic effect is observed. More recently, Scott et al. [9,10] prepared and tested mixed Fe–V sulphides. Synergy for toluene hydrogenation, which was ascribed to an optimal V dispersion within the sulphide framework, was also observed. On the other hand, nickel is known to be an efficient hydrogenating catalyst. Thus, this work deals with the preparation and characterization of mixed nickel vanadium sulphides and their activity for hydrotreating.

2. Experimental

Mixed Ni–V sulphides were prepared by homogeneous solid precipitation method (HSP) from solution containing Ni nitrate and ammonium tetrathiovanadate (ATTV) in the presence of ammonium sulphide under nitrogen atmosphere. The aqueous solution of Ni^{2+} nitrate $[Ni(NO_3)_2]\cdot6H_2O$ from Strem Chemicals, purity>98%, was slowly added dropwise to a solution of ATTV (from Strem Chemicals) and $(NH_4)_2S$ (20% in water, from Strem Chemicals). The mixture was vigorously stirred under nitrogen atmosphere. The amount of the two solutions was worked out to have the expected atomic ratio Ni/V atomic ratio in the final mixed sulphides. After stirring, the solutions were filtered off and the obtained solids were dried at room temperature, always under nitrogen atmosphere. Pure nickel sulphide was prepared in the same way but without any ATTV. The final catalysts were obtained after a sulphidation procedure which consisted of treating the dried precipitates in a flowing H_2S (15%), H_2 (85%) mixture for 4 h at 673 K. For comparison purposes, bulk MoS_2 was also prepared from ammonium tetrathiomolybdate.

All the analyses and characterizations were performed after the sulphidation procedure. Bulk chemical analyses were provided by the “Service Central d′Analyses du CNRS” at Vernaison (France). Surface area determinations (BET method, N_2 adsorption) and X-ray diffraction patterns were obtained, on the air-exposed samples, with a Quantasorb instrument and a Siemens D 5000 diffractometer (Cu anode with monochromator), respectively. X-ray photoelectron spectra were recorded with an AEI ES 200 B spectrometer equipped with an Al anode working at 300 W. C1s contamination peak at 284.6 eV was used for binding energy calibration. In this case care was taken to avoid any contact of the solids with moisture (all handling was carried out in a controlled atmosphere box filled with nitrogen). The thermoreduction experiments were performed on a Sartorius balance (temperature rate: $600^\circ C\,h^{-1}$) on the air exposed samples.

2.1. *Hydrogenation of toluene, hydrodesulphurization of thiophene and hydrodenitrogenation of pyridine*

These three reactions were carried out in a high-pressure system with an on-line gas chromatography (Intersmat IGC 131) equipped with a capillary column (WCOT fused silica, CP Sil-5 CB from Chrompack) to which the products were injected by an automatic injection valve Valco. All tubings were coated and heated to avoid condensation of reactants and products.

HYD of toluene (purity>99.5%, Fluka), HDS of thiophene (purity>98%, Fluka) and HDN of pyridine were carried out consecutively (in this order). Fresh catalysts were re-sulphided before the first reaction (HYD of toluene) according to the conditions reported in Table 1. 250 mg of catalysts were used in each test.

2.2. *Hydrodeporphyrinization of vanadyl octaethylporphyrin (VOOEP)*

The reaction was carried out in a high-pressure continuous-flow system. A solution of VOOEP ($3\times10^{-4}\,mol\,l^{-1}$) in decahydronaphtalene (purity>98%, *cis–trans* mixture, Janssen Chimica) containing 2% of dimethyldisulphide (DMDS, purity>99%, Janssen Chimica) to maintain a sulphiding atmosphere, was used as a liquid feed. The catalysts (300 mg) were sulphided prior to testing. The reaction products were analyzed by UV–vis spectroscopy. We measured the decrease in the α and β bands of the metallo porphyrin and not the reduction of the metal content in solution (Hidrodemetallization), so we will refer our activity as Hydrodeporphyrinization (HDP). However, it is usually found that this HDP, correlates well with the HDM. The experimental details of the tests are reported in Table 1. In all cases (HDS, HYD,

Table 1
Experimental conditions for hydrodeporphyrinization (HDP), hydrogenation (HYD), hydrodesulphurization (HDS) and hydrodenitrogenation (HDN)

