

Study of Fe/C and FeMo/C hydrodesulfurization catalysts : preparational aspects and metal support interaction

Citation for published version (APA):

Ramselaar, W. L. T. M., Kraan, van der, A. M., & Beer, de, V. H. J. (1986). Study of Fe/C and FeMo/C hydrodesulfurization catalysts : preparational aspects and metal support interaction. *Hyperfine Interactions*, 28(1-4), 895-898. <https://doi.org/10.1007/BF02061588>

DOI:

[10.1007/BF02061588](https://doi.org/10.1007/BF02061588)

Document status and date:

Published: 01/01/1986

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.

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STUDY OF Fe/C AND FeMo/C HYDRODESULFURIZATION CATALYSTS: PREPARATIONAL ASPECTS AND METAL SUPPORT INTERACTION

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From the Mössbauer spectra of various oxidic catalysts precursors obtained at 4.2 K, 77 K and 300 K, the sequences in particle size and thermal motions relative to the support are established.

1. INTRODUCTION

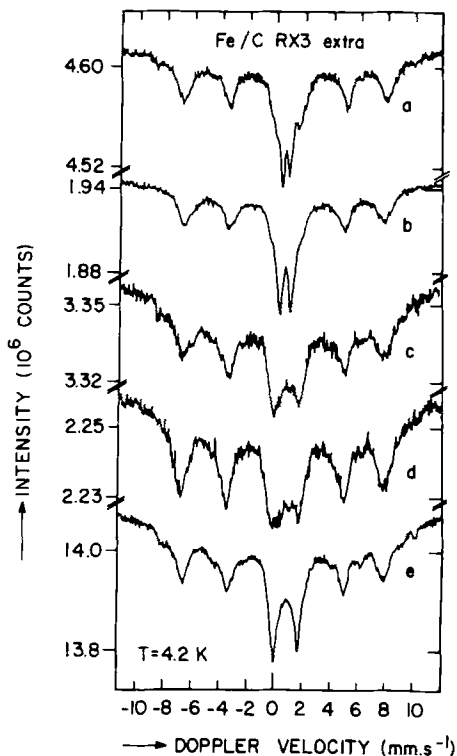
Hydrotreating catalysts are used for the upgrading of fossil fuel fractions. Several processes take place simultaneously, such as hydrocracking, removal of sulfur, nitrogen, oxygen and metals, and hydrogenation of olefins and aromatic hydrocarbons. At present, industrially employed hydrotreating catalysts consist of Mo and W promoted with Co or Ni dispersed on a high-surface area alumina support. The catalysts are active in the sulfided state. Mössbauer emission spectroscopy has been very successful in the characterization of industrial hydrotreating catalysts /1,2/.

Recently, carbon supported metal sulfides have attracted attention as favourable hydrotreating catalysts /3/. In particular, iron sulfide on carbon would be a potentially attractive catalyst, as iron is inexpensive and abundantly present. For Fe/C catalysts preparational aspects such as the kind of carbon-support and iron salt solution for impregnation, in relation to their catalytic properties, are described by Groot /4/. In his study Mössbauer spectroscopy has played an important role in characterizing the oxidic catalyst precursors. In addition, now we present the influence of the drying procedure and the solvent on the dispersion and related particle-support interaction studied by Mössbauer spectroscopy.

