

INVESTIGATION OF THE CARBURIZATION OF FE/MN-FISCHER-TROPSCH CATALYSTS WITH A MICROBALANCE

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ABSTRACT

The mass increase of Fe/Mn oxide catalysts of different compositions has been investigated in a high pressure microbalance during the reaction with CO and a CO/H₂ mixture at 543 K and 5 bar. The phase changes occurring have been investigated with XRD. The bulk carbide formation and the deposition of excess carbon on the surface of catalysts is dependent on the Mn content of the oxides and can be correlated with activity of the catalysts in Fischer-Tropsch synthesis.

INTRODUCTION

Fe/Mn oxides were first proposed by Büssemeier et al. (ref. 1) and Kölbel and Tillmetz (ref. 2) as catalysts for Fischer-Tropsch synthesis with improved selectivity for short chain olefins. New investigations dealt with the influence of Mn oxide on the phase composition of Fe containing catalysts (ref. 3-8). Depending on pretreatment conditions and Mn content different forms of carbides and manganese containing spinels and wustites are formed during synthesis. The formation of spinel and wustite is favored in the Mn containing catalysts. This suppresses the fast carburization of the iron and leads to a stabilization of the catalytic activity. In order to investigate the phase changes of Fe/Mn oxide catalysts in a simpler system than in real Fischer-Tropsch synthesis, we decided to subject the catalysts to pure CO atmosphere of 5 bar in a microbalance where the mass changes are monitored. The phase composition has been determined by X-ray diffraction. Additionally we wanted to know the influence of adding H₂ to the CO atmosphere on mass change and phase composition.

EXPERIMENTAL

The used high pressure microbalance was a Sartorius 4436. The ultimate obtainable pressure is 150 bar. The microbalance is con-

nected to an oil rotary pump and to a gas manifold for the admission of the various gases. Sample and counter weight could be heated up to 800 K by a regulated oven.

Six different Fe/Mn catalysts (100 % iron, approx. 97 %, 85 %, 53 %, 40 % and 20 % iron (atom %), designated Fe100, Fe97, etc. in the following) were used for the experiments. The catalysts were co-precipitated from a mixture of iron nitrate and manganese nitrate solutions, then dried and calcined at 773 K in Ar for 24 h. A detailed description of the preparation of the catalysts has been given elsewhere (ref. 3). About 500 mg of the catalysts were placed after calcination into the microbalance. They were reduced at 573 or 673 K in flowing H₂ for 24 h with the decrease in mass being monitored. Then H₂ was pumped off and a pressure of 5 bar CO applied. For some samples a CO/H₂ (9/1) mixture at P = 5 bar was applied to investigate the influence of H₂. The increase in mass was followed for 24 h.

The catalysts were then removed from the microbalance at room temperature under a flow of argon and immediately dropped into immersion oil to prevent oxidation of the catalysts. Afterwards X-ray diffraction patterns were made to investigate the phase composition of the samples.

RESULTS AND DISCUSSION

From the decrease in mass during reduction the degree of reduction can be calculated. Only the Fe100 samples are totally reduced to metallic iron. Already small amounts of Mn oxide lead to a certain amount of oxidic compounds in the reduced samples. A detailed description of the reduction behaviour is given elsewhere (ref. 6-9).

In Figure 1 is shown the increase in mass of the catalysts reduced at 673 K during interaction with pure CO at 5 bar and 543 K. A fast initial increase in the first 2 hours is followed by a slow further massgain. The initial rate of mass increase is dependent on the Mn content. The influence of the temperature of reduction on the massgain is shown in Figure 2 for two samples. It is obvious that the lower temperature of reduction leads to a lower increase in mass. The massgain after 24 h for all samples reduced at 573 K and 673 K respectively is shown in Figure 3. The massgain depends strongly on the Mn content and the reduction temperature, with the exception of Fe100, where there is identical massgain.

