

# Chemisorption, Desorption and Hydrogenation of CO on Fe/Active Carbon Catalysts

by

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## Introduction

Recent reviews have been reported on the anchoring and decomposition of metal carbonyl on various supports for catalyst preparations<sup>1,2</sup>. The adsorption and subsequent decomposition of metal carbonyls can be a suitable method of preparation for metal model catalysts with narrow particle size distributions<sup>3</sup>. These catalysts present a remarkable interest in the studies of the relation between metal particle sizes and activity or selectivity on supported metals.

On the other hand, carbon can be also considered an advantageous support of catalysts for these studies, because its chemical simplicity<sup>4</sup>.

In this paper the results obtained on a serie of iron catalysts supported on an active carbon and prepared from iron pentacarbonyl are described. The metal particle sizes have been determined from CO chemisorption at 373K, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The desorption of CO from Fe/active-carbon has been studied. These catalysts have been tested in the CO hydrogenation reaction, to know the effect of particle sizes on the catalytic behaviour.

## Experimental

Iron was supported on activated carbon, which was prepared from olive stones, under CO<sub>2</sub> flow, using a heating rate of 5K. min<sup>-1</sup>, up to 1123K; the final temperature was held for 24h. Some of the characteristics of this carbon are: S<sub>BET</sub>(N<sub>2</sub>77K) = 1092 m<sup>2</sup>.g<sup>-1</sup>; S<sub>D-R</sub>(CO<sub>2</sub>273K)=1084m<sup>2</sup>.g<sup>-1</sup>; ash (%)= 0.13; pore volume (mercury porosimetry)=0.33 cm<sup>3</sup>.g<sup>-1</sup>. The catalysts were prepared by adsorption of Fe(CO)<sub>5</sub> in a diethyl ether solution<sup>5</sup>. Dried samples were reduced for 12h in flowing H<sub>2</sub> at temperatures between 573 and 723K. Iron particle sizes have been determined by CO chemisorption at 373K, XRD and TEM.

The desorption and the reaction of the CO chemisorbed was followed by measuring the variation in pressure due to desorption of CO from the sample when the temperature was increased<sup>6</sup>.

The CO hydrogenation was studied in the experimental system and in the conditions previously described<sup>5</sup>.

## Results and Discussion

Metal dispersions and iron particle diameters determined from CO chemisorption, XRD and TEM are listed in Table 1. We can see that metallic dispersions are greatly decreased when the reduction temperature increase. In the average metal particle diameters calculated from the different techniques a common agreement is obtained. Then, the CO chemisorption at 373K can be considered as a good technique for the characterization of iron carbon-supported catalysts<sup>7</sup>.

In Table 1 the T<sub>r</sub> values-temperatures at which the CO desorbed is dissociated on the iron catalysts<sup>6</sup>- are shown. These T<sub>r</sub> values are a qualitative indication of the reactivity of CO on the metal surfaces. We can observe that T<sub>r</sub> decrease when increasing the iron particle sizes. A similar behaviour is observed in the specific activities for CO hydrogenation determined on these catalysts (Table 2). Therefore the specific activity is larger for the catalysts in which CO dissociation is easier. This behaviour could be interpreted as an evidence about the importance of CO dissociation as a previous step in the CO hydrogenation reaction.

Little changes in selectivity and products distribution for CO hydrogenation have been obtained on these iron/carbon catalysts, when the metal dispersions are changed. Then, we can explain the differences in catalytic activities as a consequence of the structural variations in the metal particles produced by the diminution in the iron crystallite sizes.

## References

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Table 1. Characteristics of Carbon Supported Iron Catalysts and Temperatures at which Carbon Monoxide reacts on the Catalysts ( $T_r$ )

Catalyst	Reduction Conditions		Dispersion CO/Fe <sup>a</sup>	Crystallite size $\bar{d}$ (nm)			$T_r$ (K)
	T(K)	t(h)		CO Chemisorp. <sup>a</sup>	XRD	TEM	
4.4%Fe/C	573	12	1	0.75	—	1.3	488
	623	12	0.81	0.9	—	—	471
	673	12	0.46	1.6	—	2.1	463
	723	12	0.20	3.8	4.3	—	—
12.2%Fe/C	573	12	0.38	2.0	3	2.7	459
	673	12	0.11	6.8	5.7	—	449

a.- From CO chemisorption at 373K, assuming CO/Fe stoichiometry equal to 0.5

Table 2. Activity and Products Distribution in CO Hydrogenation on Carbon Supported Iron Catalysts<sup>a</sup>

Catalyst	Reduction Conditions		CO Conversion (%)	Hydrocarbon Selectivity (%)	Specific Activity <sup>b</sup> (S <sup>-1</sup> )x10 <sup>4</sup>		olefins <sup>c</sup> paraffins	Product Distribution(%)				
	T(K)	t(h)			N <sub>CH<sub>4</sub></sub>	N <sub>CO</sub>		C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>
4.4%Fe/C	573	12	4.1	52	1.0	7.9	2.4	47	24	17	8	4
	673	12	9.0	45	3.7	36.9	3.1	47	25	13	11	6
	723	12	17.0	50	19.5	152.5	1.4	50	20	18	7	5
12.2%Fe/C	573	12	7.2	53	3.8	22.3	0.9	60	19	12	6	3
	673	12	16.6	44	21.5	150.7	1.2	57	19	19	4	1

a.- Reaction conditions: P=101KPa, H<sub>2</sub>/CO=3, T=523K.

b.- Assuming that a CO molecule defines two iron atoms on the surface.

c.- For hydrocarbons with 2 and 3 carbon atoms.