

Summary

Dear Editor,

Thank you very much for your letter and comments from reviewers. These comments are all valuable and very helpful for revising and improving our manuscript, and also provide important guidance to our research. We have studied the comments carefully and made corrections on the unsatisfying issues pointed out by the reviewers, which we hope will meet with your approval.

We have addressed the comments raised by the reviewers, and highlighted the amendments in **red font** in the revised manuscript. The point-by-point responses to the reviewers' comments are listed below in this letter.

We appreciate for you and Reviewers' warm work earnestly, and hope that the correction will meet with approval.

Thank you very much for your attention and consideration.

Sincerely yours,

Zhijiang Ni

Changzhou University

Point-by-point response to Comments and Suggestions for Authors-reviewer 3

- 1) For the equation in line 123, the authors should explain what each term is, or just write the Scherrer equation. Please explain which peak and diffraction angle was used to calculate the particle size. Also, show the peak deconvolution done to calculate the particle size.

Response: Thank you for your valuable comments. The phase of the catalyst was identified by XRD test, and the approximate size of the average particle size was calculated by the $D = K\lambda / (B \cos \theta)$ [1], where K , B , θ , λ are the Scherrer constant, the half peak width or integral width of the measured sample diffraction peak, the Bragg angle and the wavelength.

XRD analysis of the powders shows well-defined Bragg reflectance features of Fe_2O_3 . According to the XRD pattern of Fe_2O_3 within the 2θ range from 10° to 80° , the Fe_2O_3 phase can be seen. Moreover, the XRD pattern corresponded to reference code 96–900–9769 that the sharp peak with high intensity related to (311) appears at $2\theta = 35.225^\circ$, which confirms the Fe_2O_3 structure [1].

[1] S. Nasiri, M. Rabiei, A. Palevicius, G. Janusas, A. Vilkauskas, V. Nitalapati, A. Monshi, Modified Scherrer equation to calculate crystal size by XRD with high accuracy, examples Fe_2O_3 , TiO_2 and V_2O_5 , Nano Trends, 3 (2023).

- 2) Line 113: “the reaction conditions are 400 °C, 0.35 MPa, and the airspeed 113 is 2500 mL/(g*h).” What is airspeed? The reduction was not done under air!

Response: The reviewer’s idea was well taken and such changes were made: Before the formal reaction, the reduction operation is carried out, the hydrogen cylinder is connected, and the reaction is determined to be 18 hours under the premise that the whole system is not leaking, and the reaction conditions are 400 °C, 0.35 MPa, and at a flow rate of 2500 mL/g.h. Subsequently, $\text{CO}_2/\text{H}_2/\text{N}_2$ mixture cylinders (mixing ratio of 23/69/8) and argon cylinders are connected, nitrogen is used as standard gas, and argon is used as support gas. The catalytic reaction conditions were temperature 300°C, pressure 2.5 MPa, and at a flow rate of 1500 mL/g.h.

- 3) Please provide the XRD for the following samples, $\text{SiO}_2\text{-C}$, $\text{ZnO/SiO}_2\text{-C}$, $\text{Na/SiO}_2\text{-C}$, these will be good reference controls.

Response: The reviewer’s idea was well taken and such changes were made:

