

# Mössbauer emission study on $^{57}\text{Co}$ doped carbon-supported Ni and Ni-Mo sulfide hydrotreating catalysts : the influence of phosphorus on the structure

**Citation for published version (APA):**

Craijé, M. W. J., Beer, de, V. H. J., & Kraan, van der, A. M. (1991). Mössbauer emission study on  $^{57}\text{Co}$  doped carbon-supported Ni and Ni-Mo sulfide hydrotreating catalysts : the influence of phosphorus on the structure. *Catalysis Today*, 10(3), 337-344. <https://doi.org/10.1016/0920-5861%2891%2980014-Z>, [https://doi.org/10.1016/0920-5861\(91\)80014-Z](https://doi.org/10.1016/0920-5861(91)80014-Z)

**DOI:**

[10.1016/0920-5861%2891%2980014-Z](https://doi.org/10.1016/0920-5861%2891%2980014-Z)  
[10.1016/0920-5861\(91\)80014-Z](https://doi.org/10.1016/0920-5861(91)80014-Z)

**Document status and date:**

Published: 01/01/1991

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

**General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

[www.tue.nl/taverne](http://www.tue.nl/taverne)

**Take down policy**

If you believe that this document breaches copyright please contact us at:

[openaccess@tue.nl](mailto:openaccess@tue.nl)

providing details and we will investigate your claim.

## MÖSSBAUER EMISSION STUDY ON $^{57}\text{Co}$ DOPED CARBON-SUPPORTED Ni AND Ni-Mo SULFIDE HYDROTREATING CATALYSTS.

### THE INFLUENCE OF PHOSPHORUS ON THE STRUCTURE.

M.W.J. Crajé<sup>1</sup>, V.H.J. de Beer<sup>2</sup> and A.M. van der Kraan<sup>1</sup>.

<sup>1</sup>Interfacultair Reactor Instituut, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands.

<sup>2</sup>Schuit Catalysis Institute, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

### SUMMARY

In the present study it is demonstrated that Mössbauer emission spectroscopy (MES) can generate information on the various Ni phases present in sulfided Ni containing catalysts when a small amount of  $^{57}\text{Co}$  is used as a probe for Ni.

Application of MES to  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$  and  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$  revealed the formation of a so-called "Ni-Mo-S" phase in the former and a bulk sulfide in the latter catalyst. After addition of phosphorus a "Ni-(thio)phosphate" phase is found to be formed in both catalysts.

The relation between the structure of these catalysts and their activity for thiophene HDS and quinoline HDN is discussed.

### INTRODUCTION

Mössbauer emission and Mössbauer absorption spectroscopy (MES and MAS) are among the few techniques which enable one to obtain structural information about catalysts under in-situ conditions. Examples of such characterisation studies can be found in the fields of Fischer-Tropsch and hydrodesulfurisation (HDS) catalysis (refs. 1,2,3). However, one should keep in mind that MES can only be used as a fingerprint technique. Unfortunately Mössbauer spectroscopy is applicable to certain isotopes only. For example, the Mössbauer parameters of the only Mössbauer isotope of Ni ( $^{61}\text{Ni}$ ) are not sensitive enough to give useful information about the structure of Ni containing catalysts. Therefore, another approach was chosen to study some structural aspects of Ni(-Mo) hydrodenitrogenation (HDN) catalysts, namely to dope these Ni catalysts with  $^{57}\text{Co}$ . The idea behind this approach is that the  $^{57}\text{Co}$  will have only minor influence on the structure of the Ni because a  $^{57}\text{Co}/\text{Ni}$  ratio of only  $10^{-3}$  (at/at) is sufficient. Furthermore, it was expected that since the interaction between Ni and  $^{57}\text{Co}$  (both group VIII) is so large the  $^{57}\text{Co}$  will give information about the local environment of the Ni.

The catalytic problem to be solved had emerged from a quinoline HDN activity study performed by Eijbsbouts et al. (refs. 4,5) on various Ni(-Mo)/C catalysts with and without phosphorus. They concluded that phosphorus is a promoter for Ni/C while it is a poison for Ni-Mo/C. Although it was suggested that the formation of a "Ni-phosphate" might be the explanation for the observed behaviour, no experimental evidence for a link between catalyst structure and activity could be produced.

