JOURNAL OF CATALYSIS 76, 473–476 (1982)

# NOTE

## An ESR Study on the Stability of Dithiomolybdate and -Tungstate in the Presence of $H_2S$

Co (Ni)–Mo (W)/$\gamma$-$Al_2O_3$ catalysts are widely used for hydrodesulfurization of petroleum feedstocks. It is common practice to pretreat the initial oxidic catalyst with a sulfur-containing compound of low molecular weight. The sulfided modification thus obtained is considered to be the actual active catalyst. There is controversy (*1, 2*) over whether during sulfidation all oxygen ligands of the Mo(W) species present in the fresh oxidic catalyst are exchanged for sulfur, a process resulting in the formation of $MoS_2$ ($WS_2$), or whether the active phase consists of Mo (W) with mixed oxygen and sulfur ligands. In order to investigate the resistance of Mo (W) oxo-sulfo compounds against sulfiding to $MoS_2$ ($WS_2$), we prepared $(NH_4)_2MoO_2S_2$ and $(NH_4)_2WO_2S_2$ and treated them with $H_2S$/He mixtures at various temperatures.

*In situ* ESR spectroscopy was used to analyze the results because this technique was found to be more sensitive and selective than *in situ* uv reflectance spectroscopy (*3*) and XPS (*4*), as applied earlier. $(NH_4)_2MoO_2S_2$ and $(NH_4)_2WO_2S_2$ were prepared as described by Bernard and Tridot (*5*) and identified via infrared spectroscopy. They were sulfided at atmospheric pressure in a $H_2S$/He flow (volume ratio 1/10, flow rate 50 $cm^3min^{-1}$ NTP) under the following conditions: (a) 295 K for 30 min; (b) 393 K, 45 min; (c) 523 K, 90 min; (d) 673 K, 60 min. X-Band ESR spectra were recorded *in situ* at 293 K before and after each treatment.

Figure 1 shows the spectra for $(NH_4)_2MoO_2S_2$. The spectrum of fresh dithiomolybdate consists of two 2-$g$ value signals (signal I: $g_\perp = 1.92, g_\parallel = 1.89$; signal II: $g_\perp = 1.98, g_\parallel = 1.96$) and a weak signal at $g = 2.01$. The $g$ values of signal I are characteristic for $Mo^{5+}$ with oxygen ligands (*6–8*) and the $g$ values of signal II for $Mo^{5+}$ with mixed oxygen and sulfur ligands (*9*). The spectrum remains unchanged after treatment (a). Treatment (b), $H_2S$/He at 393 K, leads to a 15-fold increase of signal I and a 2-fold increase of signal II. Furthermore a 3-$g$ value signal (signal III: $g_1 = 2.029, g_2 = 2.007, g_3 = 2.003$) appears. The origin of this signal is a radical, possibly $O_2^-$ or $SO_2^-$ (*10*). Treatment (c) leads to a decrease of signal II while the intensity of signal I stays the same (note the difference in applied microwave power between Figs. 1b and c). It is difficult to estimate the intensity change of signal III since a new 3-$g$ value signal (signal IV: $g_1 = 2.039, g_2 = 2.017, g_3 = 1.999$) shows up, much stronger than signal III and most probably due to $S_n^-$ radicals (*9, 11*). After treatment (d) signals I, II, and III have almost disappeared, while signal IV has decreased 15 times in intensity, and a broad signal (signal V: $g \sim 2$, $\Delta H \sim 125$ G) has appeared which is very similar to the broad signal in vacuum-treated $MoS_2$ (*12*). The sharp signal ($\Delta H < 10$ G) at $g = 2.003$ is most probably due to impurities (grease).

