SIMILARITY OF Co—SPECIES IN Co AND CoMo—SULFIDE CATALYSTS SUPPORTED ON CARBON AND ALUMINA. A MÖSSBAUER EMISSION SPECTROSCOPIC STUDY

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It is shown that, irrespective of the application of carbon or alumina as a support, the local structure of the "Co-sulfide" phase formed during sulfidation of Co- and CoMo-catalysts is the same. A relation is found between the quadrupole splitting (Q.S. value) of the "Co-sulfide" phase and its dispersion. The higher the dispersion, the larger the Q.S. value. The so-called "Co-Mo-S" doublet is observed in all cases and it turns out to be related to a highly dispersed "Co-sulfide" phase instead of a Co, Mo and S containing phase.

1. INTRODUCTION

For several decades attempts are made to find a relation between the structure of sulfided CoMo hydrodesulfurization (HDS) catalysts and the observed synergetic behaviour of Co and Mo in these catalysts. A number of structural models are proposed, but since Topsoe et al. /1/ and Wivel et al. /2/ found a relation between the thiophene HDS activity and the presence of a certain contribution in the Mössbauer emission spectra of these catalysts, their so-called "Co-Mo-S" model has achieved widespread acceptance. However, as time elapsed several points regarding the "Co-Mo-S" model became the subject of discussion /3,4/. One of these is the question whether the so-called "Co-Mo-S" MES signal is related to a Co, Mo and S containing phase or merely to a Co and S containing phase /5,6/. In the present paper this question will be discussed.

2. RESULTS AND DISCUSSION

The "Co-Mo-S" model is based on combined Mössbauer emission spectroscopy (MES) and thiophene HDS activity studies /2/. In these studies MES had to be used as a fingerprint technique because of possible problems with chemical after effects. The MES spectra of sulfided catalysts were compared with MES spectra of bulk Co- and CoMo-sulfides /1/. It was found that sulfided CoMo catalysts exhibited a MES spectrum which did not agree with that of the bulk Co(Mo)-sulfides or that of sulfided Mo-free Co catalysts. The Co-species giving rise to this spectrum was refered to as "Co-Mo-S". Although "Co-Mo-S" was defined by its MES parameters, it turned out that the quadrupole splitting (Q.S. value) of the "Co-Mo-S" doublet could vary over a wide range, 1.03-1.21 mm/s /1/ or even 1.0-1.3 mm/s /7/. More recent, Van der Kraan et al. /8/ and Craje et al. /9/ studied a range of sulfided CoMo/C catalysts with varying Co/Mo ratio (1.0-0.00044 at/at) and they observed that the Q.S. value can vary over a still larger range (0.58-1.31 mm/s) and that the Q.S. value is related to the Co/Mo ratio. The higher the Co/Mo ratio, the smaller the Q.S. value recorded after sulfidation of the catalysts up to 673 K. A similar study on Co/C catalysts /8,9/ with various Co loadings learned that also for these catalysts the Q.S. value varies with Co loading. For Co/C catalyst with a very low Co loading the same spectrum is found as for a CoMo/C catalyst with a very high Co/Mo ratio. Although one would expect the formation of Co$_9$S$_8$ in Co/C catalysts as this is the most stable Co-sulfide phase at the sulfidation conditions applied, in none of the Co/C catalysts the spectrum of bulk Co$_9$S$_8$ (Q.S. = 0.26 mm/s) has been observed.

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The fact that for sulfided Co/C catalysts the Q.S. value varies with Co loading indicates that it is related to the dispersion of the "Co-sulfide" phase. For Fe(III)-oxide a similar relation between the Q.S. value and the dispersion was reported by Van der Kraan /10/. Further evidence for the hypothesis that this is also the case for these Co(Mo) catalysts might be obtained from MES measurements on stepwise sulfided Co/C and CoMo/C catalysts because it is very likely that sintering of the "Co-sulfide" phase will occur upon sulfidation at elevated temperatures. So, the catalysts were subjected to successive sulfidation treatments at different temperatures and after each treatment a room temperature MES spectrum was recorded /8/. Results on CoMo/C catalysts reveal that these catalysts already become sulfided during sulfidation treatments at rather low temperatures (373-473 K). It can be seen from fig. 1 and table 1 that the Co(2.25)Mo(6.84)/C catalyst (Co and Mo contents are given in wt%) exhibits a "Co-Mo-S" spectrum with a Q.S. = 1.20 mm/s already after sulfidation at 373 K. Upon sulfidation at higher temperatures the Q.S. value decreases and a value of 0.87 mm/s is recorded after sulfidation up to 673 K. For a Co(4.9)Mo(12)/C catalyst (Co/Mo = 1.0 at/at) the Q.S. value decreases from 1.11 mm/s after sulfidation at 373 K to 0.73, 0.66 and 0.58 mm/s upon sulfidation at 473, 573 and 673 K respectively /9/. This is agreement with the assumption that the Q.S. value is a measure for the dispersion of the "Co-sulfide" phase and that sintering occurs upon sulfidation at elevated temperatures.

