# Hydrodesulfurization (HDS) Poisoning by Vanadium Compounds: EPR and Metal Solid NMR Analysis

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The HDS activity of a commercial NiMo catalyst has been followed versus the amount of vanadium added to it, either by an oxidic procedure before the sulfidation step or by a sulfided route, using a highly soluble vanadyl porphyrin simulating the industrial process on the presulfided catalyst. An oxidative regeneration followed by a resulfidation transformed these porphyrin-poisoned catalysts into the oxidic preparation family. At the same time, Metal Solid NMR and EPR spectroscopies have been used to characterize the nature of the vanadium deposit. The very strong deactivation in the sulfided phase is due only to vanadyl species, well characterized by EPR; while the deactivation of the catalysts, where vanadium has been oxidized in  $V_2O_5$ , is due to vanadium sulfides, as is shown by NMR. © 1987 Academic Press, Inc.

An important body of work has already been devoted to the study of the HDM (hydrodemetallation) reaction of petroleum residues because of the need for processing more and more heavy fractions of the crude oils. In these fractions, metals, mainly in porphyrins or other organic complexes (1), are concentrated after distillation up to 1500 ppm for vanadium and 140 ppm for nickel, for instance in a Boscan residue. Such concentrations need drastic purification conditions, generally using a cheap scavenger catalyst in order to protect a second valuable catalyst (generally CoMo or NiMo) which will be used to perform the other important hydrotreatment reactions, HDS (hydrodesulfurization), HDN (hydrodenitrogenation), and hydrogenation. However, the effectiveness of the first catalyst can diminish with time or fail for a short time and allow a small amount of poisonous metals into contact with the expensive active catalyst; in addition, very low concentrations of metal in other crudes do not require a first purification step (scavenger) but, after a long run time, allow the deposition of poisonous metals on the active catalyst. It is thus interesting to

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study the HDS (HDN) activity of a conventional CoMo or NiMo catalyst at very low or low coverage of poisonous metal, which is the purpose of this paper.

Various authors have studied the deactivation of these catalysts for the HDM reaction by using either vanadium poisonous compounds (2), nickel poisonous compounds (3), or both (4) and have observed a very rapid deactivation at low coverage (<1.5 wt% metal) followed by a much slower monotonous deactivation. Only Weitkamp *et al.* (3) have emphasized these two different regimes, attributing the first one to "monomolecular layers of nickel species deposited on the active Co-Mo-S sites" and the second to the generally admitted phenomenon of pore plugging.

Deactivation for HDS or HDN reaction as a function of the percentage of poisonous metal irreversibly adsorbed on the catalyst has not been so extensively studied or published, except for a correlation between HDM deactivation and cracking of asphaltene deactivation by Takeuchi et al. (2), and an interesting work on thiophene HDS at 1 atm by Mitchell et al. (5), performed on a sulfided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. They used either vanadyl phthalocyanine or a concentrated mixture of vanadium and nickel petroporphyrins dissolved in CH<sub>2</sub>Cl<sub>2</sub> and injected in liquid form on the catalyst in the reactor working in a gas-flow system. They observed an important but monotonous deactivation correlated to the amount of solution injected, which is not necessarily correlated to the loading in poisonous metal; the ligand, phthalocyanine or porphyrin, can also poison the catalyst in these conditions. In fact, they observed no significant differences between  $H_2$ (phthalo) and VO(phthalo).

In this article, we shall show the effect of vanadium poisoning on an industrial NiMo/ $Al_2O_3$  catalyst (HR346 PROCATALYSE) for the thiophene HDS reaction by varying the vanadium deposition procedure and loading (for some of the catalysts, the pyridine HDN at 1 atm, will also be reported).

At the same time, the nature or the form of the vanadium will be followed by EPR and metal solid NMR (the same technique which has already been used for the  $^{59}$ Co study (6)).

## EXPERIMENTAL

*NiMo/Alumina characteristics.* The HR346 NiMo from PROCATALYSE contains 2.4% of Ni and 8.1% of Mo, determined by atomic absorption. The Rhône-Poulenc alumina extrudates used as support, have a mononodal pore distribution centered on 110 Å. The pore volume and the surface area of the catalyst in its oxidic form are respectively 0.5 cm<sup>3</sup>/g and 210 m<sup>2</sup>/g.

