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## **Catalytic and kinetic study of the CO<sub>2</sub> hydrogenation reaction over a K-Fe/Al<sub>2</sub>O<sub>3</sub> catalyst for gaseous and liquid hydrocarbons production.**

Carlotta Panzone<sup>1,2\*</sup>, Régis Philippe<sup>2</sup>, Alban Chappaz<sup>1</sup>, Clémence Nikitine<sup>2</sup>, Laurent Vanoye<sup>2</sup>, Alain Bengaouer<sup>1</sup> and Pascal Fongarland<sup>2</sup>

*1 Laboratoire Echangeurs-Réacteurs (LER), LITEN, CEA Grenoble, Grenoble, 38000 (France);*

*2 Université de Lyon, Laboratoire de Génie des Procédés Catalytiques (LGPC) UMR 5285*

*\*Corresponding author E-Mail: carlotta.panzone@cea.fr*

### **1. Introduction**

The recent raising needs to decarbonize the economy sector to limit CO<sub>2</sub> concentration in the atmosphere and to find a storage solution for the intermittent renewable power are leading to an increased interest in the utilisation of CO<sub>2</sub> as feedstock for the synthesis of fuels and chemicals. Among the variety of developing technologies that aim at the CO<sub>2</sub> utilization, in this work our interest is focused on Power-to-Liquid (PtL) for the synthesis of liquid hydrocarbons (HCs) that can have applications in both the transport sector and the petrochemical industry.

Iron-based catalysts have been identified as the most suitable for this reaction, as they are active for both RWGS and FT. Alkali-promoted iron catalysts have also been shown to be very active for the production of long-chain hydrocarbons by enhancing the chain-growth and simultaneously limit secondary products. [1-3] While research in the improvement of the activity and selectivity of these catalysts is very extensive, further investigation is needed in terms of kinetics and modelling of the reaction.

In this work, CO<sub>2</sub> hydrogenation is studied with attention to catalytic performances and kinetics, in order to develop a detailed mathematical model able to describe the formation of all the major products.

### **2. Methods**

The 7K-10Fe/Al<sub>2</sub>O<sub>3</sub> catalyst has been synthesized by impregnation of the alumina support with a solution of iron nitrate and potassium carbonate. After calcination under air and ex-situ reduction under hydrogen flow, a mass of 3.5 g of catalyst has been placed into a lab-scale fixed-bed reactor of 6 mm inner diameter. Experiments have been conducted by varying the operating parameters in the following ranges: 250-350°C for oven temperature, 10-20 bar for total pressure, 2-24 for H<sub>2</sub>/CO<sub>2</sub> molar ratio and 500-3600 NmL<sub>reactants</sub>/g<sub>cat</sub>/h for GHSV. A condensation unit after the reactor outlet allows the separation of heavy products (water, oxygenates and long-chain HCs) from the more volatile ones. Gas products are analysed with an on-line GC system, equipped with TCD and FID detectors, using N<sub>2</sub> as internal standard; liquid products are separated by decantation into water and organic phase and then analyzed separately with off-line GCs, equipped with a FID detector. The catalyst has been characterized by different analysis methods, such as ICP, BET, laser granulometry, TPR, XRD and Mössbauer.

### **3. Results and discussion**

The long-term stability tests showed that, after 50 hours of activation, the catalyst reaches its stationary state and keeps a stable activity for at least 150 hours. After that phase, an increase of CO selectivity is observed with a simultaneous loss in the activity towards the desired products, caused by the evolution of the iron phases of the catalyst. During stationary state and at base conditions (see Table 1), CO<sub>2</sub> conversion reaches a value of

29% with HCs selectivity of 87%. Among HCs, low olefins are the most abundant products, but the presence of olefinic and paraffinic chains until 35 carbon atoms has been observed. Non-negligible quantities of oxygenates (such as alcohols, carboxylic acids, aldehydes and ketones) as well as ramified and aromatics products have also been identified.

x <sub>CO2</sub>	S <sub>CO</sub>	S <sub>HCS</sub>	HCs distribution			HCs distribution (w/o CH <sub>4</sub> )			
			C <sub>1</sub>	C <sub>2-C4</sub>	C <sub>5+</sub>	olefins	paraffins	oxygenates	others*
29%	13%	87%	33%	50%	17%	61%	11%	24%	7%

**Table 1.** Results of the catalytic tests at base conditions ( $\tau=5.5s$ ,  $T_{oven}=300^{\circ}C$ ,  $P_{tot}=15$  bar,  $H_2/CO_2=3$ ,  $\%N_2=4\%$ ).  
\*with others we indicate aromatic and ramified products as well as non-identified products.

The distribution of products according to their carbon number shows that olefins and paraffins follow a bimodal ASF distribution, with two different alphas ( $\alpha_1$  for C<sub>2</sub>-C<sub>8</sub> and  $\alpha_2$  for C<sub>11</sub>-C<sub>30</sub>), while oxygenates follow an ideal ASF distribution with a single value of  $\alpha$ . The  $\alpha$  value for the oxygenates, reported in Table 2, is significantly lower than that of the other product groups which can be explained with the hypothesis that oxygenates are formed on a different type of active site. [4]

	Global	Olefins	Paraffins	Acids	Alcohols	Aldehydes
$\alpha_1$	0.54	0.55	0.56	0.37	0.15	0.26
$\alpha_2$	0.77	0.78	0.82			

**Table 2.** Values of alpha for each product group, obtained from the ASF distribution.

The effects of operating parameters on the catalytic performance were investigated. It was observed that increasing the temperature from 250°C to 325°C has beneficial effects for CO<sub>2</sub> conversion and HCs selectivity, however at 350°C an irreversible deactivation phenomenon was observed. Increasing the total pressure from 10 to 16 bars led to an increase of both CO<sub>2</sub> conversion and HCs selectivity, while between 16 and 20 bars, pressure seems not to have further effects. Increasing residence time also led to an increase of the global HCs yield, but it did not significantly influence HCs distribution. Finally, the study on the H<sub>2</sub>/CO<sub>2</sub> ratio showed that a H<sub>2</sub> excess is favorable for the CO<sub>2</sub> conversion and the global HCs selectivity, but among HCs, methane becomes the most favored product for H<sub>2</sub>/CO<sub>2</sub>>8.

These experimental results will be used to derive the kinetic parameters of a kinetic model developed to describe the reaction behavior in a detailed way. Two approaches have been used for the development of the kinetic model: 1. a macro-kinetic approach, based on the work of Riedel et al. [5], which has been enhanced in order to take into account the formation of the different categories of products observed and their distribution; 2. a micro-kinetic approach, based on the hypothesis of a mechanism and developed following the Langmuir-Hinshelwood-Huygens-Watson method. This latter approach will be able to describe the formation of each product, considering the existence of different sites for the formation of olefins and paraffins and for oxygenates, which could explain the difference in terms of carbon number distribution.

#### 4. Conclusions

In conclusion, some promising results have been obtained for the laboratory-scale study of the CO<sub>2</sub> hydrogenation towards long-chain hydrocarbons with an impregnated K-Fe/Al<sub>2</sub>O<sub>3</sub> catalyst. Further improvements in the catalyst synthesis are needed in order to enhance its stability. The development of a detailed kinetic model will be useful for the subsequent design of an efficient reactor-exchanger and for the estimation of the global efficiency of the process and its potential compared to other synthetic hydrocarbons production processes.

#### References

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