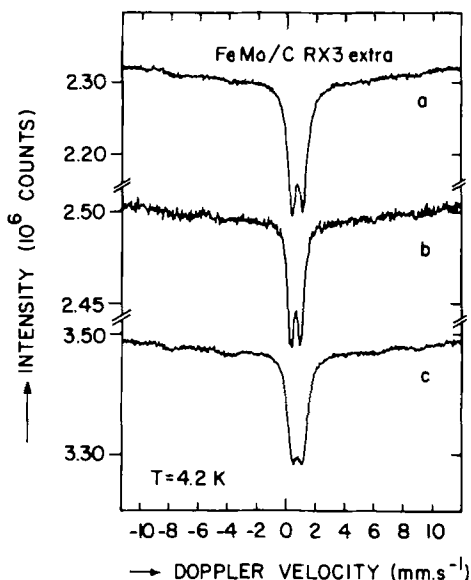
2. EXPERIMENT AND RESULTS

The carbon-supported catalyst precursors are prepared by pore volume impregnation of Norit RX3-extra active carbon (surface area 1190 m²/gr). An aqueous solution containing the desired amount of iron or molybdenum is added to the carbon support until the incipient wetness point is reached. As starting materials are used Fe(NO₃)₃·9H₂O (Merck, P.A.) and (NH₄)₆Mo₇O₂₄·4H₂O (Merck, > 99%). The impregnated samples are dried at room temperature in different ways, in order to study the influence of the drying procedure. Optimum Fe-Mo/C catalysts are obtained by a sequential pore volume impregnation in which Mo is introduced prior to iron. All catalysts contain 2.7 wt% Fe, the Fe-Mo/C catalysts in addition 15 wt% Mo.

In order to obtain a highly active catalyst, a high dispersion of the supported iron particles is desirable. Mössbauer spectroscopy can in principle yield indirectly the important information on particle size in two ways: by studying the superparamagnetic transition temperature of the particles /5/ and by analyzing the recoilless fraction as a function of temperature.



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Fig. 1. Mössbauer spectra of various Fe/C catalyst precursors. a: airflow 50 ml/min ($\theta_D=175K$); b: airflow 100 ml/min ($\theta_D=225K$); c: airflow 500 ml/min ($\theta_D=150K$); d: descicator ($\theta_D=150K$); e: solvent ethanol, airflow 100 ml/min ($\theta_D=125K$).



†
Fig. 2. Mössbauer spectra of various FeMo/C catalyst precursors. a: airflow 100 ml/min; b: evacuated descicator; c: descicator at atmospheric pressure.

From the latter an effective Debye temperature (θ_D) can be determined /6/. However, Debye temperatures derived from the temperature dependence of the resonant absorption areas will be too low, when the supported catalyst particles in their totality perform thermal motions relative to the support /7/. Therefore we determine the sequence in the mean particle size of the Fe(III)oxide particles from the spectral contribution of the magnetic hyperfine sextuplet at a certain temperature. The thermal motions of the particles depend on the interaction strength between the particles and support. The lower the interaction strength, the larger the mobility of the particles over the support, leading more easily to sintering. So, by determining the effective Debye temperature θ_D from the temperature dependence of the resonant absorption area of the spectra, information is obtained about the interaction strength between the particles and support.

In Fig. 1 Mössbauer spectra recorded at 4.2 K are presented of the oxidic Fe/C catalyst precursor after different drying treatments. The effective Debye temperatures for these samples determined from the total resonant absorption areas of the spectra at 4.2K, 77K and 300K respectively are given in the captions of Fig. 1. The impregnated sample is dried in a descicator above P₂O₅ for 7 days, or in a continuous airflow of 50 ml/min, 100 ml/min or 500 ml/min during 18 h. Due to the phenomenon of superparamagnetism, an increase in spectral contribution of the magnetic hyperfine sextuplet means an increase

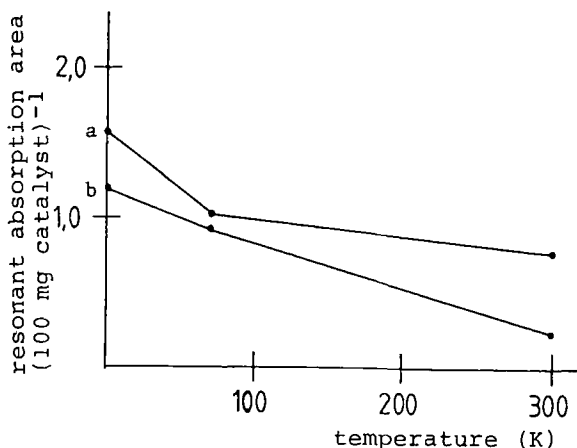


Fig.3. Temperature dependence of the resonant absorption area of Fe/C catalyst precursor (dried in 50 ml/min airflow);
 a: paraffin embedded;
 b: non embedded.

in mean particle size. Although only a little difference in mean particle size is observed for the samples dried in an airflow of 50 ml/min and 100 ml/min, it follows from Fig.1 that by increasing as well as decreasing the evaporation rate of water, an increase in mean particle size is found.