This study had two objectives. The first one was to gain information on the possibility to use  $^{57}\text{Co}$  as a probe for these sulfided Ni and Ni-Mo hydrotreating catalysts. The second objective was to obtain information about the role of phosphorus on the phases formed during sulfidation of carbon supported Ni(-Mo) catalysts, as an attempt to explain the effect of phosphorus on the HDS and HDN activity reported by Eijsbouts et al. (refs. 4,5).

## EXPERIMENTAL

The activated carbon support (Norit RX3-extra, pore volume  $1.0\text{ cm}^3/\text{g}$ , BET surface  $1197\text{ m}^2/\text{g}$ ) was sequentially impregnated with aqueous solutions of  $\text{H}_3\text{PO}_4$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (all Merck p.a.). After each impregnation step the catalysts were dried in air at 383 K (in 3 h from 293 to 383 K, 16 h at 383 K). After the last impregnation step the carbon support was impregnated with an aqueous solution of  $^{57}\text{Co}$  in 0.1M  $\text{HNO}_3$  (ex Amersham) and subsequently dried in ambient air at room temperature for 16 h. Hereafter, the catalysts were submitted to an additional drying procedure in hydrogen, during which they were kept at 313, 353 and 393 K for 24 h each. The following catalysts were prepared,  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$ ,  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$ ,  $^{57}\text{Co}:\text{Ni}(4.3)\text{P}(4.7)/\text{C}$  and  $^{57}\text{Co}:\text{Ni}(4.3)\text{Mo}(7.3)\text{P}(4.3)/\text{C}$  (Ni, Mo and P contents in wt%), or  $^{57}\text{Co}:\text{Ni}(0.5)/\text{C}$ ,  $^{57}\text{Co}:\text{Ni}(0.4)\text{Mo}(0.5)/\text{C}$ ,  $^{57}\text{Co}:\text{Ni}(0.4)\text{P}(0.9)/\text{C}$  and  $^{57}\text{Co}:\text{Ni}(0.4)\text{Mo}(0.5)\text{P}(0.9)/\text{C}$  (Ni, Mo and P contents in  $\text{at}/\text{nm}^2$ ). The  $^{57}\text{Co}$  content is about  $2\cdot 10^{-3}$  wt% or about  $2\cdot 10^{-4}$   $\text{at}/\text{nm}^2$ .

The catalysts were sulfided in a 10%  $\text{H}_2\text{S}/\text{H}_2$  gas flow. The following notation is applied (S, xK, yh+zh) which means that the catalyst was treated in the  $\text{H}_2\text{S}/\text{H}_2$  gas flow and was linearly heated upto x K in y h and kept at x K for z h, after which the catalyst was cooled down to room temperature in the sulfiding gas mixture.

The four catalysts prepared were subjected to a stepwise sulfidation treatment. In previous studies on  $^{57}\text{Fe}$  (refs. 6,7) and  $^{57}\text{Co}$  (refs. 8,9) containing catalysts it was demonstrated that the application of such a stepwise sulfidation procedure provides details which are overlooked if the catalysts are sulfided at once at temperatures commonly used in the HDS or HDN presulfiding.

The MES spectra were recorded at room temperature using a constant acceleration spectrometer. The absorber was  $\text{K}_4\text{Fe}(\text{CN})_6\cdot 3\text{H}_2\text{O}$  enriched in  $^{57}\text{Fe}$ . Calibration of the velocity scale was done by using a SNP ( $\text{Na}_2(\text{Fe}(\text{CN})_5\text{NO})\cdot 2\text{H}_2\text{O}$ ) absorber and a  $^{57}\text{Co}:\text{Rh}$  source. The zero of the velocity scale is relative to  $\text{K}_4\text{Fe}(\text{CN})_6\cdot 3\text{H}_2\text{O}$  measured with  $^{57}\text{Co}:\text{Rh}$ .

## RESULTS

In Fig. 1 the room temperature Mössbauer spectra of the stepwise sulfided  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$  and  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$  are presented. The final sulfidation temperature is 673 K.

