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Electron Spin Resonance Study of Active Centers in Nickel–Tungsten Sulfide Hydrogenation Catalysts

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Electron spin resonance absorptions have been found in nickel–tungsten sulfide and tungsten disulfide hydrogenation catalysts. One of these absorptions is identified as being due to surface tungsten ions in a coordination of low symmetry. The intensity of this ESR signal decreases with increasing sulfur content of the catalyst or by adsorption of cyclohexene or benzene on its surface. For a wide variety of tungsten-disulfide based catalysts the hydrogenation activity for benzene is proportional to the intensity of this ESR absorption. It is concluded that the active centers in these catalysts are tungsten ions, probably in the trivalent state.

1. INTRODUCTION

Ternary sulfides are important because of their catalytic action in hydrogenation, hydrocracking, and hydrodesulfurization processes (*1*). In an earlier paper (*2*) on the kinetics of hydrogenations over nickel-tungsten sulfide catalysts, it was shown that the active centers in these catalysts are anion-vacancies. The aim of the present paper is to further define the nature of the active centers in nickel–tungsten sulfide. To this end, electron spin resonance absorptions in tungsten disulfide-based compounds were studied. The relations between the intensity of the ESR signal and the catalytic activity, the adsorption of unsaturated hydrocarbons and the adsorption of sulfur compounds on this ternary sulfide are established.

2. EXPERIMENTAL METHODS

Procedures for determinations of catalytic rate constants and specific surface areas, as well as specifications of materials used, are given in an earlier paper (*2*).

The preparation of unsupported sulfide catalysts was mainly done by heating a mixture of the elements in stoichiometric proportions in closed quartz ampoules (*2*). Sometimes tungsten disulfide was heated with nickel to prepare Ni–W–S. Some catalysts with low nickel contents were prepared by impregnation of tungsten disulfide. Other preparations were obtained by coprecipitation of tungsten and nickel sulfides from solutions of ammonium tetrathiotungstate and nickel nitrate. Tungsten disulfide was also prepared by thermal decomposition of ammonium tetrathiotungstate crystals in vacuum at 300–400°C [Ref. (3)]. Alumina-supported catalysts were made by a "dry impregnation" method, starting with ammonium tungstate and nickel nitrate solutions and alumina, prepared by decomposition of aluminum triisopropylate. The impregnated alumina was dried, calcined at 500°C, and ultimately sulfided in a H_2S/H_2 mixture at 450°C. Analysis of the catalysts for nickel, tungsten, and sulfur was made by decomposing the sample in a borax melt and proceeding with an X-ray fluorescence technique.

Catalytic activities of sulfide catalysts were measured by determining the hydrogenation rate constant for benzene at 400°C, with 1% v carbon disulfide in the liquid feed. The influence of the sulfur potential of the gas phase on the properties

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of tungsten disulfide-based catalysts was studied by equilibration of the catalysts with H_2S/H_2 mixtures obtained by reaction of hydrogen with FeS/Fe mixtures for the higher H_2S/H_2 ratios and with Ni_3S_2/Ni mixtures for the lower ratios (*4*). Determinations of actual H_2S/H_2 ratios were made with a Dohrman microcoulometer.

Electron spin resonance spectra were recorded between 20 and 300°K with a Varian X-band ESR spectrometer equipped with Fieldial and 100 kcps modulation unit. The first derivative of the absorption is recorded.

3. ELECTRON SPIN RESONANCE IN NICKEL–TUNGSTEN SULFIDES AND IN TUNGSTEN SULFIDE

Fresh model catalysts such as nos. 1, 2, and 3 in Table 1 contain free nickel. Their ESR spectra show a broad resonance typical of ferromagnetic substances (*5*). During the initial periods of hydrogenation of benzene/carbon disulfide mixtures or, alternatively, during equilibration with H_2S/H_2 mixtures the catalyst takes up sulfur to reach a steady-state sulfur content. The ESR spectrum of the resulting catalyst is shown in Fig. 1. It does not show a ferromagnetic resonance any more, but instead shows:

