Innovative photocatalysts integrated in flow photoreactor systems for direct CO_2 and H_2O conversion into solar fuels

Deliverable D3.1

List of potential photocatalysts for the alcohols generation from syngas

Collaborative project within H2020-LC-SC3-2020-NZE-RES-CC

Grant agreement No. 101022202

Start date of the project: 01/07/2021

Duration of the project: 48 months

WP	WP3	Photocatalytic Flow Reactor (PCFR2) for alcohols generation

Dissemination level[1]	PU	Due delivery date	30/06/2022
Nature[2]	R	Actual delivery date	01/07/2022

Lead beneficiary	LEITAT
Contributing beneficiaries	all

Project partners:

LEITAT – NUIG – PKU – UBU – CHEM – SOCAR – ICIQ – FUNDITEC – UMICH – STRATA

Dissemination level: **PU** = Public, **PP** = Restricted to other programme participants (including the JU), **RE** = Restricted to a group specified by the consortium (including the JU), **CO** = Confidential, only for members of the consortium (including the JU)

[2]Nature of the deliverable: **R** = Report, **P** = Prototype, **D** = Demonstrator, **O** = Other

[3]Creation, modification, final version for evaluation, revised version following evaluation, final

Document history

Version	Issue date	Author	Partner	e-mail address	Comments[3]
1	23/06/2022	Alfredo Bol Santiago Aparicio Elizabeth Escamilla-Roa	UBU	alf_bol@ubu.es	Creation
2	27/06/2022	Oriol Angurell	LEITAT	Oangurell@leitat.org	Modifications
3	27/06/2022	Meng Wang	PKU	M.wang@pku.edu.cn	Modifications
4	28/06/2022	Alfredo Bol Santiago Aparicio Elizabeth Escamilla-Roa	UBU	alf_bol@ubu.es	Modifications
5	01/07/2022	Oriol Angurell Kerstin Steidle	LEITAT	oangurell@leitat.org ksteidle@leitat.org	Final Version

CONTENTS

LIST OF TABLES

1. Introduction

The Fischer-Tropsch synthesis (FTS) process consists in the transformation of synthesis gas (H_2 and CO) in presence of a catalyst to obtain hydrocarbons with a longer chain such as diesel, naphtha, synthetic crude, olefins, gasoline, and long-chain hydrocarbons or alcohols, which have a high added value.[1] The source of CO and H_2 (syngas) can be coal, biomass, natural gas (shale gas) as well as the photoreduction reaction of CO_2. The conventional FTS process has a high energy request at high temperatures (230-450 ºC) and pressure (2-5 Mpa). An alternative is the solar driven catalysis that offer a high potential for transforming CO by means of photo-thermal process. At present, the known catalysts for this process are copper for the synthesis of alcohols, nickel for fat hydrogenation, and iron and cobalt to obtain hydrocarbons.[1] These metals are suitable for photothermal processes because their electronic structure is easily changed and can be tuned up to obtain a synergistic effect between solar and thermal activation.[2] On the other hand, the study of the electronic structure is important to propose specific solutions for the production on demand of the electrons and holes needed for the photocatalytic process.[3] To form the active phase, these metals are deposited onto supported surfaces that can be metal oxides. The substrates can be crystalline, such as titania, or amorphous, such as silica.[4]

2. Objective

The main objective of this task is the bibliographic research of the potential catalysts and supports for the transformation of synthesis gas (H_2 and CO) to obtain long-chain hydrocarbons, alcohols in the case of this project. Once we have determined the suitable photocatalytic materials (catalyst and substrate), we will propose theoretical models for the simulation of the catalyst. Two main groups will be considered: surfaces (supported on a substrate) and nanoparticles (adsorbed catalysts) which could be used in the experimental process. Forthcoming theoretical studies will clarify which of both alternatives is the optimum.