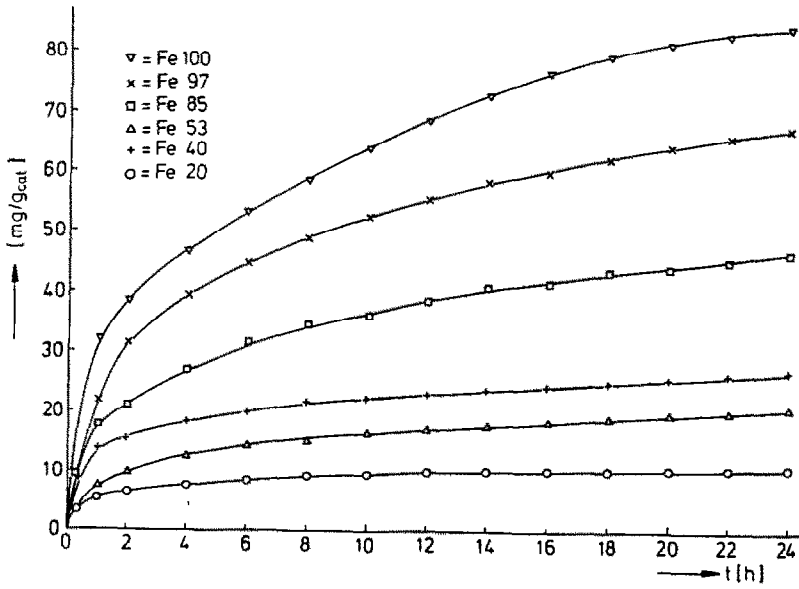


Fig. 1: Increase in mass of the catalysts reduced at 673 K ($P_{CO} = 5$ bar, $T = 543$ K) versus time

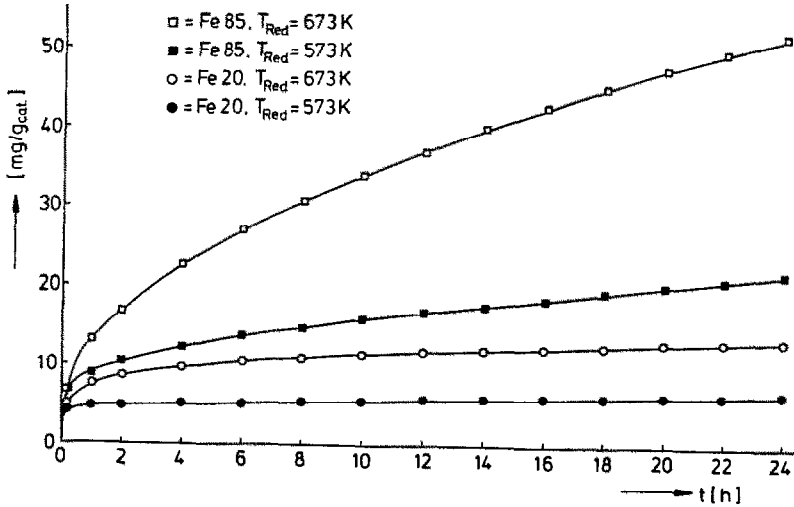


Fig. 2: A comparison of the mass gain of catalysts reduced at 673 K and 573 K respectively ($P_{CO} = 5$ bar, $T = 543$ K)

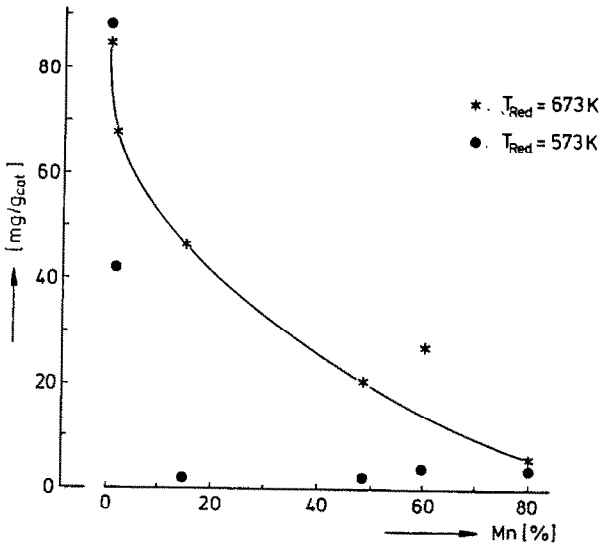


Fig. 3: Massgain after 24 h ($P_{CO} = 5$ bar, $T = 543$ K) as a function of Mn content

TABLE 1

Phase composition (vol %) of catalysts ($T_{red} = 673$ K) after 24 h at $P_{CO} = 5$ bar and $T = 543$ K

| Catalyst | Fe ₅ C ₂ | Fe | (Fe,Mn)O | (Fe,Mn) ₃ O ₄ |
|----------|--------------------------------|----|----------|-------------------------------------|
| Fe100 | 100 | - | - | - |
| Fe 97 | 36 | 59 | - | 5 |
| Fe 85 | 25 | 37 | 36 | 2 |
| Fe 53 | | 20 | 72 | 8 |
| Fe 40 | | 18 | 82 | - |
| Fe 20 | | 10 | 90 | - |