i. a spuriously occurring signal at 1500 Oe, probably produced by a minor impurity in the quartz sample tube;

ii. a sharp asymmetric peak at about 2500 Oe which is sometimes resolved into three components and is found exclusively in catalysts prepared at high temperature, irrespective of the presence of nickel;

iii. a sharp symmetric signal at about 2800 Oe, occasionally split into two components and appearing spuriously in high-temperature samples without connection with the presence of nickel;

iv. a broad wave at 3250 Oe, with a width between points of maximum slope of about 260 Oe;

v. a sharp peak at 3270 Oe, superimposed on signal (iv), and corresponding to an

TABLE 1

PREPARATION AND PROPERTIES OF CATALYSTS USED

No.	Composition[a]	Preparation	Specific surface area S (m^2/g)	Activity[b] k [ml(g cat)$^{-1}$ hr^{-1} atm^{-1}]	Surface density of active sites[c] (m^{-2})
1	$Ni_{0.50}WS_x$	WS_2 + Ni, 800°C	0.34	—	—
2	$Ni_{0.50}WS_x$	Elements, 800°C	—	—	—
3	$Ni_{0.50}WS_x$	WS_2 + Ni, 800°C	0.95	0.15	(1.1×10^{17})
4	$Ni_{0.016}WS_x$	Impregnated WS_2	2.20	0.069	(2.3×10^{16})
5	$Ni_{0.53}WS_x/Al_2O_3$	Impregnation, calcination, sulfiding	—	1.03	—
6	WS_x/Al_2O_3	Impregnation, calcination, sulfiding	—	0.0071	—
7	WS_x/Al_2O_3	Impregnation, vacuum-treated at 400°C	—	0.028	—
8	WS_2	Thiotungstate, decomposed at 400°C	20.0	0.20	5.4×10^{15}
9	WS_2	Elements, 850°C	2.55	0.0016	4.8×10^{14}
10	$WS_{1.95}$	Elements, 800°C	2.65	0.011	2.4×10^{15}
11	WS_2	Impure elements, 900°C	0.98	0.020	1.4×10^{16}
12	WS_2	Impure elements, 900°C	0.89	0.0018	1.4×10^{15}
13	WS_2	Impure elements, 900°C	2.90	0.0053	7.7×10^{14}
14	WS_2	Impure elements, 900°C	4.30	0.0013	5.5×10^{14}
15	WS_2	Impure elements, 900°C	4.25	0.0010	6.8×10^{14}

[a] The sulfur content of the catalysts is dependent on the H_2S/H_2 ratio and the temperature during equilibration. The x indicates that it is not known precisely, but $x \approx 2.0$–2.3.

[b] Benzene hydrogenation rate constants at 400°C, 1% v CS_2 admixed with benzene.

[c] Derived from ESR intensity, see text.

FIG. 1. ESR spectrum of $Ni_{0.5}WS_x$ (No. 3, Table 1) after use in cyclohexene hydrogenation.

almost pure free-spin resonance ($g = 2.0023$) which is especially strong in spent catalysts and at least partly attributed to carbonaceous radicals on the catalyst surface.

Tungsten disulfide-based catalysts supported on pure alumina show signals very similar to resonances (iv) and (v) above (compare Fig. 2a and b). Impregnated nickel–tungsten sulfide prepared at low temperature shows spectra which are again very similar, see Fig. 2c.

Signals due to surface phenomena were identified by the relation between signal intensity and specific surface area and by the effect of the adsorption of unsaturated hydrocarbons. A series of catalysts of different specific surface areas S were prepared by grinding portions of the same batch of NiW_2S_4 (No. 1 in Table 1). The intensity of the ESR signals in the spent catalysts were proportional to the area S for (iv) and (v), but not for the other signals. This result for signal (v) is in line with its assignment to adsorbed carbonaceous residues. The linear relationship (Fig. 3) between S and the intensity of signal (iv) shows that this ESR absorption is due to a surface ion. This is also borne out by the effect of the adsorption of cyclohexene and benzene on the intensity of (iv), see below.

