Carbon nanosheets supported iron oxide for Fischer-Tropsch to olefins synthesis

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ACS Spring 2019, April, 2019

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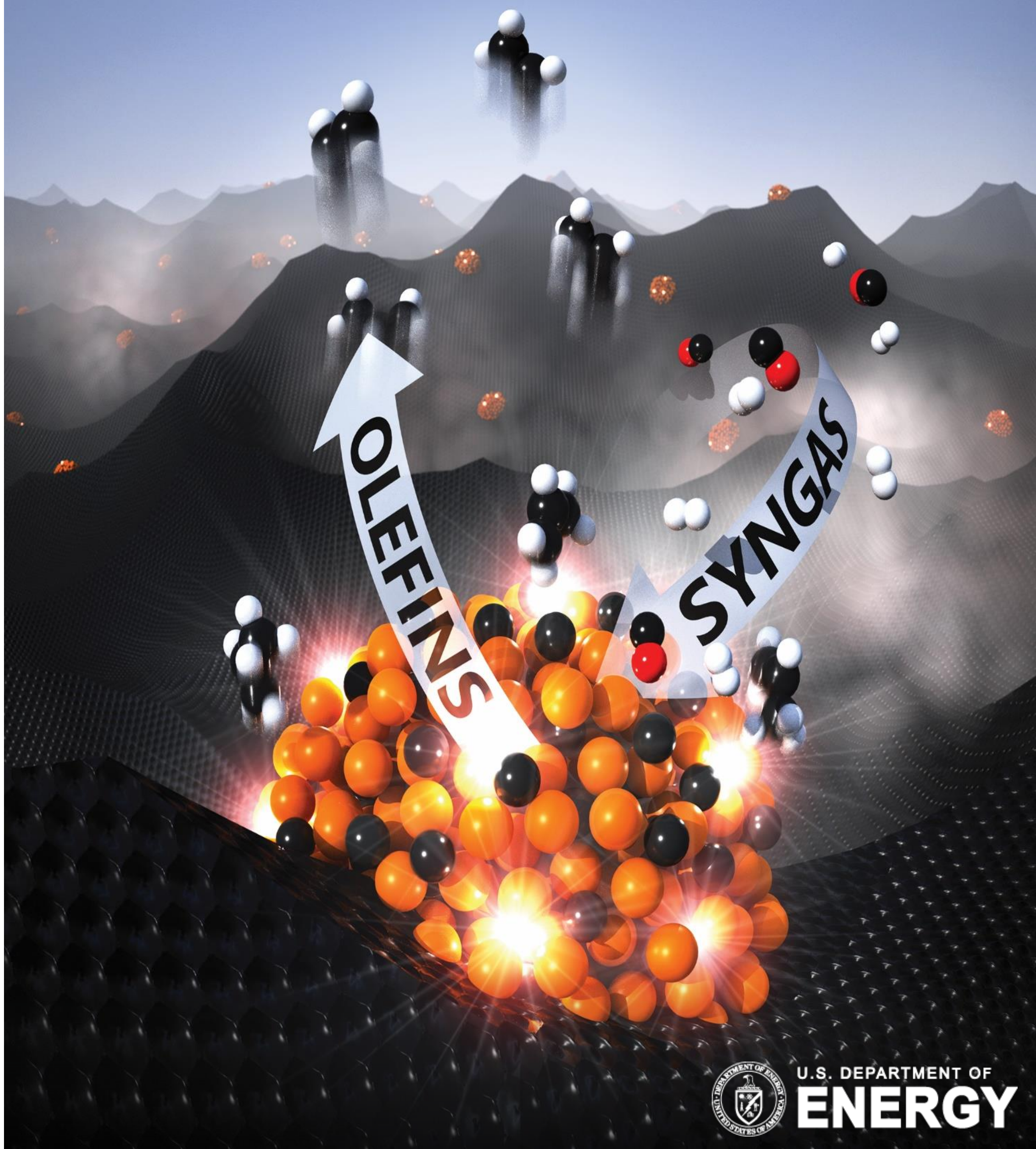

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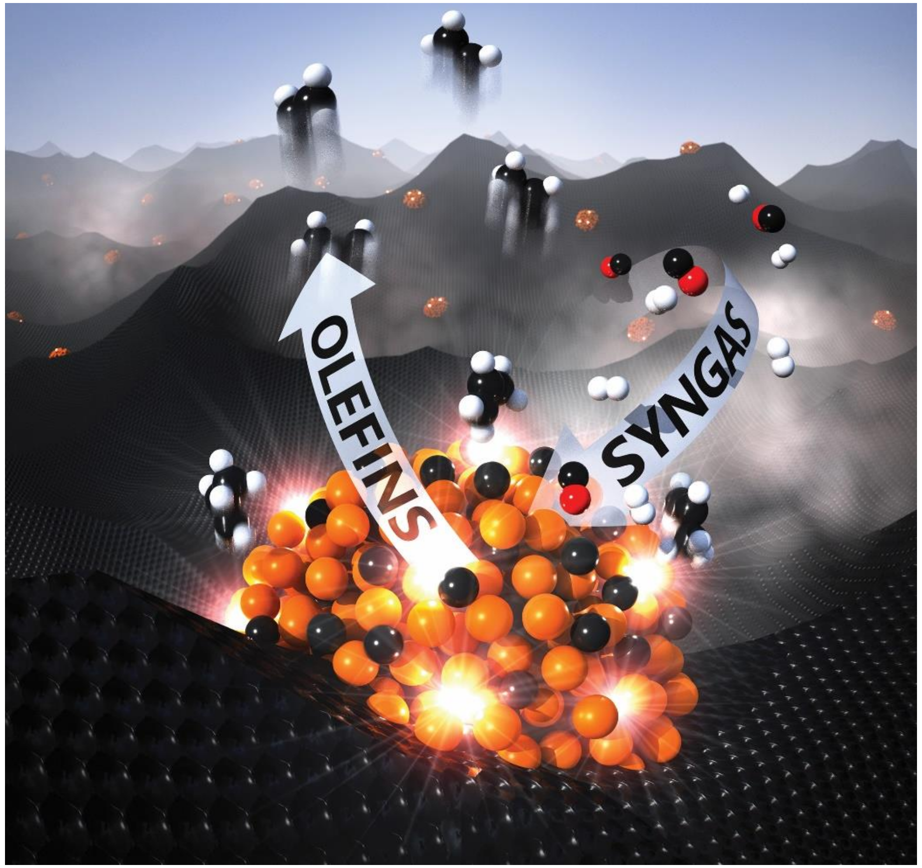
Outline

- **Introduction**
- **Carbon nanosheets supported Fe-based FTO catalysts**
  - Synthesis
  - Activity testing
  - Characterization
- **Summary and future work**



Fischer-Tropsch Synthesis

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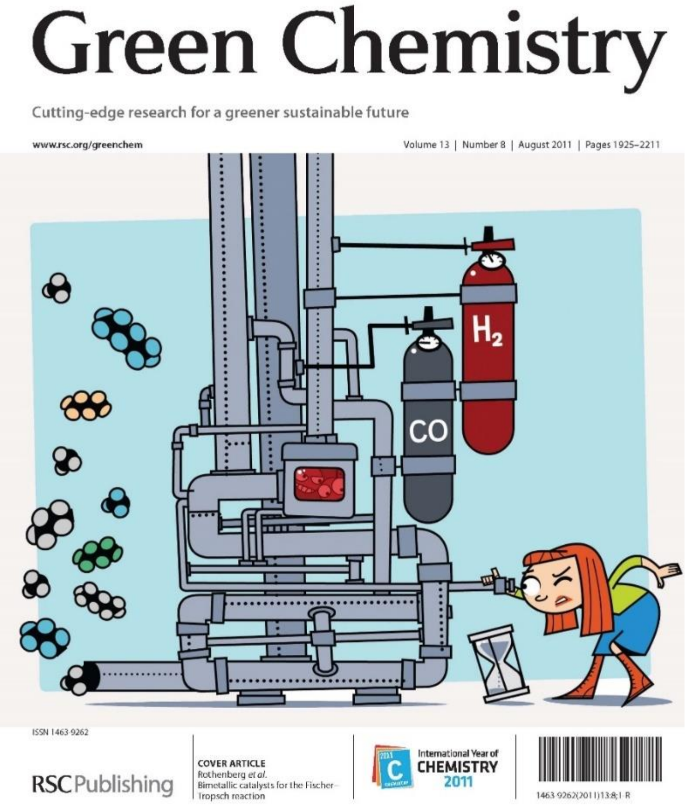


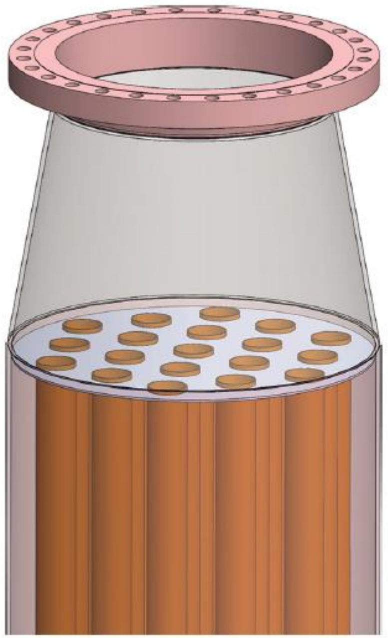


Figure 3. Multi-tube ~137 cm FT reactor (19 × 10 cm D × 6.5 m L); ~30 BPD (~4770 L/day).

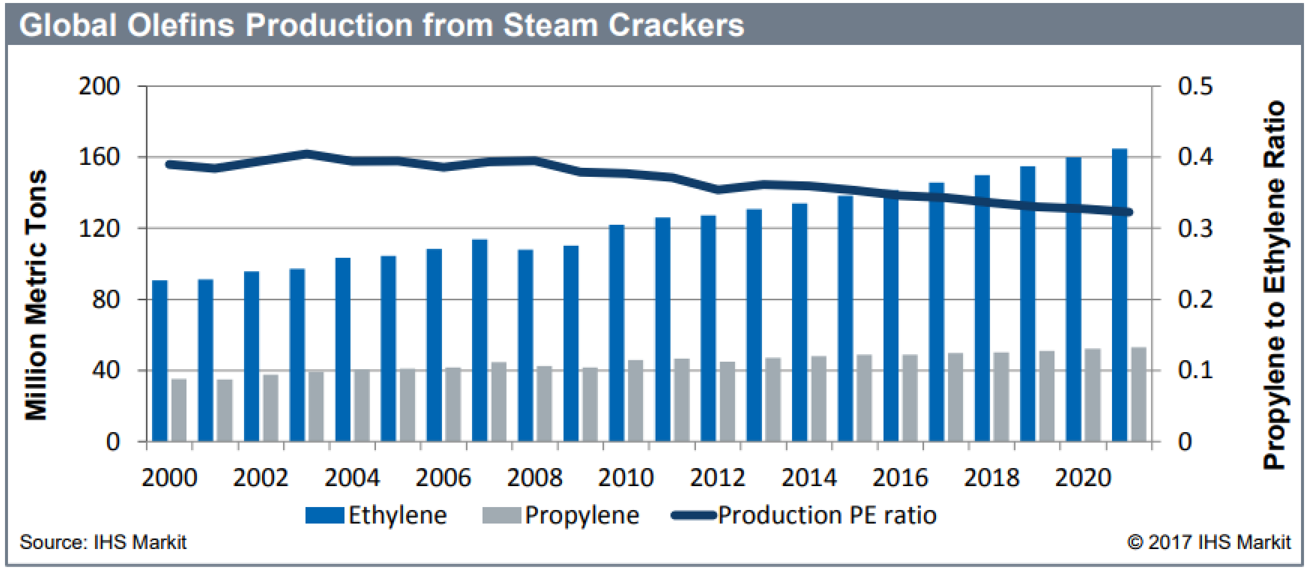
Sustainable method to produce ultraclean liquid fuels and chemicals from coal, natural gas and biomass, reducing dependence on petroleum.

The FT processes and catalysts are especially suitable for modular catalysis systems with enhanced mass and heat transfer properties.

FT catalysis is one of the most complex catalytic processes and understanding the reaction mechanism and catalyst property is also of tremendous scientific and practical value.

Frost, L. *et al.*, *Candian J. Chem. Eng.* **2016**, *94*, 636; Ceramatec Inc.

Fischer-Tropsch to Olefins Synthesis



Shell $6B ethylene cracker with polyethylene derivatives unit, under construction near Pittsburgh, PA

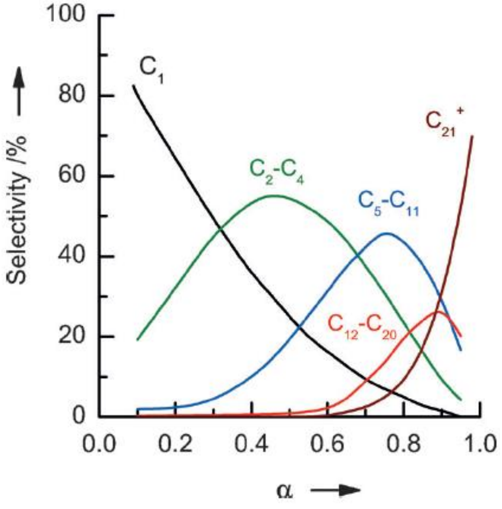
FT to olefins process (FTO) is the only technologically available method* to synthesize industrially important light olefins ($C_2^= – C_4^=$) directly from syngas, which can improve sustainability and reduce the dependence on petroleum for these chemicals.