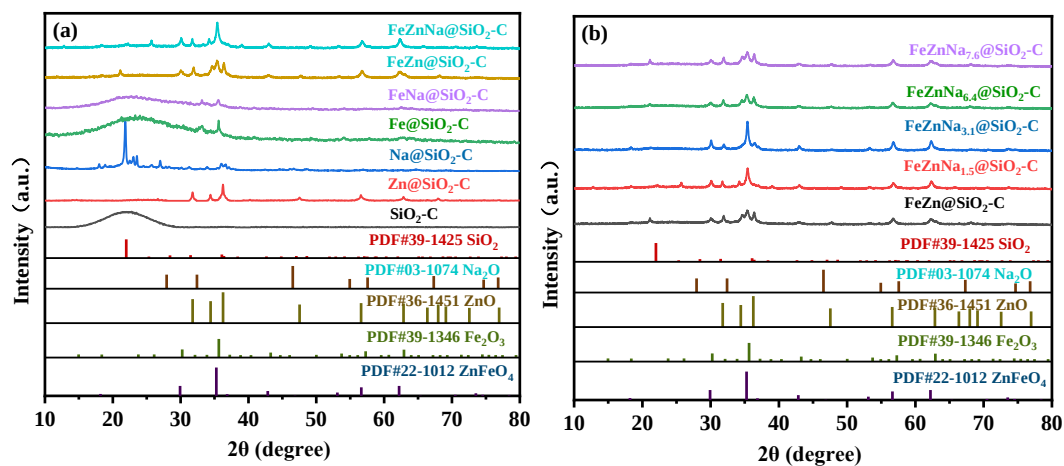


Figure 1. XRD pattern of (a) SiO₂-GC, Zn@SiO₂-C, Na@SiO₂-C, Fe@SiO₂-C, FeNa@SiO₂-C and FeZn@SiO₂-C catalysts, (b) FeZnNa_x@SiO₂-C catalysts with different Na doping.

4) Please use ONLY TWO SIGNIFICANT figures for the data provided in the tables.

Response: Thank you for your valuable comments. We have merged the contents of Table 1 and Table 2 for convenience.

Table 1. Physicochemical characteristics of the Fe@SiO₂-C, FeNa@SiO₂-C and FeZnNa_x@SiO₂-GC catalysts

Catalyst	Fe loading ^a (wt%)	Na loading ^a (wt%)	Fe ₂ O ₃ size ^b (nm)	SSA ^c (m ² /g)	PV ^c (cm ³ /g)	APS ^c (nm)
Fe@SiO ₂ -C	25.4	0	23	75.579	0.087	3.19
FeNa@SiO ₂ -C	24.2	1.5	33	78.41	0.111	4.189
FeZn@SiO ₂ -C	25.3	0	15	48.519	0.144	4.199
FeZnNa _{1.5} @SiO ₂ -C	23.7	1.5	21	9.261	0.035	4.46
FeZnNa _{3.1} @SiO ₂ -C	23.5	3.1	23	16.427	0.035	2.951
FeZnNa _{6.4} @SiO ₂ -C	22.1	6.4	16	20.572	0.047	2.956
FeZnNa _{7.6} @SiO ₂ -C	23.4	7.6	18	14.691	0.035	2.952

^a measured by XRF

^b measured with the Scherrer equation by XRD

^c measured by N₂ physical adsorption

5) With the increase in Na loading the particle size does not increase significantly, so it will be good to not use strong adjectives like “significantly” in line 127.

Response: The reviewer’s idea was well taken and such changes were made: The results indicate that the Na promoter increases the size of Fe species over FeZn/Fe catalysts.

6) Line 132-133: “With the increase of Na content, the particle size of Fe₂O₃ generally showed a trend of first decreasing, and finally rising”. Did the authors run a repeat to confirm this trend, if not then this claim is weak.

Response: Based on the comments of the reviewers, we have conducted another XRD on the sample and found that its trend has not changed. The specific results are shown in **Figure 1**, the Fe₂O₃ size in FeZn@SiO₂-C catalysts evaluated by the Scherrer equation ($D = K \cdot \gamma / (B \cdot \cos \theta)$) formula) was ~ 15 nm respectively, much smaller than those of the Fe@SiO₂-C (~ 23 nm), FeNa@SiO₂-C (~ 33 nm) and FeZnNa_x@SiO₂-C (~20 nm), Which indicate that the Zn promoter significantly decreases the size of Fe species over Fe catalysts. However, the addition of Na changes the particle size of the phase in the FeZnNa_x@SiO₂-GC catalysts. With the increase of Na content, the particle size of Fe₂O₃ generally showed a trend of first increasing and then decreasing. Thus, the trend of the particle size of Fe₂O₃ in the FeZnNa_x@SiO₂-GC catalysts was attributed to the bifunctional effect of Zn and Na.

7) In Table 1 please provide metal weight loading for each catalyst, it will be convenient for the reader to refer to it while reading the article. Provide the SSA of SiO₂-C.

Response: Thank you for your valuable comments. We have merged the contents of Table 1 and Table 2 for convenience.