To identify the surface ion producing signal (iv) the ESR spectra of nickel sulfides and tungsten sulfides were compared with (iv). Samples of Ni_3S_2 or NiS did not show any absorptions up to 13 000 Oe. On the other hand, several nonstoichiometric tungsten sulfides showed broad signals at 3250 Oe. Decomposition of ammonium tetrathiotungstate $(NH_4)_2WS_4$ produces tungsten sulfides with high specific surface areas (*3*). At decomposition temperatures below 300°C sharp ESR signals due to W^{5+} ions are found therein. Samples prepared over 330°C show a broad signal at about 3250 Oe (Fig. 4a, b) which has been ascribed to surface W^{3+} ions (*3*). Sulfur-deficient tungsten disulfide ($WS_{1.95}$) prepared by heating the mixed elements at 800°C gives an ESR signal (Fig. 4c) which is similar, except for the high-field wing A. By contrast, stoichi-

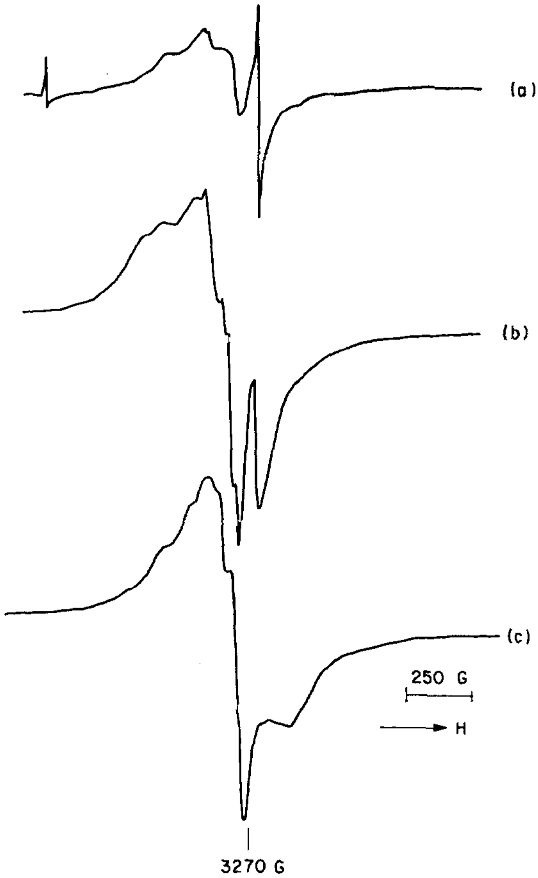

FIG. 2. ESR spectra of nickel–tungsten sulfides: (a) unsupported $Ni_{0.5}WS_x$ from the elements (No. 2); (b) $Ni_{0.53}WS_x$ on γ-Al_2O_3 (No. 5); (c) $Ni_{0.016}WS_x$ (No. 4).

ometric WS_2 prepared from the elements does not show these broad signals, but sometimes gives sharp signals (iii) and (v) as in Fig. 4d.

Comparison of the broad electron spin resonance absorptions found in tungsten sulfides around 3250 Oe (Fig. 4a–c) with those in nickel–tungsten sulfide (e.g., Fig. 4e–g) shows a great similarity indeed. The broad signals appear at very much the same field, moreover their widths and the temperature dependence of their intensities are virtually the same. The spectrum of impregnated nickel–tungsten sulfide even shows the high-field wing A that had been found in $WS_{1.95}$ also (Fig. 4c and g). The evidence is that the surface ions producing the broad ESR signal in nickel–tungsten sulfide catalysts are very probably tungsten ions, presumably W^{3+} ions.

