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Synthesis, characterisation and HDN activity of iron–vanadium sulphide prepared with the use of a chelating agent

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Abstract

The influence of the use of ethylenediamine in the preparation of iron–vanadium catalyst for toluene hydrogenation (HYD) and pyridine hydrodenitrogenation (HDN) has been studied. Both HYD and HDN activities increased significantly with Fe incorporation to vanadium sulphide and the beneficial effect of ethylenediamine was shown. Possible explanations for the enhancements in HYD and HDN conversion are discussed.

Keywords: Hydrotreating; Vanadium sulphide; Iron–vanadium sulphide; Chelating agent

1. Introduction

To process heavy and low quality feedstocks, which are rich in highly refractory nitrogen and sulphur-containing compounds and multi-ring aromatics, catalysts with high activity for hydrogenation (HYD) of aromatics rings in nitrogen-containing molecules during hydrodenitrogenation (HDN) are required. A major shortcoming of current commercial catalysts is that the HDN rate is relatively slow. Therefore improved methods for preparing catalysts with a high activity are sought. A possible strategy to overcome these problems is to develop new catalyst formulations which have to be more active and selective. Replacement of the classical Co(Ni)–MoS_2 catalysts by other transition metal sulphides (TMS), could be promising. Our strategy was therefore to focus on the use of TMS of the first row of the periodic table. Previous studies have shown the positive effect, probably catalytic, of iron-containing compounds [1]. Indeed, some publications [2–7] indicate that mixed FeMo sulphides exhibit interesting properties such as high catalytic activity in hydrodesulfurization (HDS) of thiophene [3] or, in contrast, low HDS and high HDN activities [4]. On the other hand, it has been proposed [8] that during the course of the hydrodemetallization (HDM) with clays, the initial pyrrhotite, formed by sulfurization of the clay, traps vanadium from the feed and evolves to mixed FeV sulphides. Bulk vanadium sulphides, have been shown to be efficient catalysts for HDS, HDN, and HYD of aromatic molecules [9,10]. The aim of the present work was to explore the HYD of aromatics rings in nitrogen-containing hydrocarbons, during HDN reactions.

2. Experimental

2.1. Materials

Materials used for the preparation of the catalysts were: ammonium tetrathiovanadate (ATTV, Stream

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Chemicals), ammonium tetrathiomolybdate (ATTM, Stream Chemicals), Fe(II) nitrate (Merck, >99%), ammonium sulphide (Stream Chemicals), and ethylenediamine (Aldrich, 99.9%). The gases employed were H_2 (AGA, 99.99%) and N_2 (GIV, 99%). For the reactivity test, the chemicals employed were: pyridine (Aldrich, 99.9%), toluene (Fluka, 99.5%), heptane (Aldrich, >99.5%), and dimethyl disulphide (Aldrich, 99%). All chemicals were used as-received. H_2 and N_2 were passed through water/oxygen-removing purifier.

2.2. Synthesis and characterisation of catalysts

The catalyst precursors used in this study, called iron–ethylenediamine–thiovanadate, Fe(en)VS for short, have a well-defined coordinative structure. The synthesis of this type of compounds appears to date from the works carried out by Spacu and Pop [11] and Ho et al. [4]. The preparation of the FeV catalyst precursor is typically carried out as follows: the Fe(en)VS was prepared by dissolving $(NH_4)_3VS_4$ into ethylenediamine (en). The resultant solution was cooled in an ice bath and kept in the bath for the duration of the synthesis. In a separate flask, $Fe(NO_3)_2$ was dissolved in distilled water and ethylenediamine was added slowly to Fe^{2+} solution to form $Fe(en)_2{}^{2+}$. The resulting black $Fe(en)_2{}^{2+}$ was allowed to cool to room temperature. The $Fe(en)_2{}^{2+}$ solution was then added slowly to $(NH_4)_3VS_4$/en solution with agitation. A precipitate was formed immediately. The product Fe(en)VS was further washed with ethanol. The solid was dried in vacuo and stored under inert atmosphere until use. Prior to use, the precursor compound is activated; that is, it is thermally decomposed to remove its organic constituents in the presence of sulphur-bearing stream (15% H_2S/H_2, 350 °C). We have found that this procedure is useful, even though the precursor compounds already have sufficient sulphur required for the formation of final working catalysts. Pure vanadium sulphide was prepared by treating solid ATTV by the same procedure, but without iron. Pure iron sulphide was obtained by precipitation of $Fe(NO_3)_2$ in $(NH_4)_2S$. For comparison, a bulk MoS_2 catalyst was prepared in situ by thermal decomposition of ATTM in 15% H_2S/H_2 at 350 °C.

