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EPR Studies on Unsupported and Alumina-Supported Sulfided Co–Mo Hydrodesulfurization Catalysts

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EPR has been used to investigate the paramagnetic species present in unsupported and alumina-supported sulfided Co–Mo/(Co/Mo = 0–2.3) catalysts for which the nature of the Co and Mo phases was previously characterized by Mössbauer emission spectroscopy (MES) and EXAFS. Three distinct EPR signals have been observed: MO, MS, and CMS. Signal MO (g_{av} = 1.93) corresponds to oxo-Mo^{5+} ions interacting with alumina, whereas MS ($g_{\parallel}$ = 2.06, $g_{\perp}$ = 1.98) is assigned either to bulk defect species in a MoS_2 phase or to thio-Mo^{5+} species located at the edges of the layered MoS_2 crystallites. Addition of Co decreases the intensity of signals MO and MS and generates a new EPR resonance, CMS, with g_{av} = 2.06 and ΔH = 100–200 G and best identified by its low-field peak at g = 2.08–2.10. Its intensity rapidly increases with Co content and reaches a maximum at Co/Mo $\simeq$ 1. Furthermore, the intensity of signal CMS is found to parallel both the hydrodesulfurization activity and the amount of Co observed by MES to be present as Co–Mo–S. Recent work has shown that the Co atoms in Co–Mo–S are located at the edges of MoS_2. The presence of the CMS signal does therefore provide new evidence for the presence of special Mo atoms neighboring the Co edge atoms. A two-center model is presented to explain the observed properties of the CMS signal. © 1986 Academic Press, Inc.

INTRODUCTION

By use of several techniques including Mössbauer emission spectroscopy (MES), EXAFS, and NO adsorption, it has recently been shown [for reviews see, e.g., Refs. (*1–4*)] that the active sites for hydrodesulfurization (HDS) are associated with Co atoms located at the edges of MoS_2 (in the so-called Co–Mo–S structure). It has been suggested that the surrounding MoS_2 phase plays an important role (*1–6*) and that the active sites could be, for example, a sulfur vacancy shared by the Co atoms and their Mo neighbors. Nevertheless, it has been difficult to obtain direct information on the role of the MoS_2 "support" and the Mo neighbors to the Co atoms although Mössbauer, EXAFS, and magnetic susceptibility measurements show that the MoS_2 "support" strongly influences both the structural and electronic properties of the Co atoms [see, e.g., Ref. (*3*) for a discussion]. EPR may be useful for investigating the possible influence of Co on the neighboring Mo atoms.

Many EPR studies of HDS catalysts have been carried out [see e.g., Refs. (*7–21*)] and correlations between EPR signals and hydrogenation or HDS activity have been proposed in several of these studies. An EPR signal in Ni-promoted WS_2 catalysts was found by Voorhoeve (*7*) to correlate with their hydrogenation activity. However, such a correlation was not observed in the later work by Konings *et al.* (*15*). Silbernagel *et al.* (*19*) observed a correlation between the HDS activity and the intensity of a thio-Mo^{5+} EPR signal in sulfided unpromoted Mo/Al_2O_3 catalysts. These authors did not report studies of promoted catalysts. Recently, Konings *et al.* (*17*) observed a relationship between the intensity of an EPR signal (VI, in their paper) and the

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TABLE 1

Composition of Sulfided Co–Mo Catalysts

Sample[a]	Mo (wt%)	Co (wt%)	Co/Mo[b]
I	8.6	0.00	0.00
II	8.6	0.47	0.09
III	8.6	0.95	0.18
IV	8.6	1.37	0.26
V	8.6	2.32	0.44
VI	8.6	2.80	0.53
VII	8.6	4.96	0.94
VIII	8.6	6.44	1.22
IX	8.6	12.30	2.33
X	0.0	0.50	—
XI	Mo only	—	—
XII	—	—	0.03

[a] Samples I–X are supported on η-alumina; samples XI and XII are unsupported.

[b] Atomic ratio.

HDS activity of sulfided Ni(Co)–W(Mo)/Al_2O_3(SiO_2). This signal was assigned to Mo^{3+} (W^{3+}) species in interaction with promoter ions intercalated at the surface of MoS_2 (WS_2) crystallites (*15, 17*). However, no unequivocal correlation was proposed, in particular, for catalysts prepared by the usual oxidic route.

