MÖSSBAUER EMISSION AND ABSORPTION STUDIES ON THE REDUCTION BEHAVIOUR OF SUPPORTED Co, Co-Mo, Fe AND Fe-Mo HYDROTREATING CATALYSTS

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In carbon-supported Fe-Mo catalysts an Fe-Mo alloy can be formed during reduction in H_2 at 673 K. In carbon-supported Co-Mo catalysts, instead of the formation of a Co-Mo alloy segregation of metallic Co is observed.

In alumina-supported Fe and Fe-Mo catalysts, the interaction between the alumina support and the catalyst particles hinders reduction of the ions to an Fe^0 phase. Most probably a surface “Fe(II)-aluminate” is formed.

1. Introduction

Hydrotreating catalysts are used to remove pollutioneous heteroatoms from crude oil fractions in the presence of hydrogen. The application of Mössbauer emission spectroscopy for the characterisation of these catalysts has led to the so-called “Co-Mo-S” model for the active phase in sulfidic Co-Mo/ Al_2O_3 catalysts [1]. In analogy, the presence of a so-called “Fe-Mo-S” phase should be responsible for the observed synergetic effect in sulfidic Fe-Mo catalysts [2].

Ramselaar et al. [3–5] studied sulfidic Fe and Fe-Mo catalysts by Mössbauer absorption spectroscopy (MAS). In the case of sulfidic carbon-supported catalysts they observed a large influence of Mo on the Fe phases formed. In the case of alumina-supported catalysts on contrary they observed similar spectra for Fe/ Al_2O_3 and Fe-Mo/ Al_2O_3 catalysts. So, in the alumina-supported catalysts there seems to be a much smaller influence of the Mo on the Fe phases formed.

Although hydrotreating catalysts are always used in their sulfidic state, in the present study the reduction behaviour of oxidic catalyst precursors is examined. The aim was not only to get information on the influence of hydrogen on the state of the unsulfided catalyst (precursor) but also to obtain additional information about the particle-support interaction and about the interaction between Fe or Co and Mo.

Therefore, various catalysts were subjected to a stepwise reduction procedure. During this procedure the temperature was linearly increased to a desired maximum under hydrogen flow, after which the catalyst was kept at that maximum temperature under a hydrogen flow for 1 h. The desired temperature was increased in steps of 100 K from room temperature upto 773 K. After each temperature treatment the catalyst was cooled down in the hydrogen flow and a Mössbauer spectrum was recorded at room temperature.

2. Experimental

The catalysts were prepared by the incipient wetness method. As support materials Norit RX3-Extra activated carbon (surface area 1190 m²/g, pore volume 1.0 cm³/g) and Ketjen γ -Al₂O₃ (surface area 271 m²/g, pore volume 0.7 cm³/g) were used. For the Fe-Mo (Co-Mo) catalysts these carrier materials were first impregnated with an aqueous solution of (NH₄)₆Mo₇O₂₄ · 4H₂O (Merck, min. 99.9%) after which the water was removed by drying in static air at 383 K for 16 h. Furthermore, the Mo/Al₂O₃ catalyst precursor was calcined at 673 K for 4 h.

The Fe(Co) was added by impregnation with an aqueous solution of Fe(NO₃)₃ · 9H₂O (Merck, p.a.) (Co(NO₃)₂ · 6H₂O (Merck, p.a.)). To remove the water, the catalyst was exposed to static air at room temperature for 16 h. The nitrate groups were removed by applying an additional treatment in a hydrogen flow. During this treatment the temperature of the catalyst was kept at 313, 353 and 393 K for 24 h at each temperature.

The metal contents of the catalysts are denoted as Fe(*x*), Fe(*x*)-Mo(*y*), Co(*x*) and Co(*x*)-Mo(*y*) with *x* and *y* representing atoms/mm² Fe(Co) and Mo respectively.

The reduction of the catalysts was carried out in hydrogen gas. The Mössbauer spectra were recorded in-situ.