Reaction		Feed[a]	Experimental conditions[b]
HDP	Pre-sulphidation	Decaline, 66.6 vol.%; DMDS, 33.3 vol.%	Hf=6 l h^{-1}; HCf=1.2 cc h^{-1}; P=1 bar; T=623 K
	Test	Decaline, 98 vol.%; DMDS, 2 vol.%; VOOEP, 5×10^{-4} M	Hf=15 l h^{-1}; HCf=30 cc h^{-1}; P=80 bar; T=573 K
HYD, HDS, HDN	Pre-sulphidation	Heptane, 66.6 vol.%; DMDS, 33.3 vol.%	Hf=4.4 l h^{-1}; HCf=3 cc h^{-1}; P=1 bar; T=623 K
	HYD	Heptane, 68 vol.%; DMDS, 2 vol.%; Toluene, 30 vol.%	Hf=6 l h^{-1}; HCf=1.2 cc h^{-1}; P=60 bar; T=623 K
	HDS	Heptane, 90 vol.%; Thiophene, 10 vol.%	Hf=6 l h^{-1}; HCf=2 cc h^{-1}; P=33 bar; T=573 K
	HDN	Heptane, 88 vol.%; DMDS, 2 vol.%; Pyridine, 10 vol.%	Hf=6 l h^{-1}; HCf=2 cc h^{-1}; P=33 bar; T=573 K

[a] DMDS: dimethyldisulphide; VOOEP: vanadyloctaethylporphyrin.
[b] Hf: hydrogen flow rate; HCf: hydrocarbon flow rate; P: pressure; T: temperature.

HDN and HDP) conversions were measured after, at least, 15 h on stream. It was always obtained that after this period of time four consecutive measurements gave about the same conversion (within 1%) indicating that the steady state was already achieved.

3. Results and discussion

Table 2 shows the specific surface area, the phases, as determined by XRD, and the thermoreduction peak, for the various catalysts noted as NiVS-*x*, where *x* indicates the Ni/(Ni+V) atomic ratio for the sulphided solids.

Among all the solids, pure vanadium sulphide (sample NiVS-0) has the highest specific surface area (57 $m^2 g^{-1}$), while nickel sulphide (sample NiVS-1) has a low one (about 6 $m^2 g^{-1}$). First addition of Ni into the V sulphide sample induces an important decrease in the specific surface area. Mixed Ni–V sulphides have specific surface areas between 11 and 14 $m^2 g^{-1}$ which is quite comparable to pure MoS_2 (18.4 $m^2 g^{-1}$). As already discussed [9,10] the vanadium sulphide stoichiometry (obtained by chemical analysis) is very close to V_3S_4 with a XRD diffraction pattern assigned to be NiAs like structure poorly crystallized (see [9]). The X-ray diffraction of the nickel sulphide sample indicates the presence of crystallites of millerite in which the Ni^{2+} ions are surrounded by sulphur ions located in a based square pyramid. In the mixed sulphides, NiV_2S_4 has been clearly identified and its content depends on the atomic composition. There is always a second phase together with NiV_2S_4. This second phase is either V_3S_4 or NiS (see Table 2). XPS shows that the atomic proportion of nickel surface concentration of NiVS-*x* sample increases quite linearly with Ni bulk composition. It is, therefore, assumed that nickel and vanadium are homogeneously distributed in NiVS compounds.

The thermoreduction analysis clearly shows a mutual influence of each component on the other. Pure vanadium sulphide is reduced at 520°C which could

Table 2
Specific surface area, phases and thermoreduction peaks for the various catalysts

Catalyst	Specific surface area (SSA $m^2 g^{-1}$)	Phases identified by XRD	Thermoreduction peaks (°C)
NiVS-0	57	V_3S_4	520
NiVS-0.25	13.7	V_3S_4; NiV_2S_4	325
NiVS-0.5	10.8	NiS; NiV_2S_4	301
NiVS-0.75	11.5	NiS; NiV_2S_4	225
NiVS-1	5.6	NiS (Millerite)	216
MoS_2	18.4		

correspond to the formation of V^{4+} species, while pure nickel sulphide is reduced at 216°C. Each one of the mixed sulphides is reduced at an unique intermediate temperature, which should correspond to the major component present, since we are in presence of several phases.