It is difficult to relate the previous EPR studies to the recent insight regarding the active structures in promoted HDS catalysts since the identity of Co–Mo–S was not established in these studies. In the present work we report EPR results on catalysts where both the amount of Co in the form of Co–Mo–S and the HDS activity are known.

EXPERIMENTAL

The Co/Al_2O_3, Mo/Al_2O_3, and Co-Mo/Al_2O_3 catalysts used in the present investigation are analogous to those described previously (*22, 23*). In short, a series of sequentially impregnated Co–Mo/Al_2O_3 was prepared by adding cobalt nitrate to a calcined Mo/Al_2O_3 catalyst (8.6 wt% Mo) in amounts appropriate to achieve the desired Co/Mo ratios using the incipient wetness impregnation method. The resulting materials, after drying and calcining in air at 773 K (2 h), were sulfided at 673 K (2 h) by passing over them a gas mixture consisting of about 1.7% H_2S in H_2. Table 1 gives the compositions of catalysts I–X prepared as described above. For reference purposes, two unsupported and sulfided samples were also prepared as reported elsewhere (*5, 24*) with no Co (Mo only, sample XI) and Co/Mo = 0.03 (sample XII), respectively.

The sulfided catalysts were all studied *in situ* in sealed quartz tubes containing the sulfiding gas mixture. After sulfiding, the catalysts were transferred from the reactor to a side-arm quartz tube and subsequently sealed off after reducing the pressure to about 300 Torr. With this procedure it was possible to avoid contamination by oxygen of the sulfided catalysts.

EPR spectra were obtained using a Bruker BER-420 spectrometer operating in the X band and equipped with a TE_{102} rectangular cavity. Spectra were recorded at both ambient temperature and 77 K (using a liquid nitrogen finger Dewar insert). All measurements were carried out at ca. 9.5 GHz with 25 mW of microwave power. The magnetic field was modulated at 100 kHz with an amplitude of 5 G. *g* values were calculated from accurate measurements of both the magnetic field strength and the microwave frequency. The spectra shown in the figures were obtained at 77 K and arrows point to different signals identified by their low-field peaks. The main features and our designations of the EPR signals (MO, MS, CMS, and S) observed in the present study are listed in Table 2. The relative intensities (arbitrary units) of signals MO and CMS as a function of promoter content were evaluated from the 77 K spectra, i.e., at a temperature for which the Curie–Weiss law should hold for all samples (*15*). Gaussian lineshapes were assumed. Intensities were not corrected to account for possible changes in the Weiss constant and for the progressive deterioration of the EPR cavity quality factor with higher promoter content (increasing electrical conductivity of the

TABLE 2

EPR Signals Observed in Sulfided Co–Mo Catalysts

Signal	g value	Remarks
MO	$g = 1.93$	Similar to signal in Ref. (*14*)
MS	$g_{\parallel} = 2.06$; $g_{\perp} = 1.98$	Similar to signal V in Refs. (*14, 15*)
CMS	$g_{\parallel} = 2.09$	Similar to signal VI in Refs. (*15, 17*)
S	$g_{av} = 2.014$–2.016	Anisotropic at 77 K, nearly isotropic at ambient temperature

samples). The latter effect should not affect the general trend of the observed variations nor the validity of our conclusions although actual EPR intensities at high Co content could be slightly higher than their uncorrected values.

RESULTS AND DISCUSSION

Nature of Signals MO, MS, and S

Figures 1–3 compare the EPR spectrum of sample I (supported, Mo only) to those of sample XI (unsupported, Mo only), sample V (supported, Co/Mo = 0.44), and sample IX (supported, Co/Mo = 2.33).

In addition to an axially symmetric signal, MS [$g_{\parallel} = 2.06$; $g_{\perp} = 1.98$, similar to signal V in Ref. (*14*)], characteristic of sample XI, sample I shows an almost isotropic signal, MO, with a g value of about 1.93 (Fig. 1). The latter resonance is analogous to signal I of Konings *et al.* (*14*) which was assigned to oxo-Mo^{5+} species, i.e., Mo^{5+} ions in an oxygen environment interacting with the alumina support. In agreement with this assignment the signal is not observed in unsupported catalysts (samples XI and XII). The observation that signal MO is more intense in our case relative to signal MS than in the previous study (*14*) is probably related to the somewhat less severe sulfiding which we used. It is consistent with the assignment of signals MO and MS to Mo species in an oxygen and a sulfur environment, respectively.

