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AN ATTEMPT TO CORRELATE SELECTIVITY IN CO HYDROGENATION AND MORPHOLOGY OF IRON CATALYSTS

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The influence of various pretreatments of Fe for the catalytic hydrogenation of CO have been investigated. The catalysts were prepared from $Fe(CO)_5$, and activated at 673 K in H_2 or $H_2 + N_2$ streams. Differences of catalytic behaviour (activity and selectivity) induced by the pretreatment are interpreted in the light of changes in the surface microstructure of the Fe particles.

1. Introduction

The catalytic activity and selectivity of supported metal catalysts are often sensitive to the metal particle size. In catalysis on single metal crystals, step or corner atoms show different catalytic properties than the terrace atoms [1]. Thus, the surface structure of metal particles on supports probably plays an important role in their catalytic behaviour. Not only the metallic dispersion, but also the microstructure of metal particles must be considered as factors controlling the selectivity [2]. Recently, in the design of new types of catalysts for selective conversion of synthesis gas into olefins much attention has been given to iron carbonyl-derived catalysts [3]. When the small iron particles produced from iron clusters were tested as catalysts in CO hydrogenation reaction, fairly high selectivities for lower olefins were obtained. This behaviour was interpreted as due to the small iron particles originated by the preparation procedure, and the drop in olefin selectivity and activity at increased time on stream as consequence of the metal aggregation under reaction conditions [4,5]. However, the results of iron catalysts supported on activated carbon and prepared from $Fe(CO)_5$ [6], which present average metal particle diameter between 1 and 7 nm, indicate that not only the crystallite size is responsible of the high olefins selectivity but also the particular morphology of iron crystallites stemming from the precursor used in the preparation.

On the other hand, it is well known that when the reduction of iron is carried out in a mixture of nitrogen and hydrogen the resultant catalyst is more active in ammonia synthesis compared with the catalyst reduced in pure hydrogen [7,8]. This effect has been attributed to metallic surface reconstruction. It has been shown [9,10] that the faces (100) and (110) of α-Fe are transformed to (111) during the nitrogen treatment at 670 K. Mössbauer spectroscopy studies [11] indicate that the iron catalysts treated with nitrogen or ammonia have mainly seven-coordinated (C_7) atoms. These C_7 iron atoms are characteristic of the (111) face in the b.c.c. lattice of α-Fe. On the other hand, it has been shown that nitrogen is preferentially chemisorbed on the (111) face [12,13] and that the ammonia synthesis takes place primarily on this face [14].

In this work we investigate how CO hydrogenation is influenced by the presence of different iron crystalline faces in the starting catalyst. Modification in the distribution of the various faces of the metal crystallites is produced by changing the composition of gas used for reduction (hydrogen versus nitrogen/hydrogen mixture) or by injecting a pulse of ammonia at the reduction temperature.

2. Experimental

The preparation of the Fe/activated carbon precursor has been reported previously [6,15]. Briefly, it was prepared by adsorption of $Fe(CO)_5$ from a diethyl ether solution on activated carbon (1090 m^2g^{-1}, ash content 0.13%) so as to obtain a metal weight loading of 4.4%. This precursor was dried at 383 K for 16 h. The reduction treatment was carried out in flowing H_2 (50 cm^3-min^{-1}) at 673 K using a heating rate of 5 K-min^{-1} and the final temperature was held for 12 h (sample A). Another portion of precursor was subjected in a 3 : 1 mixture of H_2/N_2 (40 cm^3-min^{-1}) to the same thermal schedule (sample B). Finally, sample C was obtained by treating the precursor with a pulse of pure NH_3 gas (5 cm^3) at 673 K in flowing H_2 before cooling down to the reaction temperature.

Catalytic hydrogenation of CO was carried out in a continuous flow reactor at 533 K under 101 KPa with a mixture of CO and H_2 ($H_2/CO = 3$). The amount of sample placed in the reactor was low enough to ensure differential conversions. Effluent gases from the reactor were analyzed using a chromatograph equiped with Chromosorb 102 columns. Fixed gases were analyzed with a thermal conductivity detector and hydrocarbons with a flame ionization detector.