Catalyst performances are reported in Fig. 1. In all cases, an increase in the activity is observed as the second metal (Ni) is added to V and the activity goes through a maximum which corresponds to an atomic ratio x=0.25 whatever the studied reaction.

Fig. 1a represents the variations in the toluene rate of reaction expressed in terms of intrinsic hydrogenation activities. Pure vanadium sulphide is slightly more active than MoS_2 ($1.6\times10^{-8}\,\mathrm{mol\,m^{-2}\,s^{-1}}$ versus $1.1\times10^{-8}\,\mathrm{mol\,m^{-2}\,s^{-1}}$). Nickel sulphide is the best among the pure TMS tested. NiVS-0.25 has a hydrogenation activity two times higher than pure nickel sulphide.

Concerning the thiophene rate of reaction, the same phenomenon is observed (Fig. 2b) but pure vanadium sulphide is a slightly less active than MoS_2

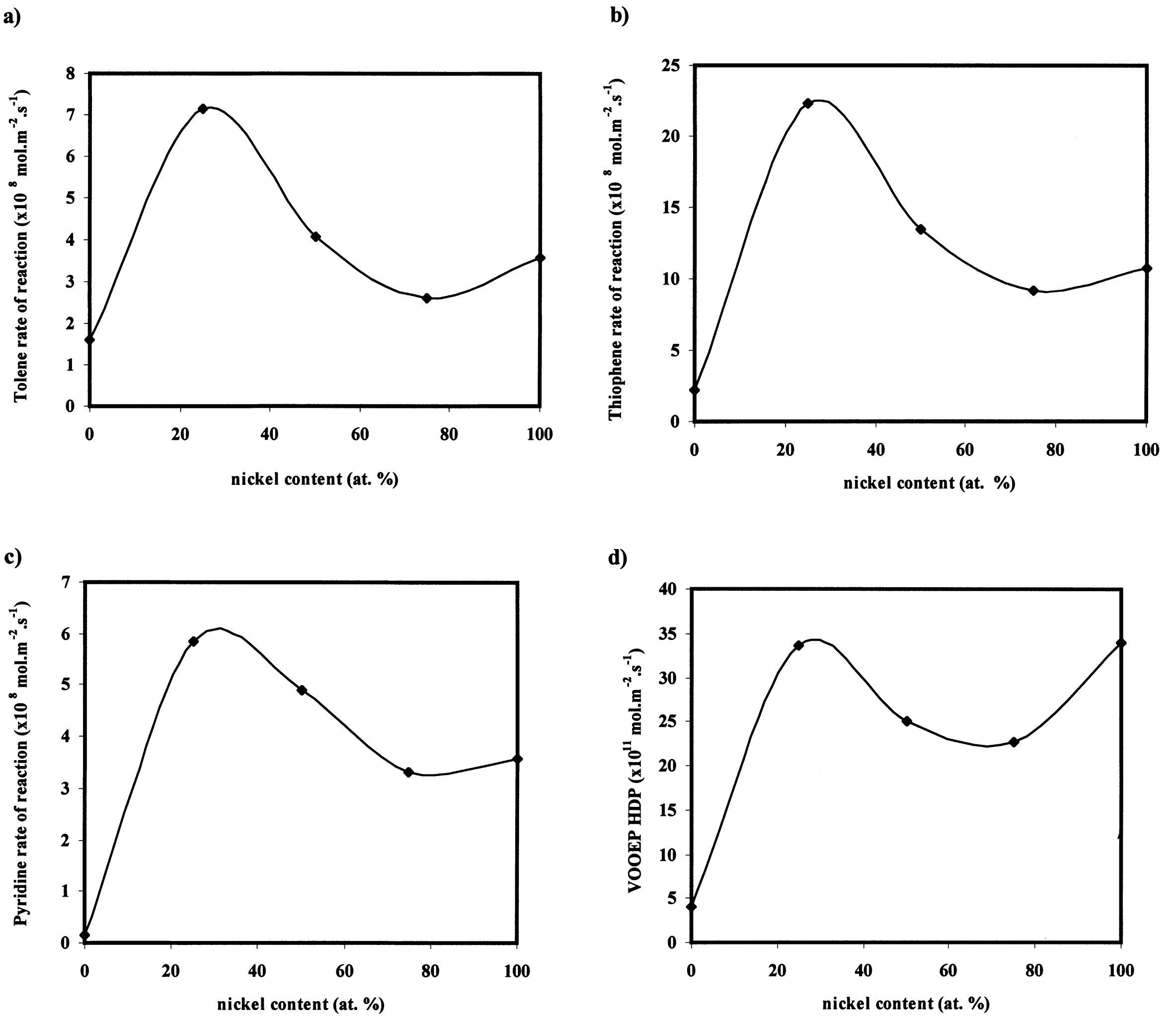

Fig. 1. Hydrotreating activities of NiVS catalysts: (a) Toluene hydrogenation rate of reaction. (b) Thiophene rate of reaction. (c) Pyridine rate of reaction. (d) VOOEP hydrodeporphyrinization.

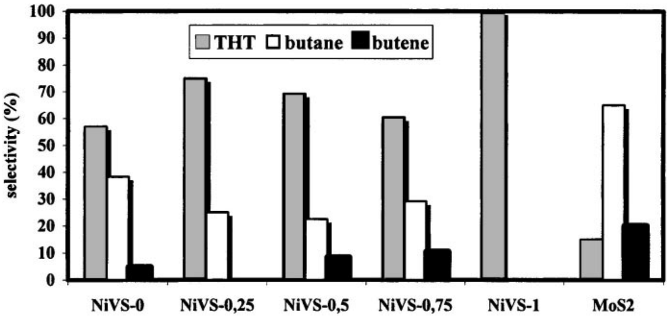

Fig. 2. Product distribution for thiophene conversion over MoS_2 and NiVS catalysts.

(2.39×10^{-8} mol m^{-2} s^{-1} versus 3.2×10 mol m^{-2} s^{-1}). Surprisingly, pure nickel sulphide has a good activity which is largely improved in presence of vanadium, as NiVS-0.25 is twice as active (22×10^{-8} mol m^{-2} s^{-1}). This value can be compared with the one obtained for FeVS-0.3 (3.67×10^{-8} mol m^{-2} s^{-1}) [10]. Ni appears to be a better promoter than Fe in the mixed TM–V sulphides for thiophene conversion. However, one of the most