Table 1. Physicochemical characteristics of the Fe@SiO₂-C, FeNa@SiO₂-C and FeZnNa_x@SiO₂-GC catalysts

Catalyst	Fe loading ^a (wt%)	Na loading ^a (wt%)	Fe ₂ O ₃ size ^b (nm)	SSA ^c (m ² /g)	PV ^c (cm ³ /g)	APS ^c (nm)
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^a measured by XRF

^b measured with the Scherrer equation by XRD

^c measured by N₂ physical adsorption

8) It is important to provide the CO₂ uptake (umol/g) for these catalysts, obtained from CO₂ TPD, to make claims like the one in Lines 185-186: “The smaller the size of the metal, the larger its surface area and the 185 more CO₂ it adsorbs”. The reviewer expects to see these numbers.

Response: Thank you for your valuable comments. We have made modifications to the CO₂-TPD spectrum and marked the positions of the relevant peaks in Figure 6 and Table 2.

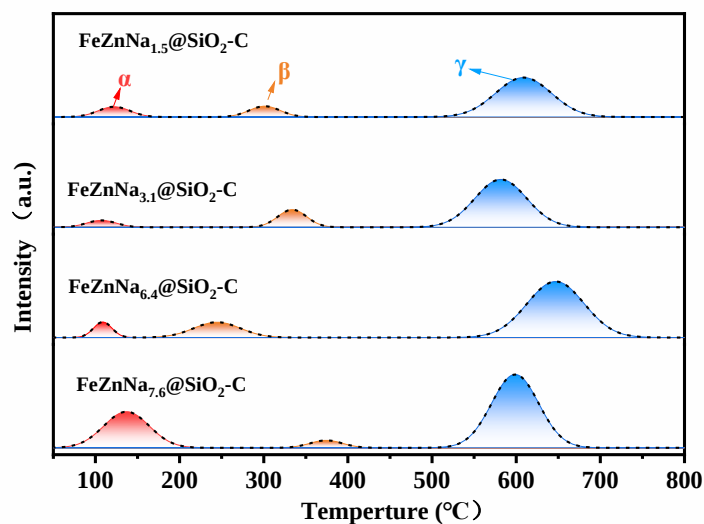


Figure 6. CO₂-TPD profiles of the FeZnNa_x@SiO₂-GC catalysts with different Na doping in 50-800 °C

Table 2. CO₂ uptake feature of the FeZnNa_x@SiO₂-GC catalysts with different Na doping

Catalysts	The amount of CO ₂ desorbed (umol/g)			
	α peak	β peak	γ peak	Total

FeZnNa _{1.5} @SiO ₂ -C	58.5	60.4	396.4	515.3
FeZnNa _{3.1} @SiO ₂ -C	36.6	91.3	446.0	573.9
FeZnNa _{6.4} @SiO ₂ -C	51.4	128.6	576.7	756.6
FeZnNa _{7.6} @SiO ₂ -C	295.4	43.1	621.7	960.2

9) The TEM image quality is low and the resolution is poor, please provide the particle size distribution chart, to make any claim about the average particle size. Can authors provide STEM-EDX for a few catalysts with high and low activity?

Response: Thank you for your valuable comments. We have replaced with higher quality images in the Figure 2, and provided the particle size distribution chart in the Figure 2a, c, e, g.

