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Behaviour of the resonant absorption area of a ^{57}Fe -doped Ni/C catalyst during sulfidation

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In-situ Mössbauer spectroscopy measurements down to 4.2 K were performed on a $^{57}\text{Fe}:\text{Ni}(0.5)/\text{C}$ catalyst after various successive sulfidation treatments. After exposure of the catalysts to the $\text{H}_2\text{S}/\text{H}_2$ gas mixture at room temperature, part of the ^{57}Fe becomes sulfidic. The rest is present as a sulfate-like intermediate species. The interaction between this intermediate species and the carbon support material is influenced by water. At temperatures below 180 K the water is rigid, at higher temperatures the water becomes mobile. This weakens the interaction with the support material, resulting in a decrease of the RAA. The interaction between the sulfidic species and the support material is not influenced by water. However, this species is not yet very well ordered; therefore, the ^{57}Fe is loosely bound. The ordering becomes better by sulfidation at higher temperatures, leading to an increase of the RAA.

1. Introduction

The hydrotreatment of crude oil fractions is one of the largest chemical processes applied in the world. In this process, heteroatoms are removed from the crude oil by leading it over a catalyst at a high temperature and pressure in the presence of an excess of hydrogen. The catalysts used generally consist of sulfided $\text{CoMo}/\text{Al}_2\text{O}_3$ when hydrosulfurization (HDS), or $\text{NiMo}/\text{Al}_2\text{O}_3$ when hydrodenitrogenation (HDN) is the main concern.

In the last three decades, extensive characterization studies have been carried out on both types of catalysts. The possibility to apply Mössbauer spectroscopy greatly facilitated the characterization studies on the sulfided CoMo catalysts [1–4]. Although nickel has a Mössbauer isotope (^{61}Ni), its Mössbauer parameters are not sensitive enough to supply useful information about the structure of the Ni-containing catalysts. However, recently it has been demonstrated that it is possible to use ^{57}Co as a probe for the Ni in these catalysts [5]. Because of the low price and non-radioactivity of ^{57}Fe , it was also investigated whether ^{57}Fe may be used as a probe for the Ni [6]. As part of this investigation, the stepwise sulfidation of a ^{57}Fe -doped

Ni(0.5)/C (at/nm²) catalyst was studied. It followed that during exposure of this catalyst to a 10% H₂S/H₂ gas mixture at room temperature, the Mössbauer parameters changed and the resonant absorption area (RAA) strongly decreased. After sulfidation at 473 K, the RAA became almost its original value. Such a decrease of the RAA during sulfidation at a rather low temperature had previously been observed [7], but not as strong as for the ^{57}Fe :Ni(0.5)/C catalyst. Since it is necessary to understand all features observed in the Mössbauer study for a thorough understanding of the structure of the catalyst, the behaviour of the RAA during the sulfidation of the ^{57}Fe :Ni(0.5)/C catalyst is studied more carefully. In-situ Mössbauer measurements are performed at temperatures down to 4.2 K in order to derive an effective Debye temperature θ_D which may reveal information about the interaction between the actual catalyst (^{57}Fe :Ni) and the support material (activated carbon).

2. Results

Details about the preparation of the catalyst and the Mössbauer measurements are given in refs. [3–5].

In fig. 1, the room temperature Mössbauer spectra of the stepwise sulfided ^{57}Fe :Ni(0.5)/C catalyst are shown after each sulfidation step. The resonant absorption areas of the spectra of the catalyst after these successive sulfidation treatments are shown in fig. 2. Clearly, the RAA strongly decreases by exposure of the catalyst to the H₂S/H₂ gas mixture. The RAA remains very small after sulfidation at 373 K, but increases strongly during sulfidation at 473 K. In addition, sulfidation at elevated temperatures results only in a slight increase of the RAA. Therefore, temperature-dependent Mössbauer measurements are performed on the fresh catalyst and on the catalyst after sulfidation at 300, 373 and 673 K.