After the final sulfidation step, the samples were analysed in the “Centro de Química analítica” for the Fe and V content (S content was determined by difference).

Surface area determinations by nitrogen adsorption using BET theory were carried out in a Micromeritics ASAP 2010C instrument. As pre-treatment, 100 mg of catalyst was placed in quartz tube and evacuated for 1 h at 150 °C. The experimental error in the surface area measures is ca. 10%.

X-ray diffraction (XRD) measurements were made using a Siemens D5000 X-ray diffractometer with monochromatic radiation Cu Kα ($\lambda = 1.5418$ nm) in step scanning mode in the range $5^\circ < 2\theta < 90^\circ$. Qualitative phase analysis was carried out using the Siemens Diffrac AT software package.

FT-IR measurements were performed using a Perkin-Elmer 1700 spectrometer with a resolution of $4\,cm^{-1}$. Samples were pressed into self-supporting wafers (ca. $10\,mg\,cm^{-2}$, $\phi = 1.6$ cm).

Diffuse reflectance spectra (UV-Vis DRS) of the catalysts in their sulfided state were obtained in a Perkin-Elmer Lambda 40P spectrophotometer, equipped with an integrating sphere.

EPR spectra have been measured at room temperature on a Varian E 104 A spectrometer operating an X band. Varian pitch was used as reference for the calibration of g values.

2.3. Toluene/pyridine activity

The activity measurements in HYD and HDN reactions were accomplished in a fixed-bed reactor working at atmospheric pressure at 350 °C, with 0.5 g catalyst diluted with SiC. The catalysts were sulfided in situ at 350 °C.

Reaction products were identified by GC–MS and the results of the identification were confirmed by injection of standard compounds. Only steady-state activity results are reported. The absence of any diffusion effects was experimentally verified by showing that similar conversions, at constant contact time, were obtained for two different weights of catalysts.

3. Results and discussion

One goal of our recent research on HYD/HDN catalysts has been the preparation of molecular catalyst precursors in which the primary catalytic metal (V),

Table 1
Atomic composition and surface specific area of the sulphides catalysts

Catalyst	Bulk composition (atomic)	SSA ($m^2 g^{-1}$)
FeS	$Fe_{0.89}S$	12
VS	$V_{0.75}S$	12
MoS	MoS_2	34
FeVS	Fe_4VS_5	4

promoter metal (Fe) and sulphur are closely mixed in a single precursor.

To corroborate the formation of the catalytic precursor, these were studied by infrared spectroscopy (IRFT). Special emphasis was given to the stretching of the nitrogen–metal (N–M) bond. In the precursor Fe(en)V, two N–M signals appears to 665 and 657 cm^{-1} (VN and FeN, respectively), which indicates the formation of the bimetallic complex with ethylenediamine. Once prepared the solid precursors were sulfided to obtain the final catalysts.

Table 1 reports the atomic composition and surface specific areas (SSAs) measured before catalytic test for pure and mixed sulphides. The SSAs are relatively low, which is expected for bulk systems. For pure Fe and V compounds, there is no variation: 12 $m^2 g^{-1}$. The smaller being that of mixed FeV sulphide (4 $m^2 g^{-1}$). This is mainly due to the large size of the thiovanadate crystal as precursor. The bulk MoS_2 showed a surface area value (32 $m^2 g^{-1}$) which is typical for samples obtained by decomposition of thiosalts [12–15].