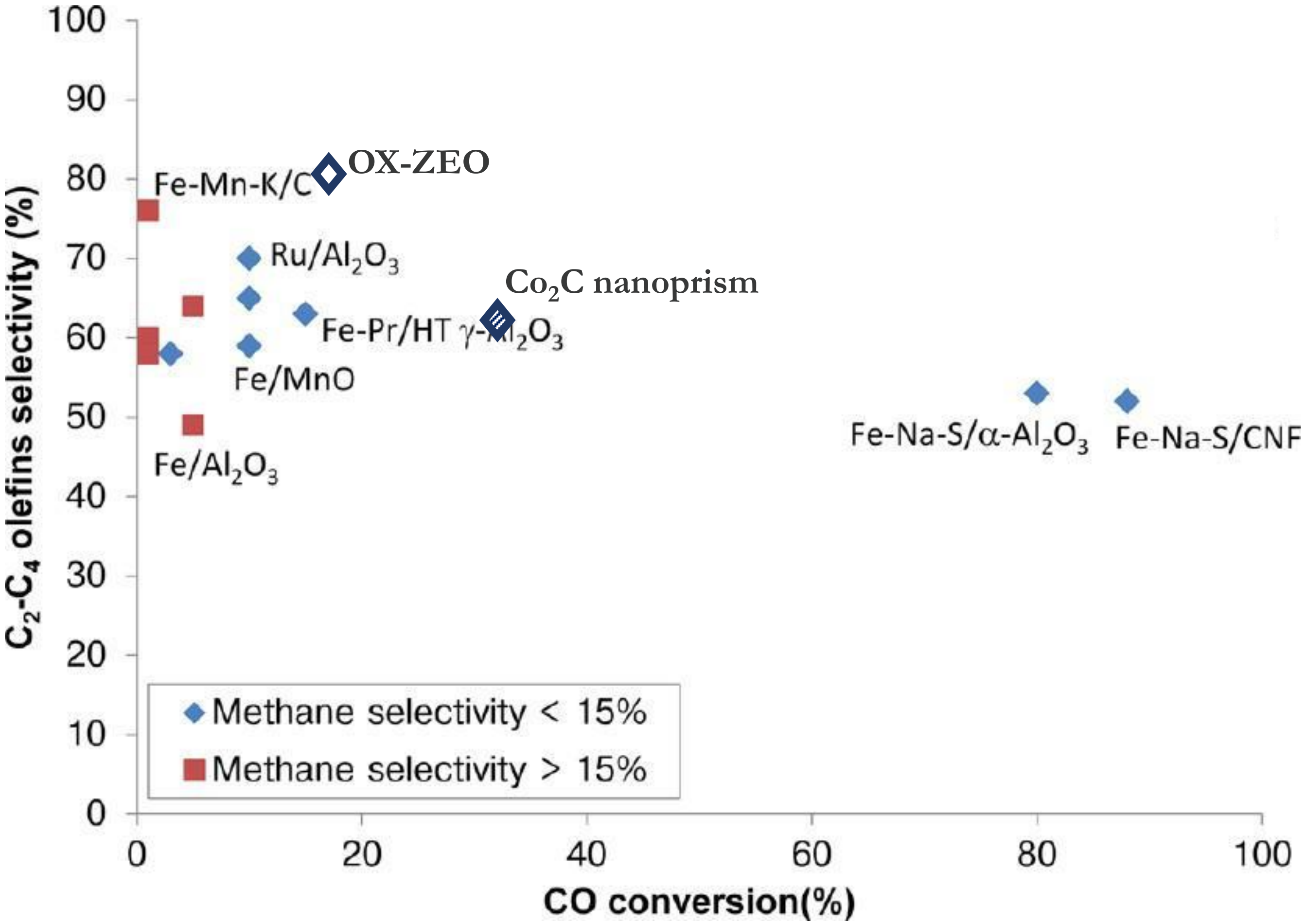
*There are hybrid processes using composite catalysts, e.g., the OX-ZEO process reported in *Science* 351, 1065 (2016) as well as recently developed Co based catalyst *Nature* 538, 84 (2016).

Steam cracking is one of the most energy-consuming processes in the chemical industry.

Challenges for FTO Synthesis

- **Selectivity**
  - Anderson-Schulz-Flory product distribution
  - Undesired products such as methane and CO_2
- **Activity**
- **Stability**





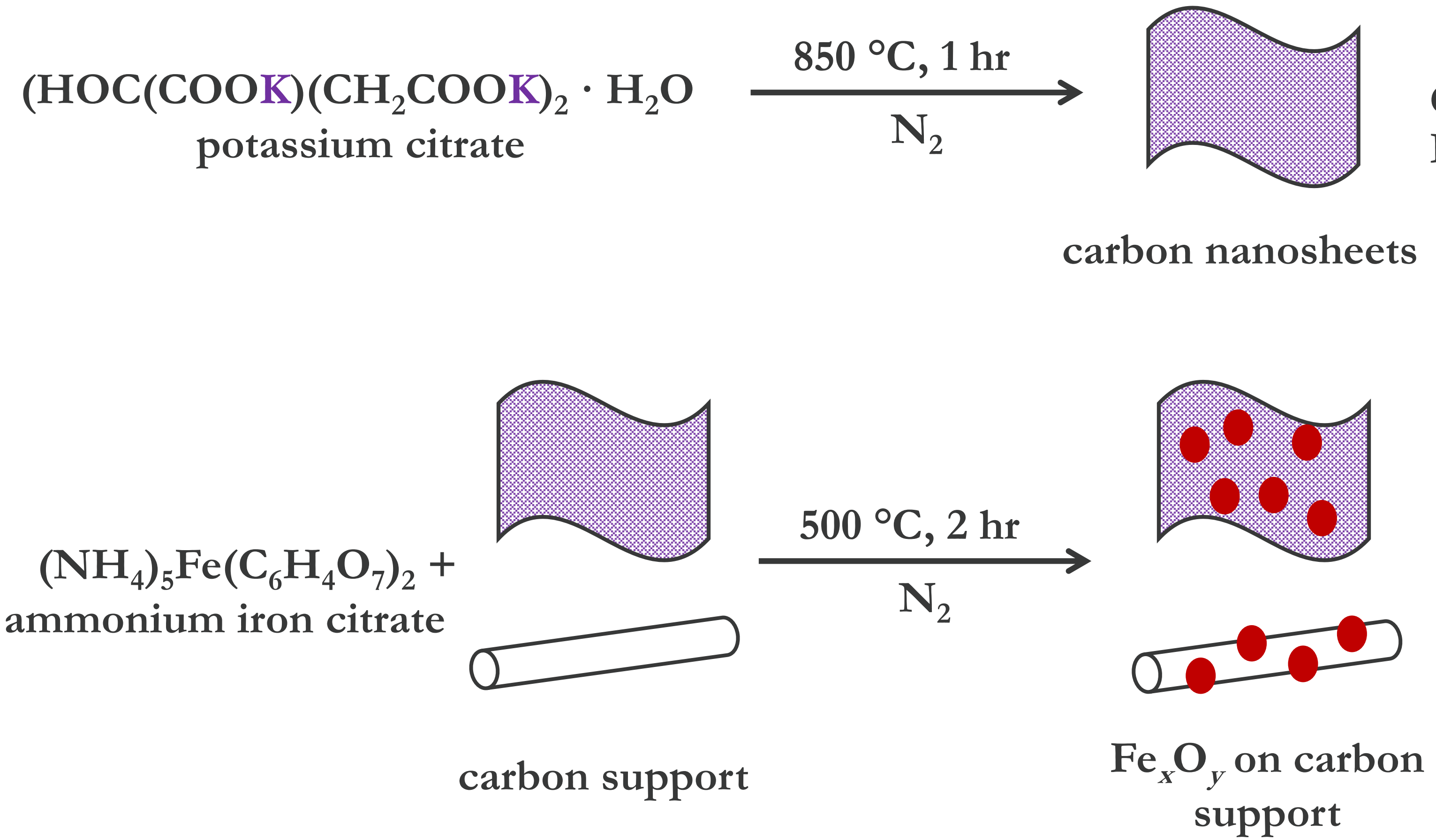
Q. Zhang, *et al.*, *ChemSusChem.* **7**, 1251 – 1264, (2014); H. M. Torres Galvis, K. P. de Jong, *ACS Catal.* **3**, 2130 (2013); H. M. Torres Galvis, *et al.*, *Science* **335**, 835 (2012); F. Jiao, *et al.*, *Science* **351**, 1065 (2016); L. Zhong, *et al.*, *Nature* **538**, 84 (2016).

Iron-based FT Catalysts

- **Advantages**
  - Inexpensive and abundant
  - High olefins selectivity
  - High reverse water gas shift reaction activity
  - One of the commercial FT catalysts
- **Disadvantages**
  - Coking
  - Formation of complex, sometimes inactive, phase during reaction

Catalyst Synthesis

Selection of catalyst support materials

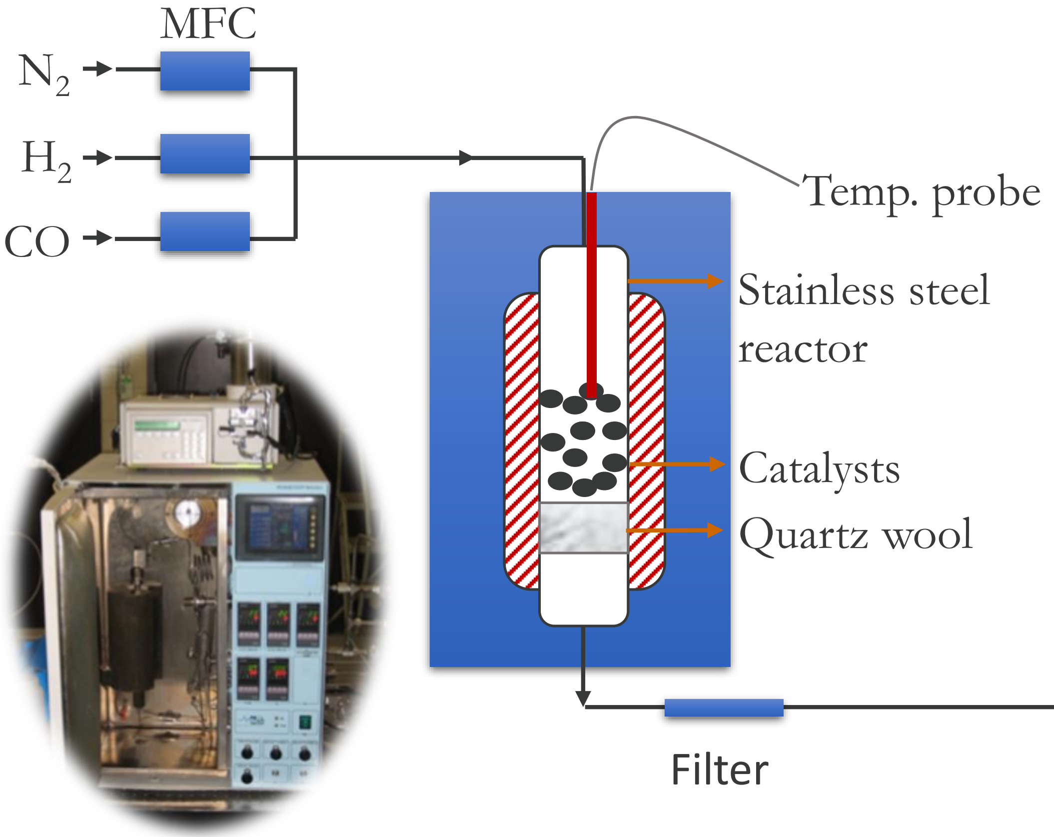


Carbon support materials have been used for FT synthesis catalysts

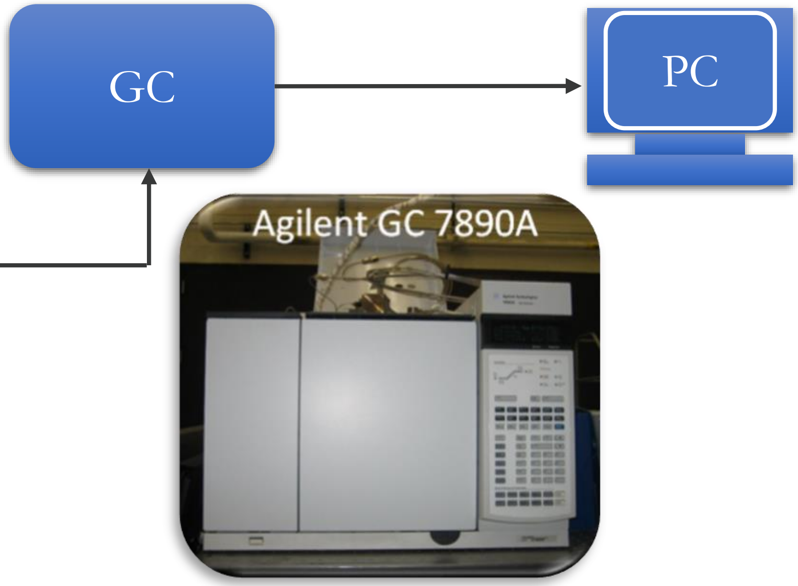
- Chemically inert – weak interaction with iron species (enhanced reducibility of iron species while preserving the integrity of catalyst particles under reaction conditions)
- Easily tailored to have high surface area
- Tunable pore structure
- Excellent thermal conductivity
- Potassium precursor

H. M. Torres Galvis, *et al.*, *Science* **335**, 835 (2012); C. Yang, *et al.*, *J. Am. Chem. Soc.* **134**, 15814 (2012); M. Cassavola, *et al.*, *Adv. Funct. Mater.* **25**, 5309 (2015); M. Sevilla, A. B. Fuertes, *ACS Nano* **8**, 5069 (2014).

FTO Catalyst Activity Testing



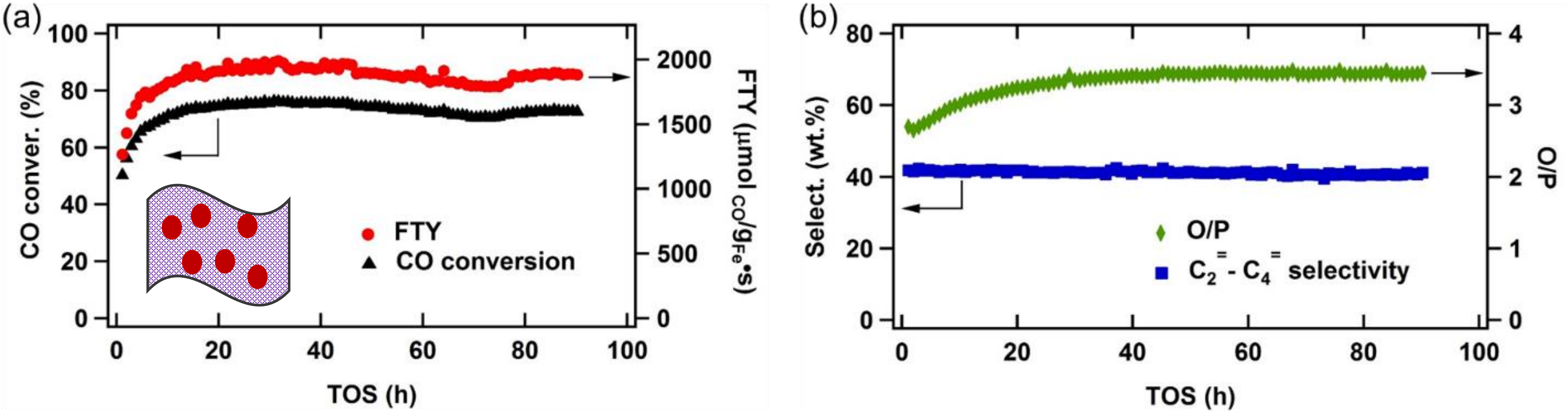
MS-13X column & TCD: CO, H_2, N_2, CH_4
Hayesep Q & FID: CO_2, C_2-C_5
Methanizer for CO detection in ppm levels



Catalysts pretreatment: H_2 @ 400℃ for 3 h, 50 SCCM
FTO Reaction conditions: 350 °C, 20 bar, $CO/H_2/N_2$= 45:45:10, 100 SCCM, W_{cat} = 200 mg, WHSV = 30000 $cc/g_{cat}/h$

Highly Active and Robust FTO Catalyst

Exceedingly high FTY and excellent selectivity for Fe_xO_y supported on CNS



Catalysts can be repeatedly used and remain robust for up to > 500 hrs on stream.