3. Results and discussion

Room temperature Mössbauer spectra of the carbon-supported Fe and Fe-Mo catalysts recorded after successive reduction treatments in H₂ are presented in fig. 1. The Mössbauer parameters are given in table 1. The spectra of the fresh precursors have been analysed by two doublets with equal isomer shift (*IS*) but different quadrupole splitting (*QS*). According to Van der Kraan [6] these two doublets can be attributed to bulk- (small *QS*) and surface-Fe(III)oxide (large *QS*). Both catalysts remain completely oxidic when they are treated in hydrogen at 373 K and 473 K for one hour.

Fig. 1. Mössbauer absorption spectra of Fe(0.15)/C, Fe(0.15)Mo(0.63)/C, Fe(0.50)/Al₂O₃ and Fe(0.80)Mo(0.63)/Al₂O₃ catalysts after various successive reduction treatments in H₂.

After reduction at 573 K the spectrum of Fe(0.15)/C contains contributions of high-spin Fe²⁺ (43%) and Fe₃O₄, whereas in the spectrum of Fe(0.15)Mo(0.63)/C only contributions of high-spin Fe²⁺ are observable. The presence of Mo seems to be causing the difference. This becomes more evident after the reduction treatments at 673 K and 773 K. The Fe/C catalyst reduces to α -Fe particles, while the Fe in the Fe-Mo/C catalyst reduces to a Fe⁰ phase which is characterised by a singlet with a rather large linewidth (simulated by a doublet with a small quadrupole splitting) due to Fe in a Fe-Mo alloy. It turned out that a Fe-Mo alloy can be formed in catalysts with a low Fe loading (upto 0.25 at/nm²),

which are mildly reduced. For higher Fe loadings or when the reduction temperature is fastly increased to 673 K, segregation of metallic Fe is observed, besides the formation of a Fe-Mo alloy.

The spectrum of the Fe/C catalyst reduced at 773 K shows besides a hyperfine field contribution of α -Fe, also contributions belonging to martensite formed via incorporation of interstitial carbon atoms in the Fe lattice [7]. Furthermore, a hyperfine field contribution ($H = 31.8$ T) is found which is probably due to Fe sites influenced by the martensite sites.

Exposure to air at room temperature of the Fe/C catalysts after the final reduction step is found to affect only a small part of the Fe despite the fact that several atom layers will be immediately oxidized on exposure to air. This indicates that the dispersion of α -Fe is poor. The dispersion of the Fe species present in the Fe-Mo/C catalyst remained much higher during the various reduction treatments which follows from the fact that after reoxidation almost the entire spectrum consists of the two Fe(III)oxide doublets. The very broad line that was observed for the Fe-Mo alloy reflects the high dispersion of the Fe species in the Fe-Mo/C catalyst because in highly dispersed Fe(III)oxide many slightly different Fe positions are available resulting in such a broad line. When the same catalyst was reduced at 815 K the line became much narrower and only 20% of the Fe reoxidised to Fe(III)oxide, indicating that at 815 K sintering of the alloy took place.

In fig. 1, also the Mössbauer spectra recorded after various successive reduction steps on Fe(0.50)/Al₂O₃ and Fe(0.80)-Mo(0.63)/Al₂O₃ are presented. The results of the analyses are given in table 2. Again, the spectra of these catalysts consist of Fe(III)oxide uptill reduction at 473 K. The dispersion of the Fe species in the Mo-containing precursor is very high, which follows from the very large surface-oxide contribution. This is in accordance with the observation of Ramselaar et al. [5] from 4.2 K measurements on these catalysts.

After reduction in hydrogen at 573 K the majority of the Fe in both samples is present as high-spin Fe²⁺ while about a quarter of the Fe is still present as Fe(III)oxide. After reduction at 673 K and 773 K the Fe(III)oxide phase has disappeared from the spectra and only high-spin Fe²⁺ phases remained.

For both catalysts, exposure to air at room temperature for several hours after reduction upto 773 K led to the reoxidation of about 70% of the Fe, which indicates that the Fe species are highly dispersed. The same fraction reoxidized Fe was found in the case of a Fe-Mo/Al₂O₃ catalyst which was reduced at 815 K instead of 773 K prior to exposure to air. This strongly suggest that even at 815 K no strong sintering occurs.

