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Fischer Tropsch and Water Gas Shift chemical regimes on supported iron-based catalysts at high metal loading

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ABSTRACT

Iron-based catalysts supported on silica for CO hydrogenation with high amounts of metal (10–50%wt) have been prepared, characterized by BET and SEM and tested. CO conversion and yield to hydrocarbons increase with iron content in catalysts. Depending on the operative conditions Water Gas Shift (WGS) becomes a competitive reaction towards Fischer Tropsch (FT) synthesis. The activation energies values highlight the presence of two different chemical regimes. In particular, for $483 < T < 533$ K, FT is the main reaction while for $543 < T < 583$ K the formation of CO_2 by WGS becomes the predominant reaction.

1. Introduction

Fischer Tropsch (FT) synthesis is a particularly complex system, in which a number of different reactions are combined to an unique mechanism: starting from H_2 and CO, irreversible FT reactions produce hydrocarbons [1–5] but equilibria among CO, CO_2, CH_4 and C are also present, such as the Water Gas Shift (WGS) reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) and the Boudouard equilibrium ($2CO \leftrightarrow C + CO_2$). Nevertheless, it is possible to suppose that FT synthesis can be simplified as a combination of the FT reactions and the WGS reaction. Water is a primary product of FT reactions, and CO_2 can only be produced by WGS reaction, a reversible parallel-consecutive reaction in respect to CO [6]. The iron-based catalysts can offer different active sites to allow both the reactions: the Fe-carbides sites are active for the formation of hydrocarbons (FT) while the magnetite (Fe_3O_4) sites are the most active phase for the WGS reaction [6–9].

Compared to cobalt systems, iron-based catalysts (FeBC) are cheaper, flexible to changes in temperature, pressure and they can work at different H_2/CO ratios (for FeBC catalysts this ratio can be between 0.5 and 2.5) [10,11]; on the contrary they are less resistant to deactivation due to the oxidizing effect of water, and have the drawback to activate the Water Gas Shift reaction producing CO_2 [2,6]. However, iron catalysts seem to be more suitable to work with biomass-derived syngas, as underlined by Corma et al. [12], that are characterized by a low ratio H_2/CO and in the presence of CO_2 (in this case the activation of WGS equilibrium becomes profitable because the above mentioned equilibrium can be oriented towards CO production, when CO_2 concentration is not negligible). They present lower methane selectivity and are less deactivated by poisons species [13].

FeBC are usually used without any support [2,5] but the major inconveniences related to the employment of massive catalysts are their physical degradation and low surface area [14]. Several advantages derived from the use of supported iron catalysts have been reported with respect to unsupported, among them the improved catalytic stability and a lower deactivation rate [15,16]. As observed by Davis et al. [17], supported FeBC usually displays a lower activity of Fe unit mass, than the unsupported ones, but many attempts have been performed to prepare a supported FeBC in a wide range of metal amount: 2.5% [18], 5% [16,19], 10% [13], 15.7% [15], 23% [17].

The lower activity of the supported iron catalysts has been attributed to the development of metal–support interactions that would affect the reducibility of the iron oxide phases [5,13]. Regarding the mechanical features of the catalyst particles, using both fixed bed and slurry reactors, these must be able to work without crushing or fracturing at any significant rate. It is very important to improve the attrition resistance of the FT catalysts using a suitable support, without sacrificing either the activity or the selectivity.

Considering the importance of WGS reaction with iron-based catalysts, particularly if promoted by alkali, it is essential to

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consider this reaction in the evaluation of the activation energy (E_a) for CO consumption reaction on all the studied catalysts. For this reason, we have tested the catalysts in a wide range of reaction temperature (483–583 K) and we have calculated the different E_a, referring the obtained values to the FT and WGS concomitant reactions. By this study, it was possible to clearly observe two different chemical regimes: the first one controlled by the FT and the second one by the WGS reaction.

The experiments presented in this paper were also carried out in order to obtain a better understanding of FeBC behaviour in a range of iron charges (10–50%) wider than those usually reported in literature, with or without the presence of the classical promoters (K and Cu).

2. Experimental

All catalysts were prepared according to the traditional impregnation method, always using the same silica as support (Fluka, BET surface area 520 $m^2 g^{-1}$, pore volume: 1.22 $ml g^{-1}$ and pore diameter: 8.7 nm). The support, after heating treatment at 393 K for 12 h, was impregnated with an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ (Riedel de Haen product) and, when required, KNO_3 (Merk product) and $Cu(CH_3COO)_2 \cdot H_2O$ (Fluka product), and then put into a vacuum oven at 313 K at 36 rpm for 24 h. The samples were heated at 373 K for 12 h and at 773 K for 4 h. In this paper, all the percentages concerning the catalysts composition are on weight basis, while the percentages concerning the CO conversion, the products selectivity and the hydrocarbons yield are on molar basis.