In fig. 3, the $\ln(\text{RAA}(T))$ of the fresh catalyst is presented. The straight line plotted through the data reveals an effective θ_D of 247 K.

After exposure of the catalyst to the H₂S/H₂ gas mixture at room temperature, a remarkable behaviour of $\ln(\text{RAA}(T))$ is observed (fig. 3). The data do not lie on one, but on two straight lines. One straight line can be drawn through the data up to 180 K and a second line through the data above this temperature. These two lines have a different slope. Analysing the measured spectra by two doublets (one doublet with $IS = 0.42$ and $QS = 0.79$ mm/s, and a high-spin 2+ doublet with $IS = 1.54$ and $QS = 2.25$ mm/s), for each doublet a $\ln(\text{RAA}(T))$ plot can be made. The doublet with $IS = 0.42$ and $QS = 0.79$ mm/s shows a straight line up to room temperature, yielding a θ_D of 148 K. The high-spin 2+ doublet shows a straight line up to a temperature of about 180 K, giving rise to a θ_D of 183 K, while above this temperature the RAA quickly decreases, becoming almost zero at room temperature.

The data obtained after sulfidation at 373 K as well as 673 K lie in both cases on straight lines. After sulfidation at 373 K, an effective θ_D of 140 K is determined for the catalyst. After sulfidation at 673 K, a much larger θ_D of 214 K is observed which is, however, still not as large as the value of 247 K in the fresh catalyst.

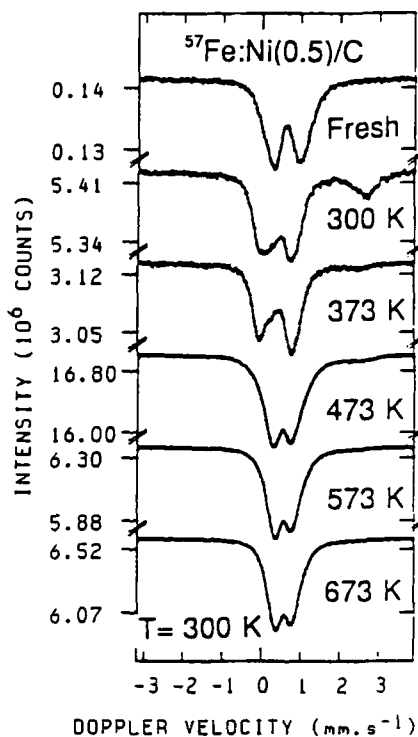


Fig. 1. Room temperature Mössbauer spectra of the stepwise sulfided ^{57}Fe : Ni(0.5)/C catalyst. The catalyst has been sulfided up to the temperatures indicated.

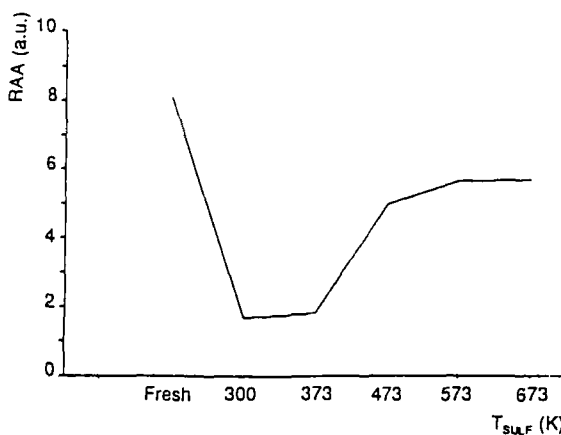


Fig. 2. Resonant absorption areas of the spectra shown in fig. 1.

