

BEHAVIOUR OF IRON AND IRON-COBALT CATALYSTS DURING CARBON FILAMENT DEPOSITION

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INTRODUCTION

Carbon filaments have been prepared by CO disproportionation over metal catalysts dispersed into a porous substrate [1]. A decrease of the reaction rate was observed until complete deactivation. Different mechanisms for deactivation have been proposed in the literature concerning catalytic deposition of carbon [2,3]. The aim of this paper is to determine precisely the relation between Fe or (Fe + Co) catalyst state and its deactivation.

EXPERIMENTAL

Catalysts were prepared by incipient wetness impregnation of around 1.2 g of an aluminosilicate-fiber substrate with a solution of ethanol containing iron nitrate or a mixture of iron and cobalt nitrate containing equal amounts of Fe and Co. The nominal metal content was about 14 weight percent of the fiber substrate. Impregnated substrates were dried in air at 363 K for 20 hours before being introduced in a cylindrical silica reactor (on a frit) and pyrolysed under a helium flow at 523 K in order to decompose metallic salts into oxides. One hour later, helium was replaced by a hydrogen flow of $120 \text{ cm}^3 \cdot \text{min}^{-1}$ and the reactor heated to 808 K during at least three hours. After a rapid helium flushing, carbon monoxide was then introduced at the same temperature, with the same flow rate.

Chromatographic analyses of the CO + CO₂ mixture issued from the reactor allowed computation of the rate of the disproportionation reaction (checked with the weighed amount of carbon after each experiment). The catalytic reaction was stopped after times varying from 5 minutes to 31 hours by flushing the reactor with helium and quenching it to room temperature.

Besides the usual TEM [1,4] and XRD observations, magnetic and Mössbauer characterization were performed on the samples. Magnetic measurements were carried out by the "axial extraction method" [5]; saturation magnetization was obtained by plotting magnetization (measured in magnetic field H up to 20 kOe at 300 K) versus 1/H and extrapolating at 1/H = 0. Moreover, samples were characterized in a microprocessor controlled Mössbauer spectrometer using a ⁵⁷Co/Rh source.

Solids were observed either after the disproportionation reaction (and under these conditions were partially oxidized by handling under air) or after the hydrogen treatment (in a reduced state). All characterizations were carried out at room temperature except an in situ Mössbauer observation during an experiment at 765 K.

PURE-IRON CATALYST

Saturation magnetization value after hydrogen treatment was $207 \text{ uemcgs} \cdot \text{gFe}^{-1}$, close to the α Fe value (218). Mössbauer spectrum was characteristic of pure iron; the slight difference in magnetizations may perhaps be due to a lack of cristallization.

After different times under pure CO, Mössbauer spectra have been recorded at room temperature. They have been fitted with two sextuplets and one doublet, revealing:

- α Fe in large particles,
- a carbide (its Fe₃C nature was revealed by XRD),
- α Fe₂O₃ issued from small α Fe particle oxydation by air handling.

Table I. Weight distribution of Fe after various times under CO disproportionation.

Time under CO	% Fe ₃ C	% Fe	% Fe ₂ O ₃
5 min	18	8	74
9 min	22	13	65
12 min	26	37	37
4 h	87	13	0
19 h	100	0	0

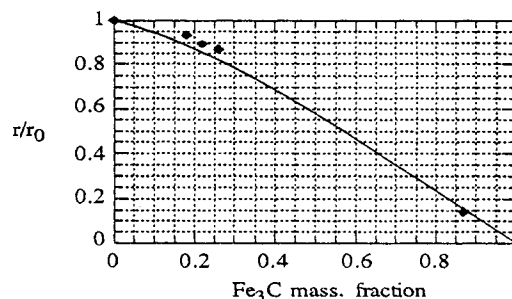


Figure 1. Evolution of reaction rate v.s. Fe₃C fraction.

From Mössbauer data and magnetization results, weight distribution of Fe into different species could be established (table I).

These results could then be correlated with rate of disproportionation at different times. Rate decreased as the carbide percentage increased (figure 1).

IRON-COBALT CATALYST

Saturation magnetization after 2h30 hydrogen treatment was close to 200 uem cgs.gFeCo⁻¹. This value was slightly higher than the the average (189) of literature values for pure Fe (218) and Co (161). It was nethertheless lower than the expected value of 230 (for an alloy containing 50 wt% Fe [6]). These measurements suggest that Fe and Co are alloyed, but badly crystallized. Alloying of Fe with Co is confirmed by XRD spectra obtained after CO treatment which exhibit peaks from which the alloy composition could be established at 50 ± 5 wt%.

After 3 hours under CO, the rate of disproportionation began to decrease until full deactivation (about 30 hours). XRD spectra did not reveal carbide as for the Fe case. Because these spectra were drawn at room temperature, products obtained at reaction temperature may have been converted during cooling down (this phenomenon is well-known in the case of cobalt carbide). An in situ Mössbauer observation was therefore carried out after a CO disproportionation of one day. Results (table II) evidences two iron species :

- a metallic iron corresponding presumably from isomer shift value to the FeCo alloy,
- an unknown compound ; its Mössbauer characteristics were consistent with those of a carbide.

Deactivation (slower than in the pure Fe case) could be due to the formation of this carbide.

Table II. In situ Mössbauer characterization of FeCo alloy.

Sites	δ (mm.s ⁻¹)	W (mm.s ⁻¹)	Δ (mm.s ⁻¹)	Phase
Fe1	-0,08	0,34	0,53	metal (9%)
Fe2	0,13	1,42	1,05	carbide (91%)

Unfortunately, our experimental device did not allow us to perform this in situ experiment at our usual temperature (808 K) but only at 765 K. Nevertheless, the obtained carbon filaments look like those obtained from the same catalyst at 808 K [1].

DISCUSSION

The state of in situ-generated iron particles during CO disproportionation was previously studied by GEUS et al. [7,8]. They evidenced the formation of Fe₃C which they demonstrated to be an inactive side product (without

studying its part in deactivation) and considered that filaments grew from an other carbide (ϵ Fe₂C or ϵ' Fe_{2,2}C). ALSTRUP's modelling [9] was in agreement with these hypotheses. Our results corroborate only the hypothesis of a poisoning by Fe₃C, previously formulated in the case of other gaseous systems [2,10].

Before our study, catalysis of carbon deposition by FeCo alloys was only studied by using massive metals [11] or filings [12]. BONNETAIN and co-workers [12] considered carbide(s) as poisons. In contrast, GEURTS et al. [11] demonstrated that rates of carbon deposition was significantly enhanced in experimental conditions favoring Fe₃C formation. Although no carbide was evidenced from our post-mortem analyses, in situ Mössbauer observation is consistent with the explanation of deactivation by the formation of an (unknown) carbide. The difference of nature between carbides involved in deactivation in the two studied cases (pure Fe and alloy) may explain the observed difference in deactivation rates, faster in the pure-iron case.

Significant differences in sizes and shapes of filaments were previously reported [1], depending on the catalyst used : filaments issued from alloy are thinner and straighter than those from pure Fe. This can be correlated with particle sizes which may be larger in the case of pure Fe because of sintering evidenced during the first minutes under CO.

CONCLUSION

Deactivation of CO disproportionation over Fe catalysts is due to Fe₃C formation. An unknown carbide could be the cause of the slower deactivation observed over FeCo alloy.

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