Preparation of vanadyl porphyrins. Two model vanadyl porphyrins were prepared, the (VO)TPP (vanadyl mesotetraphenylporphyrin) and the (VO)MTHOPP (vanadyl meso-tetra-(*p*-*n*-hexyloxiphenyl)porphyrin; see Fig. 1).

The synthesis of  $H_2$ TPP is adapted from (7). An equimolecular solution of benzaldehyde and pyrrole in proprionic acid was refluxed for 30 min. After cooling the purple crystals were filtered, washed (acetone), and dried (typical yield: 20%). The vanadyl group was introduced by refluxing a solution of H<sub>2</sub>TPP and vanadyl acetylacetonate (VO)acac2 (large excess) in phenol at 220°C. After cooling, a selective dissolution of phenol with methanol left the product which was recrystallized from CHCl<sub>3</sub>–CH<sub>3</sub>OH (yield > 95%). The purity was controlled by UV/visible spectroscopy. The solubility of the (VO)TPP in boiling toluene is approximately  $3.10^{-4}$ mole/liter or 20 ppm of vanadium metal.

To improve the solubility, we planned to prepare a more soluble vanadyl porphyrin. The access to the corresponding mesotetraalkylporphyrins being limited by low reaction yields (8), we switched to porphyrins possessing alkyl chains attached to the meso-phenyl groups. Using an original synthesis (9) in which benzaldehyde was replaced by *p-n*-hexyloxybenzaldehyde,



FIG. 1. Structure of the two vanadyl porphyrins.

 $H_2$ MTHOPP was obtained in ca. 20% yield. The metallation step was effected as above (>95% yield) to give (VO) MTHOPP whose solubility in boiling toluene is in excess of 2000 ppm of vanadium.

A dehydrated Boscan distillate (>210°C) containing (VO)porphyrins and a mixture (>25 components) of hydrocarbon free vanadyl petroporphyrins extracted from Moroccan Timhadit oil shale were also examined by EPR spectroscopy.

Vanadium salts. Ammonium-monovanadate p.a. (Merck)  $NH_4VO_3$  and Vanadyl acetylacetonate >99% (Janssen Chimica)  $VO(acac)_2$  were used without further purification.

Catalysts preparations. A first series of catalysts was impregnated with a water solution of NH<sub>4</sub>VO<sub>3</sub> on the oxidic NiMo-HR346 form, using the incipient wet impregnation method. After drying at 120°C for 12 h, the catalyst was calcinated at 500°C in pure air for 2 h. These catalysts will be called VAN-0 (a blank without vanadium which has been treated by water and the different calcinations in the same way) to VAN-x, where x is the percentage of vanadium metal weight (code VAN for vanadate). A catalyst containing 8% of vanadium has been prepared from an ammonium vanadate water solution on the same alumina support, but without the active NiMo phase, and called V-8.

A catalyst containing 2.3% of vanadium

on NiMo-HR346 was prepared from an alcohol solution of vanadyl acetylacetonate and called VAC-2 (VAC for Acac). The same calcination procedure was followed for this catalyst.

In order to reproduce the in situ poisoning process realized by the vanadyl porphyrins contained in oil, a second series of catalysts was prepared from the (VO) MTHOPP; they were called VAP-x (VAP for porphyrin). The NiMo-HR346 extrudates were presulfided by the procedure we always used, i.e., room temperature and 15 min under pure  $H_2$ , then under  $H_2S/H_2-2\%$ ; from room temperature to 450°C over 35 min, then 2 h under these conditions; cooling from 450 to 227°C for HDS test reaction or down to room temperature over 2 min for other purposes. The extrudates were then transferred under pure argon in a reactor containing a solution of the required amount of (VO)MTHOPP in toluene + thiophene (0.5%). The high solubility of (VO)MTHOPP allowed us to use a reasonable amount of toluene ( $\sim 25 \text{ cm}^3$  of solution per gram of extrudate); for the same amount of vanadium one needed 2.5 liters of toluene with (VO)TPP. We did not want to use a more efficient chlorinated solvent because of the unpredictable effect of chlorine on the catalyst and because toluene satisfactorily reproduced the environment of the porphyrin in the crude oil. The mixture was then stirred and left under