In Fig. 2 the spectra of $(NH_4)_2WO_2S_2$ are shown. Fresh dithiotungstate shows no ESR signals and neither does the sample after treatment (a) or (b). Treatment (c), $H_2S$/He at 523 K, induces a 3-$g$ value signal ($g_1 = 2.048, g_2 = 2.027, g_3 = 1.994$) most probably due to $S_n^-$ radicals. Treatment (d) results in a three-fold decrease in the intensity of the 3-$g$ value signal and in a new broad signal ($\Delta H \sim 300$ G, $g \sim 1.98$), together with an impurity signal at $g = 2.003$. The broad signal resembles the signal found in vacuum-treated $WS_2$ (*12*).

The assignment of the signals to 2-$g$ or 3-



0021-9517/82/080473-04$02.00/0

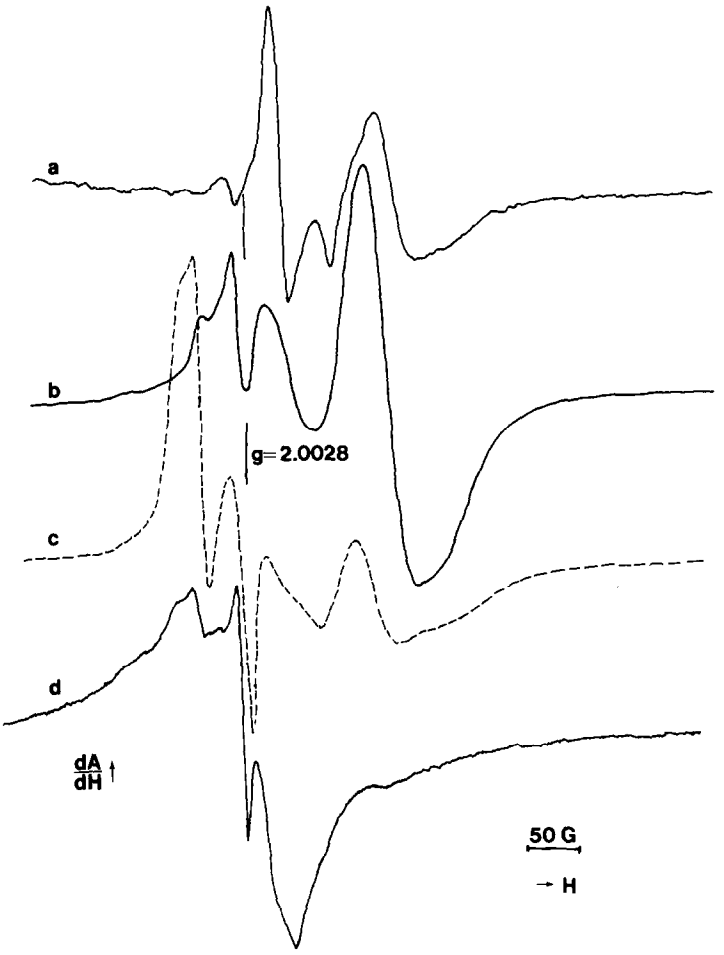


FIG. 1. ESR spectra (recorded at 293 K) of $(NH_4)_2MoO_2S_2$: (a) fresh, microwave power ($P$) = 6 dB of 200 mW, receiver gain ($R.G.$) = $5 \times 10^2$. Treatment (a) yielded the same spectrum; (b) treated with $H_2S$/He at 393 K, $P$ = 6 dB, $R.G.$ = $1 \times 10^2$; (c) treated with $H_2S$/He at 523 K, $P$ = 18 dB, $R.G.$ = $1 \times 10^2$; (d) treated with $H_2S$/He at 673 K, $P$ = 24 dB, $R.G.$ = $5 \times 10^2$.

$g$ value signals was done by means of microwave power saturation measurements at 4.2 K using a liquid helium continuous-flow cryostat (Oxford Instruments). With respect to the 3-$g$ value signal detected in $(NH_4)_2WD_2S_2$ after treatment ($c$), it is worthwhile to mention that Voorhoeve and Wolters (*13*) interpreted similar signals obtained after vacuum treatment at 523 K of $(NH_4)_2WS_4$ as originating from $W^{5+}$ ions. In view of the present data and literature data (*9, 11*) the assignment to sulfur radicals seems more appropriate.