Y. Zhou, *et al.*, *ChemCatChem*, in press (2019).
U. S. Provisional Patent Application No. 62/792,051.

High Performance FTO Catalyst

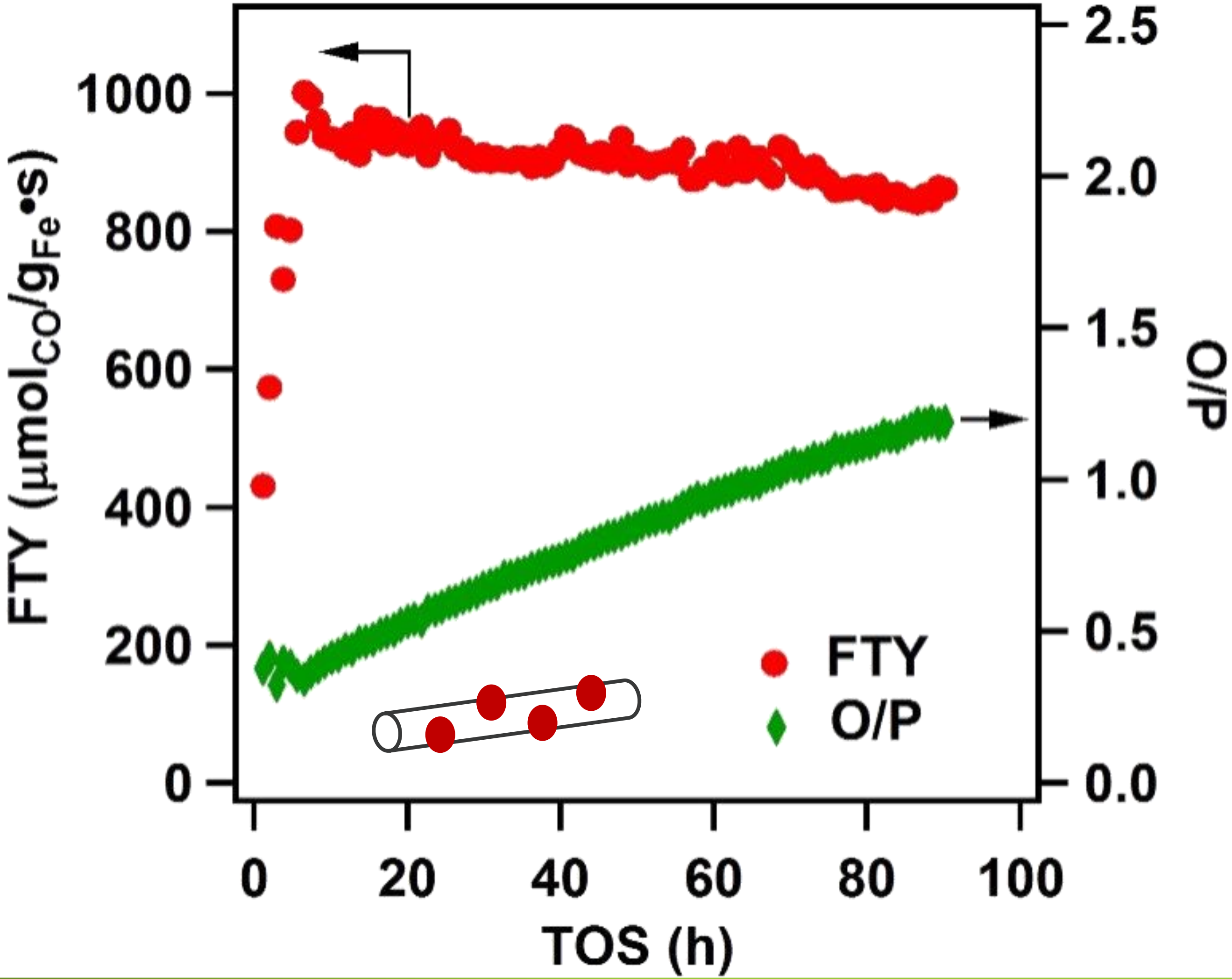
Sample	TOS (h)	CO Conversion (%)	FTY ($\mu mol_{CO}/g_{Fe} \cdot s$)	Selectivity (%wt.)			
				CH_4	C_2-C_4	$C_2^=$-$C_4^=$	C_5^+
Fe_xO_y/CNS	**90**	**72.6**	**1882**	**29.9**	**53.5**	**41.2**	**16.6**
Fe_xO_y/CNT	90	42.1	861	29.7	61.0	22.4	9.0
1K-Fe_xO_y/CNT	10	4.1	89.2	26.3	64.5	54.4	9.1
Fe-Cu-K-SiO_2	18	52.3	161	47.1	47.5	26.0	6.4
Fe_2O_3/CNF[1]	64	88	29.8	13 (%C)	64 (%C)	**55.5** (%C)	18 (%C)

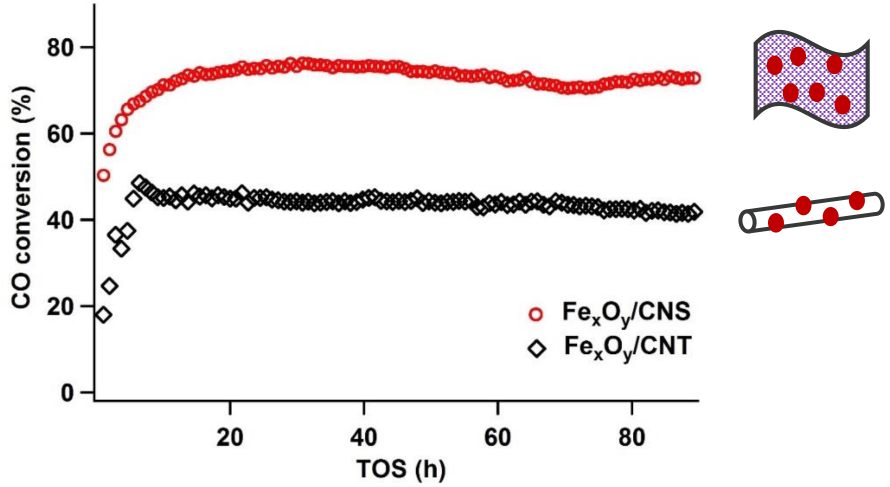
The activity of our catalysts is between 40 to 1000 times higher compared to other Fe-based FTO catalysts with similar light olefins selectivity reported in the literature.

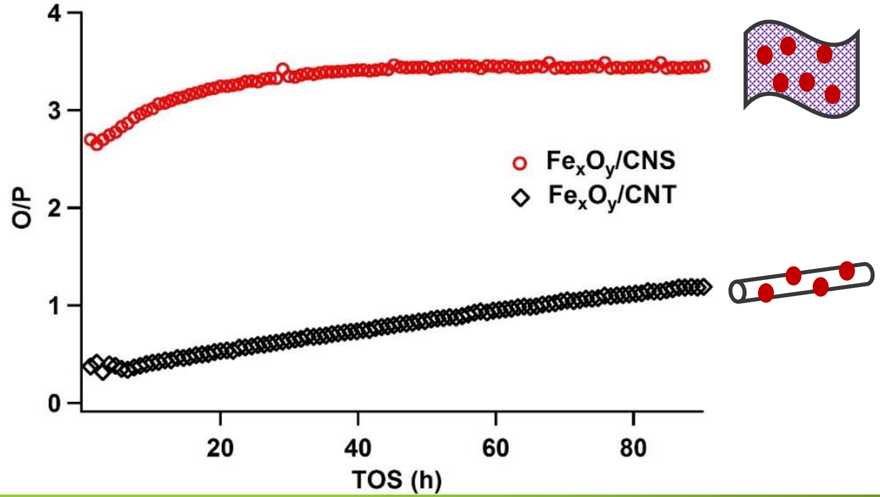
[1]H. M. Torres Galvis, *et al.*, *Science*, **335**, 835, (2012).

