Standard Experimental Report

Proposal title: Integrated CO_2 Capture and Conversion into Valuable Hydrocarbons
Proposal number: 20201159
Beamline: FAME
Shifts: 12
Date(s) of experiment: from: April 28th 2021 to: 2 May 2021
Date of report: July 13 2022

- Objective & expected results (less than 10 lines): -

We have noted that the modification of USY with Ti and Zr promotes classical reactions catalyzed by Brønsted acid sites, such as n-hexane cracking and o-xylene isomerization reactions, increasing their reaction rates by 25 and 50% respectively, compared to the undoped USY counterpart. Although more active, the Ti,Zr-USY the early stage of the o-xylene isomerization reaction, unlike the pristine USY catalyst.
The aim of the study is to establish the relationship between the local structural order around metals, the resulting acidic properties (Bronsted and Lewis site), and the catalytic performances. *Operando* X-ray absorption spectroscopy operated at Zr and Ti K-edge is applied to unravel the structural order around those atoms during o-xylene isomerization (T = 350 ºC, P(oxylene)= 0.05 bar).

- Results and the conclusions of the study (main part): -

The *operando* XAS study regarding the metal characterization of an ultra-stable Y (USY) zeolite after modification with small quantities (less than 1 wt.%) of Ti and Zr under realistic conditions was performed in May 2021 in the CRG-FAME beamline (BM30). The experiment was performed at the Ti and Zr K-edges (4.9 and 17.9 keV respectively). Figure 1 shows the Ti K-edge XANES spectra of different monometallic and bimetallic Ti-based catalysts. The XANES features of the spectra suggest a similar local environment in all the as-prepared samples either mono or bimetallic.

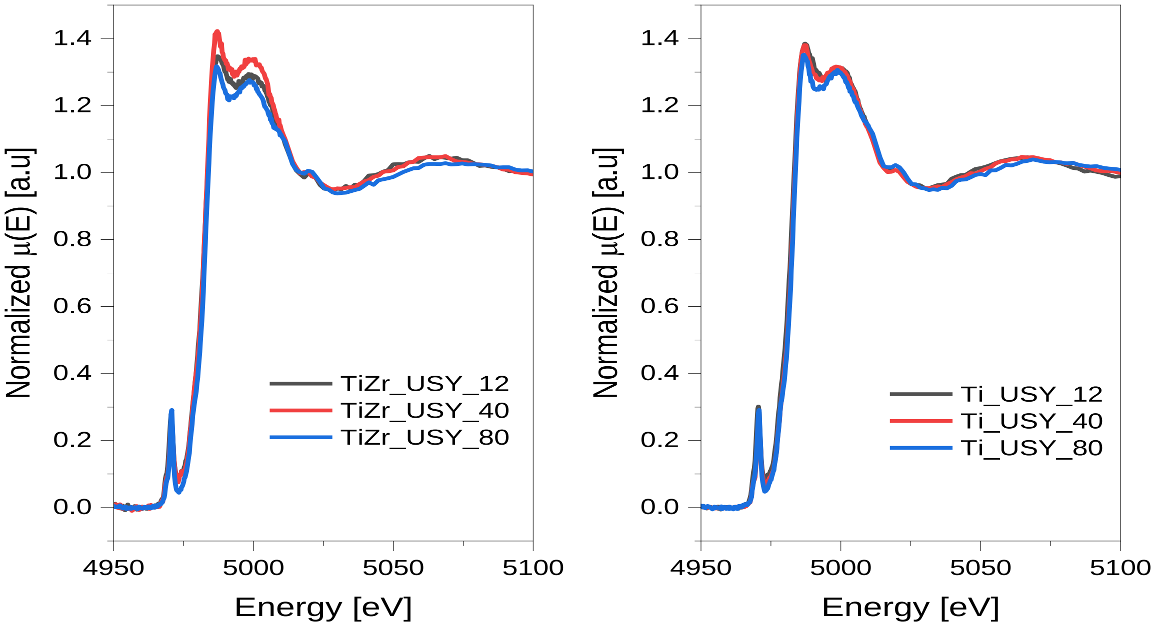

Figure 1. Ti K-edge XANES spectra of different monometallic and bimetallic Ti-based catalysts