From the spectra of  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$  it is clear that the sulfidation of the catalyst takes place at rather low temperatures. After sulfidation at 300 K the spectrum mainly consists of a doublet with a quadrupole splitting  $Q.S. = 1.02$  mm/s and an isomer shift  $I.S. = 0.19$  mm/s. Only a small fraction of the  $^{57}\text{Co}$  is present in a high-spin 2+ phase. After sulfidation at 473 K all the Co is present in a phase with a  $Q.S. = 1.01$  mm/s and an  $I.S. = 0.17$  mm/s. Such a spectrum is typical for the so-called "Co-Mo-S" phase, defined by its Mössbauer parameters by Topsøe et al. (ref. 10). (However, Van der Kraan et al. (refs. 3,8,9) have found that in accordance with this definition the "Co-Mo-S" type of Co species can also be present in the absence of molybdenum.) Sulfidation at higher temperatures only results in minor changes. The mean  $Q.S.$  of the observed doublet decreases slightly and it ends up with  $Q.S. = 0.88$  mm/s. A similar behaviour was observed for a  $\text{Co}(2.3)\text{Mo}(6.8)/\text{C}$  catalyst (ref. 3).

The sulfidation of the  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$  catalyst occurs between room temperature and 473 K. During sulfidation at room temperature and 373 K a high-spin 2+ phase is formed which is the only remaining phase after sulfidation at 373 K. After sulfidation at 473 K this high spin 2+ phase has disappeared completely from the spectrum, and instead a doublet arises with a rather small  $Q.S. = 0.65$  mm/s and an  $I.S. = 0.22$  mm/s. Results obtained on Co/C catalysts with varying Co contents have shown that the  $Q.S.$  is a function of the Co content (refs. 3,9). The doublet with a  $Q.S. = 0.65$  mm/s of the  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$  catalyst corresponds to that of a Co/C catalyst with a Co content higher than 2.5 wt%. Sulfidation at higher temperatures reduces the  $Q.S.$  even more. After sulfidation at 673 K during 4 h, the doublet with a  $Q.S. = 0.46$  mm/s of the  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$  catalyst is more pronounced than the doublet with a  $Q.S. = 0.40$  mm/s observed for the  $\text{Co}(2.5)/\text{C}$  catalyst, and which merely was a broadened single line and could be assigned to a  $\text{Co}_9\text{S}_8$  like phase. The spectrum of the  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$  catalyst suggests that  $^{57}\text{Co}$  has taken part in the formation of a Ni sulfide phase.

From a comparison of the results on the  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$  and the  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$  catalyst the influence of the Mo on the sulfidic state of the  $^{57}\text{Co}$  in the catalysts is obvious. A "Co-Mo-S" phase characterised by a doublet with a larger  $Q.S.$  is formed in the presence of Mo, and this  $Q.S.$  remains much larger at increasing sulfidation temperatures, indicating that this "Co-Mo-S" phase is much more stable than the one formed in the catalyst which does not contain Mo. The same difference was observed between Co/C and Co-Mo/C catalysts (refs. 3,9) and between Fe/C and Fe-Mo/C catalysts (refs. 6,7).

In Fig. 2 the results obtained for the phosphorus containing catalysts are presented. It is

clear that the phosphorus has an enormous influence on the  $^{57}\text{Co}$  in both the catalyst with and without Mo. In both catalysts a high-spin 2+ phase is formed after sulfidation at low temperatures. Increase in sulfidation temperature only results in small changes in these high-spin 2+ spectra. The influence of the Mo turns out to be nihil now. In none of the catalysts a  $^{57}\text{Co}$  phase with the parameters of "Co-Mo-S" is found, although it can not be excluded that a small fraction of the  $^{57}\text{Co}$  (less than 5%) is present in such a phase. These results are in agreement with previous results on phosphorus containing Fe(-Mo)/C catalysts (ref. 11).