![Mössbauer emission spectra](image)

Figure 1. Mössbauer emission spectra of Co(2.25)Mo(6.84)/C and Co(2.45)/C after various successive sulfidation treatments. For experimental details see e.g. /8/.

Table 1. Quadrupole splittings of Co(2.25)Mo(6.84)/C and Co(2.45)/C after various successive sulfidation treatments.

<table>
<thead>
<tr>
<th>Sulfidation Temperature (K)</th>
<th>Q.S. (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co(2.25)Mo(6.84)/C</td>
</tr>
<tr>
<td>373</td>
<td>1.20</td>
</tr>
<tr>
<td>473</td>
<td>0.90</td>
</tr>
<tr>
<td>573</td>
<td>0.85</td>
</tr>
<tr>
<td>673</td>
<td>0.87</td>
</tr>
</tbody>
</table>
The stepwise sulfidation treatment is also performed on a series of Co/C catalysts. From fig. 1 and table 1 it follows that also these Mo-free catalysts become sulfided at rather low temperatures (373-473 K). At these temperatures a phase is formed which gives rise to the "Co-Mo-S" spectrum. In-situ MES measurements down to 4.2 K /11/ and in-situ EXAFS measurements /12/ have revealed that the Co-species which exhibits this "Co-Mo-S" spectrum is equally surrounded (same nearest neighbours with same coordination number and distance) as the one causing the "Co-Mo-S" spectrum in CoMo/C catalysts. This is very remarkable with respect to the "Co-Mo-S" model in which this particular doublet is supposed to be uniquely related to a Co, Mo and S containing phase /1/. However, the appearance of the "Co-Mo-S" doublet in the spectrum of a Mo-free catalyst recorded after sulfidation at rather low temperatures can be understood when a relation exists between the Q.S. value and the dispersion. At low sulfidation temperatures the dispersion is still high and thus the Q.S. value will be large. Upon sulfidation at higher temperatures both the dispersion and the Q.S. value decrease. However, it is important to note that in none of the Co/C catalysts the parameters of bulk Co₉S₈ are observed. Furthermore, the finding that the resonant absorption area increases from 1.47 a.u. (at 373 K) to 1.87 a.u. (at 673 K) indicates that the Co becomes more rigidly bound in a lattice. This phenomenon can also be understood in terms of sintering.

In-situ EXAFS measurements /12/ on a Co(2.45)/C catalyst sulfided at 373 K (MES: "Co-Mo-S" doublet, Q.S. = 1.19 mm/s) and 673 K (MES: doublet with Q.S. = 0.44 mm/s) showed that the number of Co-Co neighbours increases very strongly with increasing sulfidation temperature. This proves that indeed the sulfidation temperature influences the sintering process. So, it can be concluded that the Q.S. value is a measure for the dispersion of the "Co-sulfide" phase.

Similar MES studies are performed on Co/Al₂O₃ and CoMo/Al₂O₃ catalysts. A series of CoMo/Al₂O₃ catalysts was sulfided up to 673 K and the Q.S. value of the "Co-Mo-S" phase was again found to decrease with increasing Co/Mo ratio. Stepwise sulfidation of a series of Co/Al₂O₃ and CoMo/Al₂O₃ catalysts revealed the formation of a species characterised by the "Co-Mo-S" doublet upon sulfidation at rather low temperatures (473 K) whereas the Q.S. value drastically decreased upon sulfidation at higher temperatures. It is remarkable that the Co/Al₂O₃ catalysts with Co loadings of 0.7 and 3.0 wt% sulfided at 673 K exhibit a spectrum which resembles that of bulk Co₉S₈. This result strongly suggests that the "Co-sulfide" phase sinters more easily on the alumina than on the carbon support.

3. CONCLUSIONS

By applying MES on series of carbon- and alumina-supported Co and CoMo catalysts subjected to successive sulfidation treatments we were able to show the existence of a relation between the Q.S. value of a "Co-sulfide" phase and its dispersion. This allows one to conclude that the nature of the "Co-sulfide" phase in sulfided Co and CoMo catalysts is the same and that only their degree of dispersion is different.

REFERENCES

/6/ H. Topsoe, N.-Y. Topsoe and B.S. Clausen, Proc. 12th Ibero American Symposium on


