On the EXAFS determination of the site for the chemisorption of selenophene on sulfided Ni–Mo/Al_2O_3

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Simulation of the Mo and Ni K-edge EXAFS spectra of sulfided Ni–Mo/Al_2O_3 catalysts shows that the Mo EXAFS spectrum is rather insensitive to the chemisorption of selenophene; this means that, in contradiction to a former claim, the site for selenophene chemisorption cannot be determined from a comparison of the influences of selenophene chemisorption on the Mo and Ni EXAFS spectra. Experimental EXAFS spectra of a carefully sulfided Ni–Mo/Al_2O_3 catalyst showed no difference between Mo and Ni K-edge spectra taken before and after adsorption of selenophene.

A few years ago the results of an EXAFS investigation of the chemisorption of selenophene on a sulfided Ni–Mo/Al_2O_3 catalyst were published.[1] In this study it was shown that the Mo K-edge EXAFS spectrum of the Ni–Mo/Al_2O_3 catalyst did not change upon selenophene adsorption, while the Ni K-edge EXAFS spectrum did change. Thus, it was concluded that chemisorption of selenophene proceeds *via* coordination to Ni but not to Mo on the surface of the Ni–MoS_2 catalyst particles. Assuming that the adsorption of thiophene occurs analogously to that of selenophene (its Se analogue), these results have important implications for the understanding of hydrodesulfurization reactions at metal sulfide surfaces. For instance, they would support the proposal that the so-called promoter atoms (Ni or Co) are not promoters of Mo at all but should rather be considered as the true catalytic sites, as suggested about a decade ago.[2] Furthermore, additional quantitative studies might reveal the mode of selenophene adsorption (*e.g.* η^1 or η^5 coordination).

It is the purpose of this communication to show that, although the basic conclusion that Ni rather than Mo is the catalytic site may still be true, this conclusion cannot be proved from a comparison of Mo and Ni K-edge EXAFS spectra before and after adsorption of selenophene.

The first reason why no judgement can be made about the site of selenophene adsorption is that the Mo EXAFS spectrum is quite insensitive to selenophene adsorption. If it is assumed that no more than one selenophene can be adsorbed per surface Mo site and that 50% of the Mo atoms are accessible for selenophene (which is a strong overestimation according to the high Mo–S coordination numbers observed in Co–Mo and Ni–Mo catalysts[3,4]), the influence of selenophene adsorption on a sulfided Ni–Mo/Al_2O_3 catalyst can be calculated by adding 0.5 Se atom per Mo atom. As can be seen in Figure 1 this hardly changes the EXAFS spectrum [Figure 1(*a*)] or its Fourier transform k.χ [Figure 1(*b*)]. It was assumed in the calculation that every Mo atom is surrounded by 5.5 S atoms at a distance of 2.41 A and by 3.5 Mo atoms at a distance of 3.16 A as in the catalysts described in the literature.[3,4] Every Ni atom was assumed to be surrounded by 4.5 S atoms at 2.22 A and 0.8 Mo atom at 2.85 A.[4,5] For Mo–Se and Ni–Se coordination numbers and distances, the values $N = 0.5$ and $R = 2.85$ A, and $N = 1.0$ and $R = 2.65$ A were used respectively. Backscattering amplitudes and phase factors were obtained from MoS_2 for Mo–Mo and Mo–S, from CoS_2 for Ni–S, and from $MoSe_2$ for Mo–Se, while for Ni–Se the FEFF values[6] were used.

The calculation of the Ni EXAFS spectrum demonstrates that the addition of one Se atom to the first coordination sphere of Ni leads to a new peak in the Fourier transform around 2.3 A [Figure 2(*b*)]. If every Ni atom in the Ni–MoS_2 structure were to adsorb one selenophene *via* Ni–Se coordination, this would be easy to detect in the Ni EXAFS spectrum [Figure 2(*a*)]. Ni–Se coordination numbers of 0.5 or lower, however, will be difficult to detect, because the change in the Ni spectrum, effected by adding 0.5 Se per Ni atom, is small.

The Fourier transforms of the Ni EXAFS spectra of a sulfided Ni–Mo/Al_2O_3 catalyst before and after addition of