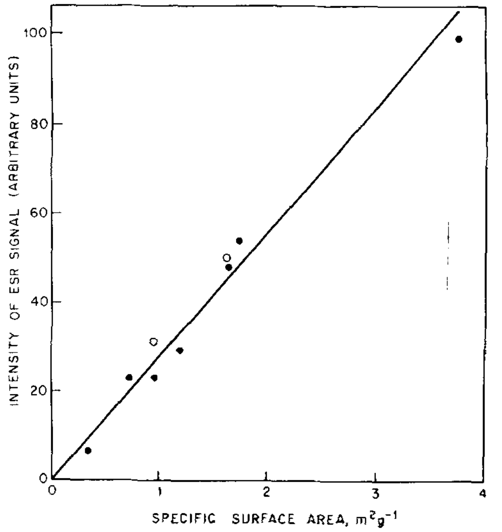

FIG. 3. Intensity of ESR signal (iv) in ground $Ni_{0.50}WS_x$ after use in hydrogenation of CS_2/cyclohexene: (●) ground in air; (○) ground in nitrogen.

4. CORRELATION OF ESR INTENSITY WITH ADSORPTION AND HYDROGENATION ACTIVITY

The number of active hydrogenation sites in nickel–tungsten sulfide catalysts has been found (2) to depend on the hydrogen sulfide content of the gasphase through the equilibrium

$$\square + H_2S \rightleftarrows S(ads.) + H_2. \quad (1)$$

Here, $\square$ is an active site. If the surface tungsten ions giving rise to the ESR signal (iv) were the active sites, the intensity of this signal would be expected to be influenced by equilibration of the catalysts with H_2S/H_2 mixtures at elevated temperatures. Specifically, the number of free active sites, and hence the intensity of the ESR signal, would drop with increasing H_2S/H_2 molar ratio and with decreasing temperature. Experiments with Ni–W–S catalysts prepared from the elements and with alumina-supported Ni–W–S show that indeed there is a strong correlation of the ESR intensity with the H_2S/H_2 ratio (Fig. 5), less so with the temperature. By contrast, tungsten disulfide prepared from thio-

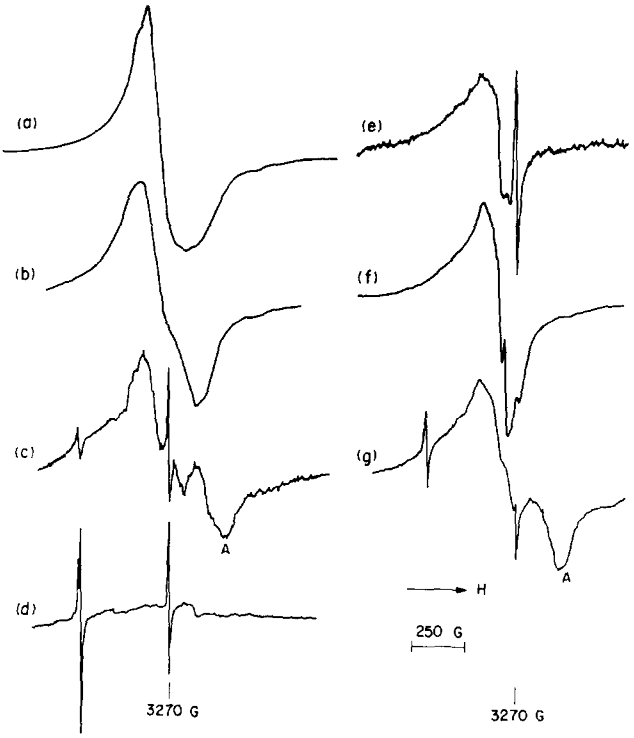

FIG. 4. ESR signals of tungsten disulfide and nickel–tungsten sulfide: (a) WS_2, prepared by decomposing $(NH_4)_2WS_4$ in vacuum, 3 hr at 400°C; (b) Same, 5 hr at 400°C; (c) $WS_{1.95}$ prepared from the elements (No. 10); (d) $WS_{2.0}$ prepared from the elements (No. 9); (e) $Ni_{0.53}WS_x$ prepared from the elements, treated with H_2S/H_2; (f) $Ni_{0.53}WS_x$ on γ-Al_2O_3 (No. 5); and (g) $Ni_{0.016}WS_x$ (No. 4).

