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"*Studies of CO$_2$ hydrogenation reaction mechanism by FT-IR measurements*"

Host Institution

Laboratoire Catalyse et Spectrochimie LCS (ENSICAEN)

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INTRODUCTION AND RESEARCH OBJECTIVE

The Short Term Mobility has been carried out at the "Laboratoire Catalyse et Spectrochimie" LCS. It is one of the Laboratory managed by the "Institut de Chimie (INC)" of CNRS of the Normandy delegation. The Catalysis and Spectrochemistry Laboratory works on the preparation and the study of solid catalysts for applications in environment and sustainable development, but it is also the leader in the observation of catalytic materials inside a working reactor, in real time, during the chemical reaction (*operando* spectroscopy).

The research activity performed during this period has been focused towards the study of CO_2 hydrogenation reaction by exploiting *operando* FT-IR measurements. Specifically, the activity has been addressed to the investigation of the reaction pathways of methanol (MeOH) and dimethyleter (DME) formation from CO_2-H_2 mixtures by using a series of solid catalysts based on copper/zinc oxide/zirconia (CZZ) and hybrid system containing zeolites (CZZ-Ferrierite), respectively. The measurements have been carried out under the real reaction conditions, in the temperature range of 160-280°C at 9,3 bar. These spectroscopic studies allowed determining the nature of active sites, intermediate compounds and main reaction steps involved in CO_2 conversion. Besides characterizing the reactivity of adsorbates, the dynamics of CO_2/hydrogen reactant mixtures has been monitored over unreduced catalyst, with the aim of acquiring information on the MeOH and DME synthesis mechanism.
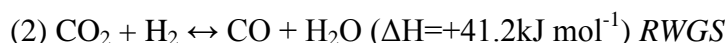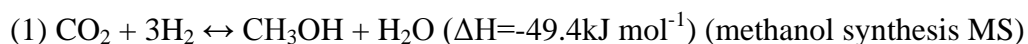
1. CO₂ HYDROGENATION TO METHANOL OR DIMETHYLETHER

1.1 State of Art

New technologies based on the CO_2 capture, storage or conversion have recently received much attention, since the reduction of greenhouse emissions represents the main challenging issue on the climate change. For example, the use of CO_2 as reagent looks very attractive for producing chemicals of fuels like MeOH and DME which can be used as alternative to gasoline and gasoil respectively.

In particular, DME is one of the most promising environmentally friendly alternatives to conventional fossil fuels due to its high cetane index, low emission of CO, NO_x and particulates as well as reduced noise [1]. DME is biodegradable; it has low toxicity and does not corrode any metals. Moreover, it is an important intermediate for production of gasoline, ethane, aromatics and chemicals [2].

From a thermodynamic point of view, in the CO_2 hydrogenation, the temperature plays a negative role on dimethylether selectivity considering that DME formation is an exothermic reaction, so a decrease in reaction temperature or an increase in reaction pressure should favor the synthesis of DME (Figure 1). However, from a kinetic point of view, only an increase of reaction temperature over 220°C/240°C facilitates the CO_2 activation rate the formation of DME being paralleled by the competitive formation of methanol (1) and/or carbon monoxide (2)

(1) $CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$ (ΔH=-49.4kJ mol^{-1}) (methanol synthesis MS)