striking results is the product distribution as a function of the atomic ratio (Fig. 2). Even though, activity measurements were not carried out at the same conversion levels, some preliminary observations can be made. Thus, the selectivity for tetrahydrothiophene (THT), the direct hydrogenation product, is within the range of 60–100%. It is noteworthy to recall that with MoS_2, a large quantity of butane (≅65%) is produced, whereas THT is in small amounts. Pure NiS shows only one product, which is THT. This result means that the good activity observed with this solid is in fact due to the disappearance of thiophene to form THT, which is not really a desulphurization activity.

The increase in the activity obtained with the bulk mixed sulphides is not surprising, since it has been reported [8] that vanadium sulphide has the same catalytic properties, in thiophene HDS, as those of conventional supported sulphides, which is in agreement with this work. However, the presence of THT was not reported before. This discrepancy is probably due to the difference in experimental conditions. In the present report, we work under high pressure (3.3 MPa) which favours hydrogenation reactions over hydrogenolysis. Moreover, vanadium [8] have been found to have better hydrogenating properties than molybdenum. Also, different metal sulphides can show different selectivities in thiophene HDS, e.g. bulk ruthenium sulphide shows a high selectivity towards THT (more than 50%) even at atmospheric pressure [11]. On the other hand, the fact

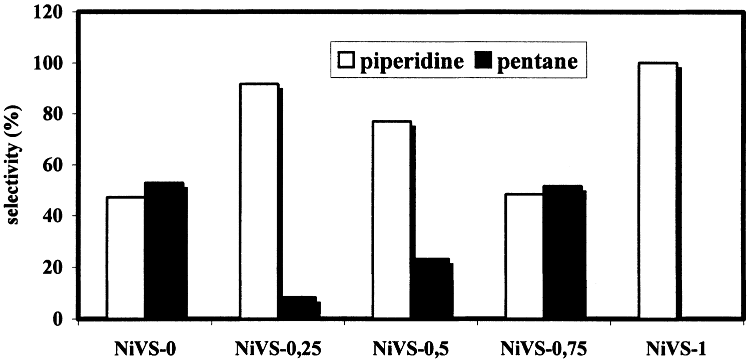

Fig. 3. Product distribution for pyridine conversion over NiVS catalysts.