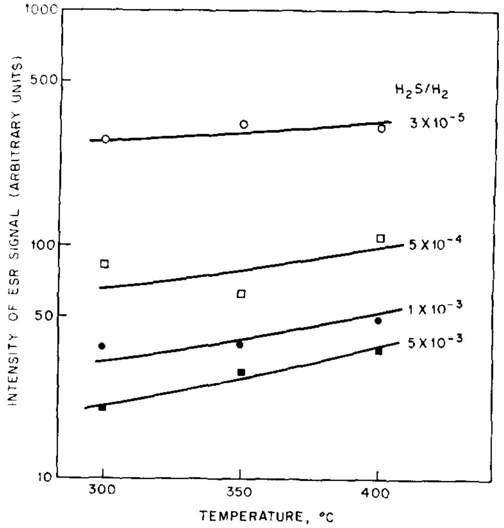

FIG. 5. Dependence of ESR intensity on H_2S/H_2 treatment: (○, □) $Ni_{0.53}WS_x$ on γ-Al_2O_3; (●, ■) $Ni_{0.53}WS_x$ from the elements.

tungstate or from the elements and similarly treated at the conditions given in Fig. 5, did not experience a change in the intensity of its ESR absorption. This is in line with observations that its catalytic activity is not affected either (*6*). However, its ESR intensity and catalytic activity do depend on the sulfur deficiency "frozen in" after preparation (Table 1, Nos. 9 and 10).

Another link between the catalytic activity and the W^{3+} ESR signal (iv) is found in the effect of adsorption of benzene and cyclohexene on the intensity of the signal. Nickel–tungsten sulfide prepared from the elements (No. 2 in Table 1) and equilibrated with 0.2 mole % H_2S in hydrogen at 400°C was treated for 1 hr with nitrogen saturated at room temperature with either benzene or cyclohexene. Recording the ESR spectra before and after treatment shows (Fig. 6) that the intensity of signal (iv) decreases

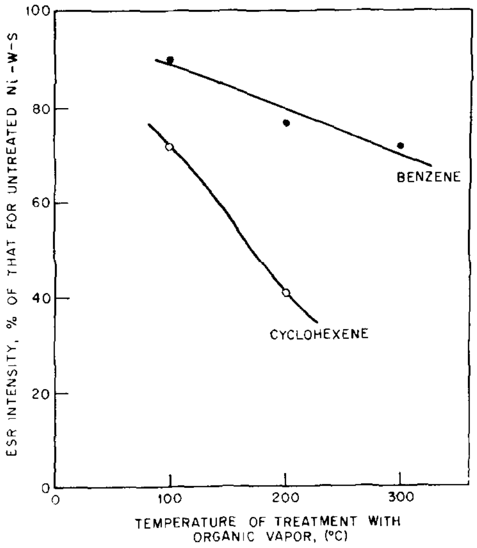

FIG. 6. Effect of treatment with unsaturated hydrocarbons on intensity of ESR signal due to tungsten ions.

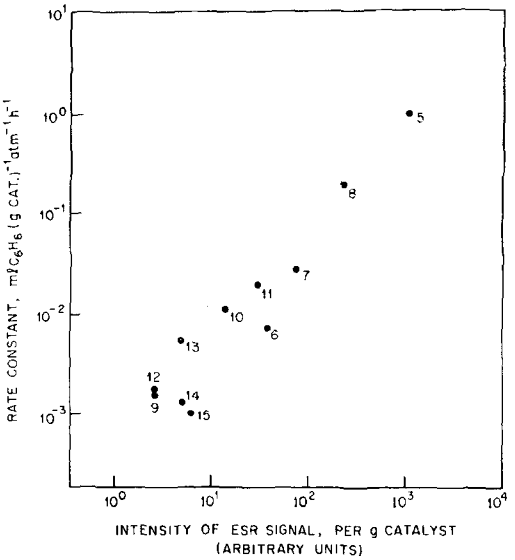

FIG. 7. Correlation of catalytic activity in benzene hydrogenation with intensity of tungsten ESR signal. Numbers refer to Table 1.

by reaction of the catalyst with the organic molecules. There is a concurrent increase of signal (v) which had been assigned to organic radicals on the surface. The effects are irreversible by evacuation at 200°C. Similar results were obtained with WS_2 (Table 1, No. 8).