Addition of Co (Figs. 2 and 3) decreases the intensity of signals MO and MS. The effect of Co addition on signal MO is also illustrated in Fig. 4 which shows a strong attenuation of signal MO in the Co/Mo ratio

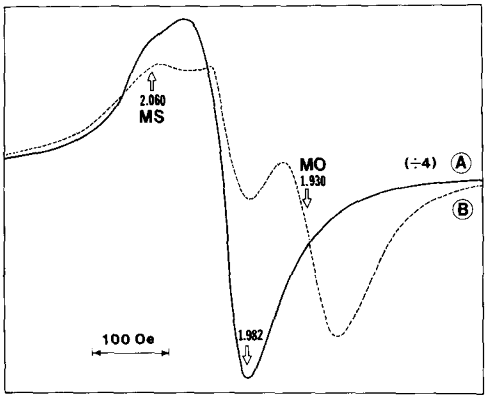

FIG. 1. EPR spectra at 77 K of unsupported (A, sample XI) and alumina-supported (B, sample I) Mo-only containing sulfided catalysts.

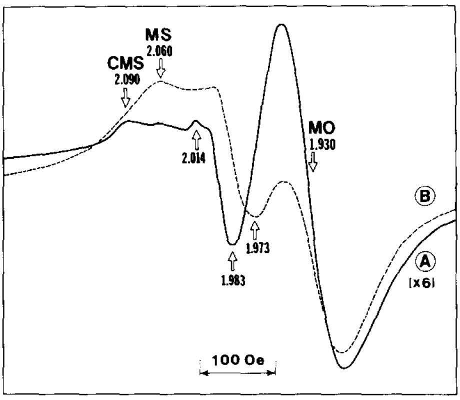

FIG. 2. EPR spectra at 77 K of alumina-supported sulfided catalysts. (A) Sample V, Co/Mo = 0.44; (B) sample I, Mo only.

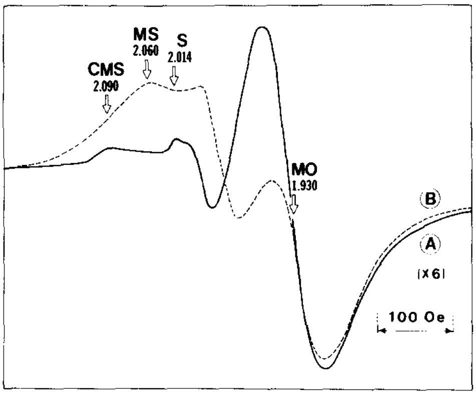

FIG. 3. EPR spectra at 77 K of alumina-supported sulfided catalysts. (A) Sample IX, Co/Mo = 2.33; (B) sample I, Mo only.

range 0–0.5. Analogous variations are observed at 77 and 293 K, the relative signal intensities for each sample being well-accounted for by the Curie law. The results suggest that the addition of Co decreases the number of oxo-Mo^{5+} species interacting with the alumina support.

In contrast to signal MO, signal MS is also observed in unsupported sulfided phases (samples I and XI, Fig. 1). MS is absent in sample X which contains only supported Co. Therefore, MS is related to Mo in a sulfur environment. Signal MS is analogous to signal V reported in Ref. (*14*) and further discussed in Ref. (*15*) by Konings *et al.* These authors assign this resonance to bulk defects in a MoS_2-like phase as it is insensitive to evacuation or equilibration. Signal MS also resembles the signal observed by Silbernagel *et al.* (*19*) ($g_{\parallel} = 2.04$ and $g_{\perp} = 2.004$) in sulfided Mo species (MoS_2-like) on high-surface-area alumina supports. However, in contrast to Konings *et al.*, these authors assigned this resonance to thio-Mo^{5+} species located at low-symmetry edge sites of the MoS_2 crystallites because of the spectral anisotropy and of the existence of correlations among EPR intensity, oxygen chemisorption, and HDS activity measurements.

We also believe that MS could arise from Mo^{5+} entities although it has unusually high g values. Oxomolybdenum (V) ions with $g_{\parallel} > g_{\perp}$ and with $g_{\parallel}$ values greater than 2 were observed previously (*25, 26*). The apparently anomalous cases of $g_{\parallel} > g_{\perp}$ can occur for such species when the covalent character of the equatorial ligand–molybdenum bonds increases as demonstrated by Che *et al.* (*26*). Such a change from octahedral to axial symmetry leads to an increase of the spin-orbit coupling on the ligating atoms. This situation can be expected for Mo^{5+} located in the bulk or at the edge of the MoS_2 structure. We will return to the point whether MS corresponds to bulk or edge defects or even other species.