The atomic composition of pure iron sulphide corresponds to the general formulae $Fe_{1-x}S$ very close to Fe_7S_8. Its diffraction pattern exhibit five sharp and intense diffraction peaks in 2θ range: 30.02, 33.99, 44.03, 53.32 and 71.45; relative (2 2 0), (2 0 3), (2 0 6), (2 0 2) and (4 0 6) planes of the Pyrrhotite phase, which is agreement with elemental analysis.

The atomic composition of pure vanadium sulphide is $V_{0.75}S$. Its XRD pattern shows intense peaks (2θ: 15.60, 35.32 and 45.14) corresponding to V_3S_4 phase.

The FeVS system shows a single and weak diffraction peak (34.08°). This compound is not well crystallised as revealed by its XRD pattern (Fig. 1). The bulk composition is reported in Table 1. This result suggests that FeVS catalyst is not a mixture of Fe and V sulphides, but rather a new type of compound or crystallographic phase.

From systematic synthesis of crystals in FeVS system, it is known that Fe can easily replace V in V_3S_4 and is stable over a wide range of composition [16,17]. Some indications of metal ordering can be perceived in previous reports [18–20], where only the *c* cell edge of FeV sulphide decreases almost linearly with increasing the mole fraction of replaced Fe atoms. This linear shrinkage of the unit cell was explained assuming that Fe atoms occupy the corner site preferentially. Even if we have no evidence of atomic substitution, the used synthesis method should allow the formation of a solid solution. It is good to notice that no oxide phase was observed by XRD which suggests that a complete sulfurization of the solids was obtained.

Diffuse reflectance spectra for bimetallic catalyst were obtained and compared with a vanadium sulphide. This technique was carried out in order to observing any modification in the coordination sphere, probably due to interactions between the V and Fe. The range studied was between 240 and 800 nm. The solid FeVS, showed broad bands centred at approximately 270, 325, 400, 450, and 500 nm. The right position of the bands was not easy due to the broadness of them. In this range charge transfer band for metal complexes are usually found. Thus the bands at 325 and 400 nm, could be due to vanadium(IV) in octahedral environment (d–d, $^2E_g \rightarrow {}^2T_{2g}$ transitions). The remaining bands, could be assigned to iron in octahedral (450 and 500 nm) and tetrahedral (270 nm) coordination.

Fig. 2 shows the EPR spectra of catalysts investigated in sulphided state. Iron sulphide shows a wide signal with a value of $g = 2.793$. For the solid VS a strong and symmetrical signal with $g = 1.955$ was observed. The broad signal is due to dipolar coupling arising from the strong interaction of near-neighbour vanadium atoms. For the FeVS catalyst (Fig. 2) the iron signal overlaps the signal of vanadium ($g = 2.234$). This behaviour for VS_4^{3-} entities was reported by Hubaut et al. [21]. The only V signal observed by EPR corresponds to vanadium sulphide.

The catalytic performances are reported in Table 2. For toluene HYD, pure V sulphide is about 1.5 times less active than pure MoS_2. On the other hand, pure iron sulphide exhibits a low but detectable activity in HYD. The results show that the mixed catalyst show higher conversion in toluene HYD than their respective sulphide constituents. The bimetallic catalyst, exhibit a conversion of 37.52%, which is five times