Strong evidence that the active sites on tungsten disulfide-based hydrogenation catalysts are identical with the tungsten ions giving rise to the broad signal at 3250 Oe is presented by the correlation of the intensity of this signal with the activity in benzene hydrogenation (Fig. 7). The data points in Fig. 7 have been numbered, referring to Table 1. Rate constants for hydrogenation of benzene with 1% v CS_2 were determined at 400°C. ESR spectra were taken of the same samples after treatment at 400°C with 0.1 mole % H_2S in H_2. The intensity of the ESR signal was determined by double integration of the low-field wing of the broad signal at 3250 Oe in the first-derivative spectrum. Thus the influence of high-field signal A (Fig. 4) occurring in some spectra was eliminated as far as possible. The correlation obtained encompasses tungsten disulfide-based catalysts with and without nickel, prepared in six or seven different ways,* with catalytic activities spanning three orders of magnitude. In this range the slope of the correlation in Fig. 7 is unity, indicating a proportionality:

$$k(\text{benzene}) = C \times (\text{number of } W^{3+} \text{ surface ions}). \quad (2)$$

Calibration of the ESR spectrometer with a standard sample of vanadyl disalicylal ethylenediamine yields a value of 4.5×10^{14} electron spins for the equivalent of the arbitrary intensity unit used. This corresponds to an equal number of W^{3+} ions in the low spin state (*3*), provided that no delocalization of electrons lowers the absorption per free electron. It is now possible to calculate the surface density of W^{3+} ions from the specific surface area and the ESR intensity. Results are given in the Table 1. In the case of unsupported nickel–tungsten sulfides, which show low ESR intensities because of their electrical conductivity, the W^{3+} surface density has been calculated

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* Only nickel–tungsten sulfides prepared at high temperatures without alumina are excluded because their electrical conductivity decreases the sensitivity of the ESR measurement.

from the catalytic activity by applying the correlation in Fig. 7. Results have been placed in parentheses in Table 1. It should be noted that the surface density of active sites is low compared with the number of atoms in the surface (10^{14}–10^{17} per m^2 versus about 10^{19} per m^2).

No correlation was found between the activity of the catalysts in cyclohexene hydrogenation and the intensity of their ESR absorptions. This will be discussed in the next paper (*6*).

5. DISCUSSION AND CONCLUSIONS

It has been demonstrated above that nickel–tungsten sulfide catalysts and sulfur-deficient tungsten sulfide show very similar broad ESR signals around 3250 Oe which are due to surface tungsten ions. A significant correlation of the intensity of this ESR signal has been found not only with the adsorption of unsaturated hydrocarbons and with the sulfur deficiency of the catalysts but also with the activity of the catalysts in the hydrogenation of benzene. The ESR signal due to the active sites was discussed earlier (*3*) and attributed to W^{3+} ions. It is concluded that the active sites for benzene hydrogenation in both tungsten sulfide and nickel–tungsten sulfide are tungsten W^{3+} ions. Nickel thus appears to have an indirect influence on the hydrogenation activity in Ni–W–S rather than acting as the active center.

The active sites for cyclohexene hydrogenation do not give an ESR absorption. In this connection it is interesting to note that a comparative study of cyclohexene and benzene hydrogenations on Ni–W–S catalysts led to the conclusion that several sulfur-deficient sites were present (*2*). It is quite possible that cyclohexene and benzene are hydrogenated on tungsten ions in different sulfur coordinations. This will be discussed in a subsequent paper (*6*).

In Ni–W–S model catalysts no new ternary compound could be found by X-ray analysis. Only WS_2 and Ni_3S_2 phases were present. This, and the similarity of the ESR signal in WS_2-based catalysts with or without nickel lead to the conclusion that the active tungsten sites are located in the surface of the WS_2 layer structure.

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