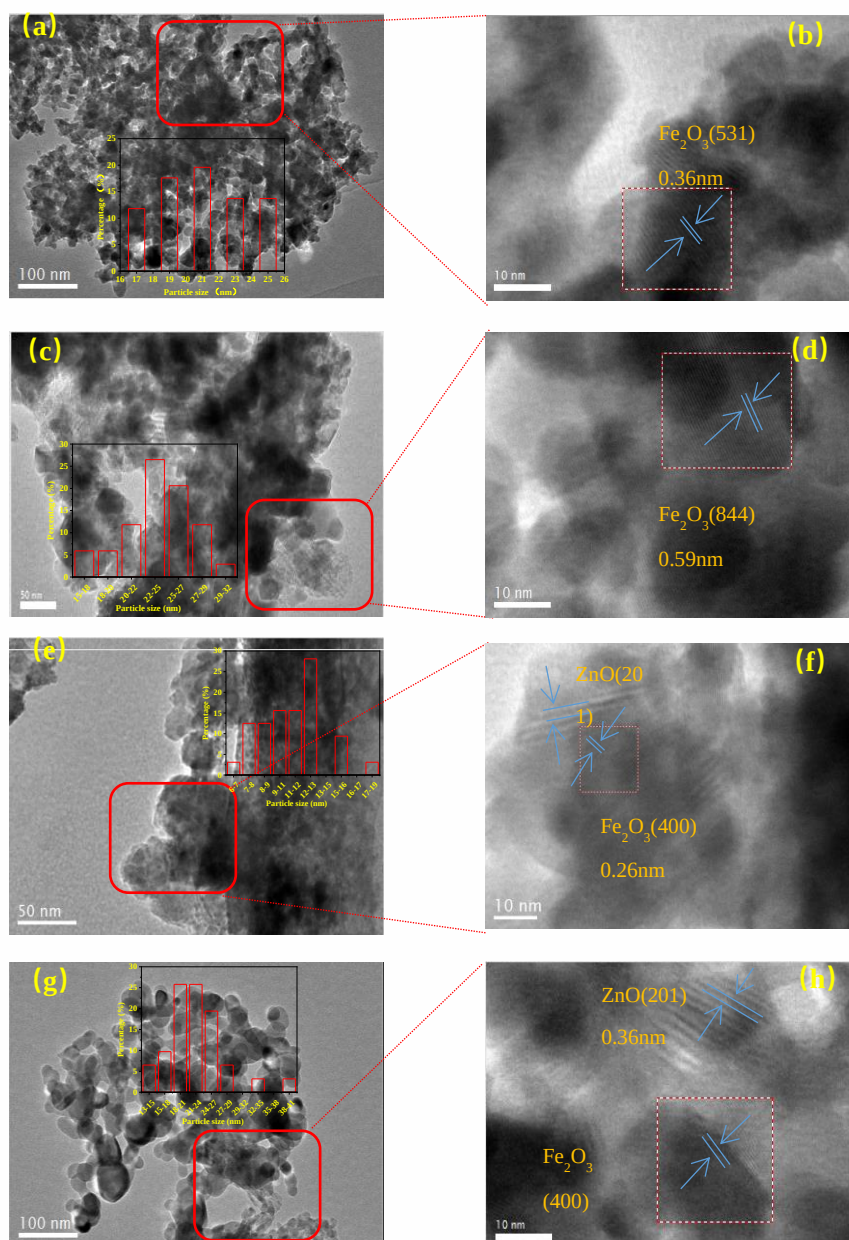


Figure. 2 TEM images and High-resolution TEM images of (a) and (b) $\text{FeZnNa}_{1.5}@\text{SiO}_2\text{-GC}$, (c) and (d) $\text{FeZnNa}_{3.1}@\text{SiO}_2\text{-GC}$, (e) and (f) $\text{FeZnNa}_{6.4}@\text{SiO}_2\text{-GC}$, (g) and (h) $\text{FeZnNa}_{7.6}@\text{SiO}_2\text{-GC}$

10) Why is the SSA data duplicated in both Tables 2 and 3?

Response: Thank you for your valuable comments. We have merged the contents of Table 2 and Table 3 for convenience.

11) Please provide DETAILED information on how each catalyst characterization was done.

Response: In this study, Fe-based catalysts with accurately controlled amounts of Na are successfully synthesized by incipient wetness impregnation method, which allows systematic and quantitative investigation of the inherent relationship between the catalyst promotion and the corresponding performances. The effect of Na on the structure of the catalysts and their performance in CO₂ hydrogenation to alkenes reaction has been explored in detail. The analysis of XRD, XPS, CO₂-TPD spectroscopy reveals the relationship between the amount of Na and the generation and stability of Fe₅C₂ in the catalyst. The findings through this systematic study may shed light to how to enhance the catalytic performance by modulation of the promoter effect and provide scientific guidance to design sophisticated novel catalyst systems.

12) Did the authors do air-free XPS for the catalyst? Authors do not have enough data to make this claim, “Among them, the existence of C-O bonds 222 indicates that there may be close interactions between C-Fe₂O₃-SiO₂ in the form of C-O- 223 Fe/Fe-C-O or C-O-Si”, C-O can be from the adsorbed CO₂ from the air, graphitic carbon, the XPS for reference samples are missing, without those data it difficult to agree with authors discussions and conclusions.

Response: Thank you for your valuable comments. We have made modifications to the XPS spectrum and marked the positions of the relevant peaks, as shown in Figure 4a indicated that the introduction of Na promoter leads to a lower binding energy of Fe 2p_{3/2} of FeZnNa_x@SiO₂-GC catalyst.