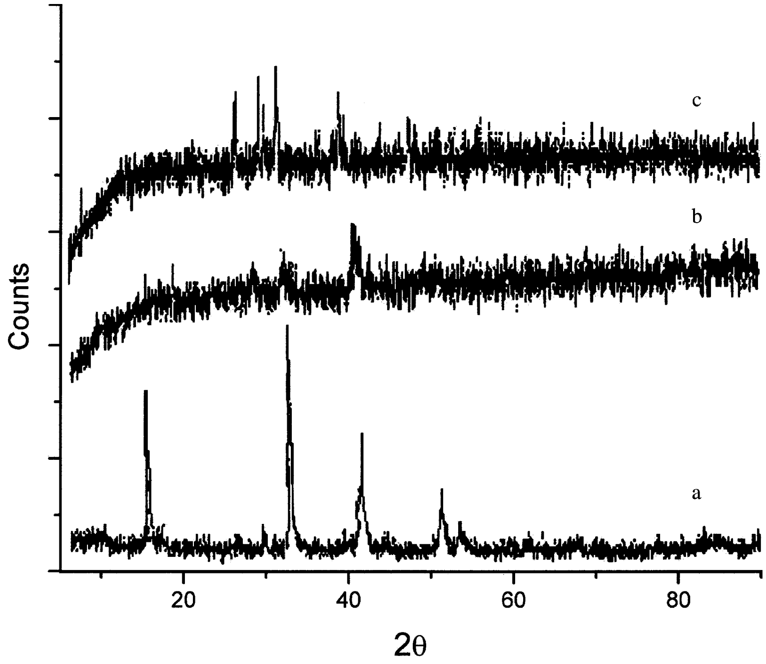

Fig. 1. XRD patterns of catalysts (a) VS, (b) FeVS and (c) FeS.

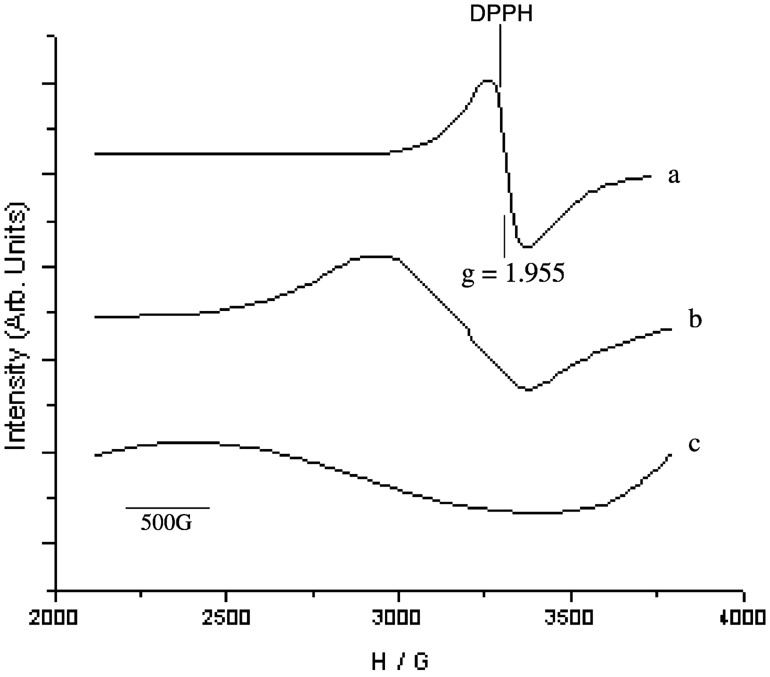

Fig. 2. EPR spectra of catalysts (a) VS, (b) FeVS and (c) FeS recorded at room temperature.

Table 2
Conversion measurements for toluene HYD and pyridine HDN[a]

Catalyst	Conversion (%)	
	Toluene HYD	Pyridine HDN
FeS	0.55	0.01
VS	7.53	0.12
MoS	11.04	2.3
FeVS	37.52	24.31

[a] Conversion normalised per gram of catalyst.

higher than the sum of their individual components and three times that of molybdenum sulphide (MoS_2). This suggests that the mixed sulphide FeVS is not composed of separate phases of V_3S_4 and $Fe_{1-x}S$. This synergetic effect is more marked for pyridine HDN (see Table 2).

The results of HDN experiments are shown in Table 2. The reaction products in the pyridine HDN were: piperidine and pentane, with the latter being the larger product.

Monometallic sulphides show low HDN conversion. FeVS catalyst shows the higher conversion for pyridine decomposition (24.31%). The increase in conversion induced by iron was more pronounced for HDN than for HYD. Compared to vanadium sulphide, conversion increases by a factor of 202 while for HYD conversion increases only five times. Even though, surfaces areas for the solids are different, expressing the conversion by surface area would only change the relative ration between them, but the trends are the same.

