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

A. GUERRERO-RUIZ 1 and I. RODRÍGUEZ-RAMOS 2

1 Departamento de Química Inorgánica, Facultad de Ciencias, UNED, Madrid, Spain
2 Instituto de Catálisis y Petroquímica, CSIC, Serrano 119, 28006 Madrid, Spain

Received 21 September 1988; in final form 6 March 1989

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 H2 or H2+N2 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 (C₇) atoms. These C₇ 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 m²g⁻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 H₂ (50 cm³·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 H₂/N₂ (40 cm³·min⁻¹) to the same thermal schedule (sample B). Finally, sample C was obtained by treating the precursor with a pulse of pure NH₃ gas (5 cm³) at 673 K in flowing H₂ 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 H₂ (H₂/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 equipped 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