Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1991, **1(1)**, 6–7

Mendeleev Communications

Direct Observation by EXAFS of Selenophene Chemisorption by Sulphide Hydrodesulphurization Catalysts

Anatolii N. Startsev, Sergey A. Shkuropat, Vladimir V. Kriventsov, Dmitrii I. Kochubey and Kirill I. Zamaraev*

Institute of Catalysis, Prospekt Akademika Lavrentieva, 5, 630090 Novosibirsk, USSR

After adsorption of C_4H_4Se at ambient temperature, two intense peaks appeared in the radial atomic distribution curves obtained from the Ni *K*-edge EXAFS spectra of the sulphide catalysts Ni–Mo/Al_2O_3, which have been attributed to the coordination of selenophene to Ni with Ni—Se distance *R* 2.5 Å and Ni—C distance *R* 3.0 Å; no evidence for the coordination of selenophene to Mo was obtained from Mo *K*-edge EXAFS.

The mechanism of C—S bond hydrogenolysis on sulphide catalysts attracts the attention of many researchers owing to the great practical importance of hydrodesulphurization processes. The idea that S-containing molecules are activated by chemisorption on the anionic vacancies of MoS_2 or the 'Co—Mo—S phase' is widespread in the literature (see *e.g.* ref. 1). Recently an alternative hypothesis has been advanced, according to which chemisorption and activation of S-containing molecules take place on Ni (or Co) atoms of the sulphide bimetallic species, while activation of H_2 is performed with the participation of Mo (or W).[2] In this work EXAFS data are presented showing that selenophene (Se analogue of thiophene) is indeed adsorbed on Ni, rather than on Mo. This conclusion was made from EXAFS studies of selenophene adsorption on sulphide catalysts Ni–Mo/Al_2O_3, obtained *via* the anchoring of metal complexes.[3] Note that this preparation technique provides the maximum dispersion of the Ni—Mo sulphide active species over the Al_2O_3 support.[3]

The Ni *K*- and Mo *K*-edge EXAFS spectra were registered with a step of 1.5 eV at the EXAFS Station described in ref. 4, using a channel-cut Si(III) crystal as monochromator. Radial atomic distribution (RAD) curves were obtained *via* Fourier analysis of the EXAFS spectra in the intervals 3.8–15 $Å^{-1}$ for the Mo *K*-spectra and 3–15 $Å^{-1}$ for the Ni *K*-spectra with weight coefficients k^2 and k^1, respectively. Extraction of oscillations was performed by the double substraction procedure of the smooth part found using spline functions. The value of E_0 was selected by comparison with Ni—S and Mo—S distances from model compounds and tables.[5] To obtain the EXAFS spectra, the sulphide catalysts were re-loaded into cells with beryllium windows, avoiding contact with air. Adsorption of C_4H_4Se was performed at room temperature.

In the RAD curves obtained from the Mo *K*-edge EXAFS spectra of sulphide catalysts 8% Mo/Al_2O_3 and 1% Ni–8% Mo/Al_2O_3 two intense peaks were detected which correspond to the distances Mo—S (2.43 Å) and Mo—Mo (3.17 Å). When C_4H_4Se was adsorbed on both Mo and Ni–Mo catalysts, no change in the RAD curves was observed [Fig. 1(*a*)]. Thus the Mo *K*-edge EXAFS spectrum demonstrates the absence of any strong interaction between selenophene and Mo-sites.

