

# Mössbauer study of the evolution of a laterite iron mineral based catalyst: Effect of the activation treatment

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The syngas reaction has been studied using a laterite iron mineral, promoted with K and Mn. In situ activation under syngas, as well as pre-treatment with H<sub>2</sub> followed by CO under mild and more severe conditions were tested. These activation procedures led to different iron phase compositions and to different catalytic selectivities. The C<sub>2</sub>–C<sub>4</sub>/CH<sub>4</sub> ratio was significantly lower for those catalysts which after reaction showed the presence of hexagonal carbide and magnetite compared to the solid, which showed the highest proportion of Hägg carbide.

## 1. Introduction

The selective production of light alkenes through Fischer–Tropsch synthesis (FTS) has received much attention in recent years. Iron catalysts are considered the best choice when light alkenes are desired [1]. Moreover, promotion with potassium [2] and with manganese [3] improves alkene formation. As a line of investigation in which natural catalysts have been used, a laterite-based iron catalyst was developed for the production of light alkenes. Laterites are produced by weathering of rocks under tropical conditions. In addition to iron, they contain non-reducible oxides (alumina, silica), which can act as textural promoters.

Iron does not remain in the metallic state under reaction conditions, but is converted to carbide phases and can also be oxidized by reaction products such as water and carbon dioxide. This fact has made the identification of the active phases in the FTS difficult and as a consequence, there has been disagreement in the literature about which of the present phases,  $\alpha$ -Fe, carbides or magnetite, is responsible for the catalytic activity [1, 4–7]. Pre-treatment and reaction conditions both appear to be important parameters for the catalytic behaviour.

In an attempt to elucidate the previous point, in the present work the influence of the activation procedure in the activity–selectivity behaviour of the laterite-based catalyst has been studied.

## 2. Experimental

The catalyst was prepared by successive impregnation (incipient wetness) of the previously washed original laterite with manganese and potassium, as nitrate and carbonate salts, respectively, followed by calcination in air for 3 h at 450 °C.

$^{57}\text{Fe}$  Mössbauer spectra were recorded in zero field at room temperature. The Mössbauer source was  $^{57}\text{Co}$  in a Pd matrix. About 0.1 g of the sample was ground and sealed with araldite immediately after treatment or reaction. The isomer shifts are quoted relative to an  $\alpha$ -Fe absorber. Fits were performed using a standard least-squares fitting routine.

The catalytic tests were performed in a flow system with a tubular reactor using 1 g of catalyst at 300 °C, 1.1 MPa, 5.0 l/(g<sub>cat</sub> h) and premixed syngas with H<sub>2</sub>/CO ~ 1 (5% N<sub>2</sub>). Heating was carried out at 5 °C/min under syngas flow until the reaction temperature was attained. The composition of feed and gas products was analyzed by on-line chromatography.

Test 1 was performed with the calcined solid without any other treatment. Pre-treatment conditions for tests 2 and 3 were: H<sub>2</sub> at 335 °C for 16 h followed by CO at 230 °C for 21 h, and H<sub>2</sub> at 450 °C for 16 h followed by CO at 150 °C (5 h)–300 °C 21 h, respectively.

## 3. Results and discussion

### 3.1. CALCINED CATALYST

The major components of the laterite are: iron, aluminum, silicon and titanium. The weight percentages of iron, potassium and manganese of the promoted catalyst are 21%, 4% and 5%, respectively. The Mössbauer spectrum of the calcined solid showed a broad sextet with a hyperfine magnetic field distribution (490–358 kG) which could be attributed to the presence of mixed oxide phases with different degrees of substitution by aluminum and manganese in the iron oxide framework. A doublet of Fe<sup>3+</sup> (14%) was also detected.

### 3.2. PRE-TREATED CATALYSTS

Only paramagnetic doublets of Fe<sup>3+</sup> (73%) and Fe<sup>2+</sup> (27%) appeared in the spectrum of the solid after pre-treatment 2, which suggests an incipient transformation of the iron oxide. Under the more severe reduction conditions of pre-treatment 3 (H<sub>2</sub> at 450 °C), 60% of the iron oxide in the calcined solid was transformed to  $\alpha$ -Fe and in the second step (CO at 150–300 °C), this species was totally converted to Hägg carbide ( $\chi$ -Fe<sub>5</sub>C<sub>2</sub>). The results indicate that the laterite-based solid is not easily reduced, which is correlated to the interaction of iron with the other constituents of the solid (aluminum, manganese, titanium) [8].

## 3.3. CATALYSTS AFTER SYNGAS REACTION

The syngas in the reaction conditions (300 °C, 1.1 MPa) effectively reduces and carburizes the catalyst. The proportion of iron carbided in the non-pre-treated catalyst (table 1) after syngas exposure is similar to that obtained after pre-treatment 3. This in situ activation produces  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> and O-Fe<sub>2</sub>C carbides [9] in an approximately 2:1 proportion; magnetite, probably produced by an incomplete reduction, was also detected.

Table 1

Percentage of spectral composition of the laterite-based catalyst after reaction.

Test	$\chi$ -Fe <sub>5</sub> C <sub>2</sub>	O-Fe <sub>2</sub> C	Fe <sub>3</sub> O <sub>4</sub>	Fe <sup>3+</sup>	Fe <sup>2+</sup>
1	39	19	11	21	10
2	16	23	8 <sup>a)</sup>	37	16
3	69	–	–	18	13

<sup>a)</sup>Oxides, mainly magnetite. Hyperfine fields (kG):  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> (220, 185, 107) ± 3; O-Fe<sub>2</sub>C 167 ± 3.