The increase in HDN and HYD activities for FeVS sulphides, compared to pure Fe and V sulphides, could be explained by (i) formation of a new FeV sulphided phase, or (ii) a decrease in crystal size, as proposed by Ho et al. [4] for FeMo sulphides prepared in a similar way as the sulphides prepared in this work. XRD and ESR results are in favour of the first explanation rather than the second one.

Thus, the promotion observed for the unsupported material would be the result of an interaction between Fe and V in the final sulphide, and this interaction is favoured by the decomposition of the ethylenediamine complex to form the FeVS catalyst. The increase in activity could be associated with the facility for the formation of vanadium coordinatively unsaturated sites (CUS) in the new FeVS phase, since it is agreed in the literature that CUS are responsible for HDS/HDN activity in sulphided catalysts.

It is worthwhile to consider that being prepared from the decomposition of precursors containing an organic amine, these bulk catalysts invariably have some carbon and nitrogen species on their surface. These species may also be a contributing factor to the unusual selectivity observed.

4. Conclusions

From the above results it can be concluded that the incorporation of iron to vanadium sulphide by means of a ethylenediamine complex leads an increase in HYD conversion and HDN conversion. The effect being more marked for HDN. The higher HDN and HYD conversion for FeVS catalysts can probably be attributed to the formation of a new FeV sulphide phase. The formation of this new phase is promoted by the use of a FeV ethylenediamine complex.

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References

[1] A. Attar, Fuel 57 (1978) 201.
[2] S. Göbölös, Q. Wu, J. Ladriere, P. Grange, B. Delmon, Acta Chim. Hung. 124 (1987) 177.
[3] M.A. Villagarcía, J. Lindner, A. Sachdev, J. Schank, Appl. Catal. 56 (1989) 281.
[4] T.C. Ho, A.J. Jacobson, R.R. Chianelli, C.R.F. Lund, J. Catal. 138 (1992) 351.
[5] J.Y. Koo, T.C. Ho, Catal. Lett. 28 (1994) 99.
[6] T.C. Ho, R.R. Chianelli, A.J. Jacobson, Appl. Catal. A 114 (1994) 127.
[7] M.A. Luis, A. Rives, R. Hubaut, B.P. Embaid, F. Gonzalez-Jimenez, C.E. Scott, Stud. Surf. Sci. Catal. 127 (1999) 203.
[8] F. Gonzalez-Jimenez, D. Basin, H. Dexpert, F. Villain, H. Constant, M. Rosa-Brussin, Physica B 158 (1989) 215.
[9] C. Guillard, M. Lacroix, M. Vrinat, M. Breyse, B. Mocaer, J. Grimblot, T. Des Courieres, D. Faure, Catal. Today 7 (1990) 587.
[10] C.E. Scott, B.P. Embaid, M.A. Luis, F. Gonzalez-Jimenez, L. Gengembre, R. Hubaut, J. Grimblot, Bull. Soc. Chim. Belg. 104 (1995) 331.
[11] G. Spacu, A. Pop, Bull. Sect. Sci. Acad. Roum. 21 (1938) 188.

[12] D.G. Kalthod, S. Weller, J. Catal. 95 (1985) 455.

[13] R. Frety, M. Breysse, M. Lacroix, M. Vrinat, Bull. Soc. Chim. Belg. 93 (1984) 697.

[14] M. Zdrazil, Catal. Today 3 (1988) 269.

[15] S. Pedraza, S. Fuentes, Catal. Lett. 65 (2000) 107.

[16] H. Wada, Bull. Chem. Soc. Jpn. 51 (1978) 1368.

[17] H. Wada, Bull. Chem. Soc. Jpn. 53 (1980) 668.

[18] H. Wada, Bull. Chem. Soc. Jpn. 52 (1979) 2130.

[19] H. Wada, Bull. Chem. Soc. Jpn. 52 (1979) 2918.

[20] H. Nozaki, H. Wada, H. Yamamura, Solid State Commun. 44 (1982) 63.

[21] R. Hubaut, C.F. Aissi, S. Dejonghe, J. Grimblot, J. Phys. Chim. 88 (1991) 1741.