

RATE OF CARBON FILAMENT GROWTH FROM CO DISPROPORTIONATION OVER FeCo SUPPORTED PARTICLES

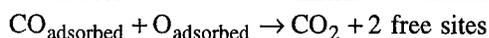
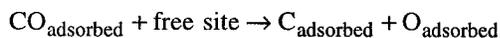
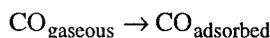
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Introduction

The wide range of experimental conditions under which a gaseous species can decompose into carbon over a catalyst probably explains the variety of kinetic results and of published mechanistic interpretations. There is nevertheless a consensus concerning the existence of four stages :

- external diffusion (of active gas to catalytic surface),
- gas-solid process (adsorption followed by a reaction between adsorbed species or between an adsorbed species and a gaseous molecule),
- diffusion of carbon through the catalyst particles from where it is formed as atoms (by the previous stage) to where it coalesces as separate solid phase,
- segregation and organizing of this solid phase.

Different kinetic laws can be derived, depending on the nature of the rate-limiting limiting step(s). In the case of CO disproportionation, several surface steps may be assumed as limiting, for instance :



From these assumptions, it is possible to derive the following linearized forms of kinetic laws (V = rate, α and β = constants) :

$$\frac{P_{\text{CO}}}{V} = \alpha + \beta \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \text{ or } \alpha + \beta P_{\text{CO}_2}$$

$$\sqrt{\frac{P_{\text{CO}}}{V}} = \alpha + \beta \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \text{ or } \alpha + \beta P_{\text{CO}}$$

$$\frac{P_{\text{CO}_2}}{V} = \alpha + \beta P_{\text{CO}} \quad \frac{P_{\text{CO}}}{\sqrt{V}} = \alpha + \beta P_{\text{CO}}$$

When diffusion through the catalyst particles is the rate-limiting step, reactions at both interfaces are at equilibrium. Thermodynamical activity of dissolved carbon near the metal-carbon interface is then equal to that of the obtained form of solid carbon :

$$a_{\text{C}(\text{dis})} = a_{\text{C}(\text{solid})}$$

At the gas-metal interface, carbon atoms are often assumed to be dissolved from the gaseous phase by an equilibrium as $2\text{CO}(\text{gas}) \rightleftharpoons \text{CO}_2(\text{gas}) + \text{C}(\text{dissolved})$.

Their activity is therefore calculated by $a_{\text{C}(\text{dis})} = K P_{\text{CO}}^2 P_{\text{CO}_2}^{-1}$ (K = constant of the above equilibrium). When diffusion is the rate-limiting step,

rate is then equal to $D \frac{K P_{\text{CO}}^2 P_{\text{CO}_2}^{-1} - a_{\text{C}\downarrow}}{L}$ (D : diffusion coefficient, L = mean diffusion length).

Alstrup [1] hypothesized that the leading face of catalyst particles was covered with an intermediate carbide. In this case, a diffusion-limiting rate would be

$$D \frac{a_{\text{carbide}} - a_{\text{C}\downarrow}}{L}, \text{ independent of the gas phase}$$

composition (provided sufficiently CO - rich to form this carbide). Studying carbon growth from methane over iron, Bianchini and Lund [2] observed two different regions in the kinetical curve (rate vs. gaseous composition) which were consistent with the diffusional equations above.

The aim of this paper is to find a kinetical modelling related to carbon filament growth from CO disproportionation over FeCo particles.

Experimental

Catalysts were prepared by incipient wetness impregnation of 0.4 to 2 g of an aluminosilicate-fiber substrate with a solution of ethanol containing a mixture of iron and cobalt nitrate (equal amounts of Fe and Co). The nominal metal content was typically 9 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. One hour later, helium was replaced by hydrogen and the reactor was heated to 800 K during at least 20 hours. After helium flushing and heating (or cooling) to the desired temperature (in the 773 - 823 K range), a mixture of ultra-pure CO and CO₂ in definite proportions was introduced with a constant flow rate

On-line chromatographic analyses of the CO + CO₂ mixtures allowed computation of the disproportionation rate (checked with the weighed amount of carbon after each experiment). The catalytic reaction was stopped after

times varying from 0.25 to 31 hours by flushing the reactor with helium and quenching it to room temperature. The carbon deposits were observed by TEM.

Results

Rates were measured vs. time at 788 K in experiments performed under different gaseous compositions. Plots exhibited typically two regions : a rapid (some minutes) increase, followed by a slow decrease. We considered the intermediate maxima of rate as representative of steady states which were established without deactivation of the catalyst particles.