13) I have similar comments for H₂-TPR, please provide the data for reference samples, like SiO₂-C, FeO_x/SiO₂-C, etc. Without these data, it is difficult to appreciate the discussion. Also, for FeZnNa_{3.1} there is a small shoulder around 1200 K, what is this peak? Authors should also do a peak deconvolution to properly identify the reduction temp, rather than marking the maxima of the TPR profile.

Response: Thank you for your valuable comments. We have made modifications to the H₂-TPR spectrum and marked the positions of the relevant peaks in Figure 5. When compared to the TPR profile of purified SiO₂-C support, the second reduction peak at 890 °C for the FeZnNa_{3.1}@SiO₂-C can be attributed to the catalytic decomposition of the support. As for the peaks located at the high-temperature region (>550 °C), which were related to the reduction of Fe³⁺ species to Fe⁰, a shift

to high temperature and a increase in their intensities were noticed in $\text{FeZnNa}_x\text{@SiO}_2\text{-C}$ catalysts and this could be attributed to a stronger interaction between the iron oxides and the $\text{SiO}_2\text{-C}$ support, as suggested by the XPS results.

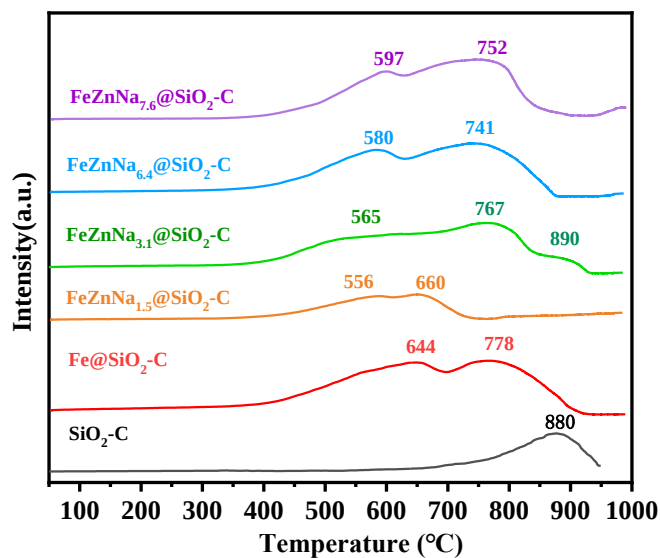


Figure 5. H_2 -TPR profiles of the $\text{SiO}_2\text{-C}$, $\text{Fe@SiO}_2\text{-C}$ and $\text{FeZnNa}_x\text{@SiO}_2\text{-C}$ catalysts

14) Please provide the catalyst stability data, by providing the TOS data for CO_2 conversion

Response: Thank you for your valuable comments. The variations of CO_2 conversion with time on stream (TOS) for the $\text{FeZnNa}_x\text{@SiO}_2\text{-GC}$ catalysts with different Na content are shown in Figure 6.

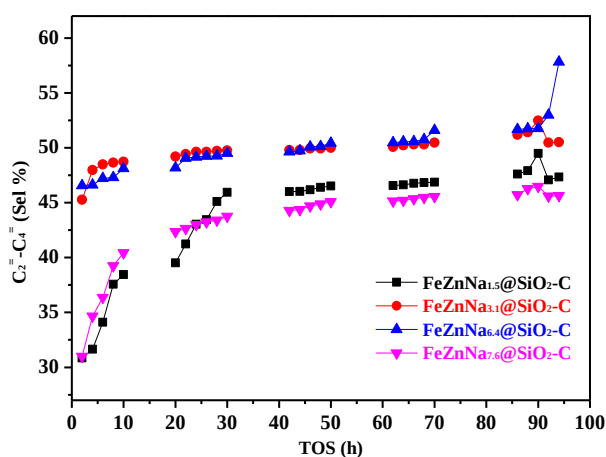


Figure10. Change in CO_2 conversion with time on-stream for the $\text{FeZnNa}_x\text{@SiO}_2\text{-C}$ catalysts.

15) What is the active site for this reaction, please provide the TOF for these catalysts and compare it with the other catalysts from literature.

Response: Thank you for your valuable comments. As mentioned by the reviewer, Hägg iron carbide (Fe_5C_2) was the active site for CO_2 hydrogenation, and the data of TOF (the density of Fe_5C_2 and assuming 14 Fe atoms/ nm^2) have been added in Table 3. Meanwhile, we had add some comparison with other related reports in the manuscript.