In order to elucidate the reason for this behaviour, we show the results of XRD for the samples reduced at 673 K in Table 1. The Fe100 sample is totally converted to X-carbide, whereas for Fe97 and Fe85 a much smaller amount of carbide is formed with an appreciable amount of the catalysts still in the form of metallic iron. Additionally small amounts of spinel and in the case of Fe85 wustite is formed. From Fe53 to Fe20 a distinction between metallic iron and carbide is no longer possible in the XRD patterns because of poor crystallinity and overlapping of peaks. But it is clear that only a small amount of the precursor is carburized, the rest being mainly wustite as after reduction. In the case of the samples reduced at 573 K only Fe100 and Fe97 show carbide formation, where-

as in the rest no bulk carbide is detected. From these results it is clear that the addition of Mn strongly suppresses the carbide formation. The reasons for this is firstly enrichment of MnO in the catalyst surface as detected by ESCA and AES (ref. 9, 10), which causes a strong decrease in CO adsorption and dissociation (ref. 9). The metallic iron particles are obviously screened from carburization by the MnO matrix. Secondly, as already mentioned, small amounts of MnO hinder the reduction of the samples considerably (ref. 4-7). When comparing carbide formation as found by XRD (cf. Table 1) with the mass increase after 24 h it can be calculated that a small amount of surface carbon is deposited on the samples reduced at 573 K and the samples Fe53 to Fe20 reduced at 673 K.

A correlation between activity data in FT synthesis (ref. 3) and the massgain data is possible. Both Fe100 samples show a high initial activity and a fast deactivation. This is connected with a fast carburization of the bulk followed by surface carbon deposition. The catalysts Fe97 and Fe85 reduced at 673 K show high initial activity but due to the slower carbide formation a slower deactivation. The rest of the catalysts have fairly low initial activity but show no deactivation, sometimes even a slight increase in activity.

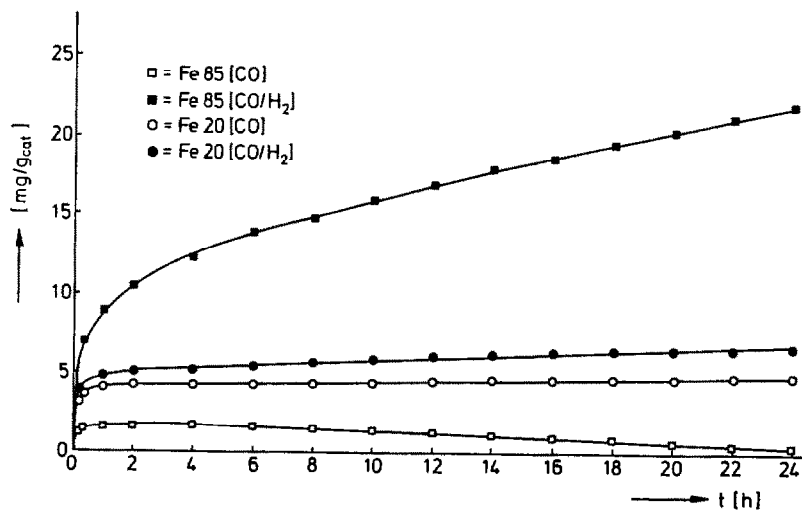


Fig. 4: Massgain of Fe85 and Fe20 in pure CO (□,○) and a mixture of CO/H₂ (9/1; ■,●) as a function of time

The influence of H₂ on the massgain is shown in Figure 4 in the case of the samples Fe₈₀ and Fe₂₀ reduced at 573 K. A higher massgain is observed with H₂ addition but in XRD no additional carbide formation is observed. The additional surface carbon deposition is in accordance with results of Bianchi and Bennet (ref. 11, 12) which explained this effect by the interaction of adsorbed CO and adsorbed hydrogen.

CONCLUSIONS

The investigation of the massgain of Fe/Mn oxide catalysts subjected to pure CO in a microbalance combined with XRD analysis can be used to explain activity data obtained in the Fischer-Tropsch synthesis, where things are much more complicated. A strong dependence of the carbide formation on the Mn content and the temperature of reduction is observed.

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