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An ESR Study on the Stability of Dithiomolybdate and -Tungstate in the Presence of \( \text{H}_2\text{S} \)

Co (Ni)–Mo (W)/γ-Al₂O₃ 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 MoS₂ (WS₂), 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 sulfidation to MoS₂ (WS₂), we prepared \((\text{NH}_4)_2\text{MoO}_2\text{S}_2\) and \((\text{NH}_4)_2\text{WO}_2\text{S}_2\) and treated them with \(\text{H}_2\text{S}/\text{He}\) 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. \((\text{NH}_4)_2\text{MoO}_2\text{S}_2\) and \((\text{NH}_4)_2\text{WO}_2\text{S}_2\) were prepared as described by Bernard and Tridot (5) and identified via infrared spectroscopy. They were sulfided at atmospheric pressure in a \(\text{H}_2\text{S}/\text{He}\) flow (volume ratio 1/10, flow rate 50 cm³min⁻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 \((\text{NH}_4)_2\text{MoO}_2\text{S}_2\). The spectrum of fresh dithiomolybdate consists of two 2-g value signals (signal I: \(g_1 = 1.92, g_{\parallel} = 1.89\); signal II: \(g_1 = 1.98, g_{\parallel} = 1.96\)) and a weak signal at \(g = 2.01\). The \(g\) values of signal I are characteristic for Mo⁵⁺ with oxygen ligands (6–8) and the \(g\) values of signal II for Mo⁵⁺ with mixed oxygen and sulfur ligands (9). The spectrum remains unchanged after treatment (a). Treatment (b), \(\text{H}_2\text{S}/\text{He}\) 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 \(\text{O}_2^-\) or \(\text{SO}_2^-\) (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 \(\text{S}_\text{n}^-\) 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: \(g \sim 2, \Delta H \sim 125 \text{ G}\)) has appeared which is very similar to the broad signal in vacuum-treated MoS₂ (12). The sharp signal (\(\Delta H < 10 \text{ G}\)) at \(g = 2.003\) is most probably due to impurities (grease).

In Fig. 2 the spectra of \((\text{NH}_4)_2\text{WO}_2\text{S}_2\) are shown. Fresh dithiotungstate shows no ESR signals and neither does the sample after treatment (a) or (b). Treatment (c), \(\text{H}_2\text{S}/\text{He}\) 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 \(\text{S}_\text{n}^-\) radicals. Treatment (d) results in a three-fold decrease in the intensity of the 3-g value signal and in a new broad signal (\(\Delta H \sim 300 \text{ G}, g \sim 1.98\)), together with an impurity signal at \(g = 2.003\). The broad signal resembles the signal found in vacuum-treated WS₂ (12).

The assignment of the signals to 2-g or 3-
Fig. 1. ESR spectra (recorded at 293 K) of (NH₄)₂MoO₄S₂: (a) fresh, microwave power (P) = 6 dB of 200 mW, receiver gain (R.G.) = 5 × 10⁴. Treatment (a) yielded the same spectrum; (b) treated with H₂S/He at 393 K, P = 6 dB, R.G. = 1 × 10⁴; (c) treated with H₂S/He at 523 K, P = 18 dB, R.G. = 1 × 10⁵; (d) treated with H₂S/He at 673 K, P = 24 dB, R.G. = 5 × 10⁵.

The present work shows that bulk dithiomolybdate contains Mo⁵⁺ ions with oxygen ligands only, as well as Mo⁵⁺ ions with oxygen and sulfur ligands. Treatment with H₂S/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 MoS₂. When treating dithiotungstate no W⁵⁺ ions are detected, probably due to a direct reduction of W⁶⁺ to W⁴⁺ ions. At higher temperatures (NH₄)₂WO₂S₂

The assignment to sulfur radicals seems more appropriate.
is converted to a metal disulfide like in the case of \((\text{NH}_4)_2\text{MoO}_4\text{S}_2\).

These results demonstrate that dithiomolybdate and dithiotungstate anions are unstable in an atmosphere of \(\text{H}_2\text{S}\) 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 oxy-sulfides 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 oxo-sulfo anions initially formed are converted into metal sulfide when contacted with \(\text{H}_2\text{S}/\text{H}_2\) 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).

REFERENCES

NOTE.


A. J. A. Konings¹
A. Valster²
V. H. J. de Beer
R. Prins

Laboratory for Inorganic Chemistry
Eindhoven University of Technology
P.O. Box 513
5600 MB Eindhoven
The Netherlands

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¹ Present address: Prins Maurits Laboratory, TNO, P.O. Box 45, 2280 AA Rijswijk (ZH), The Netherlands.
² Present address: Philips Research Laboratories, Prof. Holstlaan, 5600 MD Eindhoven, The Netherlands.