Compared with $\text{FeZnNa}_{1.5}@\text{SiO}_2\text{-C}$, $\text{FeZnNa}_{3.1}@\text{SiO}_2\text{-C}$ and $\text{FeZnNa}_{7.6}@\text{SiO}_2\text{-C}$, $\text{FeZnNa}_{6.4}@\text{SiO}_2\text{-C}$ exhibited higher CO_2 conversion, which probably had appropriate particle sizes and surface areas, providing more active sites and thereby increasing the CO_2 hydrogenation catalytic activity. Moreover, it is noteworthy in Table 3 that turnover frequencies for CO_2 conversion (TOF) for the $\text{FeZnNa}_x@\text{SiO}_2\text{-C}$ catalyst ($3.51 \times 10^{-3} \text{s}^{-1}$) is substantially higher than those over FeSb ($3.6 \times 10^{-5} \text{mol/g}\cdot\text{s}$), FeBi ($3.2 \times 10^{-5} \text{mol/g}\cdot\text{s}$)[2]. Although a higher TOF is reported to be $3.6 \times 10^{-5} \text{mol/g}\cdot\text{s}$ over FeSb, it should be noted that the value was obtained by addition of promoter Sb. All of these indicate that the catalysts (addition of promoters such as Na, Sb and Bi) that obviously promote TOF and STY, but Na was the lowest cost in all of the above promoters.

Table 3. Comparison of CO_2 hydrogenation Catalytic Performances: STY, selectivity of CH_4 , $\text{C}_2\text{-C}_4$ olefins ($\text{C}_2^=-\text{C}_4^=$), $\text{C}_2\text{-C}_4$ paraffins ($\text{C}_2^0\text{-C}_4^0$) and C_{5+}

Catalyst	CO_2 Con(%)	Selectivity ^b (%)				O/P ^c	TOF ^d (10^{-5} $\text{mol/g}\cdot\text{s}^{-1}$)	STY
		CH_4	$\text{C}_2^=-\text{C}_4^=$	$\text{C}_2^0\text{-C}_4^0$	C_{5+}			
$\text{Fe}@\text{SiO}_2\text{-C}$	52.17	83.06	5.93	5.59	5.45	1.06	3.14	0.0057
$\text{FeZn}@\text{SiO}_2\text{-C}$	53.78	64.32	1.54	30.87	3.29	0.05	3.23	0.0015
$\text{FeNa}@\text{SiO}_2\text{-C}$	52.26	66.56	6.48	20.23	8.33	0.32	3.14	0.0090
$\text{FeZnNa}_{1.5}@\text{SiO}_2\text{-C}$	58.41	22.89	29.15	14.50	33.42	2.01	3.51	0.0315
$\text{FeZnNa}_{3.1}@\text{SiO}_2\text{-C}$	59.03	33.00	29.40	13.67	23.83	2.15	3.55	0.0321
$\text{FeZnNa}_{6.4}@\text{SiO}_2\text{-C}$	58.32	18.30	40.40	9.60	31.69	4.21	3.51	0.0436
$\text{FeZnNa}_{7.6}@\text{SiO}_2\text{-C}$	58.4	18.63	41.07	8.68	31.72	4.73	3.51	0.0400

Reaction condition: T = 300 °C, P = 2.5 MPa, $\text{H}_2/\text{CO}_2 = 3$, GHSV = 1.5 L/g.h, TOS = 100 h; Reduced in 5% H_2/Ar for 16 h at 400 °C before CO_2 hydrogenation.

^b Hydrocarbon selectivity was normalized with the exception of CO.

^c O/P is the molar ratio of olefin (C₂=-C₄=) to paraffin (C₂⁰-C₄⁰).

^d TOF: turnover frequencies for CO₂ conversion, i.e. the number of CO₂ molecules converted per surface catalytic site per second at present CO₂ hydrogenation.

[2] A.J. Barrios, D.V. Peron, A. Chakkingal, A.I. Dugulan, S. Moldovan, K. Nakouri, J. Thuriot-Roukos, R. Wojcieszak, J.W. Thybaut, M. Virginie, A.Y. Khodakov, Efficient Promoters and Reaction Paths in the CO₂ Hydrogenation to Light Olefins over Zirconia-Supported Iron Catalysts, ACS Catalysis, 12 (2022) 3211-3225.