reflux at 120°C for 2 to 3 h; the solvent was then distilled to dryness and the catalyst transferred back to the reactor to be retreated by H<sub>2</sub>S/H<sub>2</sub> for 2 h. In order to analyze these catalysts either by EPR or by NMR, the samples, after rapid cooling, were transferred under pure argon, in a glove box, into the cells (Pyrex or quartz for EPR and Teflon for NMR) and sealed. For catalytic test, the extrudates were ground and sieved between 0.2 and 0.5 mm, and stored. A VAP-0 catalyst was prepared by following the same procedure but without porphyrin in the toluene solution and a VAP- $H_2$  catalyst with the same amount of  $H_2MTHOPP$  as the amount of (VO) MTHOPP used for the preparation of VAP-1. Finally, the alumina support was also impregnated with (VO)MTHOPP under the same conditions in order to check the effect of the presence of the active phase of the catalyst on the nature of the vanadium species after the preparation; this catalyst was called VAPAL-1 (1% of vanadium from porphyrin on pure alumina, sulfided).

A fraction of VAP-0.5 and VAP-1 was then calcinated in dry air at 500°C for 2 h in order to simulate an oxidative regeneration where coke-like and coke poisons are burnt off; these catalysts were called VAP-0.5R and VAP-1R (R for regenerated).

In order to have standard spectra for the NMR analysis, three other samples were prepared: bulk  $V_3S_5$  and  $V_5S_8$ , obtained by direct synthesis between vanadium metal and sulfur and V/SiO<sub>2</sub>-20 wt% obtained by impregnation of ammonium vanadate followed by a calcination in air at 500°C (SiO<sub>2</sub> Kieselgel 60 from Fluka with 550 m<sup>2</sup>/g).

Activity measurements. HDS of thiophene and HDN of pyridin were used as test reactions in a gas-flow fixed bed reactor working under differential conditions. The partial pressure of thiophene was 20 Torr at a reaction temperature of 227°C and the partial pressure of pyridin 4 Torr at a reaction temperature of 450°C. The total pressure was 1 atm with H<sub>2</sub> as complement. The conversions were always kept very low (below 2.5%) and the rate (in mole/s g(of catalyst)) was determined by plotting the conversion  $\alpha$  versus the reverse of the space velocity (10). The conditions of sulfidation of the catalyst have been detailed above.

*EPR measurements*. The EPR experiments were performed at room temperature and at 120°K, using a Brucker ER420 X-band spectrometer equipped with a TE<sub>104</sub> cavity, an NMR gaussmeter, a frequency meter, and a BNC 12 computer for data-handling facilities. All the spectra were recorded at low enough power to prevent saturation effects and with a sufficiently low modulation amplitude (100 kHz) to prevent distortion.

All the spectra show the general features, characteristic of VO(IV) complexes in the solid state (12). The hyperfine structure due to the coupling of the electron with the nuclear spin ( $s = \frac{1}{2}$ ,  $I = \frac{7}{2}$ ) is often well resolved and may be described by the principal values of the hyperfine coupling and g-factor tensors, obtained from the powder spectra; in the case of a planar symmetry:  $a_{\parallel}$ ,  $a_{\perp}$ ,  $g_{\parallel}$ , and  $g_{\perp}$ . In the following the a values have to be understood as absolute values since they are probably all negative (12).

Metal solid NMR measurements. The NMR measurements were performed in a first series of analyses at 4.2°K (liquid helium) for the sake of sensitivity. A commercial Bruker CXP100 pulsed spectrometer equipped with a box-car integrator was used. The spectra were obtained using a spin-echo technique by scanning the magnetic field and digitally recording the spinecho intensity yielded by the box-car integrator versus the field intensity, H. The apparatus frequency was set at 19,124 kHz and the field was swept between 15.8 and 18.3 kOe to cover the <sup>51</sup>V NMR spectrum. In addition, the spectra were recorded for different time intervals (TI) between the spin-echo generating  $\pi - \pi/2$  pulse sequence. This technique allowed us to discriminate between different V sites and between aluminium and vanadium resonances according to their possibly different longitudinal relaxation time  $T_1$ .

In a second series of analyses, the frequency was set at 15,200 KHz, the field was swept between 12.3 and 14.7 kOe, and the temperature after optimization was selected at 80°K.

#### RESULTS

HDS activity. The HDS activity of the various catalysts is reported in Table 1 together with the concentration in vanadium obtained by atomic absorption.

In Fig. 2, obtained from the values reported in Table 1, two main features must be emphasized.