The intensity of the pics of Fourier transform (Figure 2) of the EXAFS oscillations of the samples indicates an increase of Ti-O coordination with higher Si/Al ratio. The same effect is observed in either the mono or bimetallic samples

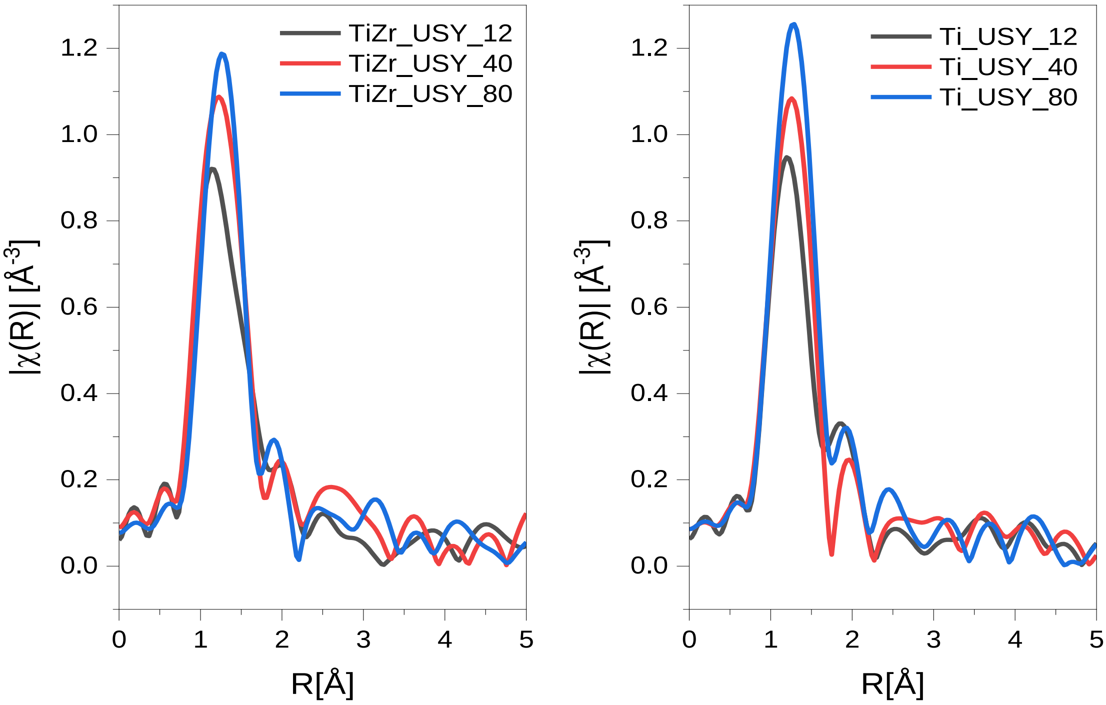

Figure 2. Fourier transform of EXAFS oscillations different monometallic and bimetallic Ti-based catalysts

Figure 3 shows the comparison of the Ti K-edge XANEs of the TiZr USY-40 under He at 300 °C, TS-1 hydrated and dehydrated and the anatase, amorphous TiO_2 and $TiOSO_4$ references. This results suggest a probable mixture of under coordinated Ti (< 6+) and amorphous TiO_2

