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A NGR STUDY OF IRON CATALYSTS IN CO HYDROCONDENSATION REACTIONS

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Several iron 10 % by weight containing supported on alumina catalysts were studied using transmission M ssbauer Spectroscopy in situ, in addition to magnetic measurements, X Rays diffraction, thermodesorption and measurements of catalytic activity and selectivity. The aim of this work was to study (I) the evolution of the catalyst during the first steps of the CO hydrocondensation reaction up to the stationary conditions, (II) the differences during the same treatment between catalysts modified by an additive : molybdenum which improves the light hydrocarbons formation, manganese and potassium which increase the olefin content.

The catalyst precursor was prepared by a modification of Pichler's method (1), wherein a hot suspension of $\gamma\text{-Al}_2\text{O}_3$ in aqueous $\text{FeCl}_2/\text{FeCl}_3$ was treated with Na_2CO_3 . The resulting mixture was briefly boiled and the precipitate washed with boiling water prior to being dried 20 hours at 378 K. This precursor was modified by impregnation with solutions of K_2CO_3 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$, or $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$. The final atomic percentages of K, Mo, Mn with respect to Fe are respectively 50, 6 and 6.

Magnetic and radiocrystallographic measurements and NGR spectra taken at 293, 77 and 4 K describe the precursor as a mixture of finely dispersed $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$.

The reduction is performed in a stream of hydrogen during 18 hours at 873 K and followed by NGR. The final composition of the solids (Table 1) has been obtained from spectra recorded at 523 K.

Table 1 - Reduced catalysts

Catalyst $\text{Fe}/\text{Al}_2\text{O}_3$ - Reduction (magnetism) : 77 %				
IS (SNP)	Γ_{exp} (mm s^{-1})	QS	H (kOe)	Attribution (% in spectra)
0.18	0.30	0	312	Fe (74.5)
0.66	0.19	0.25	0	Fe^{3+} (3.5)
1.10	0.80	1.55	0	Fe^{2+} (22.0)
Catalyst $\text{Fe}/\text{Al}_2\text{O}_3 + \text{K}$ - Reduction (magnetism):82%				
0.17	0.28	0	313	Fe (90.0)
1.17	0.40	1.10	0	Fe^{2+} (10.0)
Catalyst $\text{Fe}/\text{Al}_2\text{O}_3 + \text{Mo}$ - Reduction (magnetism):76%				
0.18	0.32	0	313	Fe (71.0)
0.99	0.58	1.55	0	Fe^{2+} (17.0)
1.22	0.34	1.08	0	Fe^{2+} (13.0)
Catalyst $\text{Fe}/\text{Al}_2\text{O}_3 + \text{Mn}$ - Reduction (magnetism):84%				
0.16	0.30	0	312	Fe (100.0)

It results that additives influence the final reduction percentage and the phase composition. Moreover no Fe alloy formation is detected.

A desorption at 873 K of hydrogen from the $\text{Fe}/\text{Al}_2\text{O}_3$ catalyst results in oxidation of surface iron atoms (2). It is a reversible process, which can be described as a whole by the equilibrium : $\text{Fe} + 2 \text{H}^+ \rightleftharpoons \text{Fe}^{2+} + \text{H}_2$ where alumina plays a role, as previously reported in the case of Fe/MgO catalysts (3). A similar behaviour is evidenced by magnetic measurements on the modified catalysts.

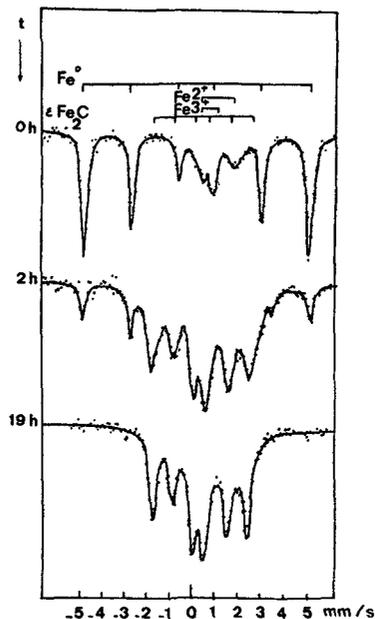


Figure 1 and Table 2.-Evolution of $\text{Fe}/\text{Al}_2\text{O}_3$ catalyst during CO hydrocondensation reaction.

t : reaction time ; T : temperature of the sample.

t (h)	T (K)	IS (SNP)	Γ_{exp} (mm s^{-1})	QS (kOe)	H (kOe)	Attribution (% in spectra)
0	523	first set of data in Table 1				
2.5	523	0.17	0.30	0	313	Fe (12.0)
		0.61	0.50	0	0	Fe^{3+} (12.0)
		0.90	0.62	1.57	0	Fe^{2+} (18.5)
		0.39	0.54	0	136	$\epsilon\text{-Fe}_2\text{C}$ (67.5)
		0.40	0.24	0	196	
19	523	0.35	0.46	0.53	0	Fe^{3+} (18.0)
		1.15	1.22	1.34	0	Fe^{2+} (30.0)
		0.41	0.40	0	131	$\epsilon\text{-Fe}_2\text{C}$ (52.0)
4	4	0.24	0.44	0	184	$\epsilon\text{-Fe}_2\text{C}$
		0.6			500	Fe^{3+}

The evolution of the $\text{Fe}/\text{Al}_2\text{O}_3$ solid during CO hydrocondensation is represented by the set of spectra in figure 1, recorded at 523 K in the mixture $1\text{CO}/1\text{H}_2$. Metallic iron is no longer detected after 3 hours. It is replaced by $\epsilon\text{-Fe}_2\text{C}$ (4,5,6) and a species the isomeric shift of which could be that of a Fe^{3+} . This is confirmed by the spectrum taken at 4 K, where it appears as a sextet with a maximum effective field about 500 kOe. The carbide and the ferric phase could arise from the dissociative adsorption of CO on iron.

The study of $\text{Fe}/\text{Al}_2\text{O}_3 + \text{K}$ solid in the same conditions shows a similar behaviour. In the case of $\text{Fe}/\text{Al}_2\text{O}_3 + \text{Mn}$ the main feature of the evolution is the formation of cementite Fe_3C in addition to $\epsilon\text{-Fe}_2\text{C}$. As to $\text{Fe}/\text{Al}_2\text{O}_3 + \text{Mo}$, no carbide appears during the first hours. Since the formation of hydrocarbons is evidenced as soon as the reaction is started, it is to be thought that bulk carbide is not an intermediate in the reaction mechanism.

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