## DISCUSSION

As outlined in the introduction, one of our aims was to get information about the relevance of  $^{57}\text{Co}$  MES measurements for studies of the structure of Ni containing hydrotreating catalysts. The MES analyses of the  $^{57}\text{Co}$  doped Ni(-Mo) catalysts resulted in the following findings: (i)  $^{57}\text{Co}$  is not randomly distributed over the catalyst, (ii) the apparent  $^{57}\text{Co}$  content is much higher than the actual one and (iii) the behaviour of a  $^{57}\text{Co}/\text{C}$  and a  $^{57}\text{Co-Mo}/\text{C}$  ( $2 \cdot 10^{-3}$  wt%  $^{57}\text{Co}$ ) catalyst without Ni is completely different from that of the examined Ni containing catalysts. These observations which can be understood only if the  $^{57}\text{Co}$  probes the Ni will be discussed below.

Although  $^{57}\text{Co}$  was added in the final impregnation step, the results on the  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$  and the  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$  catalyst show that  $^{57}\text{Co}$  is not randomly deposited on the carbon support. The behaviour of  $^{57}\text{Co}$  in the  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$  catalyst is completely different from that in the  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$  catalyst. In the case of a random  $^{57}\text{Co}$  distribution, a "mixed"  $^{57}\text{Co-Mo}/\text{C}$  and  $^{57}\text{Co}/\text{C}$  behaviour would have been expected in the  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$  catalyst. As this is not the case the results indicate that  $^{57}\text{Co}$  is probing the Ni.

A second indication that  $^{57}\text{Co}$  is probing the Ni is found in the Q.S. value of the Co-sulfide phases formed in the  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$  and the  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$  catalysts. The mean Q.S. of the "Co-Mo-S" phase in  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$  sulfided at 673 K is 0.88 mm/s which is comparable to the mean Q.S. of "Co-Mo-S" in  $\text{Co}(2.3)\text{Mo}(6.8)/\text{C}$  (ref. 3). In the Co-Mo/C catalysts the mean Q.S. of the observed "Co-Mo-S" doublet turned out to be a function of the Co content (refs. 3,9). Following this empirical relation between the magnitude of the Q.S. and the Co content the apparent Co content in the present  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$  catalyst would be 2.3 wt%. It is rather unlikely that the very small amount of  $^{57}\text{Co}$  added to the catalysts will be present in spots with such a high  $^{57}\text{Co}$  concentration. It is more likely that the Q.S. of  $^{57}\text{Co}$  reflects the Ni content and that the promoter dispersion of the  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$  is as high as that of the  $\text{Co}(2.3)\text{Mo}(6.8)/\text{C}$  catalyst (ref. 3). The same holds for the  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$

catalyst. The Q.S. of the "Co-Mo-S" phase formed at intermediate sulfiding temperatures suggests a much higher Co content than the one which is actually present in the catalyst. The apparent Co content in this case is higher than 2.5 wt%. So, in the absence of MoS<sub>2</sub> the Ni sulfide seems to be as poorly dispersed as the Co sulfide. Furthermore, the sulfidic phase formed at the highest sulfidation temperature (673K) turns out to be different from Co<sub>9</sub>S<sub>8</sub>, which is the thermodynamically stable Co-sulfide phase. NiS (ref. 12) and Ni<sub>3</sub>S<sub>2</sub> (ref. 13) are reported to be present in sulfided Ni/C catalysts. Although the MES spectrum of <sup>57</sup>Co in these Ni-sulfides is not known, the fact that another sulfide than Co<sub>9</sub>S<sub>8</sub> is formed, is also an indication that <sup>57</sup>Co probes the Ni.

