



CAMURE-11 11th International Symposium on Catalysis in Multiphase Reactors

ISMR-10 10th International Symposium on Multifunctional Reactors

MILANO, ITALY - 21-24 March, 2021

Gaseous phase Fischer-Tropsch synthesis on solid iron catalysis promoted with liquid metals

Alan Barrios¹, Deizi Peron¹, Bang Gu¹, Mirella Virginie¹, Robert Wojcieszak¹, Ovidiu Ersen²,
Vitaly Ordonsky¹ and Andrei Khodakov^{1*}

¹ Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France; ²IPCMS, Université de Strasbourg, France

*Corresponding author E-Mail: andrei.khodakov@univ-lille.fr

1. Introduction

The growing demand for light olefins in the context of depletion of oil reserves has stimulated development of alternative olefin manufacturing processes. Fischer-Tropsch (FT) synthesis represents a promising and sustainable alternative for light olefins synthesis, which can be generated from renewable feedstocks such as organic waste, used plastics and biomass. The selectivity to specific products is a great challenge of carbon monoxide and carbon dioxide hydrogenation, because of unselective broad Anderson-Schulz-Flory (ASF) distribution of the produced hydrocarbons [1, 2]. Iron based catalysts are efficient for the synthesis of light olefins from the syngas due to their selectivity and high activity in the Water Gas Shift reaction [3]. The catalytic properties and rate of the reaction elementary steps strongly depend on the chemical and structural catalyst characteristics. The evolution of atom coordination, crystal size faceting and chemical composition under the reaction conditions are key parameters controlling the catalytic performance with the reaction time.

Recently, we found that promotion of iron catalysts with soldering metals such Bi and Pb resulted in major increase in the reaction rate and improved the light olefin selectivity [2, 3]. Interestingly, both the Bi and Pb promoters are present in liquid state on the catalyst surface at the conditions of high temperature FT synthesis. In the present work, we uncovered that other metals such Sn and Sb, which also have low melting points, could remarkably promote the reaction rate. The goal of the present work is to provide insights into the mechanisms of the promotion of iron catalysts supported in carbon nanotubes (CNT) and silica for gaseous phase FT synthesis with liquid metals such as Bi, Pb, Sn and Sb by using a combination operando XANES/EXAFS, in-situ TEM and near atmospheric pressure NAP- XPS.

2. Methods

Iron-based catalysts (10 wt. % Fe) supported on CNT and silica were prepared by classic incipient wetness impregnation method. These catalysts were promoted with different mobile metals (Bi, Pb, Sn, and Sb) 100/2 molar ratio. They were characterized by XRD, TPR, in-situ TEM, operando XAS/EXAFS and in-situ NAP-XPS. The catalytic tests were conducted in a micro fix-bed reactor at 10 bar, 350 °C, and GHSV 3.6 L/gh.

3. Results and discussion

Catalytic studies of the iron catalysts promoted with liquid metals show a major enhancement of stability and they also have a direct impact on the FT reaction rate activity (Table 1). The promotion effect of liquid metals on iron carbide (active phase) has been reinforced by the continuous promoter migration (mobility) during the catalyst activation and reaction, which leads to the preferential localization of promoters at the interface with iron carbide nanoparticles (Figure 1). Characterization data and catalytic tests suggest that the promotion effect

of liquid metals on the catalytic performance of supported iron catalysts can be tentatively attributed to three phenomena: enhancement of iron carbidisation and reducibility, facilitation of carbon monoxide dissociation via scavenging of oxygen atoms by the promoters, slower carbon chain growth.

Table 1. Catalytic performance data showing a major increase in the FT reaction rate (FTY) over iron catalyst promoted with mobile promoters.

Catalyst	Activity		Selectivity				
	FTY, 10^{-4} mol $\text{g}_{\text{Fe}}^{-1}$ s^{-1}	XCO, %	SCO ₂ , %	S _{CH₄} , %	S _{C₂-C₄} , %	S _{C₂-C₄} , %	S _{C₅⁺} , %
Fe/SiO ₂	0.20	11	15	24	31	5	40
FeSb/SiO ₂	0.87	47	47	14	17	10	59
SbFe/SiO ₂	0.61	33	43	21	20	12	47
FeSn/SiO ₂	0.98	53	49	23	17	13	47
FeBi/SiO ₂	1.11	60	49	15	25	10	50
FePb/SiO ₂	0.82	44	46	16	34	7	43

A combination of *in situ* characterization techniques provided further detailed information about evolution of liquid Bi on the surface of iron catalyst under catalyst activation and reaction. Operando XANES, in-situ STEM and NAP-XPS conducted under CO and syngas suggest that Bi reduction to metallic state coincides with its migration and formation of iron carbide-bismuth core-shell structures. Quasi-liquid bismuth also agglomerates into larger Bi nanoparticles on the catalyst surface. In-situ TEM was indicative of iron sintering

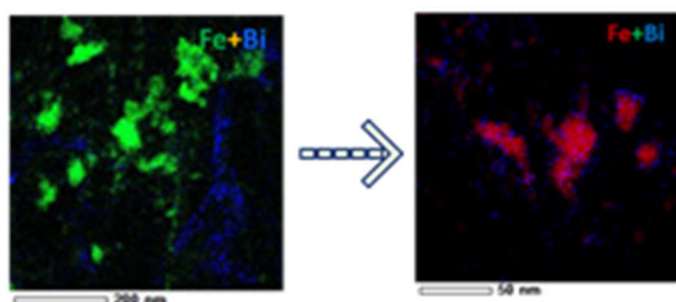


Figure 1. TEM images and EDX mapping of the FeBi/CNT catalysts before and after reaction showing formation of core shell structures.

during catalyst activation in carbon monoxide at 350°C. The presence of liquid metal seems to slow down iron sintering. Both in-situ NAP-XPS and operando XANES suggest easy oxidation and reduction of Bi as a function of reaction conditions, which is consistent with the role of the promoters in oxygen scavenging during CO dissociation.

4. Conclusion

Promotion of iron catalysts with liquid and highly mobile metals (Bi, Pb, Sn and

Sb) results in major increase in FT reaction rate and strongly affect light olefin selectivity. The effect of liquid promoters on iron carbide has been reinforced by their preferential localization at the interface with iron carbide nanoparticles.

In-situ characterization techniques suggests continuous migration of liquid promoters on the catalyst surface under the reaction conditions, while its oxidation state oscillates between oxide and metallic state. The observed phenomena explain facilitation of CO dissociation over iron carbide and scavenging oxygen in the working catalysts by metal leading to oxide. A combination of in-situ, operando characterization techniques and catalytic tests has provided information about the effect of different reaction conditions on the major increase in the FT reaction rates and olefin selectivity over the promoted iron catalysts.

References

- [1] Galvis, H.M.T. and De Jong, K., ACS Catal. 3 (2013) 2130-2149.
- [2] Gu, B., Ordonsky, V., Bahri M., Ersen, O., Chernavskii, P., Filimonov, D., and Khodakov, A. Appl. Catal. B Environ. 234 (2018) 153-166.
- [3] Ordonsky, V., Luo, Y., Gu, B., Carvalho, A., Chernavskii, P., Cheng, K., and Khodakov, A., ACS Catal. 7 (2017), 6445-6452.