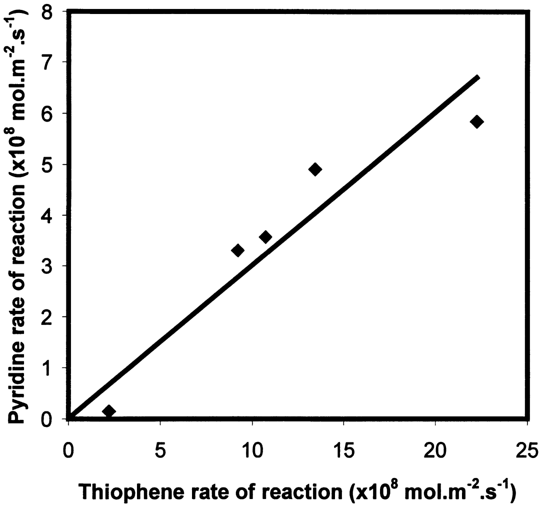

Fig. 4. Correlation between pyridine and thiophene rate of reactions.

that molybdenum sulphide also produces THT could be explained according to a previous report [12], where it has been shown that changes on stacking of molybdenum sulphide produces changes on the selectivity (hydrogenation/hydrogenolysis) for HDS of dibenzothiophene.

Changes in butene–butane selectivities complements the trends obtained on THT production. For MoS_2, selectivity for butane is higher than that for butene. NiVS-0 presents the same behaviour (Fig. 2). However, in this case THT is the most important reaction product. Incorporation of Ni induces a decrease in butane production and an increase in butene selectivity.

The results obtained for pyridine rate of reaction is very similar to the latter ones (Fig. 1c), i.e. we observed a synergetic effect with the NiVS-0.25 catalyst showing the maximum activity. Clearly, the presence of nickel, particularly as NiV_2S_4 solid solution, largely favours pyridine react of reaction, in which the first-step is well known to be a hydrogenation reaction. The presence of nickel has a drastic effect in the rate of formation of piperidine. This can be seen in Fig. 3, where the selectivities obtained in this reaction are presented. The most active catalysts mainly produce piperidine. This result is in agreement with those observed in the conversion of thiophene. In Fig. 4 pyridine versus thiophene rate of reaction is plotted. This plot shows a very good correlation indicating that both reactions are carried out in same catalytic sites.

The selectivity for piperidine is in the range of 48–100% (versus 40% on pure MoS_2) (Fig. 3). Besides, the changes in the formation of these hydrogenated intermediates parallel the trends in toluene hydrogenation. This result suggests that the synergy effect is mainly related to the hydrogenation step. Moreover, this synergy is observed for the mixed sulphides with different structures (e.g. in the presence of solid solutions, as in NiVS-*x*, RuNiS-*x* [13–16], or in their absence, as in CoMoS-*x*, RuMoS-*x* [17–19]). We can therefore suggest that the synergy is most probably related to electronic effects rather than to structural effects, as already proposed by several authors [18,20–21].

Lastly, Vanadyloctaethyl Porphyrin HDP is in agreement with previous results, as we observe a synergy effect for the NiVS-0.25 (Fig. 2). For this reaction pure nickel sulphide is almost as active as the best mixed sulphide. This is not really surprising because we report the deporphyrinization activity (that means the disappearance of VOOEP and not the reduction on the metal content). It is well known that the first-step for the HDM reaction is the hydrogenation of the porphyrinic ring to successively form vanadyl octa ethyl chlorine and vanadyl octa ethyl isobacteriochlorin, and that is partially a thermal phenomenon [22] and not only a catalytic one. Thus, the synergy effect on the hydrogenation step is less evident.

4. Conclusions

Mixed nickel vanadium bulk sulphides prepared from ammonium tetrathiovanadate exhibit a synergy effect for hydrotreatings reactions, the important of which depends on the reaction considered, but is always located near the NiVS-0.25 formulation. The product distributions obtained for thiophene and pyridine conversions, and its comparison with the toluene hydrogenation, seems to show that the synergy effect is related to the hydrogenation properties of the mixed sulphides. Thus, clearly the V based catalysts appear better than MoS_2 for hydrogenation of aromatic ring, but they are less active for the hydrogenolysis of the C–S bond.

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