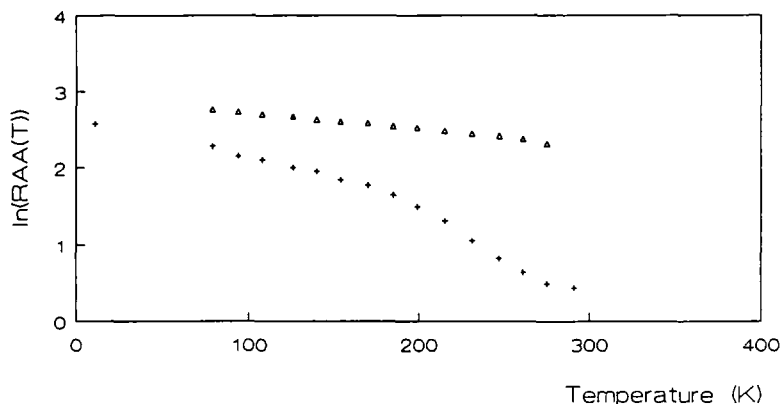


Fig. 3. Plot of $\ln(\text{RAA}(T))$ of the fresh catalyst (Δ) and of the catalyst exposed to the $\text{H}_2\text{S}/\text{H}_2$ gas mixture at room temperature (+).

3. Discussion

From previous studies, it is known that the catalyst is oxidic after preparation. From the clear changes in shape as well as the RAA of the room temperature spectrum of the catalyst, it follows that sulfidation of the catalyst starts by exposing it to the $\text{H}_2\text{S}/\text{H}_2$ gas mixture at room temperature. However, it cannot be derived to what extent the catalyst is sulfided after this treatment, because the spectrum is dominated by a doublet with $IS = 0.42$ and $QS = 0.79$ mm/s, which might be attributed either to an oxidic or a sulfidic species. However, the temperature dependence of the RAA discriminates between the both of them. It is found that the species to which the doublet is assigned has a θ_D of 148 K, resembling the one observed for the doublet recorded after sulfidation at 373 K. From previous studies [5, 6, 9] and from the absence of a high-spin 2+ species (which should be regarded to be an intermediate sulfate-like species), it is concluded that the catalyst is completely sulfidic after sulfidation at 373 K. The agreement between IS , QS and θ_D of the dominating doublet obtained after sulfidation at room temperature and the parameters of the sulfidic doublet obtained after sulfidation at 373 K makes it clear that the former doublet most likely should be assigned to a sulfidic species.

The second doublet formed during room temperature sulfidation originates from a high-spin 2+ species. The species has a small spectral contribution at room temperature, but a large one below 180 K. Based on previous studies [7, 8] and because it disappears during sulfidation at higher temperature, the high-spin 2+ doublet is assigned to an intermediate species between oxidic and sulfidic species, most probably a sulfate-like species. As mentioned above, this sulfate-like species has a θ_D of 183 K, which drops to almost zero at temperatures above 180 K. A similar behaviour has been observed for a high-spin 2+ species formed in CoMo/C catalysts. This high-spin 2+ species, formed by oxidation of a sulfidic CoMo/C catalyst, has

a θ_D of 175 K [10]. Also for this species, the RAA dropped almost to zero at temperatures above 180 K. For the CoMo/C catalyst, it was demonstrated that the interaction between the high-spin 2+ species and the support material was influenced by the presence of water [10]. The water is mobile at temperatures above 180 K, but becomes rigid below this temperature, thus explaining the increase of the RAA below this temperature. The behaviour of $\ln(\text{RAA}(T))$ of the high-spin 2+ doublet observed for the $^{57}\text{Fe}:\text{Ni}(0.5)/\text{C}$ catalyst is explained in the same way.

Since $\ln(\text{RAA}(T))$ of the sulfidic doublet observed after sulfidation at room temperature shows a straight line up to room temperature, it is clear that the interaction between this species and the support material is not influenced by water. The same holds for the sulfidic species formed after sulfidation at 373 K. The QS of 0.79 mm/s is indicative for poorly ordered sulfide species [4]. These species show a very small RAA. Sulfidation at 473 K leads to a strong decrease of the QS value, indicative of a better ordering of the sulfide species [4]. This induces a strong increase of the RAA. Sulfidation at even higher temperatures leads to a small decrease of the QS value and the concomitant increase of the RAA.

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