The spectra of supported Co-promoted catalysts (for example, samples V and IX shown in Figs. 2 and 3, respectively) also indicate the presence of another signal, signal S, with an average g value of about 2.014. It reaches a rather constant intensity for Co/Mo greater than 0.26. This resonance is observable at both 77 K and ambient temperature and is not present in samples containing Co only. Signal S is more prone to microwave saturation than signal MO. Furthermore, its axially symmetric g tensor (at 77 K) is nearly averaged at ambient temperature. This indicates that the corresponding species must have a certain

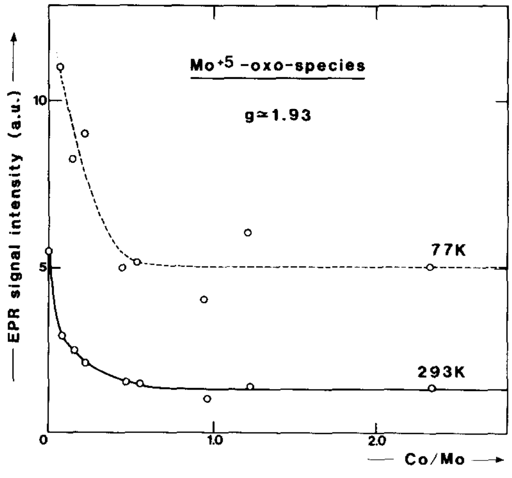

FIG. 4. EPR signal intensity (arbitrary units) of the MO signal as a function of the Co/Mo ratio, at 77 and 293 K, respectively.

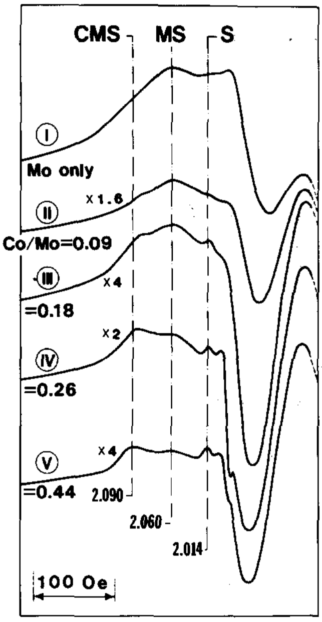

FIG. 5. Low-field region of the EPR spectra at 77 K of samples I–V (Co/Mo = 0.0–0.44).

freedom of motion. We attribute this resonance to paramagnetic sulfur species (*27*), such as disulfur radicals or polysulfur species produced during sulfidation and held at the alumina surface since their presence does not appear to affect the behavior of the MO, MS, and CMS signals.

Nature and Behavior of Signal CMS

Apart from the changes discussed above, addition of Co results in the appearance of a new resonance, CMS, characterized by a low-field peak corresponding to $g_{\parallel} = 2.09$. Considering its apparent linewidth, the average g value is probably about 2.06.

A comparison of Figs. 2 and 3 shows that the CMS signal decreases with Co content at high Co loading. The opposite situation prevails at low Co loading (Co/Mo < 1) as illustrated in Fig. 5 which compares the low-field regions of the spectra of samples I–V. As Co is progressively added, the increase of the CMS intensity is accompanied by a decrease of the MO and MS signals. The incorporation of Co hence leads to new Mo species, responsible for CMS, while simultaneously decreasing the contribution of oxo-Mo^{5+} entities (MO) and thio-Mo^{5+} species (MS).

Signal CMS is definitely not associated with the formation of Co_9S_8 since it appears in a Co concentration range where this sulfide phase is not observed by MES in the samples (*22*).

Figure 6 illustrates the intensity variation of CMS and the HDS activity vs the Co/Mo ratio. In both cases, maxima are observed for Co/Mo ~ 1.0. The variation of the intensity of the CMS signal follows the amount of the Co–Mo–S structure present in identical sulfided Co–Mo/Al_2O_3 catalysts as evaluated by MES (*22*) and NO adsorption using IR (*29*). The EPR signal CMS thus appears to be another feature characteristic of the catalytically active Co–Mo–S phase.