A third argument that <sup>57</sup>Co functions as a probe for the Ni is based on a comparison of the present results with those obtained on <sup>57</sup>Co/C and <sup>57</sup>Co-Mo/C catalysts with a similar low <sup>57</sup>Co content (2\*10<sup>-3</sup> wt%) as their Ni containing counterparts. So, if the Ni has no influence on the behaviour of the <sup>57</sup>Co the results should be similar. However, in the <sup>57</sup>Co-Mo/C catalyst a "Co-Mo-S" phase is observed with a Q.S. of 1.14 mm/s which is larger than the Q.S. of "Co-Mo-S" in the Ni containing catalyst. Furthermore, the Q.S. tends to increase on sulfidation at higher temperatures whereas the Q.S. of the "Co-Mo-S" in the <sup>57</sup>Co:Ni(4.5)Mo(8.0)/C catalyst shows a tendency to decrease, as was also observed for the Co(2.3)Mo(6.8)/C catalyst (ref. 3). The behaviour of the <sup>57</sup>Co/C and the <sup>57</sup>Co:Ni(5.6)/C catalysts is entirely different. Besides a doublet with a large Q.S. (1.42 mm/s) in <sup>57</sup>Co/C, a phase with a Q.S. of 4.2 mm/s (ref. 14) is formed at intermediate sulfidation temperatures which is not observed in the <sup>57</sup>Co:Ni(5.6)/C catalyst. After the final sulfidation a broad single line is observed in the <sup>57</sup>Co/C catalyst, indicating the formation of a Co<sub>9</sub>S<sub>8</sub>-like phase, while an unknown sulfide phase is formed in the <sup>57</sup>Co:Ni(5.6)/C catalyst.

Although it will never be possible to prove that in the catalysts investigated the <sup>57</sup>Co probe acts the same as Ni, the present measurements produce ample evidence that the <sup>57</sup>Co MES technique may be used to investigate the structure of the Ni in these catalysts.

So, in the <sup>57</sup>Co:Ni(4.5)Mo(8.0)/C catalyst sulfided at 673 K the Ni is present in a "Ni-Mo-S" phase. The existence of such a "Ni-Mo-S" phase was made plausible by other techniques (refs. 15,16), but such strong evidence as presented here was not yet provided. In the <sup>57</sup>Co:Ni(5.6)/C catalyst a bulk sulfide is formed. According to Bouwens et al. (ref. 17) and Eijssbouts (ref. 4), the thiophene HDS activity of Ni-Mo/C is much higher than that of Ni/C. This is in agreement with the assumption that "Ni-Mo-S" is the active phase and the observation that in the <sup>57</sup>Co:Ni(5.6)Mo(8.0)/C catalyst "Ni-Mo-S" is the dominant phase while in the <sup>57</sup>Co:Ni(5.6)/C catalyst a bulk sulfide is formed. Furthermore, according to Eijssbouts et al. (refs. 4,5), the quinoline HDN activity of the Ni-Mo/C catalyst is much higher than that

of the Ni/C catalyst. This agrees with the general accepted idea that also for HDN the "Ni-Mo-S" sites are the active sites. However, it must be mentioned that the MES spectra are recorded at atmospheric pressure while the quinoline HDN tests are performed at 30 bar.

The introduction of phosphorus clearly changes the type of Ni-compounds formed. Instead of a bulk Ni-sulfide or "Ni-Mo-S", in both catalysts a "Ni-(thio)phosphate"-like phase is formed. So far, we were not able to distinguish between the "Ni-phosphate" - and the "Ni-thiophosphate"-like phases. The formation of this phase has a large influence on the catalytic properties of the catalysts. The thiophene HDS activity (measured at 1 bar and 673 K) of Ni/C and especially that of Ni-Mo/C is poisoned by the introduction of phosphorus (ref. 4). As a result, the difference in activity between the two phosphorus containing catalysts is much smaller than that between their phosphorus free counterparts. The effects of phosphorus on the structure, sulfidability and thiophene HDS activity of Ni(-Mo)/C catalysts are also observed for Co(-Mo)/C (refs. 17,18) and Fe(-Mo)/C (refs. 11,17)

Although for both Ni/C and Ni-Mo/C the HDS activity is lowered by introduction of phosphorus, this is not the case for the quinoline HDN activity (refs. 4,5). The quinoline HDN activity of the Ni-Mo/C catalyst is decreased in the presence of phosphorus, while the activity of Ni/C is strongly enhanced. The resulting activities of the Ni-Mo-P/C and the Ni-P/C catalysts are quite similar. This seems to be in good agreement with the obtained MES results. In both catalysts a "Ni-(thio)phosphate" is formed. This "Ni-(thio)phosphate" apparently has a low activity for HDS but turns out to have an interestingly high activity for HDN.