[1] Araujo-Ferrer, S. C.; De Almeida, A.; Zabala, A.; Granados, A. Uso de catalizadores en los procesos Fischer-Tropsch. *Revista mexicana de ingeniería química* **2013**, *12*, 257-269.
[2] Sharma, P.; Sasson, Y. A photoactive catalyst Ru–g-C3N4 for hydrogen transfer reaction of aldehydes and ketones. *Green Chemistry* **2017**, *19*, 844-852.
[3] Yang, C.; Zhao, H.; Hou, Y.; Ma, D. Fe5C2 Nanoparticles: A Facile Bromide-Induced Synthesis and as an Active Phase for Fischer–Tropsch Synthesis. *Journal of the American Chemical Society* **2012**, *134*, 15814-15821.
[4] Ponec, V. On the role of promoters in hydrogenations on metals; α,β-unsaturated aldehydes and ketones. *Applied Catalysis A: General* **1997**, *149*, 27-48.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101022202. This publication reflects only the author's views, and the European Union is not liable for any use that may be made of the information contained therein.

3. Methodology

Systematic bibliographic search.

4. Results

The development of photo-thermal processes for the synthesis of alcohols from the reduction of CO is a capable route for the conversion of CO_2. The development of new catalysts includes a wide range of organic and inorganic materials, nanoparticles such as Fe_5C_2[4] and metals as Au, Pd, Ag, carbon-based materials, metal oxides (Fe_3O_4, and TiO_2-x, etc.), metal sulfides (Cu_3BiS_3, Cu_9S_5, MoS_2) and composite materials ($Ag/MoS_2/TiO_2$-x, Fe_2O_3-NPS-Au) that have showed enhanced activity or selectivity in the FT processes.[4,5,6] An example is the Fe_5C_2 selectivity for CO molecule in hydrogenation reaction produced under photo-irradiation. Gao et al.[7] have shown high selectivity of the Fe_5C_2 with respect to Fe/Al_2O_3 (Table *1*).

Table 1. Catalytic Performance of Various Catalysts in the Photo-Driven FTO Reaction

Entry	Catalysts	Catalyst Bed Temperature (°C)[a]	CO Conversion (%)	CO_2 Selectivity (%)	Product Selectivity (%, CO_2-free)				Olefin/Paraffin Ratio
					CH_4	C_{2-4}=	C_{2-4}^0	C_{5+}	C_{2-4}
1	blank[b]	–	0	–	–	–	–	–	–
2	Fe/Al_2O_3	356	0.3	–	–	–	–	–	–
3	Fe_5C_2[c]	490	0	–	–	–	–	–	–
4	Fe_5C_2	490	49.5	18.9	33.1	55.5	5.1	6.3	10.9
5	Fe_5C_2(passivated)[d]	488	13.6	16.9	33.7	51.4	7.8	7.1	6.6
6	Fe_5C_2 (air treated)[e]	404	<0.1	–	–	–	–	–	–
7	Fe_5C_2 (H_2 treated)[f]	421	0.4	–	–	–	–	–	–
8	Fe_5C_2[g]	491	52.2	28.9	30.9	54.0	8.8	6.3	6.1

Reaction conditions: no external heating, catalyst mass 180 mg, CO/H_2 = 1/2, irradiation time 0.5 hr, 300-W Xe lamp.
[a]Monitoring of the catalyst bed temperature of various catalysts under photo-irradiation.
[b]Blank experiment; irradiation in the absence of any catalysts under above conditions.
[c]Reaction conditions: H_2/Ar (10/90), irradiation time 0.5 hr, 300-W Xe lamp.
[d]The fresh Fe_5C_2 catalyst was passivated with O_2/He (0.5/99.5) for 12 hr before reaction.
[e]The fresh Fe_5C_2 catalyst was calcined in air at 500°C for 2 hr before reaction.
[f]The fresh Fe_5C_2 catalyst was reduced in H_2/Ar (10/90) at 800°C for 5 hr before reaction.
[g]Reaction conditions: 180 mg, CO/H_2 = 1/3, irradiation time 0.5 hr, 300-W Xe lamp.