The CMS signal is similar to signal VI in the studies by Konings *et al.* (*15, 17*). They assigned their signal to Mo^{3+} ions strongly interacting via superexchange with Co^{2+} ions. In view of the decoration, or pseudo-intercalation model of Farragher and Cossee (*28*), the authors consider that the Co^{2+}

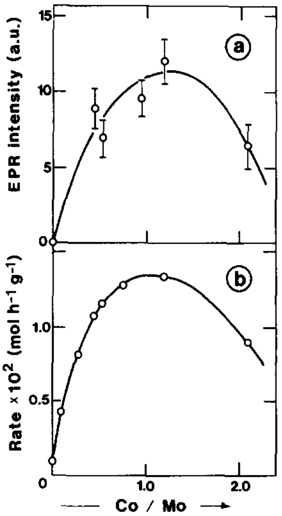

FIG. 6. EPR signal intensity (77 K, arbitrary units) of signal CMS (A) and catalytic activity from thiophene HDS (B) vs Co/Mo ratio. [Activity data adapted from Ref. (*22*).]

ions may occupy octahedral intercalation sites at the MoS_2 edges. The recent measurements on Co–Mo–S have provided direct evidence for Co atoms occupying edge positions but the measurements have shown that the positions are not intercalation sites.

Below we will discuss an interpretation of the signal CMS other than that given by Konings *et al.* (*15, 17*). The CMS signal is assigned to an almost isotropic species with $S = 1/2$. We reach this conclusion because a system with $S = 1$ is highly unlikely to give signals corresponding to $g \sim 2$ due to zero-field splittings. Quite often such systems show no resonances at all within the fields and frequencies normally available. Furthermore, systems with $S = 3/2$ tend to exhibit many peaks, and in cases with strong distortions from octahedral symmetry intense positive peaks are observed at fields corresponding to a g factor around 4 (in terms of a fictitious spin of 1/2) and a weak negative peak for g around 2 (*30, 31*). These signs are based on the phase convention used in our figures. Similar behavior is observed for other d-electron configurations, d^n. Systems with n even and odd resemble the $S = 1$ and $S = 1/2$ systems, respectively.

The simple interpretation in terms of a strong two-center interaction between a Co^{2+} ion (d^7, $S = 3/2$ or $1/2$) and a Mo^{3+} ion (d^3, $S = 3/2$ or very rarely $S = 1/2$) is, therefore, very unlikely since the resulting spin value of the ground state would be of the type $S = n/2$ with n being even.

The EPR spectra do not exclude systems with low-spin Mo^{3+}, due to very strong distortions (*32, 33*), nor magnetically isolated and EPR-silent Co^{2+}, due to fast-spin relaxation. This interpretation, however, disagrees with the static magnetic susceptibilities corresponding to very small magnetic moments per cobalt ($\lesssim 1$ Bohr magneton) (*34, 35*).

In view of the above discussion a more likely interpretation of the CMS signal, still within the two-center model, is based on antiferromagnetic coupling between Co^{2+} and Mo^{4+}. Independent of Co^{2+} being high or low spin, the consequence of this is a ground state with $S = 1/2$ as it is actually observed. The nearest excited state is then a spin quartet. Its energy is expected to be many hundreds of reciprocal centimeters above the ground state due to strong exchange interaction, and it could, therefore, easily escape detection by the present methods.

Thus, the present work supports the original observation (*15, 17*) of signal VI and furthermore identifies it to signal CMS pertaining to the Co–Mo–S structure, and establishes unequivocally its correlation with HDS activity.

Behavior of MO, MS, and CMS: Model for Co–Mo/Al_2O_3 Catalysts

It may be valuable at this point to speculate about the factors which govern the concentrations of MO, MS, and CMS species in order to provide additional insight into the nature of Co–Mo/Al_2O_3 catalysts.

The oxo-Mo^{5+} species (MO), which are observed in the sulfided catalysts, are most probably related to species present in the calcined Mo/Al_2O_3 precursor. This suggests that part of the Mo species resists complete sulfiding at moderate temperatures. Such species in the calcined catalyst could be thought of as very small Mo domains or isolated Mo atoms (e.g., tetrahedral Mo species) which are probably difficult to sulfide. The observation that the intensity of the MO signal decreases rapidly with increasing Co loading indicates that the presence of Co in some way aids the sulfiding of these Mo species. This also means that by increasing the severity of the sulfiding treatment, the concentration of such species should, as discussed above, decrease accordingly.