Effect of Carbon Support

Fe_xO_y supported on CNT

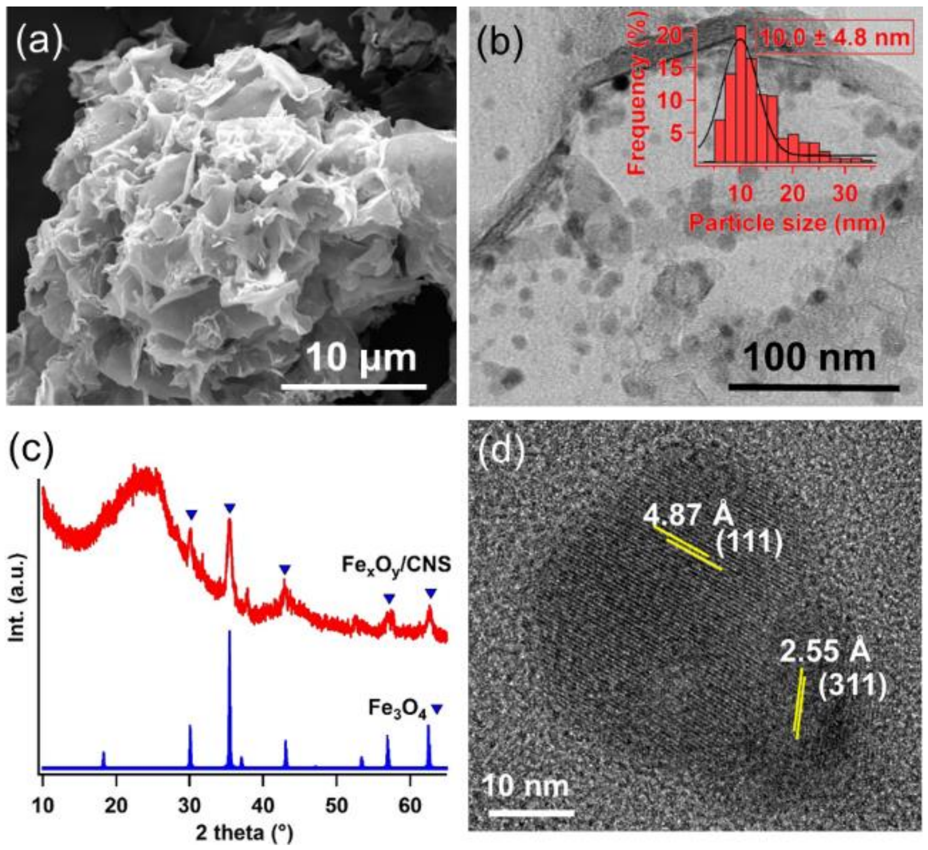




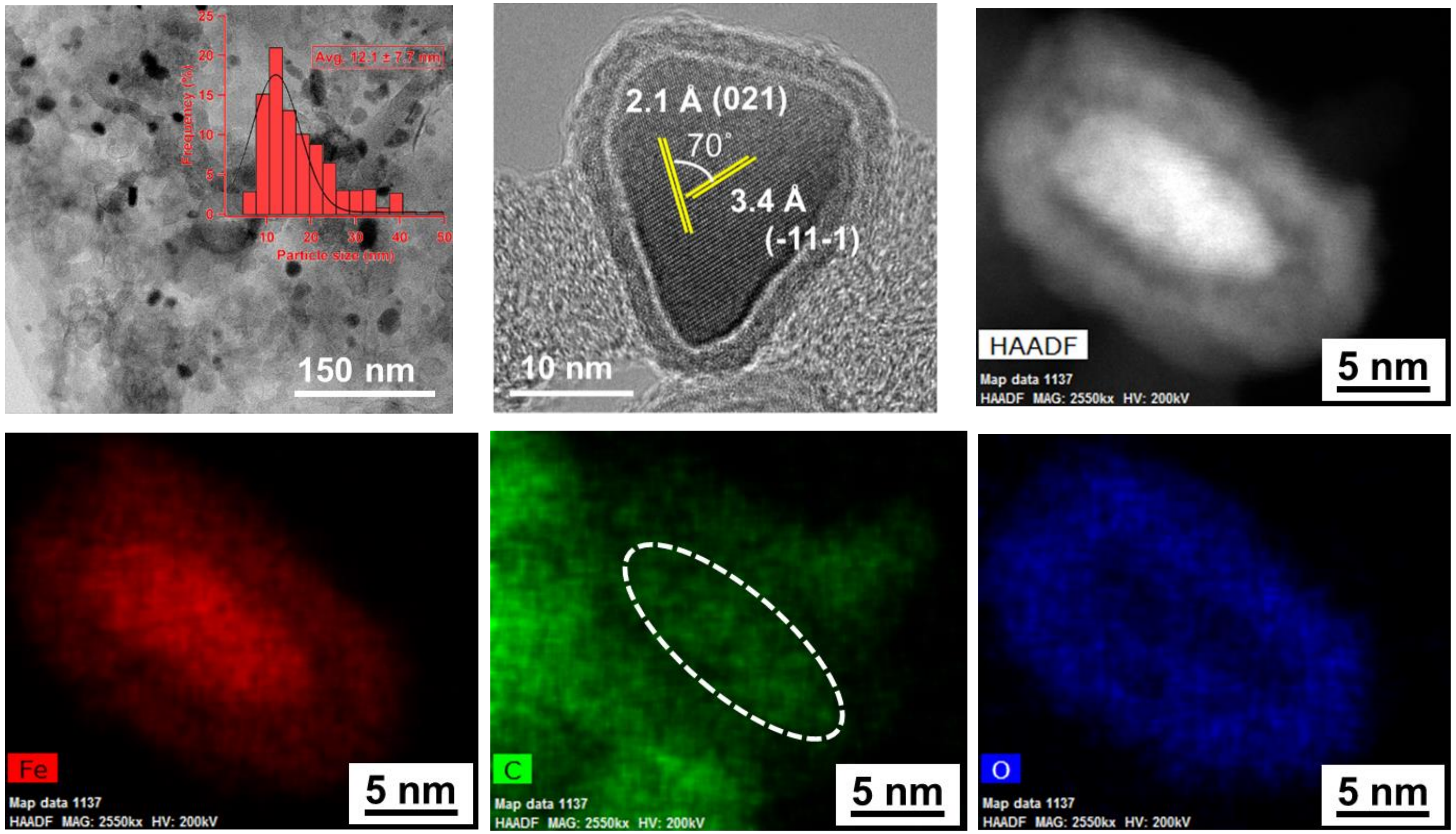


Fe-based FTO Nanocatalysts on CNS

More readily reducible Fe_3O_4 advantageous for the formation of active Fe_5C_2

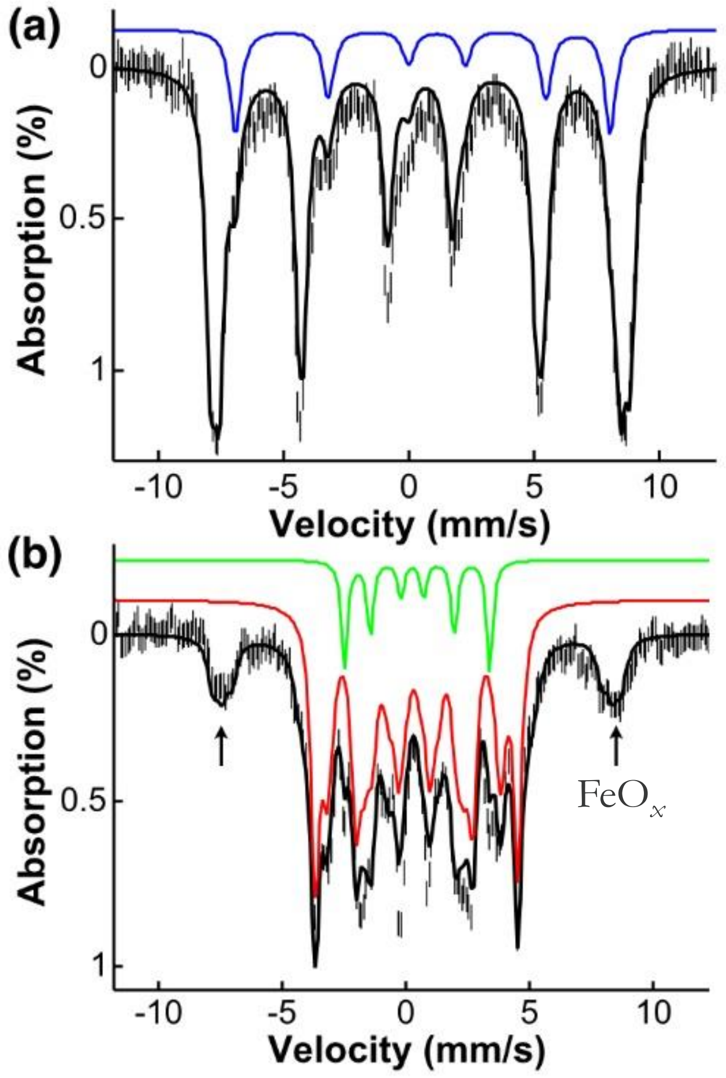


Fe_3O_4 is identified as the main phase in the fresh catalyst.



Formation of Fe_5C_2@FeO_x core-shell structure in post-reaction catalyst.

Mössbauer Spectroscopy Characterization

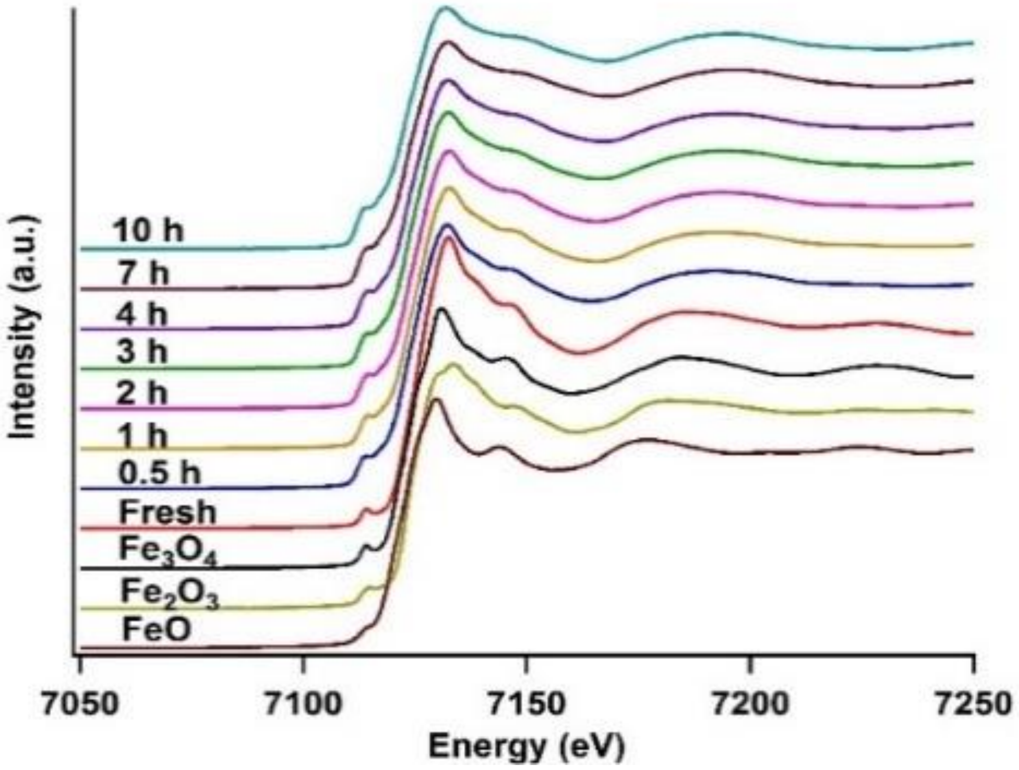


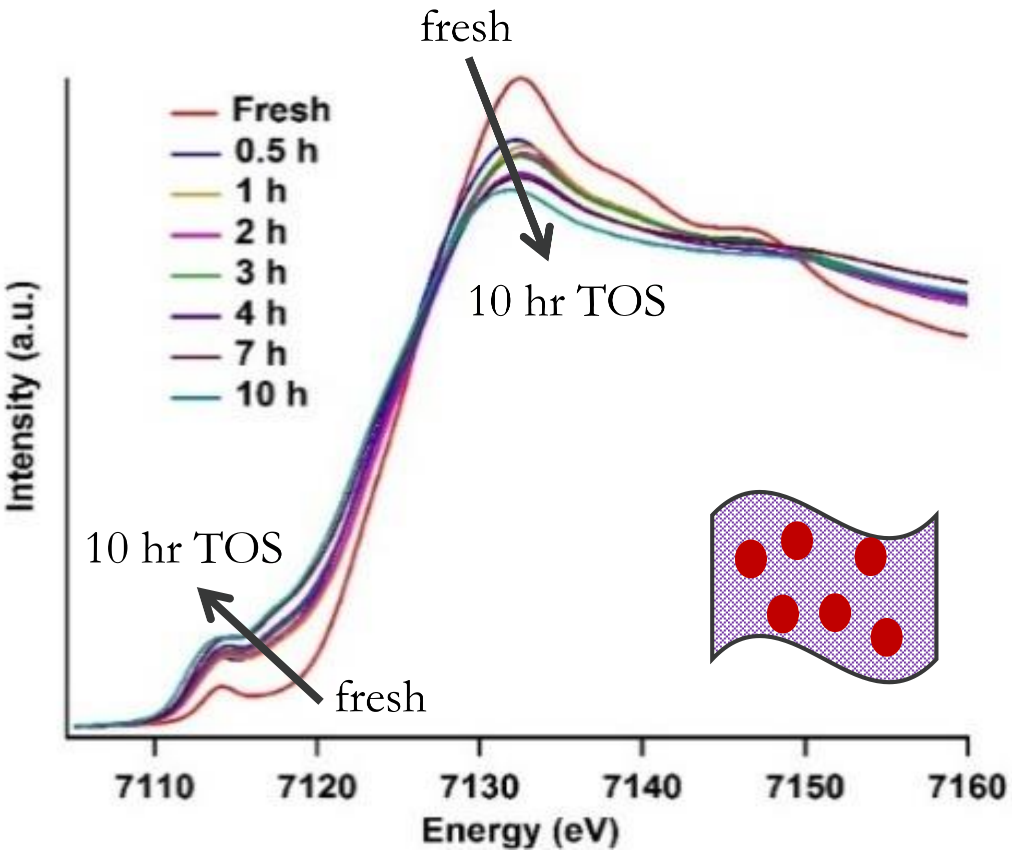
Sample	Phase	δ (mm/s)	ΔEq (mm/s)	B_{hf} (T)	Γ (mm/s)	%
Fresh Fe_xO_y/ CNS	Fe_xO_y-I	0.46	0	52.1	0.5	35
	Fe_xO_y-II	0.43	0	49.8	0.5	37
	Fe_xO_y-III	0.83	-1.14	46.3	0.5	16
Spent Fe_xO_y/ CNS	Fe_xO_y-I	0.46	0	52.1	0.5	6
	Fe_xO_y-II	0.43	0	49.8	0.5	6
	Fe_xO_y-III	0.45	0	46.5	0.5	5
	χ-Fe_5C_2-I	0.39	0.09	25.5	0.4	30
	χ-Fe_5C_2-II	0.33	0	21.8	0.55	27
	χ-Fe_5C_2-III	0.33	0.05	10.6	0.5	15
	Fe_xC	0.36	0	18.3	0.3	10

Mössbauer spectroscopy results are consistent with the presence of Fe_3O_4 phase in the fresh catalyst, and the conversion to Fe_5C_2 in the post-reaction catalyst.

XANES Spectra of FTO Catalyst

Fe_xO_y supported on CNS

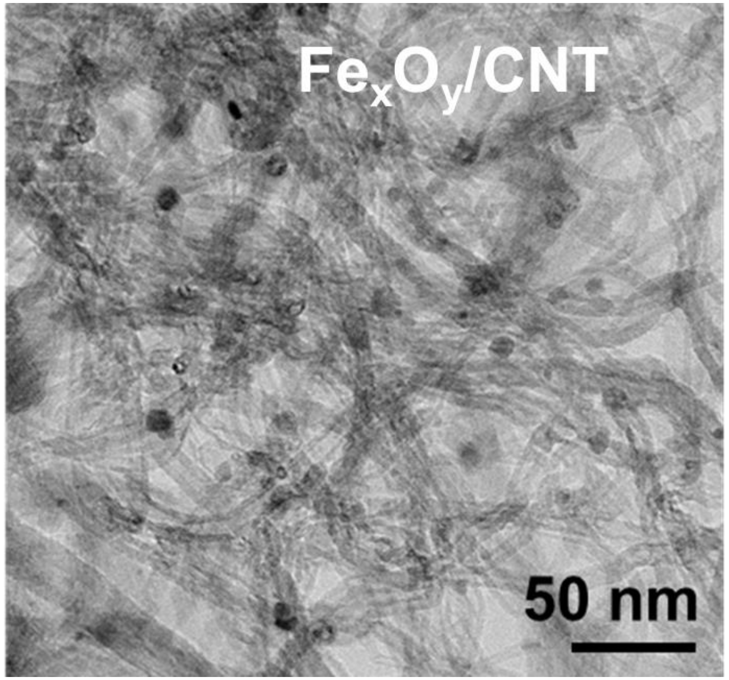


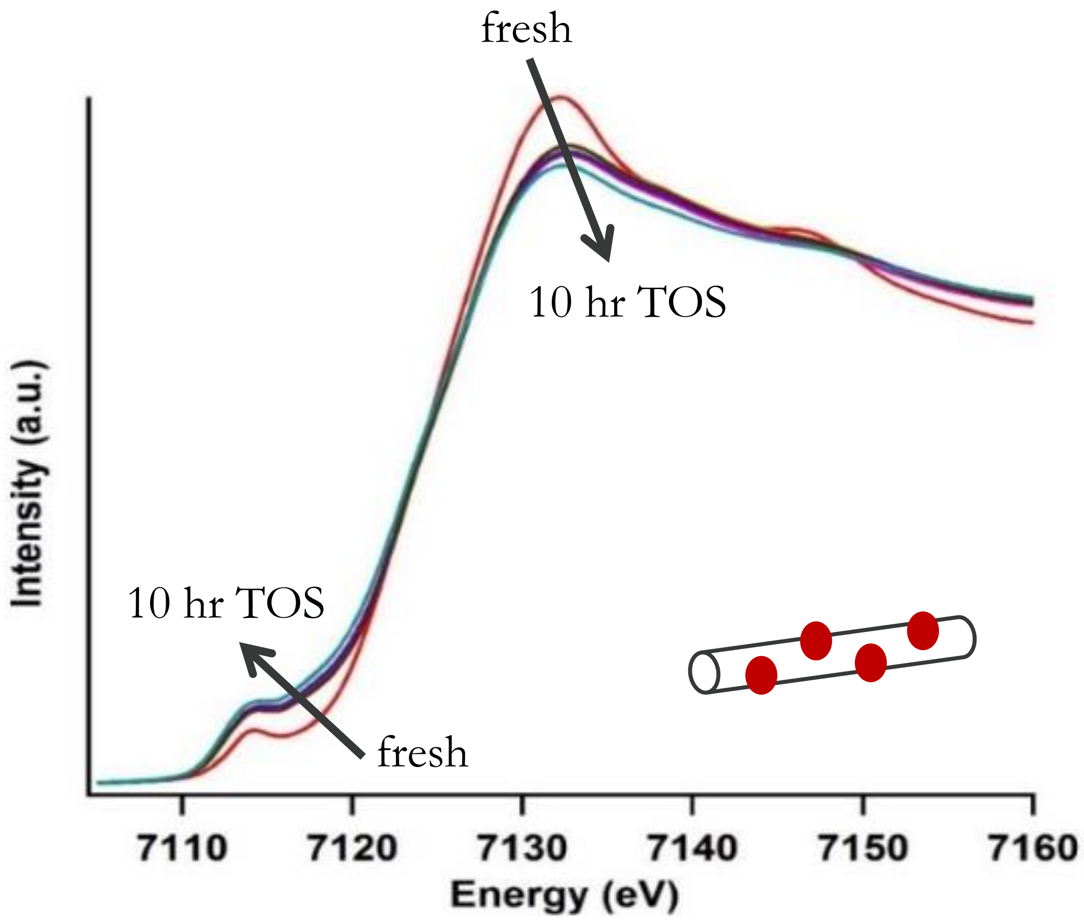


Fe K-edge XANES spectra illustrate the similarity of fresh catalyst to Fe_3O_4, consistent with TEM, XRD, Mössbauer spectroscopy results. The oxide phase gradually decreases, whereas the iron carbide feature increases, as a function of TOS.