(i) Whatever the source and the procedure of deposition of the vanadium, one observes a sharp deactivation of the catalyst, depending on the amount of vanadium (the blank experiments VAN-0, VAP-0 or

TABLE 1

Thiophene HDS Activities and Vanadium Concentration on NiMo-HR346

Catalysts	V wt%	$r \times 10^{-10}$ (in mole/s g)	α (in %)	
HR346 fresh	0	18,200	2.0	
VAN-0	0	15,000	2.0	
VAN-1	0.87	7,800	1.2	
VAN-2	1.84	5,800	1.2	
VAN-5	4.65	1,530	0.5	
VAN-7	7.53	1,160	0.4	
VAN-8	7.93	1,050	0.6	
VAN-10	11.78	630	0.8	
V-8	7.81	640	0.9	
VAC-2	2.30	5,340	0.9	
VAP-0	0	16,200	2.2	
VAP-H <sub>2</sub>	0	13,500	2.45	
VAP-0.5	0.48	6,150	1.3	
VAP-1	1.00	1,400	0.8	
VAP-0.5R	0.48	10,350	3.0	
VAP-1R	1.00	8,570	1.3	

Note. The conversion  $\alpha$  reported for each catalyst is the maximum which has been used for the rate determination, generally obtained from three measurements at three different space velocities.



FIG. 2. HDS activity versus vanadium content (logarithmic scale) and procedure of poisoning.

even VAP-H<sub>2</sub> show only small deactivation) which reaches the range of activity of poorly dispersed pure vanadium sulfide (catalyst V-8). However, one must emphasize the much stronger poisoning effect of the vanadium when it is impregnated on the sulfided NiMo (ex porphyrin) than on the oxidic phase followed by a calcination. The high activity of VAP-H<sub>2</sub> shows that it is not the porphyrin ring which is responsible for the deactivation but the vanadyl ion contained in it. In addition, if VAP-0.5 or VAP-1 are calcinated in air to simulate an oxidative regeneration, these two catalysts are partly reactivated and reach the values found on the VAN catalyst series prepared in oxidic conditions.

(ii) The two regimes of deactivation (VAN or VAP catalysts) are linear with the logarithm of the vanadium concentration. This is consistent with a statistical distribution of this metal on the whole surface of the catalyst (the classical problem of the amount of paint necessary to cover a wall!).

It was then important to study the nature of the vanadium deposit in these different conditions in order to understand the mechanisms of the poisoning.

HDN activity and selectivity. The HDN

reaction has only been studied on the VAN series because of the peculiar behavior of high vanadium loaded catalyst toward this reaction.

If the deactivation due to the vanadium (42.5 to 31.0) exists for the HDN reaction. it is far less dramatic than for the HDS reaction. In addition, it is very interesting to note that for high vanadium loading one observes an increase of the activity (42.5 to 46.5). As the pure vanadium sulfide catalyst (V-8) has been found in our reaction conditions as the best HDN catalyst, one is tempted to attribute the increase in activity at high loading to the vanadium sulfide on the NiMo. In fact the answer is not so clear because, as it can be seen by comparison of the selectivity in saturated hydrocarbon products or in the nature of the mechanism, between VAN-10 and V-8, these two catalysts are very different; VAN-10 is a much poorer hydrogenating and "acidic" catalyst than the pure vanadium sulfide V-8. In fact V-8 behaves almost like a pure  $MoS_2$  catalyst (17), and the presence of Ni in VAN-10, strongly affects the activity and the selectivity of the vanadium sulfide (see Table 2).

The interest of these results from an industrial point of view is that a large amount of vanadium sulfide (above 5% in weight) on the scavenger precatalyst could ensure a considerable amount of the required denitrogenation in addition to the demetallation and thus supply a better feed to the HDS catalyst.

*EPR analysis.* A detailed physical description of all the spectra (hyper-hyperfined coupling, temperature dependence, etc.) obtained from the various samples which were analyzed will be published elsewhere (11) because only the measures useful for the catalytic study are retained for this article. In Table 3 the main physical constants (hyperfine coupling constants and g-tensors) obtained from these spectra are reported.