It is likely that the MO species are located at the outer rim of the MoS_2 domains and that they play a role in stabilizing the MoS_2 particles toward growth. In fact, several results have provided indirect evidence for the existence of such oxidized Mo species and that such species would be located at the MoS_2 edge [see, e.g., Ref. (*3*)]. Their presence could, as discussed previously (*36, 37*), be the reason for the different catalytic and physical properties observed for the "low temperature sulfided" Type I Co–Mo–S structure.

Both signals MS and CMS are related to the MoS_2 disulfide phase. If MS is a bulk defect as proposed earlier (*15*), the decrease in MS observed upon addition of Co should imply that the promoter favors a better crystallization of the MoS_2 phase.

EXAFS measurements on these particular catalysts showed that this is not the case (*38, 39*). The EXAFS results also showed that the total edge dispersion of the MoS_2 phase did not change significantly with Co content for the present type of catalysts. IR results on NO adsorption (*29*) showed that as the Co loading increases, the number of available Mo edge sites decreases due to coverage of the edges by Co. In view of this, we prefer to relate the MS signal to the uncovered Mo edge sites. In unpromoted Mo catalysts these sites are responsible for the HDS activity (*2, 3, 29, 39*), and in agreement with the above assignment of the MS signal Silbernagel *et al.* (*19*) report a correlation between the HDS activity and the intensity of a signal similar to MS for a series of unpromoted MoS_2 catalysts.

For the promoted Co–Mo/Al_2O_3 catalysts, NO also titrates the Co edge sites (*29*), and the variation in the intensity of CMS is seen to follow the concentration of these sites, supporting the assignment of CMS to Mo atoms interacting with the Co atoms probably via sulfur in the Mo^{4+}–Co^{2+} entity.

CONCLUSIONS

From a comparison of the present EPR data on sulfided Co–Mo/Al_2O_3 catalysts with Mössbauer emission spectroscopy (MES), NO adsorption, magnetic susceptibility, and catalytic activity measurements, it has been possible to determine the catalytic significance of the different EPR-active species and to investigate to what extent their presence is related to the Co–Mo–S structures observed in such catalysts (*1–5*). Three different EPR signals have been observed: MO, MS, and CMS.

Signal MO is assigned in agreement with the previous proposals (*15*) to oxo-Mo^{5+} species, i.e., Mo species which resist sulfidation. In view of recent results (*36, 37*) on the present type of catalysts, the MO species may be located at the edges of the MoS_2 domains and may play an important role in stabilizing the structures toward growth. Furthermore, the presence of such MO species in the MoS_2 structure may also influence the physical and catalytic properties of the Co–Mo–S structures (*36, 37*).

Signal MS resembles resonances reported by previous authors (*14, 15, 19*). It was assigned to either bulk defects or edge thio-Mo^{5+} species. The present results favor the latter interpretation. The MS sites do not appear to play a major role for the catalytic activity of promoted catalysts since the intrinsic activity of these unpromoted MS sites has been shown to be low compared to that of the promoted CMS edge sites (*39*). However, for unpromoted Mo catalysts the sites characterized by signal MS will be the ones responsible for the catalytic activity.

Signal CMS appears to be similar to a signal also observed by Konings *et al.* (*15, 17*). The present results show that CMS is characteristic of the Co–Mo–S structure and its intensity varies in parallel with the HDS activity. The CMS signal suggests the presence of Mo^{4+} centers interacting with Co^{2+} neighboring centers (the Co–Mo–S Co atoms) located at the edges of the MoS_2-like structures.

Previously we have observed that the HDS activity is related to the number of Co atoms located at the edges of the MoS_2 "support" [see, e.g., Refs. (*22, 29*)]. Although these results emphasized the importance of such special promoter atoms the neighboring Mo atoms were also considered to be important (*1–6*). This was further substantiated in recent magnetic susceptibility measurements on Co–Mo–S structures (*34, 35*) which showed that extensive electron delocalization takes place and that the surrounding Mo atoms have a strong influence on the electronic properties of the Co edge atoms. The present EPR results give further evidence for the existence of special Mo atoms neighboring the Co edge atom and that the promotion of the HDS activity is related to the presence of these atoms (i.e., the Mo^{4+}–Co^{2+} centers at the edges). Presumably, electron transfer reactions are faster on catalysts with extended exchange interactions, and this may facilitate the formation of associated sulfur atom vacancies which are commonly believed to be important in HDS.

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