3. Results and discussion

The preparation of the catalysts was chosen so as to ensure that iron is in the zero oxidation state. The support of the catalysts was an activated carbon which is an inert support for metal particles, with a weak metal-support interaction and consequently facile reduction of metal particles can be achieved. Also the carbonyl is readily reduced to metal. (It has been shown [16] that iron pentacarbonyl decomposition over a high surface area graphite leads to metallic iron.) Moreover the reduction conditions were selected to produce iron crystallites with different morphology. It is known that interaction of ammonia with iron crystallites changes their structure as outlined above. The mechanism of iron surface reconstruction by interaction with nitrogen or ammonia is not well known. Recently Somorjai et al. [17] have shown that reduction by a mixture N_2/H_2 of an oxidated iron surface leads to faces (111) and (211), which are more active for ammonia synthesis. Also they found that the presence of a support phase (i.e., Al_xO_y) can prevent the reconversion of the iron into less active orientations. Consequently, we can assume that in our catalysts the (111) iron face is preferentially developed for samples C and B (treated with ammonia or reduced with a $N_2 + H_2$ mixture) compared with sample A (reduced in pure hydrogen). An order of sample C > sample B > sample A can be considered for the (111) face presence on the iron crystallites, and in the reverse order can be estimated the presence of (100) and (110) faces. For samples B and C the presence of some nitride overlayer in the catalyst surface could be possible [14], in spite of that the conditions to produce iron nitrides are more drastic [10] than those used in this paper. The study by XPS spectroscopy of the surface of a freshly prepared sample B does not reveal the presence of iron nitride.

Figure 1 shows the catalytic activity variation as a function of reaction time for the different samples in the CO hydrogenation reaction. There is for all samples an initial decrease in activity, which then remains almost constant after 200 min. This is in line with the previously reported results on Fe/activated carbon catalysts [6,18]. It is noticeable that the (111) face, which is predominant in preparations C and B, has lower turnover frequency for CO hydrogenation than other faces. However, a direct interpretation of these results as a proof of the structure sensitivity of CO hydrogenation on iron crystallites can lead to a misunderstanding because, as it is well known, metallic iron is transformed in carbide phases under reaction conditions. Then the possibility of faster kinetic for carbide formation or the production of different carbides on the divers initial metallic iron faces should be taken into account. The lower activity of the (111) face compared to other iron faces in our crystallites, is opposite to the trend found in ammonia synthesis over iron single crystal [14]. Apparently the usual parallelism between CO hydrogenation and ammonia synthesis, which are catalyzed by similar systems, is contradicted by the diferences of reaction mechanisms. Other explanations such as the possibility that surface nitridation resulting from the treatments of samples B and C could produce a loss in activity. The formation of a nitride overlayer on the surfaces of samples B and C is unlikely. The mechanism of surface reconstruction of iron catalysts in ammonia synthesis condition is not exactly known but it has not been attributed to surface nitridation [17].

In CO hydrogenation the more important requirement of a catalyst is the

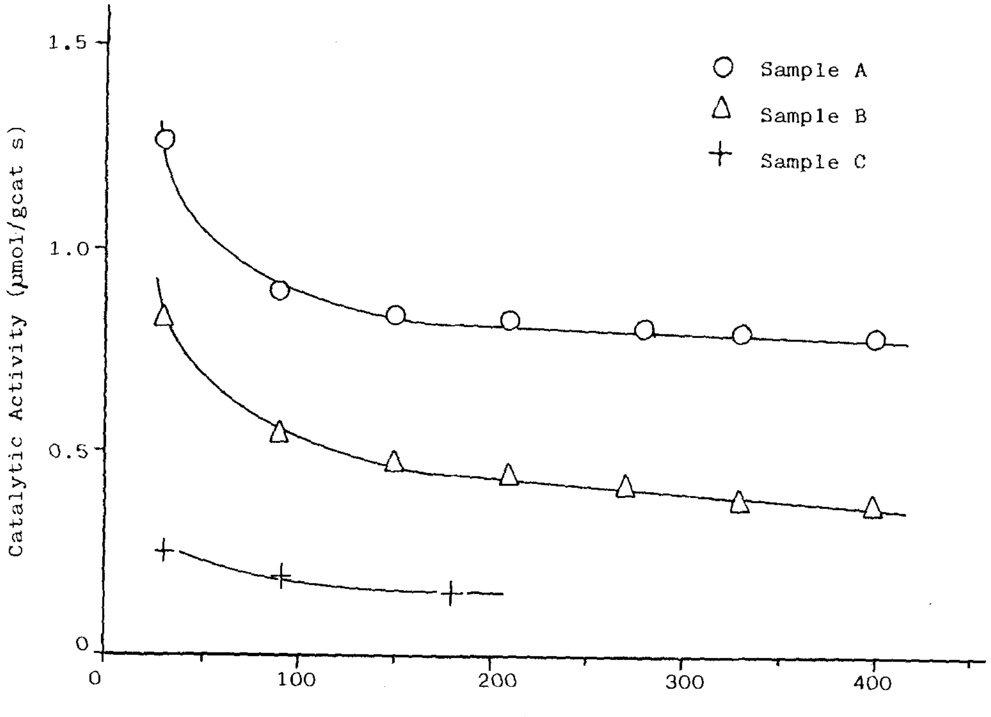

Fig. 1. Catalytic activity variation during the CO hydrogenation at 533 K.