The two vanadyl porphyrins in solution have very close spectra (Fig. 3), (for frozen



FIG. 3. EPR spectra at  $120^{\circ}$ K. (a) (VO)TPP in toluene solution; Central field (CF) = 3322.5 G; 2000 G wide. (b) (VO)MTHOPP in toluene solution; CF = 3320.0 G; 2000 G wide. (c) Boscan residue; CF = 3445.0 G; 2000 G wide.

solution,  $a_{\parallel} = 171 \pm 2$  G,  $a_{\perp} = 60 \pm 2$  G,  $g_{\parallel} = 1.973 \pm .002$ ,  $g_{\perp} = 2.012 \pm .002$ ) with, however, some differences due to the slower rotation of the molecule in the largest porphyrin compared to the (VO)TPP at room temperature. The values found for the Boscan residue and for the solution of the oil shale vanadyl porphyrins (see Table 3) show that the soluble vanadyl porphyrin used in this study is a good model for simulating the natural porphyrins.

In the solid state, the spectra differ slightly (Fig. 4); the spectrum of (VO) MTHOPP is better resolved than that of (VO)TPP because of the effect of the substituent chains which separate the magnetic species and thus decrease the dipolar broadening. This solid state analysis gives a

rynume fibly at 450 C						
Catalysts	VAN-0	VAN-2	VAN-5	VAN-7	VAN-10	V-8
$\alpha \text{ (in \%)}$ r × 10 <sup>-10</sup> (in mole/s g)	1.2 42.5	0.8 31.0	1.2 38.9	1.1 36.7	1.2 46.5	2.4 85.2
% saturated hydrocarbons	32.7	18.8	13.2	14.6	11.4	23.7
% acidic mechanism	21.5	21.4	18.2	18.7	16.3	33.8
% metallic mechanism	78.5	78.6	81.8	81.3	83.7	66.2

TABLE 2

Catalysts	VAN-0	VAN-2	VAN-5	VAN-7	VAN-10	V-8
x (in %)	1.2	0.8	1.2	1.1	1.2	2.4
$\times$ 10 <sup>-10</sup> (in mole/s g)	42.5	31.0	38.9	36.7	46.5	85.2
% saturated hydrocarbons	32.7	18.8	13.2	14.6	11.4	23.7
% acidic mechanism	21.5	21.4	18.2	18.7	16.3	33.8
% metallic mechanism	78.5	78.6	81.8	81.3	83.7	66.2

Pyridine HDN at 450°C

Note. % acidic mechanism =  $(C5 + NH_3) + (C3 + C2 + NH_3)$ . % metallic mechanism =  $(C4 + C + NH_3) + (C3 + 2CI + NH_3) + (5CI + NH_3)$ . % saturated hydrocarbons: in the C5 fraction, *n*-pentane + cyclopentane + isopentane/ $\Sigma$ C5.

TABLE 3

Physical Constants Obtained from the EPR Analysis of the Samples

Samples	<i>T</i> (°K)	<i>a</i> <sub>  </sub> (G)	$a_{\perp}$ (G)	8	$g_{\perp}$	$\overline{a}_{0}^{a}$ (G)	<i>a</i> <sub>0</sub> (G)
	300						95
solution	120	171	60	1.973	2.012	97	
(VO)TPP	300						
solid	120	173	60	1.972	1.987	98	
(VO)MTHOPP	300						83
solution	120	171	60	1.973	2.012	97	
(VO)MTHOPP	300	170	60	1.971	2.006	97	
solid	120	173	60	1.958	1.999	97	
Boscan	300	166	60	1.974	1.994	95	
residue	120	169	58	1.974	1.992	95	
Oil shale	300						93
extract solution	120	182	60	1.963	1.999	100	
VO-acac	300						100
solution	120	183	59 <sup>6</sup>	1.955			
VO-acac	300	$\Delta H = 340 \text{ G}$					
solid	120	$\Delta H = 310 \text{ G}$		g = 2.0	)08		
VAP-0.5 <sup>c</sup>	(1) 300	168	55	1.978	1.991	92	
and VAP-1	(2) 300	152	55	1.978	1.991	87	
	(1) 120	168	56	1.970	1.988	93	
VAPAL-1	(1) 300	171	56	1.966	1.984	94	
	(2) 300	154	56	1.966	1.984	89	
	(1) 120	171	56	1.971	1.986	94	

 $a \bar{a}_0 = (2a_\perp + a_\beta)/3$  mean value of the hyperfine coupling constant which must be theoretically equal to  $a_0$  in solution.

<sup>b</sup>  $a_{\perp}$  determined by considering  $\overline{a}_{0} = a_{0}$ .

<sup>e</sup> Species (1) and (2), see text. Spectra at 300 and 120°K identical.