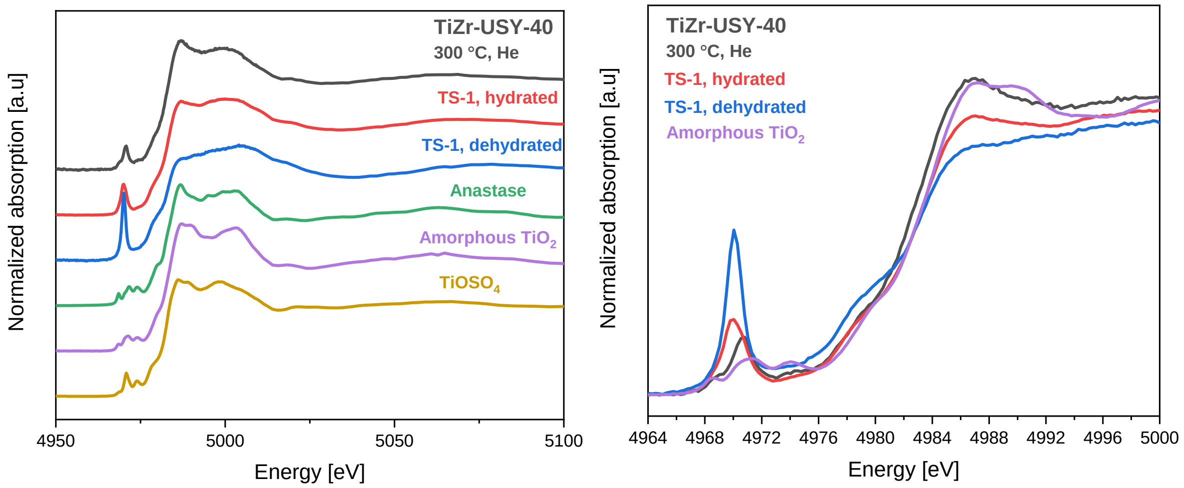

Figure 3. comparison of the Ti K-edge XANEs of the TiZr USY-40 under He at 300 °C, TS-1 hydrated and dehydrated and the Anatase, amorphous TiO_2 and $TiOSO_4$ references

A comparison of TiZr USY-40, TS-1 catalysts and Anatase, amorphous TiO_2, $TiOSO_4$ and metallic references (Figure 4) show there is not significant Ti-Ti scattering which may suggest undercoodinated Ti in the samples

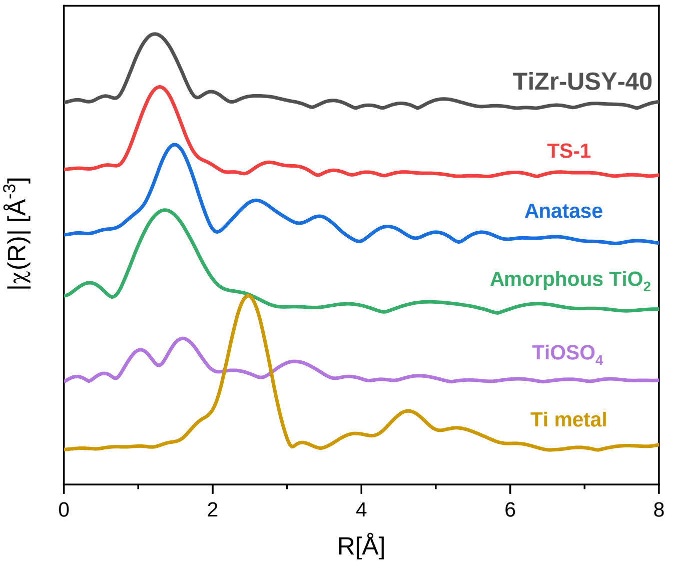

Figure 4. Comparison of EXAFS oscillations' Fourier transform of TiZr USY-40 and TS-1 catalysts and different Ti references

Additionally we present some preliminary results of the samples in the Zr K-edge. Figure 5 shows the Zr K-edge XANES spectra of different monometallic and bimetallic Ti-based catalysts. The XANES features of the spectra suggest a similar local environment in all the as-prepared samples either mono or bimetallic except for the TiZr USY-12 catalyst.