The prepared catalysts were: (i) a first series of iron samples supported on silica with 10%, 30% and 50% of metal, named Fe10, Fe30 and Fe50, respectively; (ii) a second series with the same amount of iron but with promoters, i.e. $K = 5.65\%$ and $Cu = 3.75\%$ for all samples, named Fe10KCu, Fe30KCu and Fe50KCu. The amount of promoters has been chosen taking into account the proper concentrations reported for iron-based catalysts with 10% iron content [4].

The surface area of all catalysts was determined by conventional N_2 adsorption (BET) at 77 K using a Sorptometer instrument (Costech Mod. 1042). Before the analysis, the catalyst samples were heated at 393 K for 12 h, they were then pre-treated at 473 K in a nitrogen flux. SEM images were measured using an electron microscopy Philips XL-30CP with RBS detector of back-scattered electrons.

FT synthesis was performed into a fixed bed reactor, using 1 g of fresh catalyst mixed with 1 g of diluting material (α-Al_2O_3). This diluting material must be inert for FT reactions and act as a good thermal conductor to control the process temperature avoiding hot spots into the catalytic bed [20]. The reduced catalyst was initially activated in situ in flow of H_2/CO (ratio of 2/1, 46.8 $ml min^{-1}$ at 623 K, 0.3 MPa for 4 h). Then, it was tested in the same flow conditions with the addition of 5.0 $ml min^{-1}$ of N_2 as internal standard, at 2.0 MPa in the temperature range 483–583 K. Analyses of the gas-phase products (C_1–C_7) were performed with an on-line micro gas-chromatograph (Agilent 3000). Liquid products were collected in a cold trap at 278 K and 2.0 MPa and analyzed off-line by a gas-chromatograph (Fisons Mod. 8000 Series) equipped with a Poparak-Q column at the end of the whole reaction. The aqueous phase collected in the cold trap was analyzed by a TOC (Schimadzu Mod. 5000A) to quantify the amount of carbonaceous species dissolved in water. Using all the collected data, for each run, a mass molar balance was resulted with a maximum error of ±5%mol.

3. Results and discussion

3.1. Catalysts characterization

The surface area (SA) of the prepared catalysts is strongly influenced by the high iron loading, as shown by the values in Table 1. This parameter decreases linearly from 362 $m^2 g^{-1}$ for the sample loaded with 10% of iron to 143 $m^2 g^{-1}$ for the sample loaded with 50% of iron. This important decrease can be explained considering the dilution effect, due to the presence of iron on the support. The dilution effect can be easily assessed by considering the surface area of bare silica support (520 $m^2 g^{-1}$) and assuming a negligible contribution of the iron phases to the surface area.

A further decrease can be observed when K and Cu promoters are present as already reported by Dadyburjor et al. [15].

SEM analyses are essential to evaluate the morphology of catalysts with high loading of iron and to verify the metal dispersion. In Fig. 1 pictures of catalysts loaded by 10% (Fig. 1a), 30% (Fig 1b) and 50% (Fig. 1c) are reported. It is evident that iron is always well dispersed on the support surface even in the more loaded catalyst, but both the shape of iron aggregates and the distribution are different in the three samples. In particular, in the Fe10 sample (Fig. 1a) the iron particles are visible as aggregates of different size and cover a little area of silica support; in the Fe30 sample (Fig. 1b) the metal is homogeneously dispersed as little aggregates on silica while in the Fe50 sample (Fig. 1c) the silica is totally covered by a layer of iron.

3.2. Catalytic results

Table 1 shows the FT synthesis results at the temperature of 523 K. The CO conversion is tightly related to the iron percentage of catalysts: the higher the amount of supported iron, the higher the CO conversion and, with the same iron amount, CO conversion increases in the presence of the promoters K and Cu. The combination of CO conversion and products selectivity results is taken into account calculating the total yield to hydrocarbons greater than C_1 (C_{2+}), i.e. not considering methane and carbon dioxide, usually considered as undesired products. Increasing the amount of supported iron, the C_{2+} yield raises: the best FT results in term of C_{2+} yield (53%) has been obtained using Fe50 catalyst, while, in term of CO conversion (89%), using Fe50KCu catalyst (see Table 1).

CO conversion and the selectivity in a wider temperature range (503–583 K) have been obtained for all the catalysts: an example of

Table 1
Catalysts composition, BET surface area and results of kinetic FT runs at the standard temperature of 523 K; H_2/CO molar feeding ratio = 2/1; pressure = 2.0 MPa; total flux = 46.8 N $ml min^{-1}$.

Catalyst	Composition (%wt)	BET SA ($m^2 g^{-1}$)	CO conversion (%)	C_{2+} total yield (%)	Products selectivity (%)			
					CH_4	CO_2	$<C_7$	$>C_7$
Fe10	Fe10	362	6	4	19	11	47	23
Fe30	Fe30	241	26	19	13	14	44	29
Fe50	Fe50	143	74	53	6	22	20	52
Fe10KCu	Fe10, K 5.65, Cu 3.75	143	15	9	5	30	20	45
Fe30KCu	Fe30, K 5.65, Cu 3.75	72	38	22	2	40	14	44
Fe50KCu	Fe50, K 5.65, Cu 3.75	25	89	44	2	48	11	39