The highest effective Debye temperature is found for the sample with the smallest mean particle size. So this sample will be the least sensitive to sintering.

Mössbauer spectra have been taken at room temperature of the sample dried in the desiccator, after different periods of drying. The relative total resonant absorption area is directly after impregnation 0.27, after one day in the desiccator 0.51, after two days 0.98 and after seven days 1.0. After two days in the desiccator it is hardly possible to remove more water of the catalyst precursor. The thermal motions of the particles relative to the support are still large as follows from the effective Debye temperature (in the caption of Fig.1).

In Fig.2 the Mössbauer spectra of the oxidic FeMo/C catalyst precursor after drying in airflow (100 ml/min) for 18 h, or in a desiccator above P₂O₅ or an evacuated (3.10³ Pa) desiccator above P₂O₅ are shown. Hardly any spectral contribution of a magnetic hyperfine sextuplet is found for the different samples, so the mean particle size of the iron(III) oxide particles will be the same and appears to be smaller in the FeMo/C than in the Fe/C catalyst precursors. A comparison with data obtained by Jung et al /8/ and Niemants-verdriet et al /9/ for carbon-supported iron Fischer-Tropsch catalysts shows that the mean particle size of the iron(III) oxide particles in the FeMo/C samples is below 20 Å. For the three FeMo/C samples a same temperature dependence of the total resonant absorption area is found, which leads to a θ_D of 150K.

To overcome the thermal motion of the particles relative to the support and the enhanced vibrations of the surface atoms, we have embedded a Fe/C catalyst precursor in a paraffin matrix following Hayashi et al./10/. As is shown in Fig.3 the measured total resonant absorption area is increased and the temperature dependence of A is drastically changed upon embedding the catalyst precursor. Between 77K and 300K, the temperature dependence of A in the embedded sample corresponds to the behaviour of fixed iron(III) oxide particles of this size (≈ 30 -40 Å). However, between 77K and 4.2K A of the embedded sample increases much more with decreasing temperature than A of the non-embedded sample. This indicates that due to the paraffin matrix also a fraction of the original iron(III) oxide particles, missing in

the spectrum due to the large thermal motions of the particles, becomes stronger bound to the support. However still not completely fixed.

By using ethanol as a solvent, the pore volume of the carbon-support turns out to be higher ($1.2 \times 10^{-3} \text{m}^3/\text{kg}$) than for water ($1.0 \times 10^{-3} \text{m}^3/\text{kg}$). In order to achieve a higher dispersion of the iron(III) oxide particles we have measured a Fe/C catalyst precursor obtained by impregnation with a solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in ethanol (see Fig.1e). The spectrum is more complicated than when an aqueous solution is used. A larger fraction of the spectral area is due to paramagnetic relaxation of monatomically dispersed Fe, influenced by anionic species present on the support. So it turns out that indeed a higher dispersion can be achieved by using ethanol as a solvent. Investigations of the effect on the catalytic activity are in progress.

3. CONCLUSIONS

There exists an optimum evaporation rate of the impregnated solvent in relation to the highest dispersion of the catalyst precursor. By using that drying procedure the particles are then most strongly bound to the support and so less sintering sensitive.

It seems to be worthwhile to investigate the catalytic activity of Fe/C catalysts obtained by impregnation with a solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in ethanol.

For the bimetallic FeMo/C catalyst precursor an influence of the drying procedure on the dispersion of the catalyst has not been observed. A possible explanation for this phenomenon is that in FeMo/C the Fe is supported by the molybdenum rather than by the carbon. This result would be in agreement with measurements on CoMo/Al₂O₃ catalysts /2/.

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