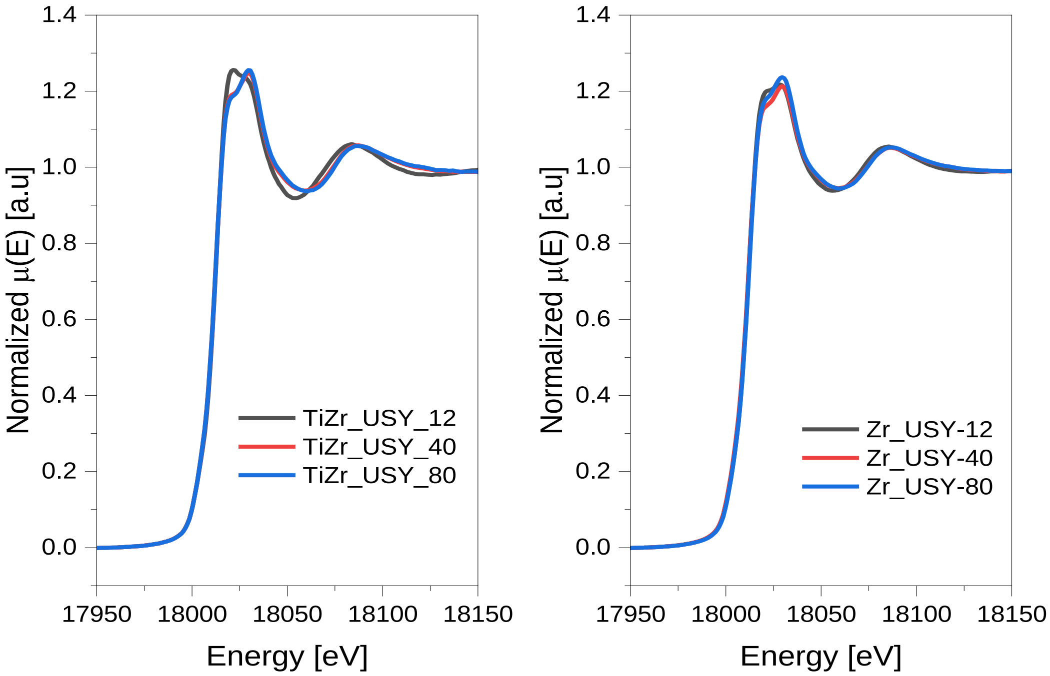

Figure 5. Zr K-edge XANES spectra of different monometallic and bimetallic Ti-based catalysts

Further qualitative analysis of the EXAFS oscillations' Fourier transform (Figure 6), show that all the samples exhibit similar local environment except for the TiZr USY-12 sample accordingly with the XANES spectra information