FIG. 4. EPR spectra at  $120^{\circ}$ K. (a) (VO)TPP solid state; CF = 3322.5 G; 2000 G wide. (b) (VO)MTHOPP solid state; CF = 3323.0 G; 2000 G wide.

standard spectrum, where the vanadyl cation is surrounded by four nitrogen atoms and will be used for the determination of the nature of the vanadyl environment on the catalysts, if any are present on the surface.

In order to obtain a standard spectrum where the vanadyl cation is surrounded by four oxygen atoms, we analyzed VO (Acac)<sub>2</sub> in solid state. Figure 5 shows that the hyperfine structure is no longer observable, the lines being strongly broadened by the dipolar coupling, and we only observe the envelope of these lines, 340 G broad.

The sulfided VAN catalysts (oxidic preparation) and the bulk  $V_3S_5$  and  $V_5S_8$  do not show any signal in EPR analysis as long as they are kept under inert (argon) atmosphere.



FIG. 5. EPR spectra at  $300^{\circ}$ K. VO(Acac)<sub>2</sub> solid state; CF = 3422.5 G; 2000 G wide.

Figure 6 reports the three spectra obtained for the catalysts VAP-0.5 and VAP-1 and the porphyrin supported on sulfided pure alumina VAPAL-1. These three spectra are almost identical, their characteristic parameters being very close (Table 3). These spectra show the presence of three vanadyl surroundings (Fig. 7): species 1, probably with four nitrogen atoms surrounding the cation because of the similar a and g parameters found for it and for the solid pure porphyrins ( $a_{\parallel} = 170 \pm 2$  G,  $a_{\perp} = 56 \pm 2$  G,  $g_{\parallel} = 1.97 \pm 0.01$ ,  $g_{\perp} = 1.987$  $\pm$  .004); species 2, similar to species 1, but with a smaller hyperfine coupling constant  $(a_{\parallel} = 153 \pm 1 \text{ G})$ ; species 3 is represented by a very broad (340 G) line (Fig. 7), which,



FIG. 6. EPR spectra at 300°K. (a) VAP-0.5; CF = 3430.0 G; 2000 G wide. (b) VAP-1; CF = 3425.0 G; 2000 G wide. (c) VAPAL-1; CF = 3433.0 G; 2000 G wide.



FIG. 7. EPR spectra at 300°K. (a) VAPAL-1 like Fig. 6c; species 1 = 4 N atoms, species 2 = probably 4 S atoms, species 3 = 4 O atoms. (b) Species 1 + 2 after substraction of species 3.

in shape and width, is identical to that of VO(Acac)<sub>2</sub> in the solid state. If this third species can easily be described as a vanadyl cation surrounded by four oxygen atoms, the second species is still a matter of controversy. One important point is the fact that species 2 disappears immediately when the sample is open to air for the benefit of species 3 with four oxygen atoms (see later for the quantitative measurements). This instability and the variation of the  $a_{\parallel}$  (18) suggest that the vanadyl cation could be surrounded in species 2 by four (or at least two) sulfur atoms on the surface of the support. These sulfur atoms are immediately replaced by four oxygen atoms in air. We hope to be able to synthesize some vanadyl sulfided compounds in order to obtain standard EPR spectra for comparison and draw conclusions on the nature of the unknown unstable species.

By double computerized integration and by using a standard sample (pure (VO)TPP), we were able to evaluate the amount of vanadyl cation contained in different catalysts and, at the same time, measure the relative abundance of the three species. For VAP-0.5, VAP-1, and VAPAL-1 the amount of species 3 (four oxygen atoms) is  $60 \pm 10\%$ ; species 1 (four nitrogen atoms) and species 2 (four sulfur atoms?) have the same "weight," with 20% of the total amount for each of them. Calculations made on VAP-1 and VAPAL-1 after air introduction show 20% for species 1 (four nitrogen atoms) and 80% for species 3 (four oxygen atoms), meaning that species 2 disappear to the benefit of species 3.

The most important result arising from these quantitative measurements is that *all* the vanadium atoms in VAP-0.5, VAP-1, VAPAL-1, and VAP-1 + air (Table 4) are present under the vanadyl form. This is demonstrated by the very good agreement between, on the one hand, the amount of vanadyl ion measured by EPR and, on the other, the amount of vanadium atoms calculated from the weight of the sample and the concentration of vanadium determined by atomic absorption.