selectivity. In table 1 are given the selectivity to hydrocarbon production (S), the main product besides hydrocarbons being CO_2, possibly resulting from secondary water-gas shift reaction between H_2O produced in the hydrocarbons formation and some CO reactant [18]. The formation of CO_2 from this reaction, instead of a Boudouard reaction between two CO molecules, is supported because the analysis during reaction of the gas effluent from the reactor shows a very small quantity of H_2O. Table 1 gives the product distributions and the probability of propagation of the hydrocarbon chain (α), stimated by application of the Schulz-Flory equation [19]. All these parameters are for steady-state conditions at 533 K and conversions below 6 per cent. Product distribution is obviously changed by catalyst pretreatment. Production of methane and light hydrocarbons rise with

Table 1
Selectivity parameters in CO hydrogenation for the iron catalysts

SAMPLE	S	Product distribution (%)						α
		C1	C2	C3	C4	C5	C6	
A	63	43	21	17	9	6	4	0.60±0.02
B	65	45	22	16	8	5	4	0.57±0.03
C	58	51	23	15	7	3	1	0.52±0.03

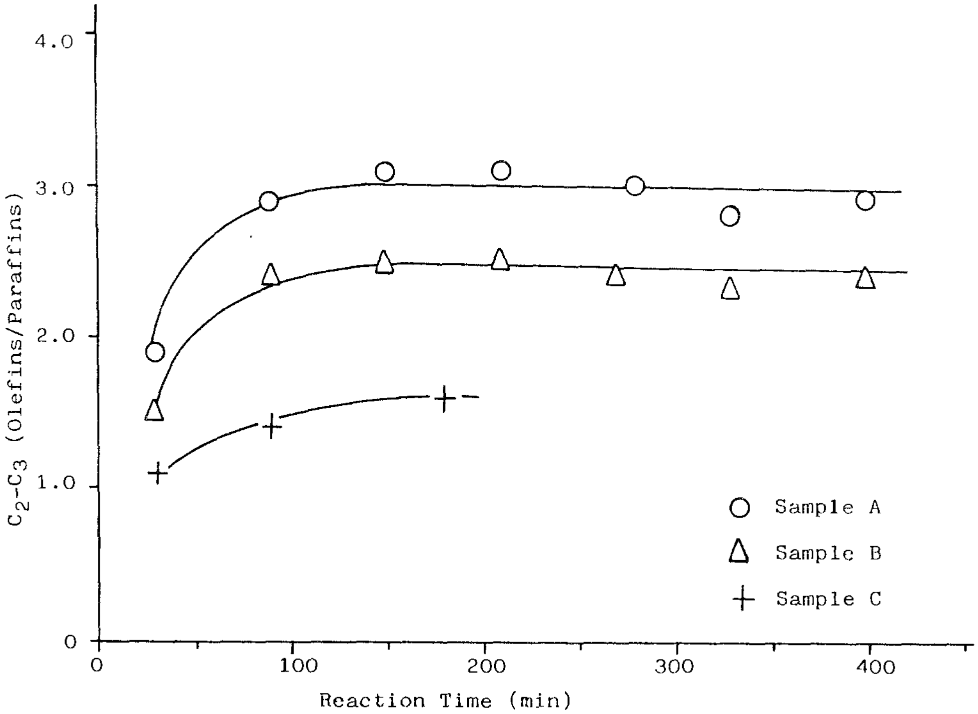

Fig. 2. Olefin to paraffin ratio versus reaction time.

the increase of (111) face in the catalyst (sample A to C). This effect is also reflected on the decrease in α values. Consequently these results indicate that there is a different chain-growth probability for the different iron faces. On the (111) face the hydrogen addition to intermediates (CH_x) with the subsequent chain growth termination and the production of light hydrocarbons is easier. A difference in the ratio of carbon intermediates species to the chemisorbed hydrogen on the various faces of metallic iron, could explain our results. In agreement with this interpretation a lower olefin production was obtained on samples containing more (111) face (see below).

Recently great interest in the CO hydrogenation studies has been paid to develop catalysts exhibing a high selectivity toward olefins of low molecular weight. Figure 2 gives the olefin-to-paraffin ratio for hydrocarbons of two and three carbon atoms obtained over our samples, as a function of time in reaction. In line with previous results on similar catalysts [6] a high selectivity for olefins is obtained. The order of olefin selectivity for our catalysts is: A > B > C. Then the olefin precursor intermediates can be hydrogenated easier on (111) face than on the other iron crystal faces, possibly as consequence of enhanced adsorbed hydrogen. On the other hand, general high olefin selectivity that is produced by catalysts prepared from iron carbonyls and reduced by conventional methods, could be attributed to a low presence of (111) face in the crystallites.

In conclusion, this work indicates that (111) face present in iron crystallites has a lower activity and a different selectivity (lower olefins production and lower chain growth probability) for CO hydrogenation than other crystal faces. Further investigations are desirable to understand the exact catalytic role of the surface faces present in small iron crystallites.

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