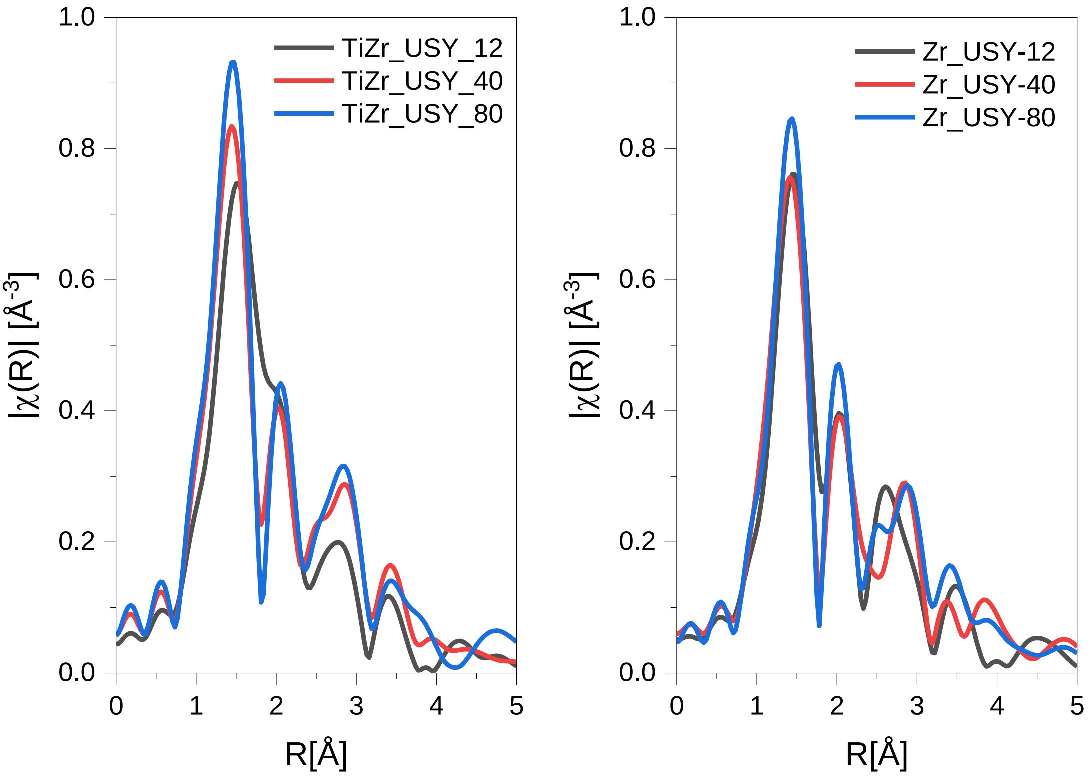

Figure 6. Fourier transform of EXAFS oscillations different monometallic and bimetallic Zr-based catalysts

The TiZr USY-40 catalyst was studied in the o-xylene isomerization reaction using the next protocol:

Experiment conducted at atmospheric pressure using our catalytic reaction cell and gas distribution system in the BM30 beamline. [1] 75 mg of TiZr USY-40 catalyst were introduced in the reactor, then a flow of 100 mL/min of He was introduced in the cell. Afterwards, the sample was heated up to 300 °C (10 °C/min) under 100 mL/min of He. At 300 °C, a flow of 100 mL/min H_2 was introduced in the reactor. After this, the reaction mixture containing o-xylene and H_2 was flowed in the cell for few hours. Finally the cell was purged using 100 mL of He and cooled down. XAS characterization was performed in each step of the test

Figure 7 shows the Zr K-edge XANES spectra of the TiZr USY-40 catalyst under different conditions. It can be observed that the main changes occurred upon water desorption, *i.e.* after heating at 300 °C under He. After this, no major changes can be observed indicating the stability of the catalyst.

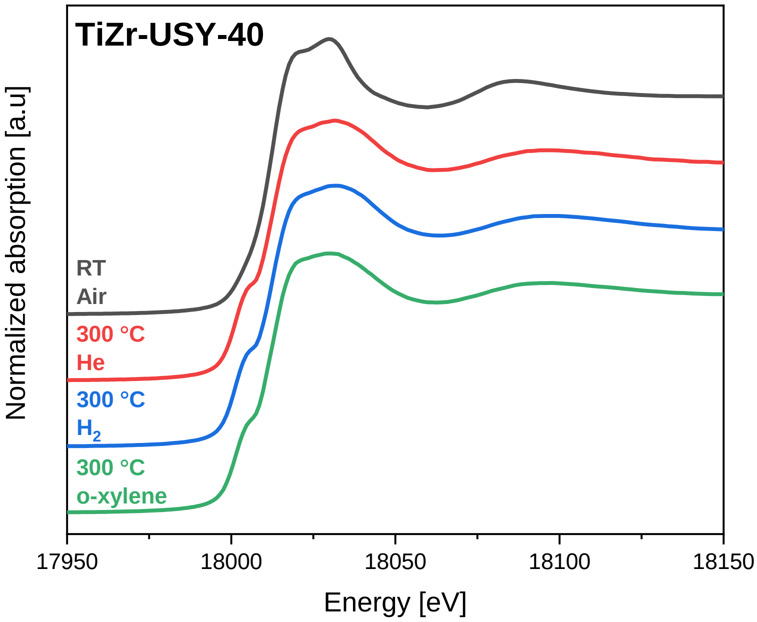

Figure 7. Zr K-edge XANES spectra of the TiZr USY-40 catalyst under different conditions: Air at RT, under He at 300 °C, under H_2 at 300 °C and under reaction mixture after few hours of reaction at 300 °C

Further qualitative analysis regarding the EXAFS oscillations (Figure 8) of the sample and the references confirms that the major changes occurs after the dehydration of the catalysts. After this, there is a stable Zr coordination at the different stages of the test.