## CONCLUSIONS

$^{57}\text{Co}$  may be used as a probe for Ni in the Ni-containing hydrotreating catalysts investigated. This follows from a comparison of the  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$  and  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$  results with those obtained for  $^{57}\text{Co}/\text{C}$  and  $^{57}\text{Co-Mo}/\text{C}$  catalysts, and with results on Co(-Mo)/C catalysts with higher Co contents.

From the MES results on  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$  and  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$  it follows that at atmospheric pressure a bulk Ni-sulfide is formed in the former whereas a "Ni-Mo-S" phase is formed in the latter. The presence of this "Ni-Mo-S" phase most likely explains the high thiophene HDS activity of the Ni-Mo/C catalyst. Addition of phosphorus leads to the formation of a "Ni-(thio)phosphate" phase in both catalysts which appears to have a very low HDS activity.

The MES results obtained at 1 bar seem also useful to explain the effect of P on the quinoline HDN activity obtained at 30 bar of Ni(-Mo)/C catalysts.

## REFERENCES

- 1 A.M. van der Kraan and J.W. Niemantsverdriet, in: "Industrial Applications of the Mössbauer Effect", eds. G.J. Long and J.G. Stevens, (Plenum, New-York and London), (1986)609-634.
- 2 H. Topsøe, B.S. Clausen, R. Candia, C. Wivel and S. Mørup, *Bull. Soc. Chim. Belg.*, **90**(1981)1189-1214.
- 3 A.M. van der Kraan, M.W.J. Crajé, E. Gerkema, W.L.T.M. Ramselaar and V.H.J. de Beer, *Hyp. Int.*, **46**(1989)567-574.
- 4 S. Eijsbouts, Ph.D. Thesis Eindhoven University of Technology, Eindhoven (1989).
- 5 S. Eijsbouts, J.N.M. van Gestel, L.M.P. van Gruijthuijsen, J. Volmer, R. Prins and V.H.J. de Beer, Extended Abstract, 19th Biennial Conference on Carbon, Penn State University, U.S.A. (1989)46-47.
- 6 W.L.T.M. Ramselaar, R.H. Hadders, E. Gerkema, V.H.J. de Beer, E.M. van Oers and A.M. van der Kraan, *Appl. Catal.*, **51**(1989)263-283.
- 7 W.L.T.M. Ramselaar, M.W.J. Crajé, E. Gerkema, V.H.J. de Beer and A.M. van der Kraan, *Appl. Catal.*, **54**(1989)217-239.
- 8 A.M. van der Kraan, M.W.J. Crajé, E. Gerkema, W.L.T.M. Ramselaar and V.H.J. de Beer, *Appl. Catal.*, **39**(1988)L7-L10.
- 9 M.W.J. Crajé, E. Gerkema, V.H.J. de Beer and A.M. van der Kraan, in: "Studies in Surface Science and Catalysis 50", eds. M.L. Occelli and R.G. Anthony, (Elsevier, Amsterdam), (1989)165-179.
- 10 H. Topsøe, B.S. Clausen, R. Candia, C. Wivel and S. Mørup, *J. Catal.*, **68**(1981)433-452.
- 11 W.L.T.M. Ramselaar, S.M.A.M. Bouwens, V.H.J. de Beer and A.M. van der Kraan, *Hyp. Int.*, **46**(1989)599-606.
- 12 R. Burch and A. Collins, *J. Catal.*, **97**(1986)385.
- 13 S.M.A.M. Bouwens, N. Barthe-Zahir, V.H.J. de Beer and R. Prins, *J. Catal.*, Acc. for Publ.
- 14 M.W.J. Crajé, V.H.J. de Beer and A.M. van der Kraan, in preparation.
- 15 N.-Y. Topsøe and H. Topsøe, *J. Catal.*, **84**(1983)386-401.
- 16 S.M.A.M. Bouwens, D.C. Koningsberger, V.H.J. de Beer, S.P.A. Louwers and R. Prins, *Catal. Lett.*, **5**(1990)273-284.
- 17 S.M.A.M. Bouwens, Ph.D. Thesis, Eindhoven University of Technology, Eindhoven (1988).
- 18 P.J. Mangnus, V.H.J. de Beer and J.A. Moulijn, *Appl. Catal.*, **67**(1990)119-139.



