



## CO<sub>2</sub> reactivity on Fe–Zn–Cu–K Fischer–Tropsch synthesis catalysts with different K-loadings



Michela Martinelli<sup>a</sup>, Carlo Giorgio Visconti<sup>a,\*</sup>, Luca Lietti<sup>a</sup>, Pio Forzatti<sup>a</sup>,  
Claudia Bassano<sup>b</sup>, Paolo Deiana<sup>b</sup>

<sup>a</sup> Politecnico di Milano, Dipartimento di Energia, Piazza Leonardo da Vinci 32, Milano 20133, Italy

<sup>b</sup> ENEA, Agenzia Nazionale per le Nuove Tecnologie, l'Energia e lo Sviluppo Economico Sostenibile, Via Anguillarese 301, S. Maria di Galeria, Roma 00123, Italy

### ARTICLE INFO

#### Article history:

Received 17 July 2013

Received in revised form

12 November 2013

Accepted 15 November 2013

Available online 17 December 2013

#### Keywords:

Fischer–Tropsch synthesis

CO<sub>2</sub> hydrogenation

Iron catalysts

Potassium

### ABSTRACT

In the presence of low cost H<sub>2</sub>, the hydrogenation of pure CO<sub>2</sub> streams (e.g., from carbon capture processes) or CO/CO<sub>2</sub> mixtures (e.g., from biomass of coal gasification) to fuels is a potential solution to convert the primary greenhouse gas into a valuable building block for the synthesis of high-added value products. Iron based Fischer–Tropsch catalysts, known for their reverse water gas shift activity, are good candidates to run such process. However, their reactivity depends on the catalyst formulation which may vary significantly in the presence of supports or promoters. Also, the H<sub>2</sub>/CO<sub>x</sub> inlet ratio may strongly influence the catalyst activity and selectivity. With the purpose of gaining more insights into the reactivity of carbon dioxide, the catalytic performances of K-promoted 100Fe/10Zn/1Cu samples have been comparatively studied in CO, CO<sub>2</sub>, and CO/CO<sub>2</sub> hydrogenation processes with low H<sub>2</sub>/CO<sub>x</sub> ratios varying from 0.5 to 1. We have found that traditional iron-based catalysts for the Fischer–Tropsch synthesis can be successfully used to obtain high added-value products from CO<sub>2</sub> even in the presence of H<sub>2</sub> deficient feed streams. In the case of pure CO<sub>2</sub> hydrogenation, the most promising results are obtained with strong potassium promoted iron catalysts which grant interesting selectivities toward middle distillates by favoring CO<sub>2</sub> adsorption. In the presence of strongly adsorbed CO, CO<sub>2</sub> is instead hardly converted independently on the K-loading. The presence of CO<sub>2</sub> does not affect the product distribution either. Nevertheless, CO<sub>2</sub> has a key-role in preventing the CO shift to CO<sub>2</sub>, thus improving the overall economy of the conversion process and avoiding a net CO<sub>2</sub> production. Interestingly, upon increasing the K-loading, the CO conversion rate is decreased, both in the presence and in the absence of CO<sub>2</sub>, possibly as a result of the very strong CO adsorption on the catalytic surface. Such result is however complicated by the presence of initial deactivation phenomena, whose rates may be also related to the K-loading of the catalyst. Accordingly, the best catalyst formulation appears to be significantly different depending on the presence of CO in the feed.

© 2013 Elsevier B.V. All rights reserved.

### 1. Introduction

Carbon dioxide is the primary greenhouse gas (GHG) arising from life and human activities. In recent years, the growing consciousness of the dramatic impact of its atmospheric concentration on the climate has brought to conclusion that the reduction of CO<sub>2</sub> emissions from all anthropogenic processes is mandatory [1]. In addition to the improvement of the efficiency of energy conversion and utilization processes, GHG reduction strategies proposed in the last decades also include secondary measures such as the carbon dioxide capture and the storage (CCS). Apart from the open

technological issues associated to these technologies, it has been recently shown that the costs related to the CO<sub>2</sub> re-injection are extremely high, thus making CCS hardly convenient even in the presence of carbon-emission taxes [2]. This paves the way to the so-called CO<sub>2</sub> capture and utilization (CCU) technologies, where it is no more considered as a waste to be dumped but is used as feed-stock (C<sub>1</sub> building unit) to produce highly added-value products such as chemicals or fuels.