These maximum rates were checked against theoretical kinetic laws. No accordance was found with any of the interfacial laws : for instance, considering the linearized forms above, $P_{CO}V^{-1}$ was neither linear vs. $P_{CO_2} P_{CO}^{-1}$ nor vs. P_{CO_2} . On the contrary, plotting rates vs. $P_{CO}^2 \times P_{CO_2}^{-1}$ (figures 1 and 2) revealed three domains : a linear growth at low activities, a constancy at high activities as in [2] and an intermediate region.

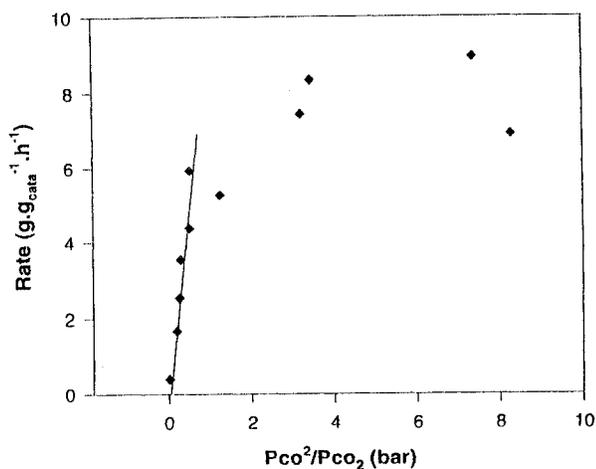


Figure 1 : Evidence of a linear growth of rate vs. carbon activity at low activities.

Experiments were carried out at different temperatures in each of the above three regions (the two straight lines and the intermediate region of the 1 & 2 figures). Each of the three runs was performed under constant carbon activity, i.e. with a constant value of the product : $P_{CO}^2 \times P_{CO_2}^{-1} \times K$ (K depends on T).

T.E.M. revealed neither change in filamentous shape nor change of metallic particle dimensions. Consequently, the parameters $a_{C\downarrow}$ and L in the rate formula were constant. Rate evolution had therefore to be correlated with a modification of D.

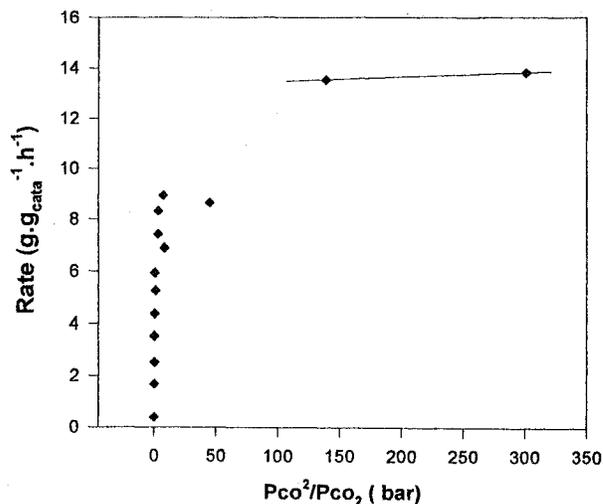


Figure 2 : Evidence of a constant level at high activities.

Figure 3 shows the linear dependance of $\ln V$ against T^{-1} (Arrhenius law) in the low activity region ($a_C = 23$). The obtained activation energy of D is consistent with the litterature.

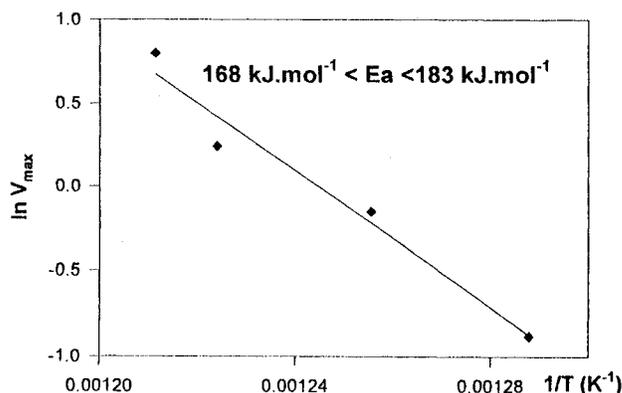


Figure 3 : Arrhenius plot at low carbon activities.

On the contrary, no Arrhenius straight line was obtained in other regions (high or middle activity) and rates seemed to be, at high temperature, non or slightly activated (influence of external diffusion ?).

Conclusion

Rates of filament growth from CO disproportionation were measured over supported FeCo particles in the 773-823 K range and checked with kinetical modelling. At low carbon activities, they were consistent with a postulated rate-limiting diffusional step through catalyst particles, the leading face being at equilibrium with the CO + CO₂ mixture.

- [1] Alstrup I., *J. Catal.*, 1988, 109, 241.
- [2] Bianchini E.C. and Lund C.R.F., *J. Catal.*, 1989, 117, 455.