For the catalyst submitted to pre-treatment 3, the amount of Hägg carbide increases during reaction and only this phase, together with paramagnetic contributions, appears in the Mössbauer spectrum (fig. 1(b)). The type of carbide phase formed depends on the nature of the catalyst as well as on the reaction conditions [10]. Formation of hexagonal carbides is often associated with the presence of small particles of metallic iron compared to Hägg carbide formation [6]. In the in situ activation under syngas exposure, formation of small metallic iron particles that are rapidly carbided will be favored in comparison with a two-stage procedure.

After the reaction with the solid in a state of incipient reduction (pre-treatment 2), the formation of hexagonal carbide was 1.4 times larger than that of Hägg carbide (table 1, fig. 1(a)). The paramagnetic Mössbauer spectrum of the initial solid suggests the presence of small superparamagnetic particles of reduced iron, favoring the formation of hexagonal carbides, as mentioned previously. The fact that the solid was heated from room to reaction temperature under syngas exposure could be involved in this result; hexagonal carbide formation is favored at lower temperatures.

The results of the catalytic tests indicate that syngas acts as an activating agent, increasing the carbon monoxide conversion with time on stream for the three tests. The higher activation rate is observed for the solid submitted to the mildest pre-treatment (table 2). Since carburization of the solids occurs during the three tests, the observed catalyst activation could be ascribed to the continuous formation of iron carbides [6, 7].

Hydrocarbon selectivities differ among the three tests (table 2) The C<sub>2</sub>-C<sub>4</sub> to methane ratio for similar carbon monoxide conversions are 3.5 for test 3, 2.2 for

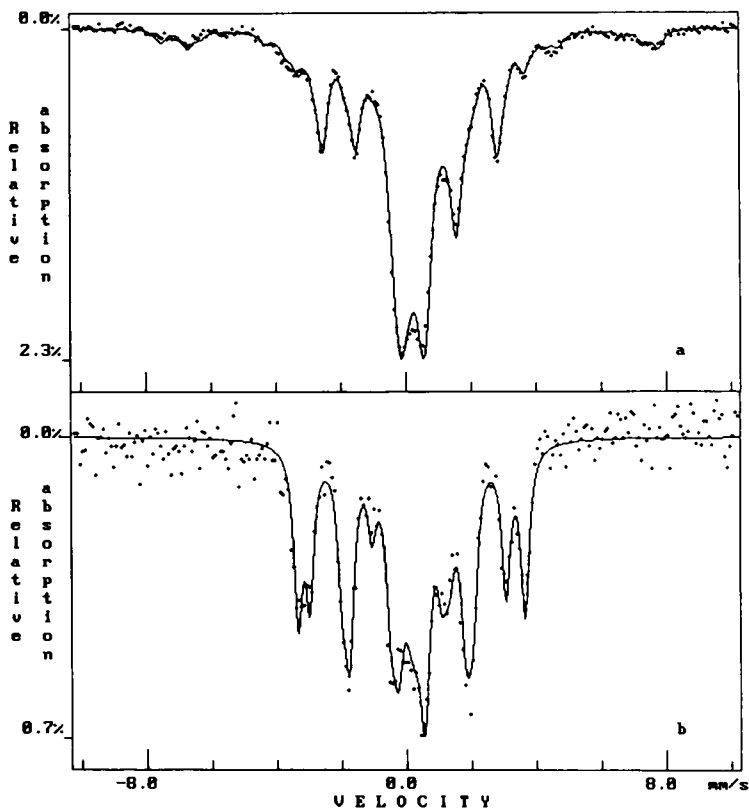


Fig. 1. Mössbauer spectra of the potassium and manganese promoted laterite after reaction. (a) Test 2: mildest pre-treated catalyst. (b) Test 3: strongest pre-treated catalyst.

Table 2  
Catalytic tests results.

Test	1	2	2	3
time on stream (h)	71	44	54	72
CO conversion (%)	57	58	67	51
$C_1-C_6$ distribution (wt.%)				
$C_1$	22.9	27.8	28.9	17.0
$C_2-C_4$	51.1	51.2	49.6	59.1
$C_5-C_6$	26.0	21.0	21.4	23.6
alkenes in $C_2-C_4$ (wt.%)	77.8	75.1	72.9	78.3

test 1 and 1.8 for test 2. The higher ratio is attained with the solid whose Mössbauer spectrum showed Hägg carbide as the only magnetic species, followed by the solids which showed a mixture of Hägg and hexagonal carbides together with magnetite. The results allow us to correlate a better hydrocarbon distribution in the presence of Hägg carbide compared to O-Fe<sub>2</sub>C carbide and magnetite [8]. Soled et al. [11], comparing bulk Fe<sub>3</sub>O<sub>4</sub> and Hägg carbide, found that more methane as well as less C<sub>5</sub>+ and alkenes were obtained for magnetite, which was related to the more acidic oxide surface. The results obtained for the 1 and 2 catalytic tests suggest that hexagonal carbides also favor the methane formation.

#### 4. Conclusions

The pre-treatment of the potassium and manganese laterite catalyst, which transforms an important portion of iron into Hägg carbide, improves the catalytic selectivity (lower methane and higher C<sub>2</sub>-C<sub>4</sub> alkenes) compared with an in situ activation during reaction starting with a calcined or mildly reduced catalyst, in which hexagonal carbides and magnetite appear. These results lead us to conclude that Hägg carbide favors the formation of C<sub>2</sub>-C<sub>4</sub> alkenes.

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