The compared EPR analyses of VAP-0.5 and VAP-0.5R (Fig. 8) or of VAP-1 and VAP-1R show that all the vanadyl ions have disappeared after the oxidative regeneration (oxidation to  $V_2O_5$ ) followed by a resulfurization. The surface is now probably covered with a vanadium sulfide devoid of EPR signal and is equivalent to the VAN catalysts prepared through the oxidic path where we do not observe any signal. This finding is in agreement with the increase of the HDS activity of VAP-0.5R and

TABLE 4

EPR Quantitative Analysis of the Vanadium

Samples	Number of V atoms $\times 10^{18}$ determined by weighting	Normalized EPR intensity (%)		
		Expected <sup>a</sup>	Measured	
(VO)TPP	$5.05 \pm 0.50$	Reference	100	
VAP-0.5	$1.62 \pm 0.16$	$31 \pm 4$	39	
VAP-1 in air	$2.58 \pm 0.25$	51 ± 6	51	
VAPAL-1	$3.34 \pm 0.33$	66 ± 8	74	

<sup>a</sup> From the number of atoms (see text).

FIG. 8. EPR spectra at 300°K. (a) VAP-0.5. (b) VAP-0.5R. The two samples are normalized to the same amount of vanadium atoms determined by weighting.

VAP-1R, which is for instance equivalent to the activity of VAN-1 (Fig. 2).

*NMR analysis.* Figure 9 reports the NMR spectra obtained for bulk  $V_3S_5$  and V/SiO<sub>2</sub> (VAN-30) in its oxidic form and in its sulfidic form.

The very strong signal due to the Al

atoms hides the vanadium signal on alumina supported catalysts. Thus, in order to show that  $V_2O_5$  is completely sulfided, in the conditions which were used throughout this work, one had to prepare this oxide on a silica support. The results obtained on this support are probably very close to those we should obtain on alumina.

No NMR signal has been detected either for pure solid vanadyl porphyrins or for the VAP catalysts before regeneration.

The long relaxation time  $(T_1)$ , 2 s, of the vanadium oxide allowed us to discriminate between the oxidic and the sulfidic form  $(T_1 \le 10 \text{ ms})$ . In varying the time interval between the impulsions in the analysis of the sulfidic form, we did not observe any change in the spectra at the value of the field corresponding to the oxide, and thus one could conclude that all the oxide was sulfided.

In addition, by comparing the sulfidic spectrum with the spectrum of the bulk  $V_3S_5$  (which are almost identical in terms of

FIG. 9. Metal solid NMR spectra. Temp.:  $4.3^{\circ}$ K. Time interval TI = 10 ms for V<sub>3</sub>S<sub>5</sub> and sulfided VAN-20 and 2 s for oxidic VAN-20. VAN-20 = V/SiO<sub>2</sub> with 20% of vanadium.







FIG. 10. Metal solid NMR spectra. Temp.:  $80^{\circ}$ K. Time interval TI = 0.5 ms. VAN-10 = NiMo/Al<sub>2</sub>O<sub>3</sub> with 11.78% of vanadium.

Knight shift and relaxation time), one could reasonably assume that the sulfidic form of the catalyst which has been calcinated before sulfidation is a vanadium sulfide of the nonstoichiometric phase  $VS-VS_2$ .

Figure 10 reports a second series of NMR spectra where we have been able "to see" the vanadium sulfide on the alumina supported NiMo VAN-10 containing 11.78% of vanadium. In order to extract the vanadium signal from the large aluminium peak, one had to increase the temperature to 80°K and to shorten the time interval TI to 0.5 ms. The vanadium is definitely under a sulfidic form because of the short relaxation time. The Knight shift of the vanadium atoms corresponds to species III of V<sub>5</sub>S<sub>8</sub> observed by Silbernagel et al. (15); but species II is not observed. This sulfide is probably very much dispersed and the two species are not discernible and one observes a single large peak as in  $V_3S_5$ .

## DISCUSSION

Two different states of the vanadium at low concentration must be considered in order to explain its poisoning effect on the HDS reaction on classical NiMo catalysts.

State 1. Before sulfidation, the vanadium is oxidized to  $V_2O_5$  by a calcination in air at

temperatures above 400°C as is shown by NMR. At the same time, either nickel and molybdenum are still in their oxidic form if the catalyst is fresh (precursor) or are oxidized by desulfuration (formation of  $SO_2$ ) of the nickel-molybdenum sulfides by an oxidative regeneration.