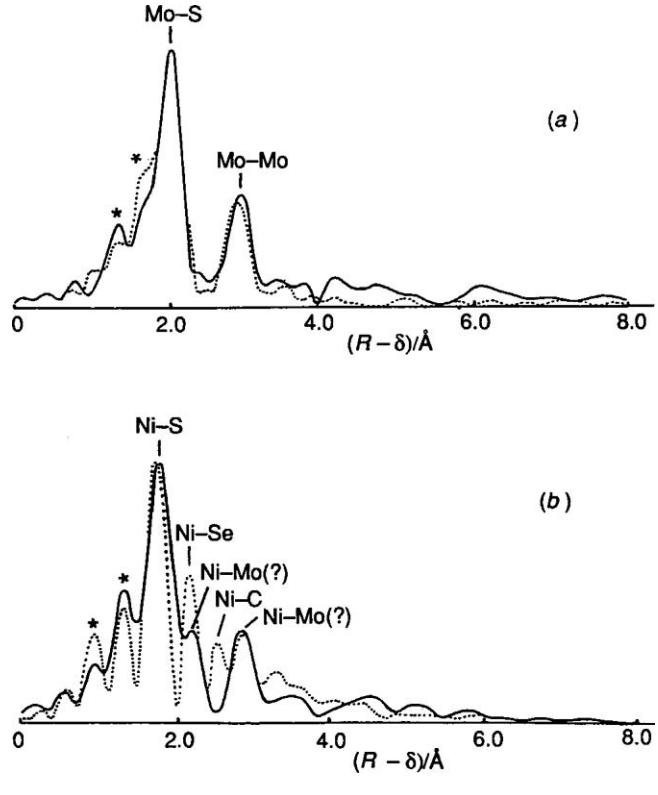

Fig. 1 Radial atomic distribution curves obtained from the Mo *K*-edge (*a*) and Ni *K*-edge (*b*) EXAFS spectra of sulphide catalyst 1% Ni–8% Mo/Al_2O_3 before (solid line) and after (dotted line) adsorption of selenophene at room temperature. The asterisks indicate 'false' peaks arising at small distances from the incomplete subtraction of the smooth part of the experimental EXAFS spectra.[7]

In the RAD curves of the Ni *K*-edge EXAFS spectra of sulphide catalyst Ni–Mo/Al_2O_3 intense peaks at ($R - \delta$) 1.76, 2.19 and 2.87 Å are observed [Fig. 1(*b*)]. The first peak corres-

ponds to the distance Ni—S (2.2 Å). The next two peaks cannot be assigned unambiguously at present. In accordance with the previously proposed model of the structure of the active component in Ni–W–S catalysts[6] these peaks may be assigned to the distances Ni—Mo (2.4 and 3.1 Å), however, other possibilities cannot be excluded. When C_4H_4Se is admitted to the catalyst, the intensity of the peak at $(R - \delta)$ 2.19 Å increases notably and a new peak appears at $(R - \delta)$ 2.55 Å [Fig. 1(*b*)]. These large changes in the Ni *K*-edge EXAFS spectrum conclusively demonstrate that there is a strong interaction between selenophene and Ni-sites. The increase in intensity of the peak at 2.19 Å may be tentatively explained by the appearance of a peak corresponding to the distance Ni—Se (2.5 Å), while the peak at 2.55 Å may be assigned to the distance Ni—C (3.0 Å). Examination of molecular models confirms the possibility of this type of selenophene coordination with the appearance of peaks for the corresponding interatomic distances. However, further studies are needed to verify the specific assignment of the two peaks.

Thus, chemisorption of C_4H_4Se on the bimetallic sulphide hydrodesulphurization catalyst Ni–Mo/Al_2O_3 proceeds *via* its coordination to Ni but not to Mo in the sulphide bimetallic species which is the active component of this catalyst.

Received in USSR, 18th September 1990
Received in UK, 3rd January 1991; Com. 0/04242K

References

1 H. Topsøe, in *Surface Properties and Catalysis by Non-Metals*, eds. J.P. Bonnelle, B. Delmon and E. Derouane, Reidel, Dordrecht, 1983, p. 329.
2. A.N. Startsev, *Kinet. Katal.*, 1990, **31**, 869.
3 A.N. Startsev and S.A. Shkuropat, *React. Kinet. Catal. Lett.*, 1990, **41**, 175.
4 D.I. Kochubey, Yu. A. Babanov, K.I. Zamaraev, R.V. Vedrinskii, V.L. Kraisman, G.N. Kulipanov, L.N. Mazalov, A.N. Skrinskii, V.K. Fedorov, B. Yu. Helmer and A.T. Shuvaev, *EXAFS Spectroscopy*, Nauka, Novosibirsk, 1988 (in Russian).
5 A.G. McKale, *J. Am. Chem. Soc.*, 1988, **110**, 3763.
6 D.I. Kochubey, M.A. Kozlov, K.I. Zamaraev, V.A. Burmistrov, A.N. Startsev and Yu. I. Yermakov, *Appl. Catal.*, 1985, **14**, 1.
7 J.W. Cook and D.E. Sayers, *J. Appl. Phys.*, 1981, **52**, 5024.