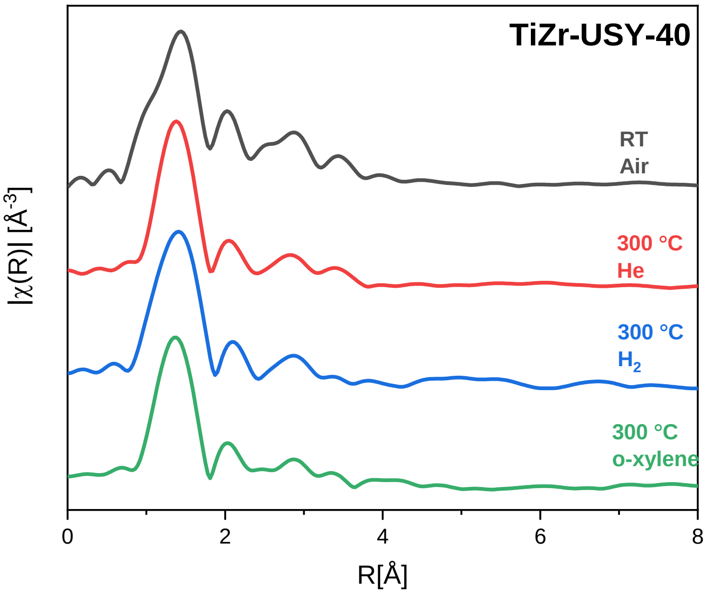

Figure 8. Comparison of EXAFS oscillations: Fourier transform of TiZr USY-40 at different stage of the operando test

A comparison of the XANES spectra of the TiZr USY-40 catalyst with the spectra of different zirconium references (Figure 9). The pre-edge feature of the XANES spectrum of the catalyst may suggest a penta or tetra coordinated Zr in the sample

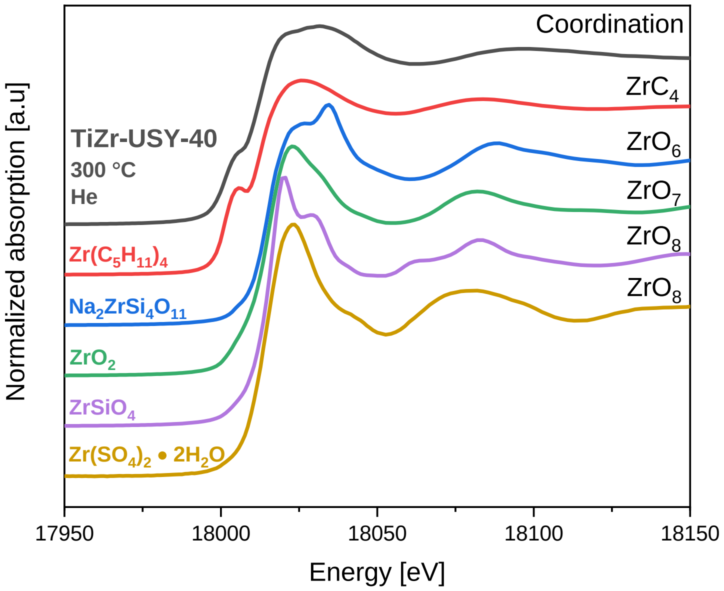

Figure 9 Zr K-edge XANES spectra of the TiZr USY-40 and different Zr references

- **Justification and comments about the use of beam time** (5 lines max.): -

Due to the COVID situation, the allocated shifts for this experiment were decreased from 18 to 12. Futhermore, the run also suffered from several and long beam downtime which had an impact on the final scope of the work. Despite those difficulties, most of the structural information required to conclude the study could be recorded except for the state of titanium during o-xylene isomerisation. One publication is currently in preparation.

- **Publication(s)**: -

[1] *Rev. Sci. Instrum. 89, 035109 (2018)*