Two different ways for the vanadium to poison the NiMo catalyst can be proposed.

(i) During the sulfidation process, the vanadium competes with the nickel on the edges of microcrystallites of  $MoS_x$  in order to form interspecies V-Mo which block the formation of Ni (or Co) "octahedral rapid" atoms which are the key of the synergy (6, 14). About 2 to 3% of vanadium (same amount as the nickel at the maximum of synergy) must thus be introduced in order to kill the synergy between nickel and molybdenum. It is exactly the same concentration that we found when the NiMo catalyst reaches the activity of a nonpromoted Mo catalyst.

(ii) The vanadium is not competing with nickel but lies on the basal plans of the  $MoS_x$  microcrystallites, using these sulfurmolybdenum-sulfur plans to develop a  $V_5S_8$ - or  $V_{1/4}VS_2$ -like structure where the  $VS_2$  plans are replaced by  $MoS_2$  plans. The vanadium will occupy the  $V_{1/4}$  plans (type I in the Silbernagel *et al.* terminology (15)) and forms a dispersed  $V_{1/4}MoS_2$  or  $VMo_4S_8$ compound. Such a compound has not yet been synthetized in bulk form, but can be stabilized on a monolayered form of  $MoS_2$ . Its stoichiometry (one V atom for four Mo atoms) also corresponds to 1 to 2% of vanadium, the amount necessary to poison severely the NiMo catalyst. This second hypothesis corresponds to the NMR analysis and, in addition, is in better agreement with the statistical distribution of the vanadium poison deduced from the logarithmic plot of the Fig. 2.

The poisoning process at high concentration of vanadium can easily be understood if one assumes that, using VMo<sub>4</sub>S<sub>8</sub> as a base, V<sub>5</sub>S<sub>8</sub> is developed on the top of the first V layer, poisoning more Mo atoms, and then plugging the pores of the catalyst for the very high concentration. Silbernagel (13) has clearly shown by using nonpulsed NMR that at high loading most of the vanadium is in a sulfided form close to V<sub>5</sub>S<sub>8</sub>.

State 2. The vanadium contained in a vanadyl porphyrin is deposited on the sulfided catalyst in a sulfidic environment. The EPR measurements clearly show that the vanadyl group is preserved even after severe treatment under  $H_2S/H_2$  at 450°C. The striking fact is that, whether or not in the presence of the active phase on the support, the same relative amounts of each vanadyl species were observed: 60% surrounded by four oxygen atoms, 20% by four nitrogen atoms, and 20% by probably four sulfur atoms. In addition, the concentration of vanadium (0.5 or 1%) did not affect this distribution. It is thus logical to deposition-decomconclude that the position of the vanadyl porphyrin is statistical on the whole surface of the catalyst as it is confirmed by the logarithmic plot on Fig. 2 for the VAP catalysts.

As it is not possible to find oxygen atoms on the active sulfided phase, only a maximum of 40% of vanadyl can interfere with the active phase. Thus, on a catalyst containing about 8% of molybdenum, only one atom of vanadium (in vanadyl form) for about nine atoms of molybdenum is enough to destroy the synergy completely and give a catalyst which has the same activity as Mo without Ni on alumina. In the model of the surface that we have proposed (6, 14), only one atom of Mo out of nine is bound to a "rapid octahedral" cobalt (or Ni) atom which confers on it a superactivity due to an electronic transfer in terms of Harris and Chianelli's theory (16), and explains most of the synergy. If one assumes that these sites on the active phase are selectively chosen by the vanadyl surrounded by four nitrogen or sulfur atoms, one has the explanation of the dramatic poisoning effect of the vanadyl porphyrins on the HDS catalysts which is well illustrated by the sharper slope of the VAP catalysts compared to the VAN catalysts (Fig. 2). An oxidative regeneration of these catalysts reactivates the catalysts not only because of the burning of the coke, but also because it transforms state 2 (vanadyl species) into state 1 (sulfide) (see Fig. 8) which allows more vanadium to be present on the catalyst for the same degree of deactivation.

An interesting route of regeneration for future study will be to extract (washing, complexing?) the vanadyl ions before calcination and formation of  $V_2O_5$  followed by a vanadium sulfide, two products which are not extractable under economical conditions.

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