In addition to these carbon management strategies, the development of CO<sub>2</sub> utilization technologies being able to co-activate CO and CO<sub>2</sub> has become more and more strategic when considering that carbon dioxide is a significant component in syngas produced through natural gas partial oxidation, and steam reforming or through biomass gasification [3]. Until now, it is generally separated from CO/H<sub>2</sub> with important heat and energy loss [4].

\* Corresponding author. Tel.: +39 0223993297; fax: +39 0223993318.  
E-mail address: [carlo.visconti@polimi.it](mailto:carlo.visconti@polimi.it) (C.G. Visconti).

As a matter of fact, the most studied CO<sub>2</sub> conversion technologies involve its hydrogenation into chemicals or fuels [1,5] or the so called dry-reforming, i.e., its conversion to syngas *via* reaction with methane [6]. The major advantage to the use of CO<sub>2</sub> for the production of fuels is that their market is big enough to guarantee a relevant CO<sub>2</sub> consumption [7].

The processes under investigation to produce fuels from CO<sub>2</sub> can be divided into two main categories: *via* methanol and *via* modified Fischer–Tropsch synthesis (FTS). In the methanol-mediated approach, CO<sub>2</sub> is first converted to methanol over a Cu–Zn based catalyst, which is then transformed into hydrocarbons through a methanol to gasoline (MTG) process [1,8]. Methanol may be eventually dehydrated to dimethyl-ether, a valid alternative to diesel fuels. At variance, in the case of modified FTS, CO<sub>2</sub> is directly hydrogenated to linear hydrocarbons.

A number of studies are available where the direct hydrogenation of CO<sub>2</sub> and CO/CO<sub>2</sub> mixtures to hydrocarbons is reported on traditional FTS catalysts. In the case of cobalt-based catalysts (in the case of ruthenium as well [8]) there is a general consensus to the fact that carbon dioxide behaves as inert when CO is co-fed while the reaction regime shifts from a Fischer–Tropsch type to a methanation type when CO is completely replaced by CO<sub>2</sub> [9–16]. The reason of the different reactivity of CO and CO<sub>2</sub>, however, is still debated, as it has been recently pointed out by Visconti et al. [10] and Gnanamani et al. [9]. In this respect, low temperature Fe-based catalysts are reported to be much more effective than cobalt to convert CO<sub>2</sub> to high molecular weight hydrocarbons. This is attributed either to the intrinsic reverse water gas shift (RWGS) activity of those catalysts [17], which is possibly the first step involved in the CO<sub>2</sub> conversion to hydrocarbons [18,19] or to their ability to directly hydrogenate carbon dioxide [20]. However, also in this case different evidences were collected by several groups and various explanations were used to justify the different reactivity of CO and CO<sub>2</sub>. Riedel et al. [11], working with a 100Fe/13Al<sub>2</sub>O<sub>3</sub>/10Cu/10K (mass ratios) catalyst, found similar products as a result of CO and CO<sub>2</sub> hydrogenations, and explained this result by assuming that the carbides irreversibly formed during CO hydrogenation, which are responsible for the formation of the FT regime over Fe-based catalysts, can be formed even when CO<sub>2</sub> is fed. On the contrary, according to Gnanamani et al. [9], the C<sub>5+</sub> selectivity drops significantly when switching from CO to CO<sub>2</sub> on a K-promoted Fe-catalyst (100Fe/4.4Si/0.9K, atomic ratios). These authors explained such a result by assuming that due to the slow RWGS, the H<sub>2</sub>/CO ratio in the reactor is higher when CO<sub>2</sub> is fed instead of CO. Similar results are also reported by Yao et al. [21] on a supported Fe/TiO<sub>2</sub> catalyst; a significant decrease of the olefin to paraffin (O/P) ratio is also observed when replacing CO with CO<sub>2</sub>. Finally, Dwyer and Somorjai [22], and Ando et al. [23], working with unpromoted bulk iron catalysts, reported different product composition during the hydrogenation of CO and CO<sub>2</sub> with a shift to light and saturated hydrocarbons in the latter case. This has been explained by speculating that the formation of the active carbide species ( $\chi$ -Fe<sub>2.2</sub>C), readily occurring on the catalytic surface in the presence of CO, is suppressed in the presence of CO<sub>2</sub> [23]; the catalytic surface would be indeed oxidized during the conversion of CO<sub>2</sub> to CO.