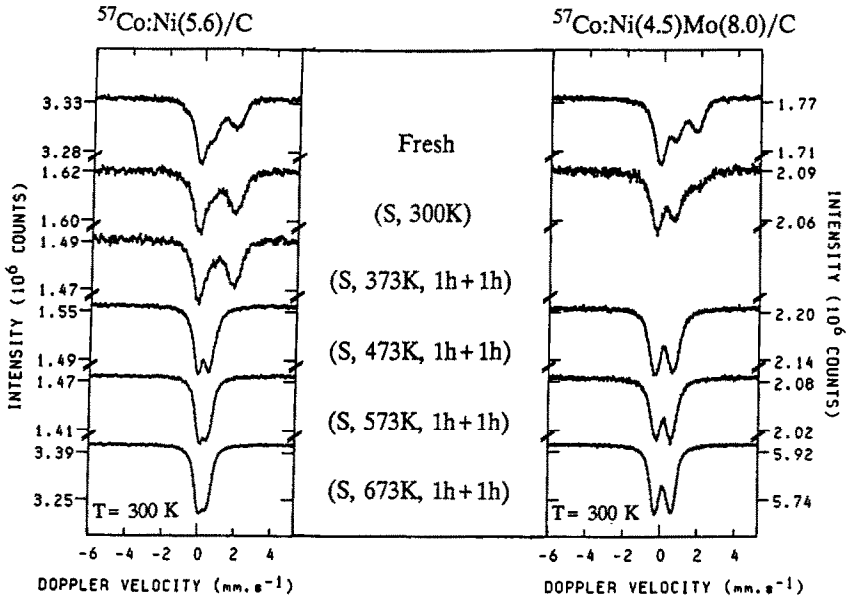


Fig. 1. Mössbauer emission spectra of  $^{57}\text{Co}:\text{Ni}(5.6)/\text{C}$  and  $^{57}\text{Co}:\text{Ni}(4.5)\text{Mo}(8.0)/\text{C}$  after successive sulfidation treatments.

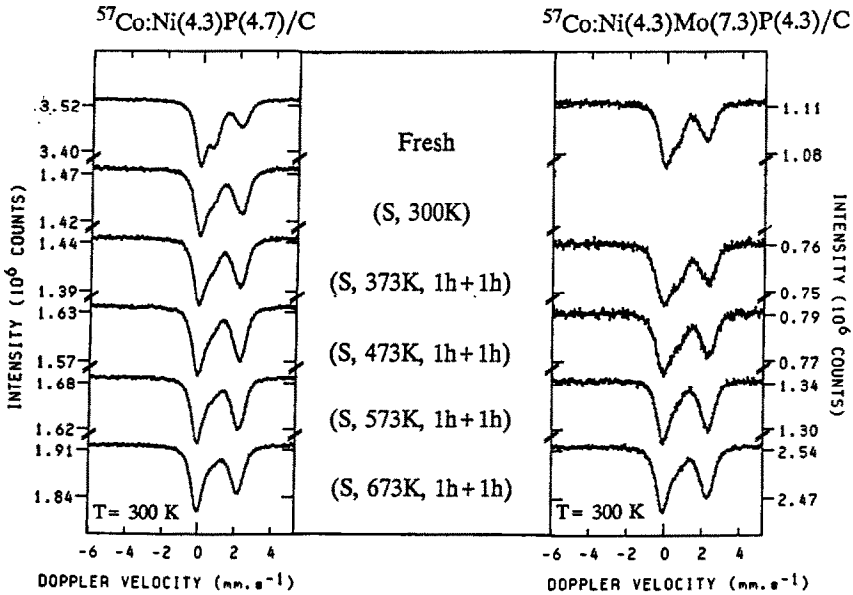


Fig. 2. Mössbauer emission spectra of  $^{57}\text{Co}:\text{Ni}(4.3)\text{P}(4.7)/\text{C}$  and  $^{57}\text{Co}:\text{Ni}(4.3)\text{Mo}(7.3)\text{P}(4.3)/\text{C}$  after successive sulfidation treatments.