E. de Smit, *et al.*, *J. Am. Chem. Soc.* **132**, 14928 (2010); S. Y. Hong, *et al.*, *Nanoscale* **7**, 16616 (2015); D. C. Bock, *et al.*, *Physical Chemistry Chemical Physics* **19**, 20867 (2017); T. E. Westre, *et al.*, *J. Am. Chem. Soc.* **119**, 6297 (1997).

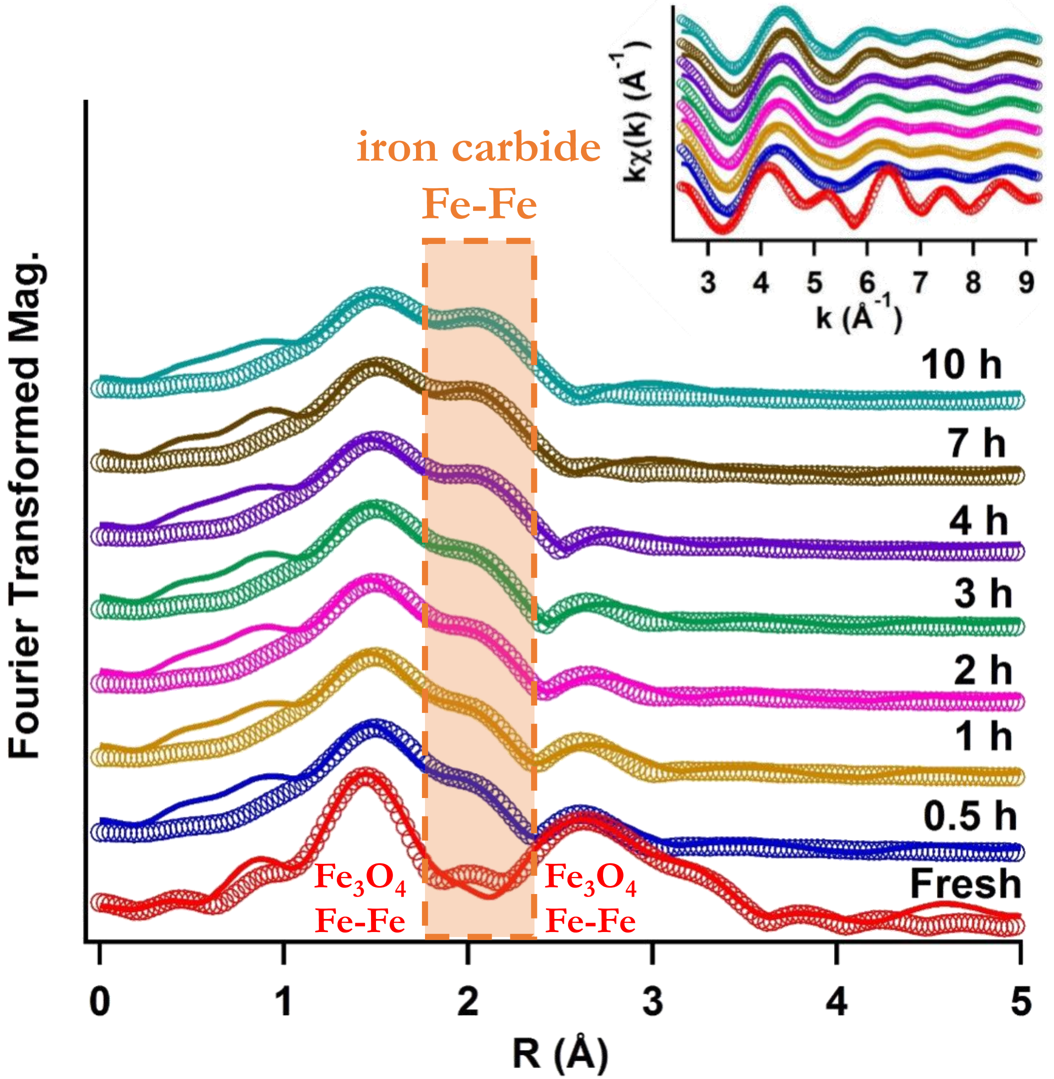
Fe-based FTO Nanocatalysts on CNT

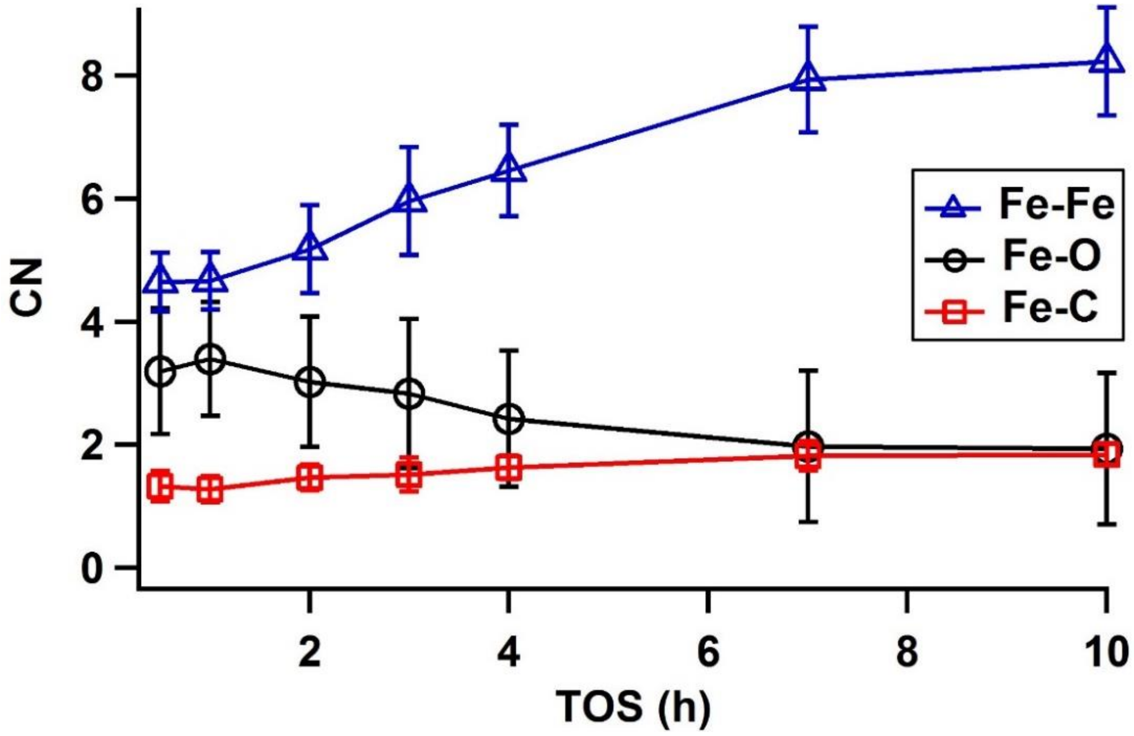




EXAFS Analysis of FTO Catalyst

Fe_xO_y supported on CNS

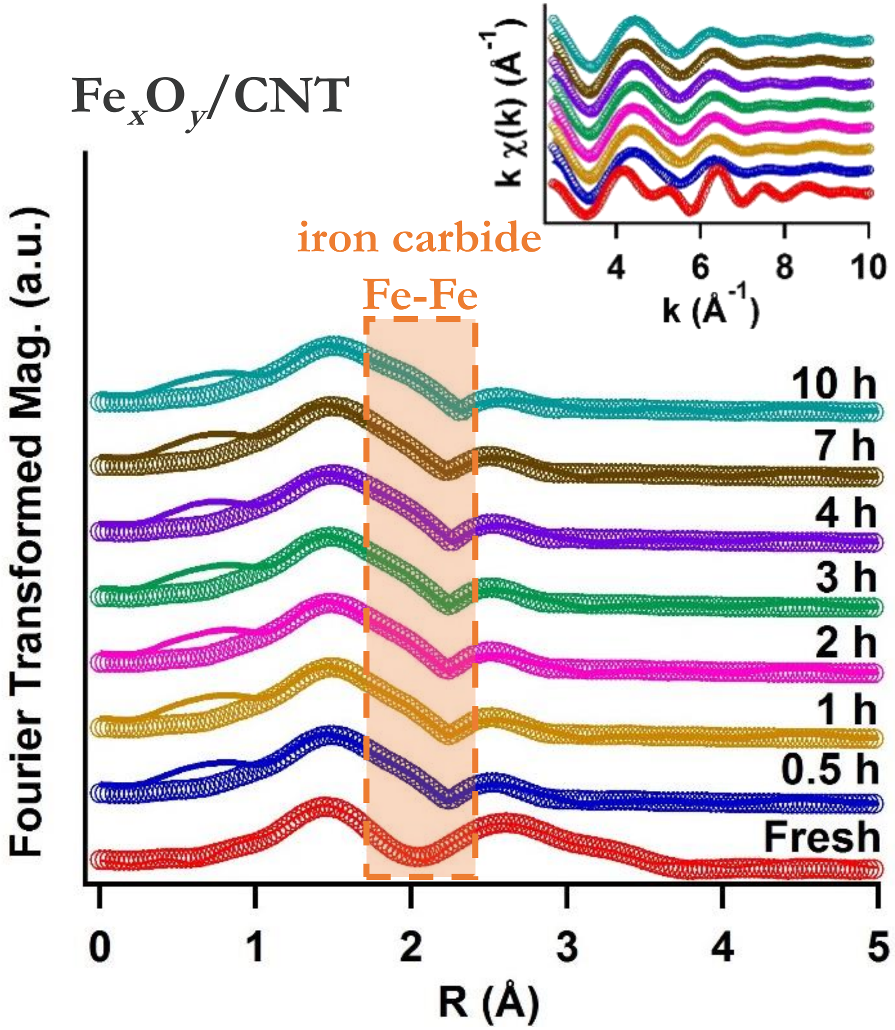


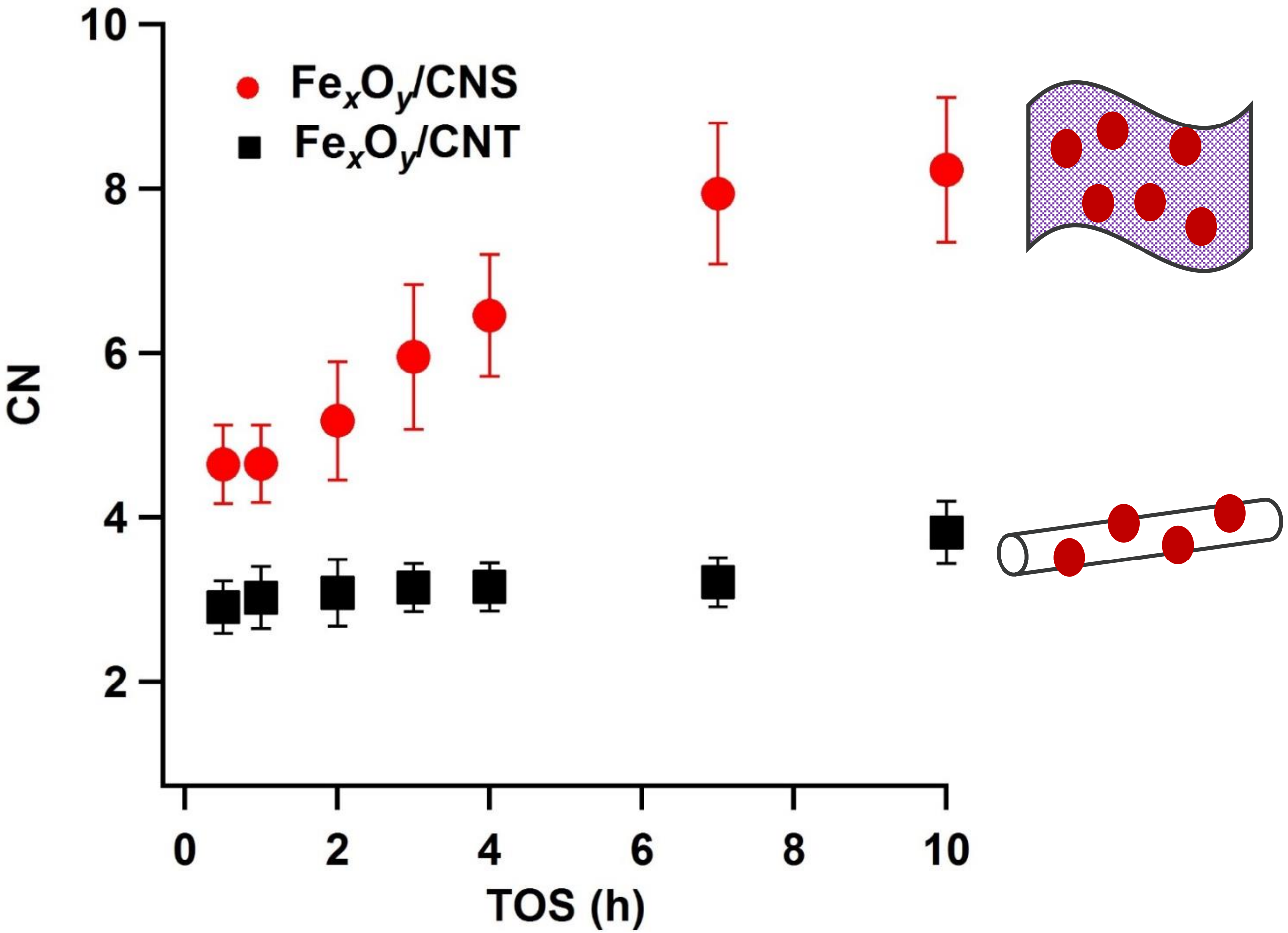


EXAFS data clearly show the reduction and conversion of Fe_3O_4 to form catalytically active iron carbides under FTO reaction conditions.

Models of Fe_5C_2 and Fe_3O_4 were used for fitting analysis.