The cofeeding of CO and CO<sub>2</sub> also leads to puzzling results. Xu et al. [24] and Yao et al. [21] found that CO<sub>2</sub> is hydrogenated only at low CO partial pressure due to a relevant contribution of the RWGS at these conditions. However, when CO<sub>2</sub> is converted, the selectivity to methane suddenly increases but decreases to C<sub>2+</sub> hydrocarbons [21]. The same authors show that O/P ratio progressively decreases when CO is replaced by CO<sub>2</sub> [13]. At variance, Gnanamani et al. [9] reported similar (always very low) CO<sub>2</sub> conversions upon varying the CO/CO<sub>2</sub> feed ratio; also, the product distribution was found to depend only on the H<sub>2</sub>/CO ratio,

independently on the presence of CO<sub>2</sub>. Chun et al. [4], working with a 100Fe/5.33Cu/5.23K/17.4SiO<sub>2</sub> (mass ratios), found an inhibiting effect of CO<sub>2</sub> in terms of hydrocarbon yield; the carbon number distribution as well as the O/P ratio was however not affected. They attributed such a decrease to a competitive adsorption of CO and CO<sub>2</sub>.

With the purpose to gain more insights on the reactivity of carbon dioxide on Fe-based catalysts, in this work, the catalytic performances of K-promoted 100Fe/10Zn/1Cu samples have been comparatively studied in the hydrogenation of CO, CO<sub>2</sub>, and CO/CO<sub>2</sub> mixtures. The effect of potassium on the catalyst activity and selectivity has been investigated by reactivity of samples having different K-loadings. Due to the fact that Fe-based catalysts are usually considered for coal to liquid (CTL) and biomass to liquid (BTL) processes which operate with H<sub>2</sub>-deficient synthesis gas (H<sub>2</sub>/CO~1 mol/mol), reactivity studies have been carried out in this work with equimolar H<sub>2</sub>/CO and H<sub>2</sub>/CO<sub>2</sub> mixtures, and results are shown in the following experiments.

## 2. Experimental

### 2.1. Catalyst preparation

Following the procedure reported in [25], potassium and copper promoted 100Fe/10Zn catalysts were prepared by semi-batch co-precipitation of ferric and zinc nitrates at constant pH to form porous Fe–Zn oxy/hydroxycarbonate powders, which were then promoted after calcination at 350 °C by incipient wetness impregnation with potassium carbonate and copper nitrate. Briefly, a ferric nitrate solution (3.0 M) and a zinc nitrate solution (1.4 M) were prepared by dissolving Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Aldrich, ≥98%) and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Aldrich, ≥98%) in deionized water. The two solutions were then mixed so as to obtain a Zn/Fe atomic ratio of 0.1. The resulting solution was continuously fed to a jacketed glass reaction cell kept at 80 °C containing a buffer solution ((NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> 1.0 M (Aldrich, ≥30% NH<sub>3</sub> basis) acidified at pH = 7 with nitric acid. This led to the co-precipitation of the Fe and Zn hydroxycarbonates. (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> 1.0 M was added to the cell through an electronic titrator (Metrohm, Titrino plus) to keep the pH of the slurry at a value of 7 ± 0.2.

The obtained slurry was filtered and the obtained solid was then washed five times with deionized water (500 cm<sup>3</sup> each time), dried in ambient air at 120 °C overnight and eventually calcined in stagnant ambient air at 350 °C for 1 h (heating rate 1 °C/min). Then, copper (Cu/Fe = 0.01 atomic ratio) and potassium (K/Fe = 0.02 or 0.04 atomic ratios) promoters were sequentially added to the Fe–Zn calcined precursor by the incipient wetness impregnation technique starting from aqueous solutions of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Aldrich, >98%) and K<sub>2</sub>CO<sub>3</sub> (Aldrich, ≥99%). After each impregnation steps, the samples were dried in ambient air at 120 °C overnight. After impregnation with potassium, samples were calcined at 400 °C in stagnant air for 4 h (heating rate 1 °C/min). This procedure led to the complete decomposition of all precursor salt except K<sub>2</sub>CO<sub>3</sub>.

Two catalysts, with different K-loadings, were prepared: 100Fe/10Zn/1Cu/2K (sample “cat2K”) and 100Fe/10Zn/1Cu/4K (sample “cat4K”) on a molar base.

### 2.2. Catalyst characterization

Both the precursors of “cat2K” and “cat4K” (named “prec2K” and “prec4K”, respectively), i.e., the samples obtained after Fe–Zn co-precipitation and the final catalysts obtained after Cu–K impregnation (“cat2K” and “cat4K”) were characterized.

Powder X-ray diffraction measurements were carried out using a D8 Advance Bruker diffractometer and Cu–K $\alpha$  radiation

Download English Version:

<https://daneshyari.com/en/article/54130>

Download Persian Version:

<https://daneshyari.com/article/54130>

[Daneshyari.com](https://daneshyari.com)