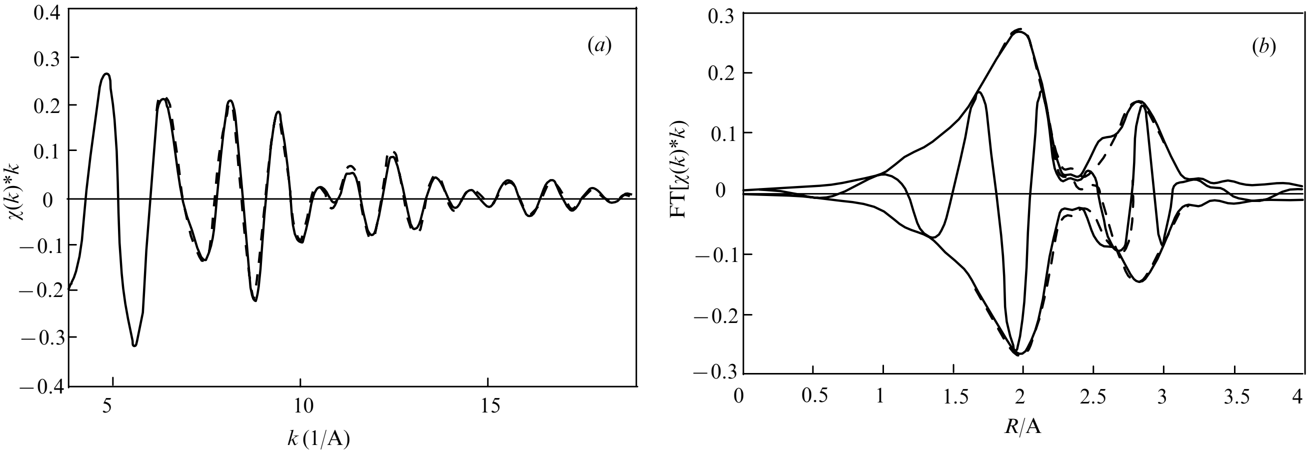

Figure 1 Simulated Mo K-edge $\chi(k)*k$ EXAFS spectra (*a*) and their Fourier transforms (*b*) of Ni–MoS_2 on γ-Al_2O_3 (- - -) and of Ni–MoS_2 on γ-Al_2O_3 with adsorbed selenophene (—). The following parameters were used: Mo–S, $N = 5.5$, $R = 2.41$ A; Mo–Mo, $N = 3.5$, $R = 3.16$ A; Mo–Se, $N = 0.5$, $R = 2.85$ A.

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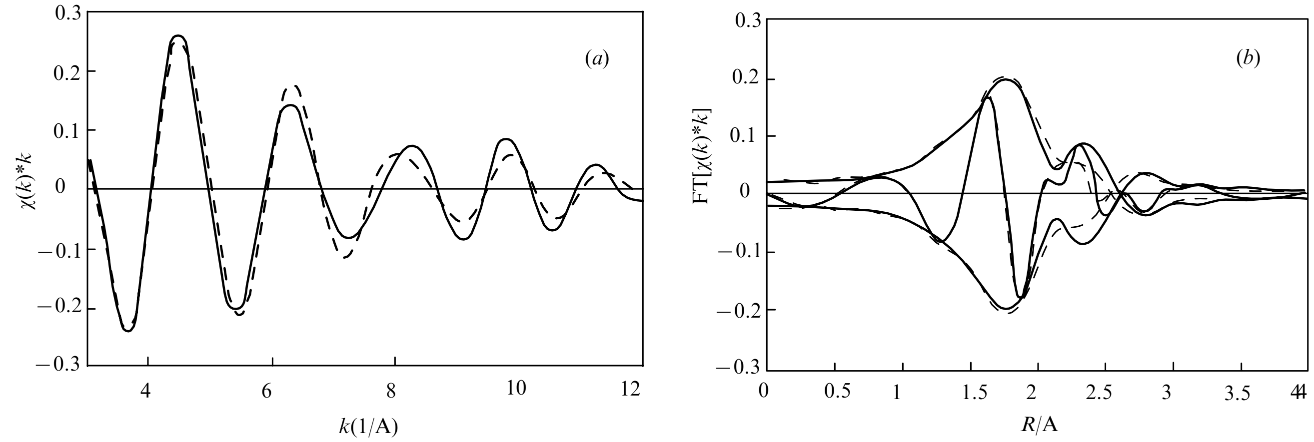

Figure 2 Simulated Ni K-edge $\chi(k)*k$ EXAFS spectra (*a*) and their Fourier transforms (*b*) of Ni–MoS$_2$ on γ-Al$_2$O$_3$ (- - -) and of Ni–MoS$_2$ on γ-Al$_2$O$_3$ with adsorbed selenophene (—). The following parameters were used: Ni–S, $N = 4.5$, $R = 2.22$ A; Ni–Mo, $N = 0.8$, $R = 2.85$ A; Ni–Se, $N = 1.0$, $R = 2.65$ A.

selenophene, published by Startsev *et al.*,[1] look completely different from the simulations presented in Figure 2(*b*) and from spectra published for sulfided Ni–Mo/Al$_2$O$_3$ catalysts.[3,5] The side lobes on both sides of the main peak at $R-\delta = 1.76$ A in the Fourier transform of the sample in the presence of selenophene[1] suggest that a neighbouring atom with a different phase factor than that of sulfur interferes. Oxygen, from contamination by air, might be the explanation.

A general reason why the mode of binding of selenophene (or of thiophene for that matter) will be difficult to determine is the fact that selenophene can coordinate in different ways. Thus, in η^5-C$_5$Me$_5$(CO)$_2$ReL complexes, with L = alkylselenophene, the selenophene was found to be η^1(S) as well as η^2(C = C) coordinated to the Re atom.[7] If this were to be true as well for the binding of selenophene to the Ni or Mo atom in the Ni–MoS$_2$, then there would be little hope of observing a single, well-defined structure in the EXAFS. In addition, the very weak bonding of thiophene in organometallic complexes[7] suggests that the corresponding EXAFS contribution should be severely broadened by the Debye-Waller factor and that the only possibility for measuring a significant Ni–Se or Mo–Se EXAFS contribution will be at very low temperatures.

Finally, we report that, even though the chances of detecting Ni–Se or Mo–Se contributions in the EXAFS spectrum of selenophene adsorbed on Ni–Mo/Al$_2$O$_3$ catalysts are meagre, we tried to measure them at about 100 K but failed to detect them. Neither in the Mo nor in the Ni K-edge EXAFS spectrum of a carefully sulfided Ni–Mo/Al$_2$O$_3$ catalyst (with an Ni/Mo atomic ratio of 0.3, so that all Ni atoms are in the Ni–Mo–S structure) did we detect any difference between spectra taken before and after adsorption of selenophene.

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