Comparison of CNT and CNS Support





Compared to CNT support, CNS leads to markedly enhanced carburization of Fe_xO_y catalyst under FTO reaction conditions.

CNS Stabilized Fe Metallic Nanoparticles

More robust formation of metallic Fe on CNS compared to CNT upon H_2 reduction

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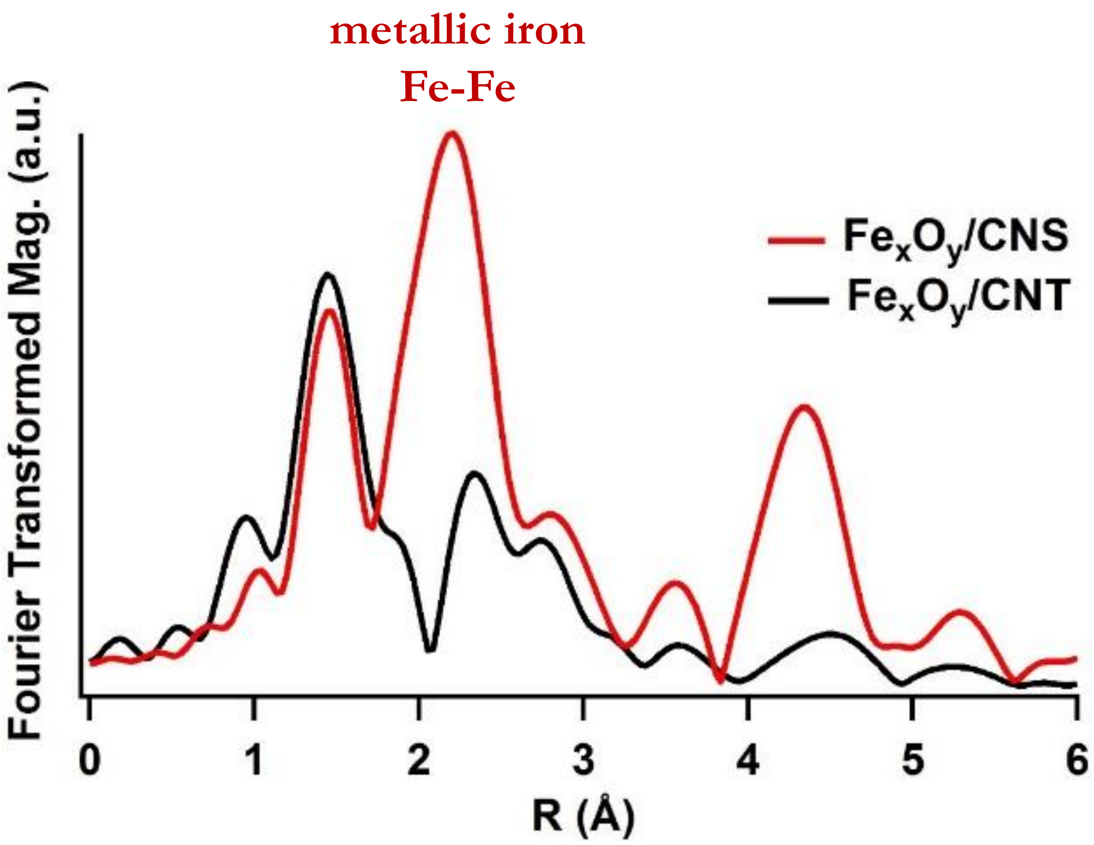
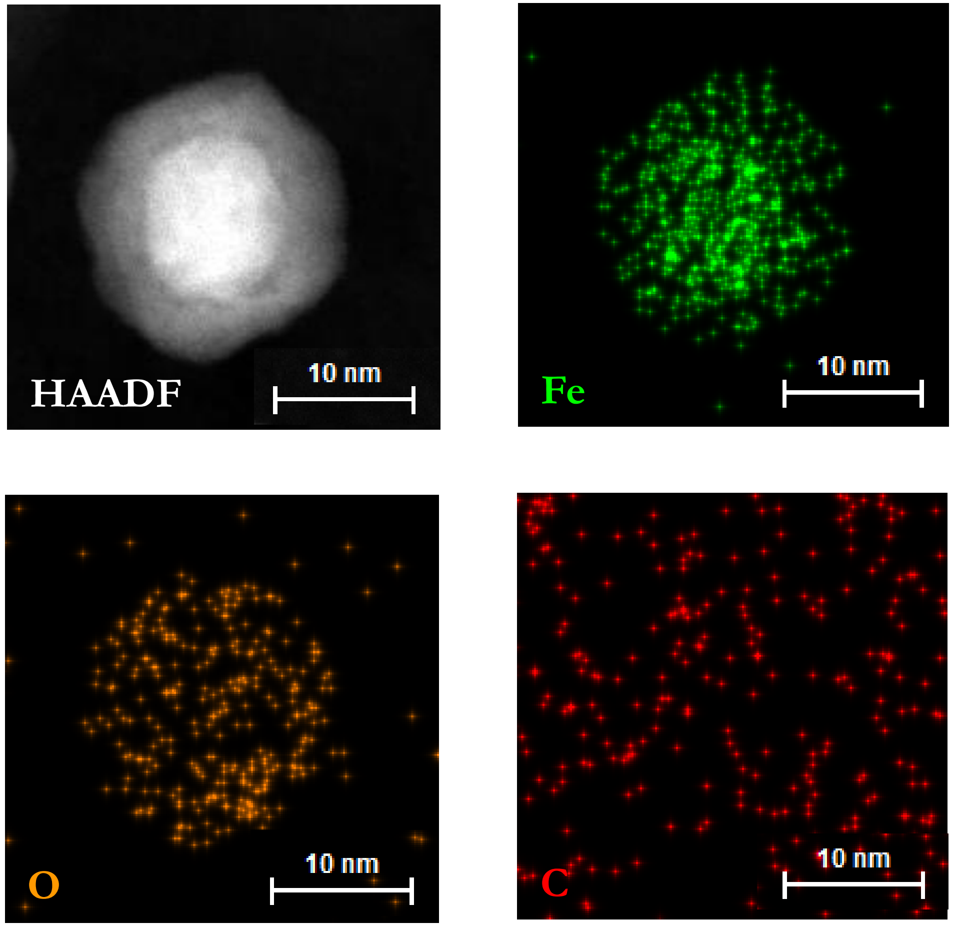
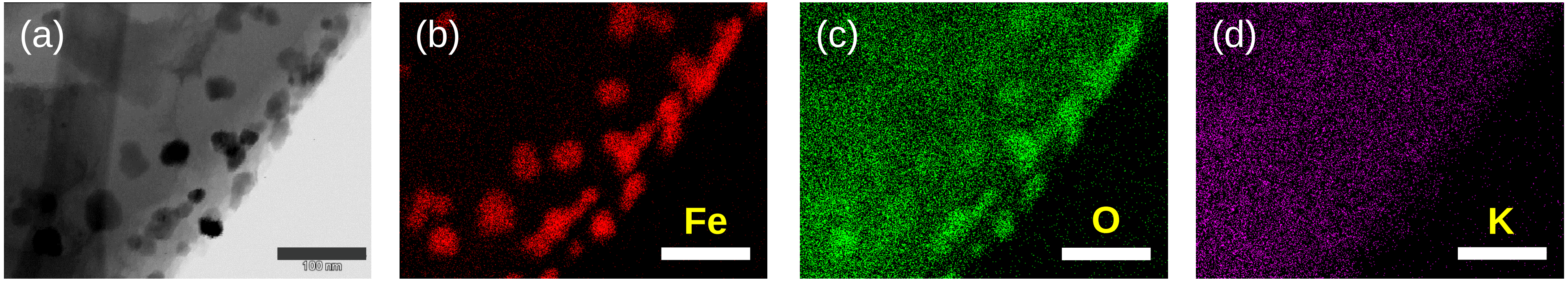


Fe K-edge EXAFS spectra of H_2 reduced Fe_xO_y/CNS and reduced Fe_xO_y/CNT catalysts.

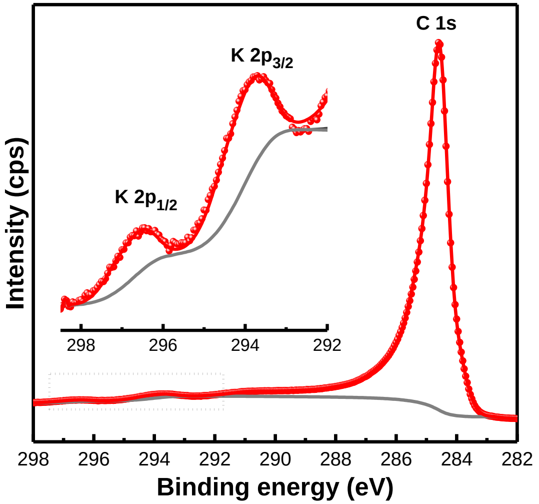


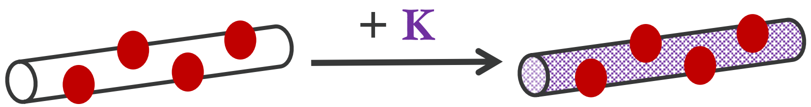
Reduced Fe_xO_y/CNS

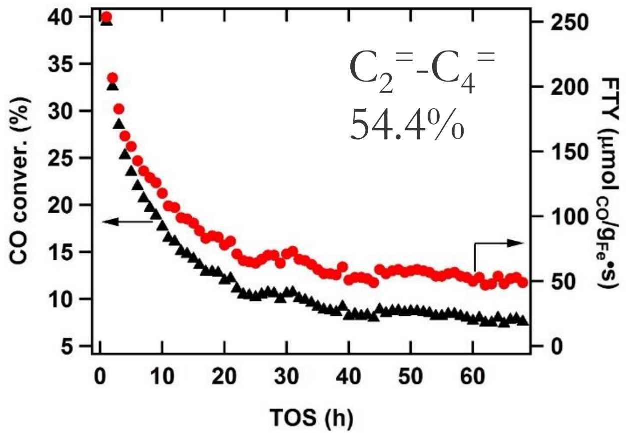
Uniformly Distributed Promoter K on Carbon Nanosheets Support



The use of potassium citrate for the synthesis of carbon nanosheets introduces promoter K uniformly distributed on the catalyst support. (Scale bar, 100 nm.)

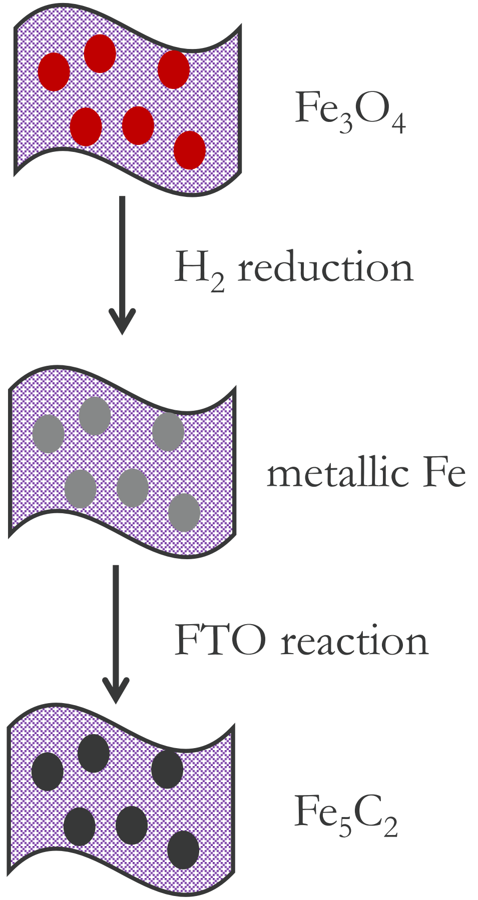






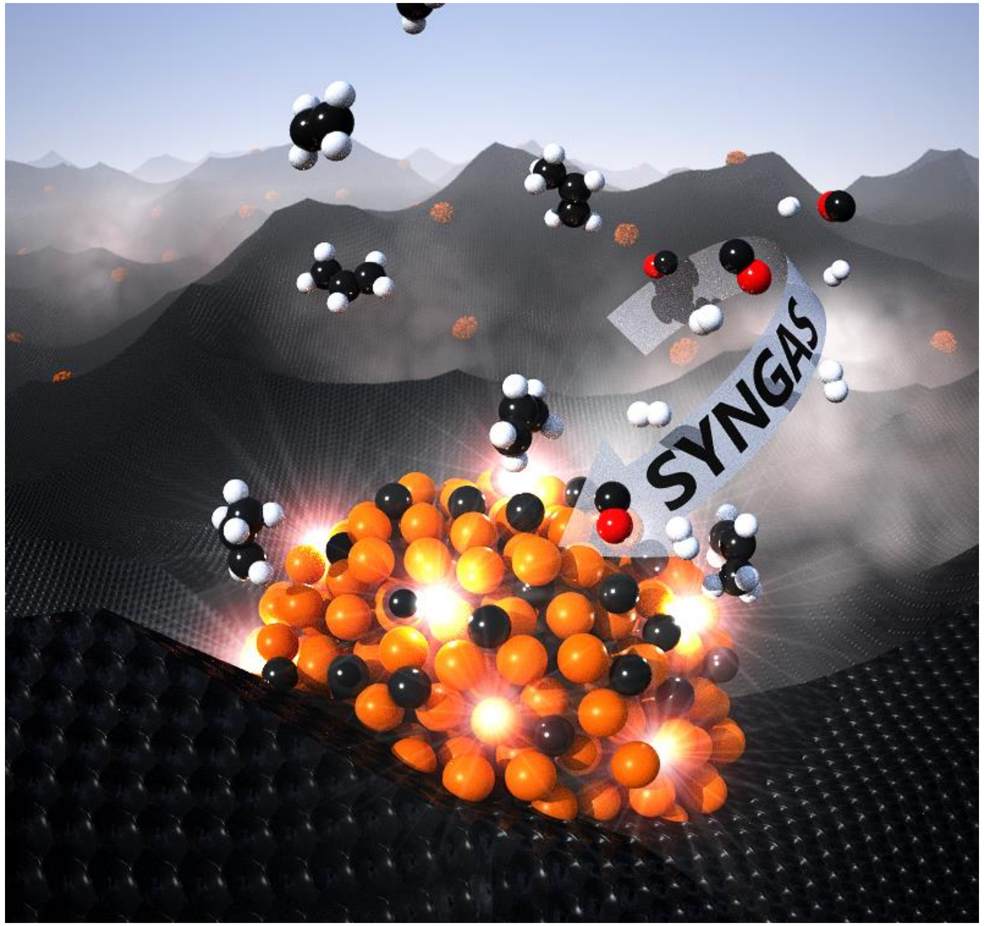
Summary

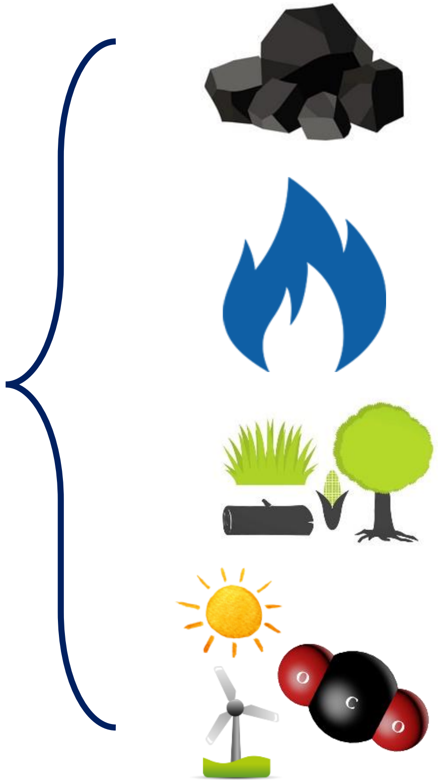
- Iron-based FTO catalysts with possibly the highest FTY open up new opportunities for Fischer-Tropsch to olefins synthesis.
- Various characterization techniques such as electron microscopy, Mössbauer spectroscopy, as well as X-ray spectroscopy have been performed showing the transformation of iron oxides to iron carbides after FTO reaction.
- CNS support with embedded K promotes more robust formation of metallic Fe nanoparticles, leading to more effective and complete transformation to catalytically active iron carbide phase under FTO conditions.