The present work shows that bulk dithiomolybdate contains $Mo^{5+}$ ions with oxygen ligands only, as well as $Mo^{5+}$ ions with oxygen and sulfur ligands. Treatment with $H_2S$/He at low temperature (393 K) increases especially the amount of the first species (reduction). At higher temperatures (523 and 673 K) sulfur radicals are formed and eventually the dithiomolybdate is converted to $MoS_2$. When treating dithiotungstate no $W^{5+}$ ions are detected, probably due to a direct reduction of $W^{6+}$ to $W^{4+}$ ions. At higher temperatures $(NH_4)_2WO_2S_2$

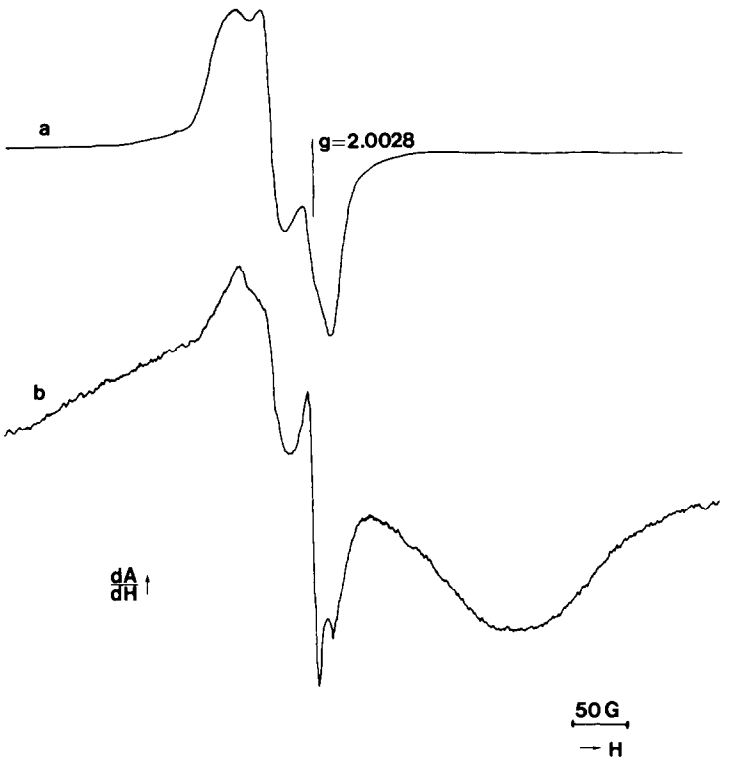


FIG. 2. ESR spectra (recorded at 293 K) of $(NH_4)_2WO_2S_2$: (a) treated with $H_2S$/He at 523 K, $P$ = 6 dB, $R.G.$ = $2 \times 10^1$; (b) treated with $H_2S$/He at 673 K, $P$ = 12 dB, $R.G.$ = $1 \times 10^3$.

is converted to a metal disulfide like in the case of $(NH_4)_2MoO_2S_2$.

These results demonstrate that dithiomolybdate and dithiotungstate anions are unstable in an atmosphere of $H_2S$ and are transformed into metal sulfides. Obviously hydrogen sulfide acts as a reducing agent, which is confirmed by the observation of polysulfide radicals. Our findings are in accordance with results reported by Tsigdinos (*14*) showing that the stability of oxysulfides is questionable. Although in real catalysts there is the additional factor of the interaction with the support, we feel safe in concluding that also in these catalyst systems any molybdenum or tungsten oxosulfo anions initially formed are converted into metal sulfide when contacted with $H_2S$/$H_2$ mixtures at elevated temperatures. In real catalysts we have never been able to observe any ESR signal (such as signal II) that could be ascribed to oxo-sulfo species (*12*).

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*Received June 23, 1981; revised February 26, 1982*

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