In contrast to the carbon-supported catalysts, on their alumina-supported counterparts interaction of the carrier with the Fe-species becomes clear. The alumina hinders complete reduction of the Fe in Fe/Al₂O₃ and Fe-Mo/Al₂O₃, while in the case of Fe-Mo catalysts the alumina also hinders the formation of an Fe-Mo alloy. Furthermore, the strong interaction of the alumina carrier with the

Table 2

Mössbauer parameters of the spectra of Fe(0.50)/Al₂O₃ and Fe(0.80)Mo(0.63)/Al₂O₃, recorded after various reduction steps. The isomer shift (*IS*) is given relative to SNP

Fe(0.50)/Al ₂ O ₃												
Red. temp (K)	<i>IS</i> (mm/s)	<i>QS</i> (mm/s)	<i>A</i> (%)	<i>IS</i> (mm/s)	<i>QS</i> (mm/s)	<i>A</i> (%)	<i>IS</i> (mm/s)	<i>QS</i> (mm/s)	<i>A</i> (%)	<i>IS</i> (mm/s)	<i>QS</i> (mm/s)	<i>A</i> (%)
bulk-oxide				high-spin Fe ²⁺								
				surface-oxide								
373 K	0.61	0.59	50	0.60	0.98	50						
473 K	0.61	0.63	46	0.59	1.02	54						
573 K				0.57	1.02	23	1.11	1.80	21	1.34	2.06	32
673 K							1.06	1.82	31	1.32	1.96	38
773 K							1.06	1.74	34	1.35	1.89	41
											1.97	25
Fe(0.80)Mo(0.63)/Al ₂ O ₃												
Red. temp (K)	<i>IS</i> (mm/s)	<i>QS</i> (mm/s)	<i>A</i> (%)	<i>IS</i> (mm/s)	<i>QS</i> (mm/s)	<i>A</i> (%)	<i>IS</i> (mm/s)	<i>QS</i> (mm/s)	<i>A</i> (%)	<i>IS</i> (mm/s)	<i>QS</i> (mm/s)	<i>A</i> (%)
bulk-oxide				high-spin Fe ²⁺								
				surface-oxide								
373 K	0.60	0.70	23	0.59	1.21	77						
473 K	0.60	0.72	25	0.59	1.24	75						
573 K				0.59	1.06	29	1.20	2.03	42	1.44	2.13	22
673 K							1.11	1.63	28	1.24	2.11	39
773 K							1.02	1.81	28	1.29	1.99	37
											2.04	35

(Experimental uncertainties: *IS* = 0.05 mm/s; *QS* = 0.05 mm/s; *A* = 5%.)

Fig. 2. Mössbauer emission spectra of Co(0.10)/C and Co(0.10)Mo(0.63)/C catalysts after reduction in H₂ at 573 K for 1 h.

Fe-species prevents the particles against sintering. All these findings point to the formation of a surface “Fe(II)-aluminate” due to diffusion of the iron atoms into the surface layers of the alumina support, during the reduction treatments at or above 573 K.

In fig. 2 the results of the measurements on a Co(0.10)/C and a Co(0.10)-Mo(0.63)/C catalyst after reduction at 573 K are presented. Both spectra consist of a sextuplet which belongs to α -iron. This indicates that sintering occurs on both catalysts and that in the case of the Co-Mo/C catalyst no Co-Mo alloy is formed like the Fe-Mo alloy formed in the case of Fe-Mo/C.

4. Concluding remarks

The interaction of the alumina support with the Fe species is very strong and dictates the reduction behaviour of the Fe in the Fe/Al₂O₃ as well as Fe-Mo/Al₂O₃ catalysts. Under the reduction conditions applied here, the Fe atoms most probably start to diffuse into the surface layer of the alumina support at about 573 K.

In contrast herewith, the carbon support showed the expected very weak interaction with the Fe species. Hence, the behaviour of the Fe in the carbon-supported Fe-Mo/C catalysts is dominated by the Mo species. By applying a mild reduction treatment to Fe-Mo/C catalysts, only a Fe-Mo alloy will be formed.

Carbon-supported Co and Co-Mo catalysts show a completely different behaviour. Although the same mild reduction procedure was applied and even the Co loading was rather low (0.10 at/nm²), segregation of metallic Co occurred.

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