Future Work

- *in situ* and operando characterization (electron microscopy, X-ray spectroscopy, Raman spectroscopy).
- Computational modeling.





Acknowledgment

This work was performed in support of the US Department of Energy's Fossil Energy Crosscutting Technology Research Program. The Research was executed through the NETL Research and Innovation Center's Process and Reaction Intensification. Research performed by Leidos Research Support Team staff was conducted under the RSS contract 89243318CFE000003.

This work was funded by the Department of Energy, National Energy Technology Laboratory, an agency of the United States Government, through a support contract with Leidos Research Support Team (LRST). Neither the United States Government nor any agency thereof, nor any of their employees, nor LRST, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Acknowledgment

Yunyun Zhou, Sittichai Natesakhawat,
Thuy-Duong Nguyen-Phan, Douglas R. Kauffman,
Chris M. Marin, Jonathan W. Lekse, Yang Yu,
John Baltrus, Yu Lu, Christopher Matranga

Kim Kisslinger, Ruoqian Lin, Huolin L. Xin,
Eli Stavitski, Klaus Attenkofer, Iradwikanari Waluyo

Yijie Tang, Yisong Guo

Amitava Roy

Thank You!

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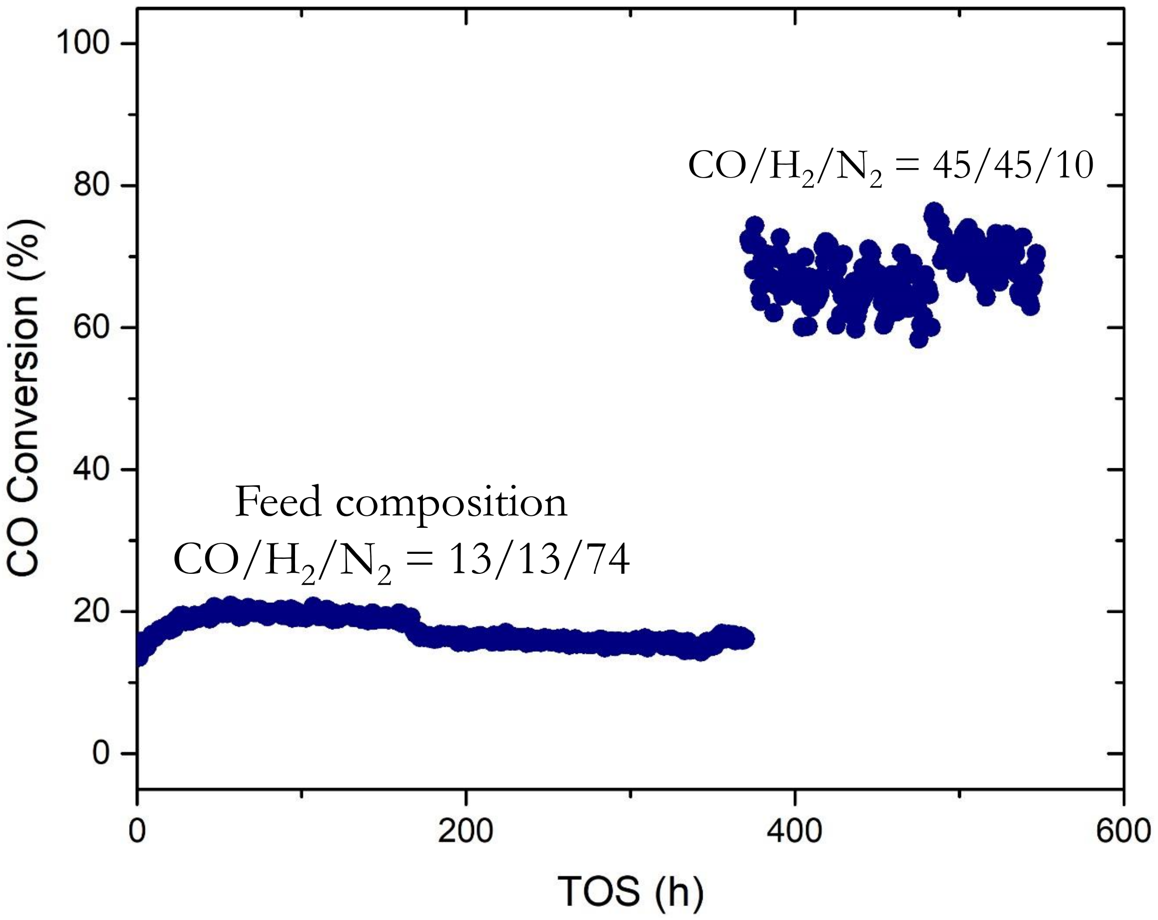
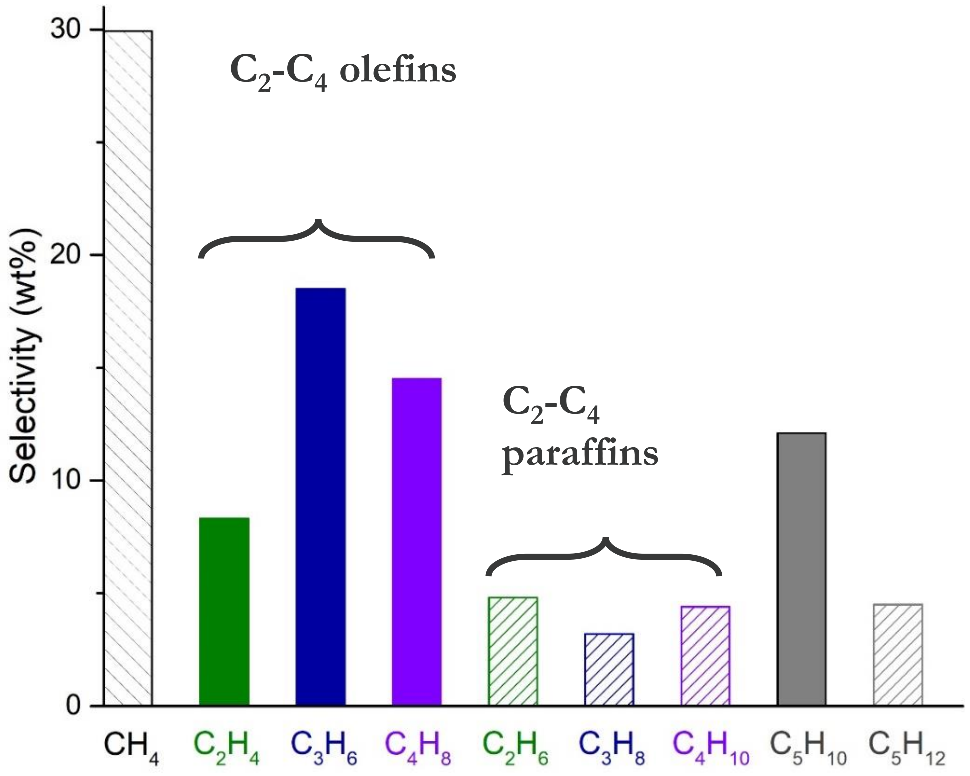
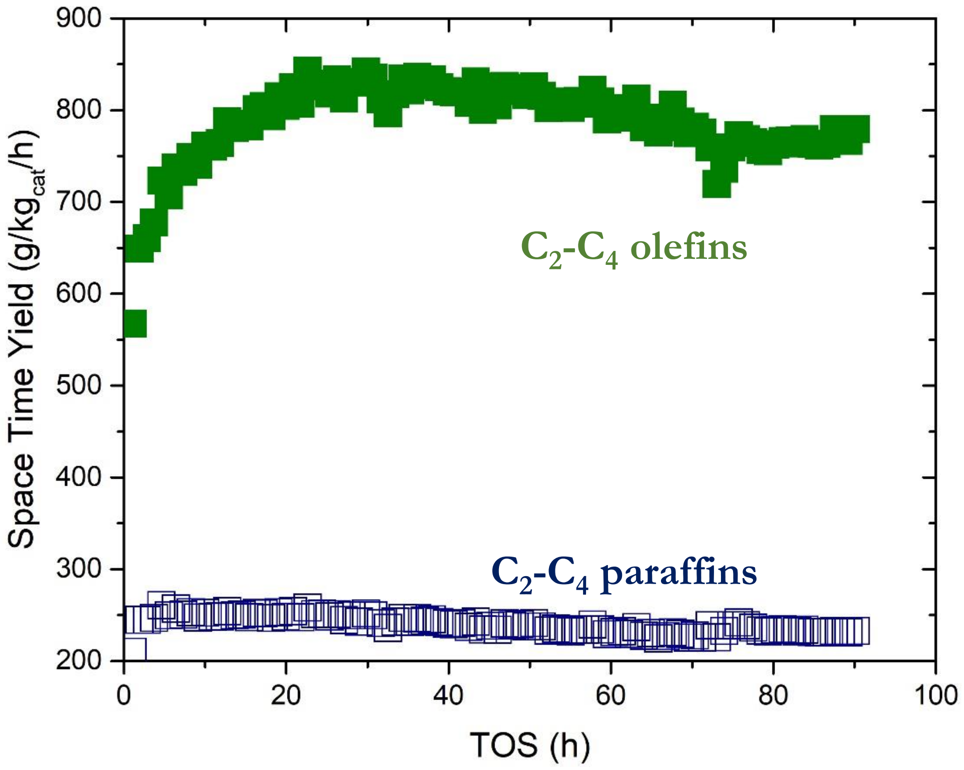
Optimization of Reaction Condition and Stability Testing

