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ON THE STRUCTURE OF COBALT SULFIDE CATALYSTS

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In a previous article [1] Bouwens et al. published XANES spectra of cobalt sulfides catalysts (fig. 2 in [1]) which confirm our preceding conclusions [2] concerning the symmetry of cobalt sulfide supported on activated carbon. We wish to comment on this point and show that the XANES spectra are in full agreement with our NMR deduction.

Bouwens et al. produced four spectra: Co_9S_8 and CoS_2 bulk, Co/C and CoMo/C sulfided. These spectra show an absorption peak near threshold, corresponding probably to a 1s → 3d transition. Schulman et al. [3] have observed more intense absorption for tetrahedral symmetry of cobalt than for octahedral symmetry. Two strong absorptions are observed between -10 and -9 eV before the threshold for Co_9S_8 and Co/C, while only very weak absorption can be detected around the same energies for CoS_2 and CoMo/C. In Co_9S_8, 8/9 cobalt atoms are tetrahedrally coordinated and 1/9 octahedrally, and in CoS_2 all cobalt atoms are octahedrally coordinated. The Shulman observations are thus confirmed by Bouwens's pre-edge XANES recording. It is therefore logical to extrapolate these conclusions to the unknown phase of Co/C and CoMo/C, i.e. Co/C showing a strong 1s → 3d absorption must contain mainly tetrahedral cobalt atoms and not "a higher percentage of octahedral cobalt as present in Co_9S_8" [1], while CoMo/C must contain mainly octahedral cobalt atoms.

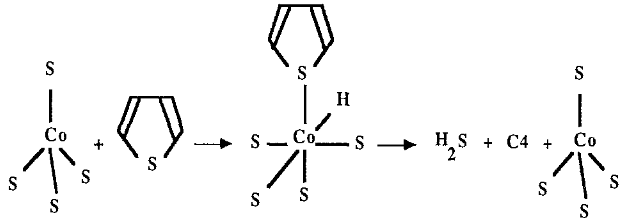
In addition, if in fact we observed tetrahedral distorted cobalt on Co/C by NMR [2], we recently proposed a model of the sulfided CoMo/C phase [4] were half of the cobalt atoms is in a tetrahedral position and the other half in an

Table 1

Compounds	number of tetra Co	number of octa Co	Ref.	Pre-edge structure		Bouwens conclusion [1]
				Found [1]	Predicted [3]	
Co_9S_8 bulk	8/9	1/9	crystal	strong	strong	OK
CoS_2 bulk	0	all	crystal	weak	weak	OK
Co/C	all	0	[2]	strong	strong	wrong
CoMo/C	1/2	1/2	[4]	weak	weak	OK

octahedral position. One can summarize these different results in a table (table 1). They seem to be totally consistent with the pre-edge structures [1].

Two arguments are in favor of tetrahedral cobalt in Co/C. It is easy to understand that a tetrahedral sulfided cobalt atom could be a very attractive site for the HDS reaction compared to an octahedral atom (Duchet et al. [5] and we [2] have found Co/C very active for HDS). Firstly, in the thermodynamic range used for the HDS tests, the cobalt sulfide "prefers" the tetrahedral symmetry to the octahedral symmetry (8 versus 1 in Co_9S_8). A tetrahedral cobalt atom can temporarily adsorb a sulfided molecule to adopt the octahedral symmetry because this symmetry is naturally possible, performs the HDS and then releases a hydrocarbon and H_2S to return to the original more stable tetrahedral form.



Such a model is a perfect description of a Sabatier system where the geometrical possibility of passing from tetrahedral to octahedral symmetry is well balanced by the more stable tetrahedral form. This concept has been applied to many other active sulfides [6].

Secondly, following the electronic theory proposed by Harris and Chianelli [7], one can expect a good HDS activity for a tetrahedral sulfided cobalt atom (HOMO containing 3 electrons in t_2 (symmetry) while an octahedral cobalt will

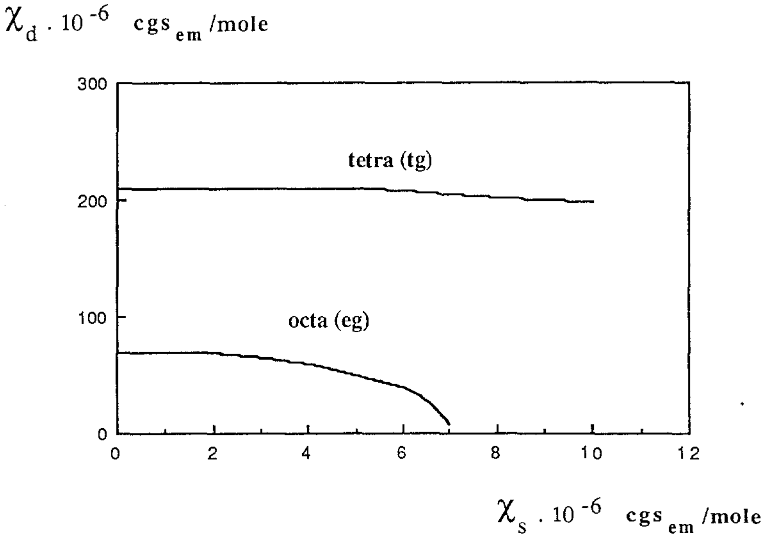


Fig. 1.

have a HOMO containing only 1 electron in e_g symmetry. By measuring of the density of state at the Fermi level in Co_9S_8 (equivalent to the electronic population in the HOMO if one assumes a similar shape for the t_2 and e_g bands and considering that both t_2 and e_g bands are less than or equal to half-populated) using the Metal Solid NMR, we have confirmed this electronic structure for the two symmetries of sulfided cobalt atom.

(χs and d : s and d electrons' contribution to the Pauli magnetic metallic susceptibility directly extracted from the measure of the Knight shift and of the longitudinal relaxion time T1 [8]). The density of state at the Fermi level is at least three time higher for the tetrahedral site than for the octahedral site.

In conclusion, by reading the article of Bouwens et al. [1] one could be led to the conclusion that the so-called synergy effect between Co and Mo is due to the addition of the activity of octahedral Co to that of Mo. But if CoMo/C is more active than Co/C, it is because of the presence of molybdenum [4] and not because the octahedral cobalt atoms are active sites.

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