Table 1. Behaviour of the photocatalysts in the CO hydrogenation reaction[7]

[5] Zhao, T.; Xing, Z.; Xiu, Z.; Li, Z.; Chen, P.; Zhu, Q.; Zhou, W. Synergistic effect of surface plasmon resonance, Ti3+ and oxygen vacancy defects on Ag/MoS2/TiO2-x ternary heterojunctions with enhancing photothermal catalysis for low-temperature wastewater degradation. *Journal of Hazardous Materials* **2019**, *364*, 117-124.
[6] Ullattil, S. G.; Narendranath, S. B.; Pillai, S. C.; Periyat, P. Black TiO2 nanomaterials: a review of recent advances. *Chemical Engineering Journal* **2018**, *343*, 708-736.
[7] Gao, W.; Gao, R.; Zhao, Y.; Peng, M.; Song, C.; Li, M.; Li, S.; Liu, J.; Li, W.; Deng, Y. Photo-driven syngas conversion to lower olefins over oxygen-decorated Fe5C2 catalyst. *Chem* **2018**, *4*, 2917-2928.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101022202. This publication reflects only the author's views, and the European Union is not liable for any use that may be made of the information contained therein.

The use of novel photocatalysts could increase alcohol production and selectivity in the CO hydrogenation reaction.[8] On the other hand, the supporting structure for the catalyst has a great importance in the dispersion as well as the particle size and activity of the metal catalysts constituents. The main used supports are Al_2O_3, SiO_2 and TiO_2, which allow a high dispersion of the metal, maximizing the available surface area.[1] Titania is a support using for the FT reaction, owing to its semiconductor character, its high surface area for the active sites and also because of its good electronic and thermal properties.[9]

During the catalysts activation, different phases are produced. In the case of iron, these phases may include metallic iron, iron carbide and iron oxides, which co-exist under stable conditions.[10] Iron carbide is the responsible for the high activity of hydrocarbon production in FT reaction,[3, 11, 12] *i.e.* using Fe_5C_2 nanoparticles as catalysts, it is possible to obtain short chain olefins from a photothermal syngas conversion process.

5. Conclusions

According to previous experimental FTS processes, TiO_2 seems to be a good option as support for this process due to its semiconductor character with high surface area for the active site and also, because it has good electronic and thermal properties. As a catalyst candidate we propose Ni, Cu, Fe-ZnOx and Fe_5C_2 nanoparticles. These materials could produce an efficient catalytic system to the photothermal catalytic Fischer–Tropsch synthesis. The adsorption process and electronic properties will be explored by mean Density Functional Theory.

[8] Yang, H.; Lin, Q.; Zhang, C.; Yu, X.; Cheng, Z.; Li, G.; Hu, Q.; Ren, X.; Zhang, Q.; Liu, J.; He, C. Carbon dioxide electroreduction on single-atom nickel decorated carbon membranes with industry compatible current densities. *Nature Communications* **2020**, *11*, 593.
[9] Wang, L.; Zhang, Y.; Gu, X.; Zhang, Y.; Su, H. Insight into the role of UV-irradiation in photothermal catalytic Fischer–Tropsch synthesis over TiO2 nanotube-supported cobalt nanoparticles. *Catalysis Science & Technology* **2018**, *8*, 601-610
[10] Kölbel, H.; Ralek, M. The Fischer-Tropsch Synthesis in the Liquid Phase. *Catalysis Reviews* **1980**, *21*, 225-274.
[11] Zhai, P.; Xu, C.; Gao, R.; Liu, X.; Li, M.; Li, W.; Fu, X.; Jia, C.; Xie, J.; Zhao, M.; Wang, X.; Li, Y.-W.; Zhang, Q.; Wen, X.-D.; Ma, D. Highly Tunable Selectivity for Syngas-Derived Alkenes over Zinc and Sodium-Modulated Fe5 C2 Catalyst. *Angew Chem Int Ed Engl* **2016**, *55*, 9902-9907.
[12] Yang, C.; Zhao, B.; Gao, R.; Yao, S.; Zhai, P.; Li, S.; Yu, J.; Hou, Y.; Ma, D. Construction of Synergistic Fe5C2/Co Heterostructured Nanoparticles as an Enhanced Low Temperature Fischer–Tropsch Synthesis Catalyst. *ACS Catalysis* **2017**, *7*, 5661-5667.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101022202. This publication reflects only the author's views, and the European Union is not liable for any use that may be made of the information contained therein.