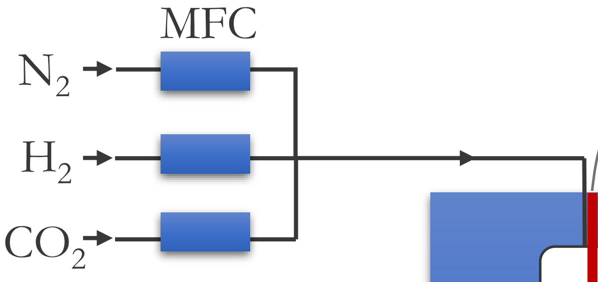


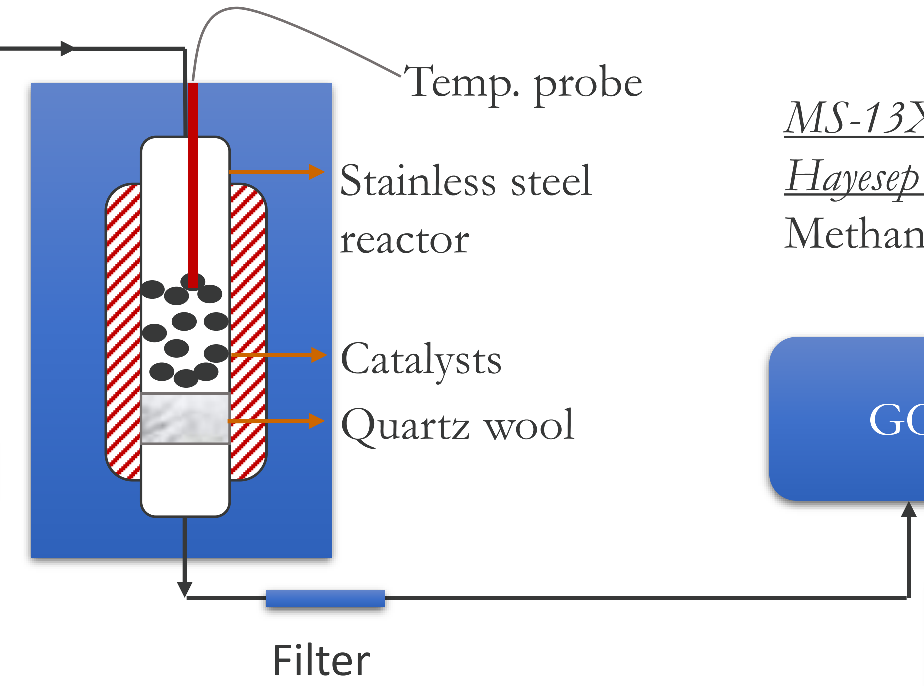
Product Distribution





CO_2 Hydrogenation Activity Testing

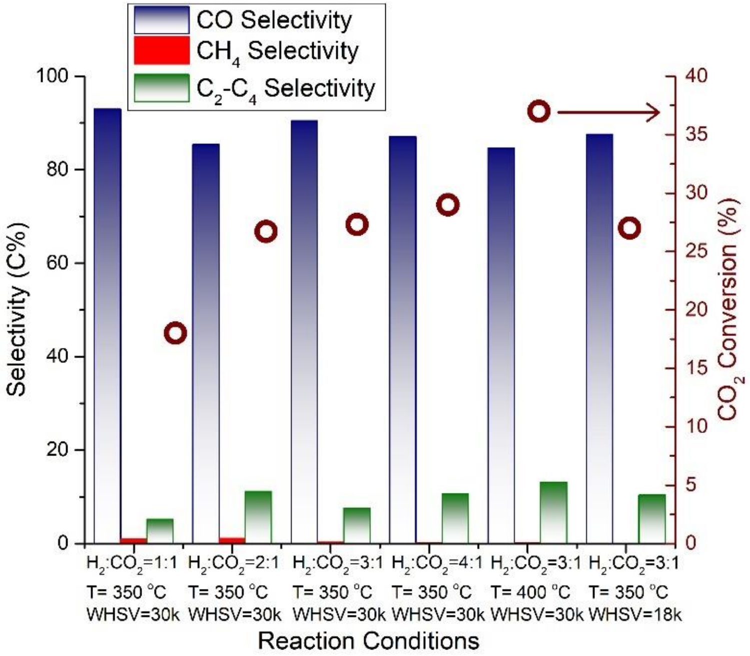


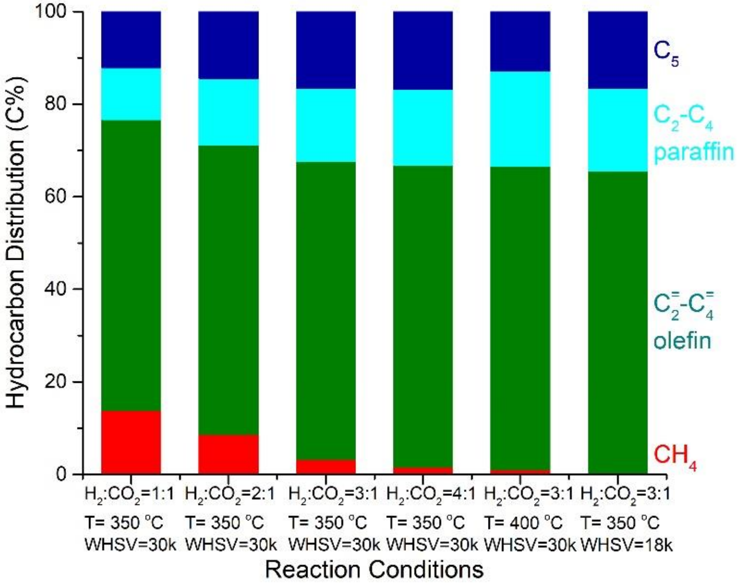


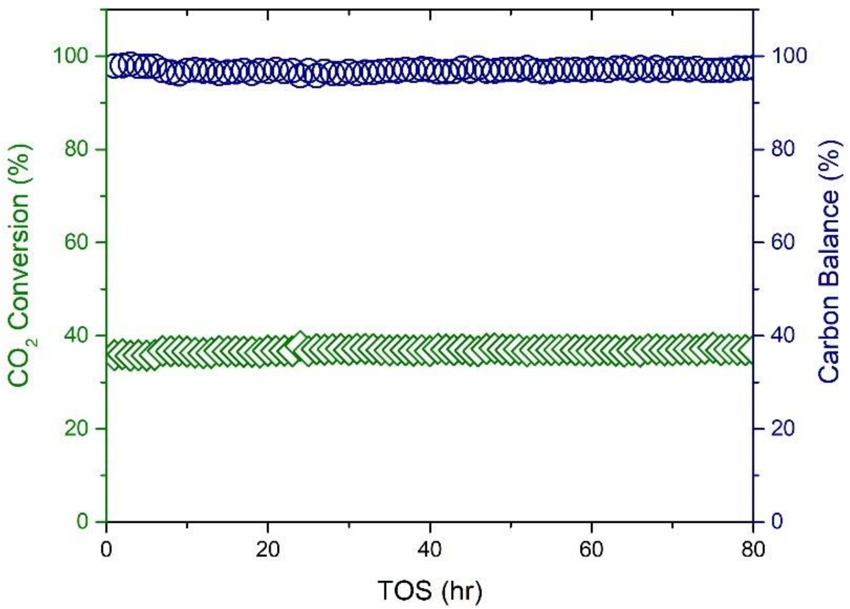
MS-13X column & TCD: CO, H_2, N_2, CH_4
Hayesep Q & FID: CO_2, C_2-C_5
Methanizer for CO detection in ppm levels

Catalysts pretreatment: H_2 @ 400 ℃ for 3 h, 50 SCCM
CO_2 hydrogenation conditions: 350 – 400 ˚C, 20 bar, CO_2:H_2 = 1:1 – 1:4, 100 SCCM, W_{cat} = 200 mg, WHSV = 18000 to 30000 cc/g_{cat}/h

Robust CO_2 Hydrogenation Activity

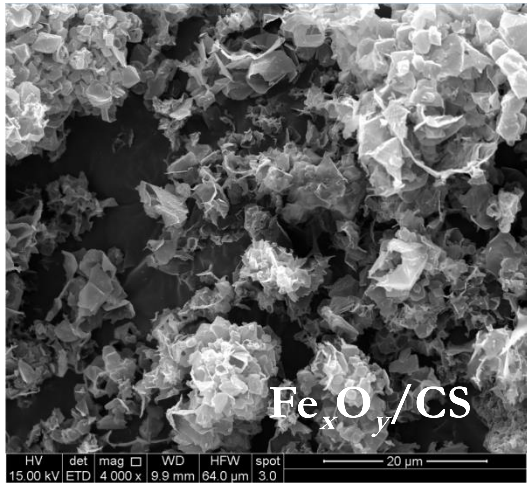


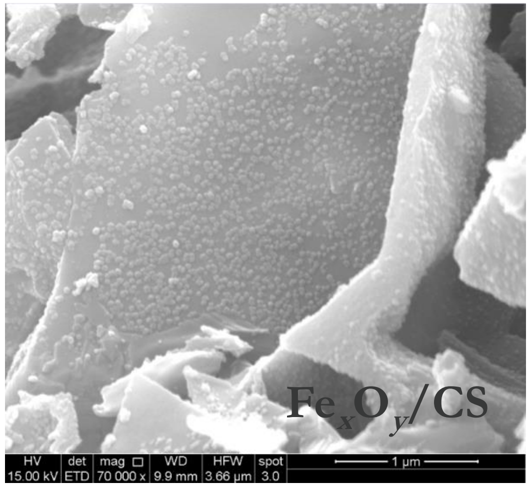


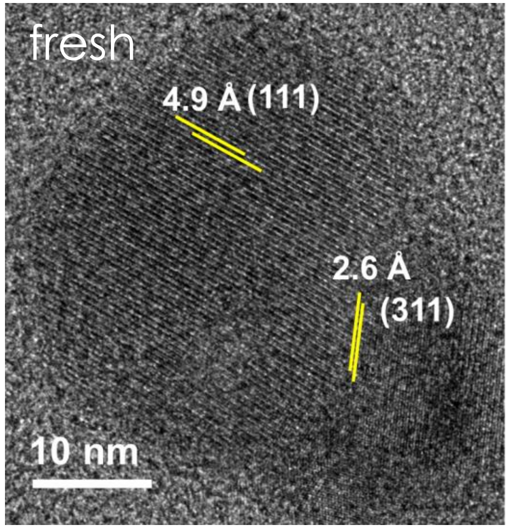


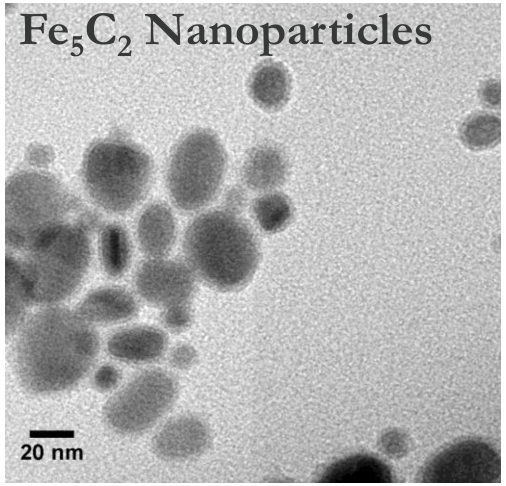
- CO_2 conversion up to ~37%
- C_2–C_4 hydrocarbon selectivity of up to ~13%
- Catalysts stable for > 550 hrs (with testing at different rxn conditions).
- Low CH_4 selectivity.
- Further optimization needed

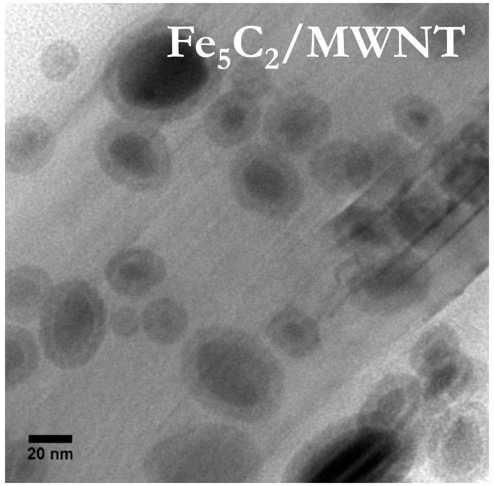
Fe-based Nanocatalysts

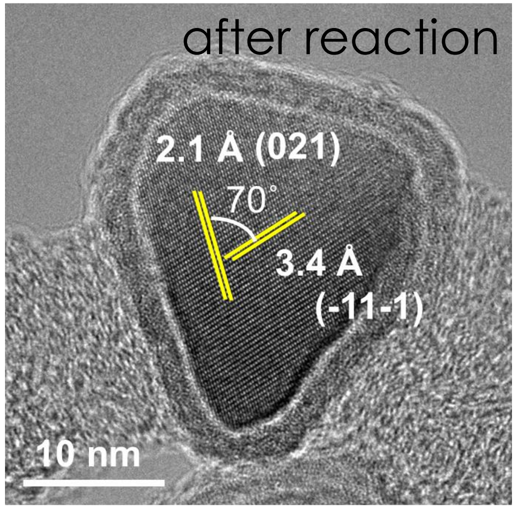






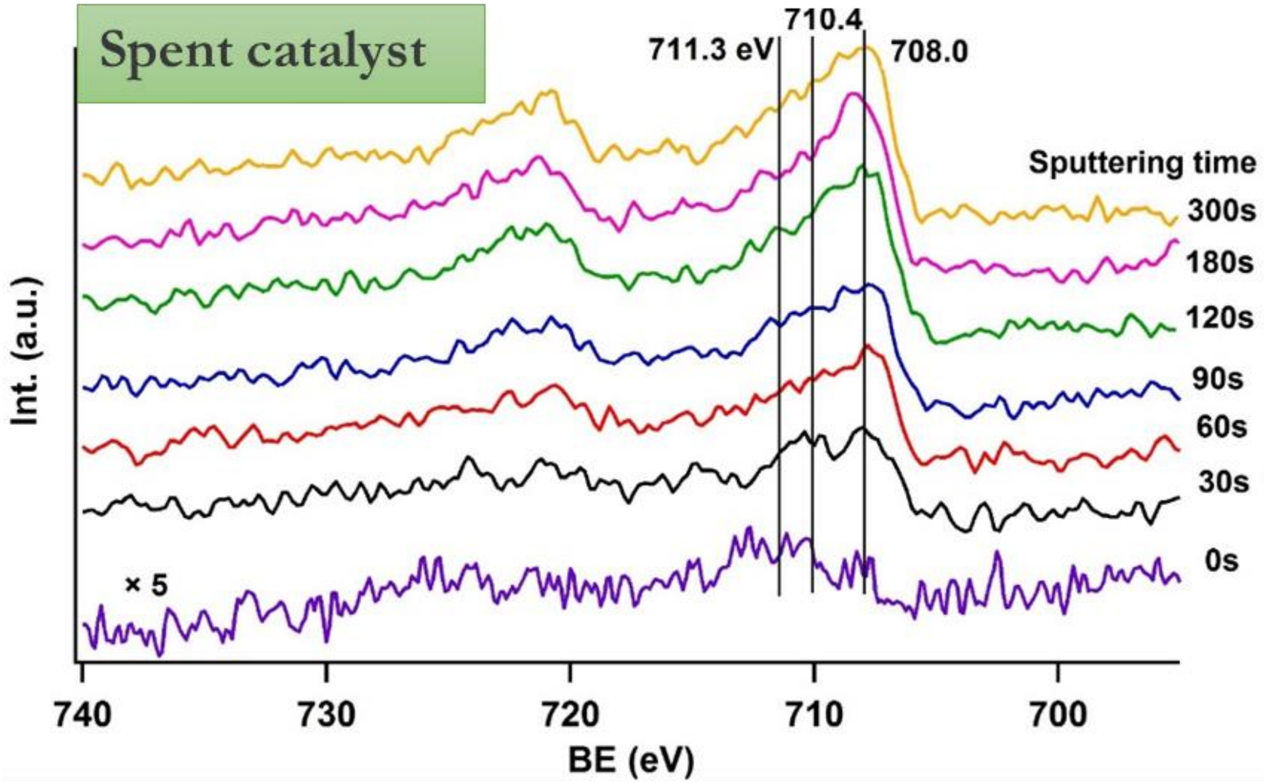




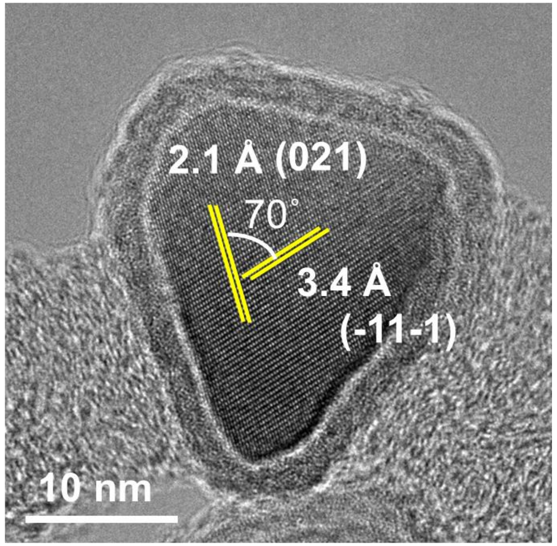


Characterization of FTO Catalysts

After catalytic reaction



Bulk Standard	Ep (ref)/ eV
Fe^0	706, 707
Fe_5C_2	708
FeO	710
Fe_3O_4	710.6
Fe_2O_3	711.0



Laboratory-based XPS results agree with the core/shell Fe_5C_2/FeO_x structure of catalyst nanoparticles after FTO reaction.

XANES Spectra of FTO Catalyst

Fe_xO_y supported on CNT