(2) $CO_2 + H_2 \leftrightarrow CO + H_2O$ (ΔH=+41.2kJ mol^{-1}) *RWGS*

During the CO_2 hydrogenation, in fact, CO is also produced by the reverse water-gas shift reaction (RWGS) (2) and this reaction reaches quickly its equilibrium.
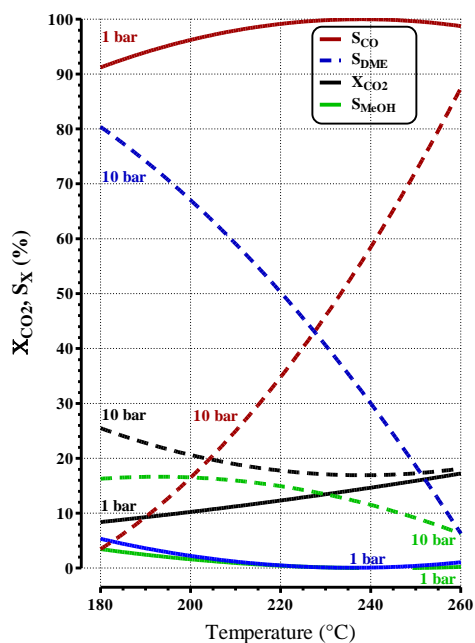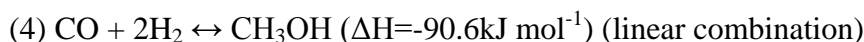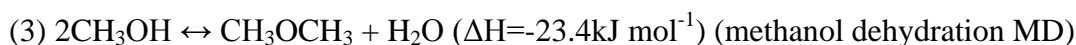
**Figure 1.** *Thermodynamics of DME by CO$_2$ hydrogenation.*

Subsequently, DME is produced though methanol dehydration/condensation (3), thereby enhancing the forward reaction and limiting the CO$_2$ consumption via-RWGS reaction

(3) $2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$ (ΔH=-23.4kJ mol^{-1}) (methanol dehydration MD)

(4) $CO + 2H_2 \leftrightarrow CH_3OH$ (ΔH=-90.6kJ mol^{-1}) (linear combination)

In the direct CO$_2$ hydrogenation process, the net reaction is given by the reaction:

(5) $2 CO_2 + 6 H_2 \leftrightarrow CH_3OCH_3 + 3H_2O$ (ΔH=-122.2kJ mol^{-1}) (linear combination)
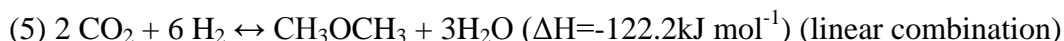
The DME synthesis could be also affected by the decomposition of methanol to CO

(6) $CH_3OH \leftrightarrow CO + 2H_2$ *(ΔH=+90.62kJ mol^{-1})*
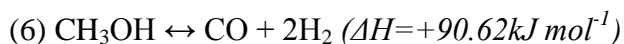
Currently MeOH synthesis is run mostly starting from a syngas feed containing 5%CO-5%CO$_2$ and H$_2$, whereas the two steps technology is considered as the most mature route to obtain DME. So, in the first step, syngas is converted into methanol over copper-based catalysts. In the second step, methanol is dehydrated into DME over acid catalysts. Anyhow, the direct production of DME by CO$_2$ hydrogenation has become an important issue widely studied by employing hybrid catalysts characterized by multifunctional sites to overcome the thermodynamic constraints and to lead to higher per-pass CO conversions and higher DME productivity.

On this account, new Cu-Zn-Zr/zeolites systems with suitable extent of metal-oxide interfacial area for CO$_2$ conversion and acid sites for MeOH dehydration have been prepared by CNR-ITAE and tested in the DME production with very important results already published in papers of international relevance [1, 3-5]. Besides, to further improve the catalytic behavior by optimizing the catalyst design, studies on the reaction mechanism, the nature of active sites and intermediate products formation is fundamental considering that in literature a great debate in this area is still opened.

During the last decades, in fact, the mechanism of methanol synthesis from $CO/CO_2/H_2$ feedstock over copper-based catalysts has been the subject of much controversy [6]. It is generally agreed that a linear relationship exists between copper metal surface area and methanol synthesis activity, for CO_2 containing mixtures [7-8]. In apparent contrast to the results of Chinchen et al. [6] Burch and co-workers [9-10] argued that also the nature of the support oxide present could have a significant effect on the catalytic activity. For zinc oxide/alumina supported copper catalysts ($Cu/ZnO/Al_2O_3$) it was clearly shown that CO_2 is the main carbon source of methanol in the presence of water by means of isotope labeling experiments. In contrast, over zirconia-supported systems, it remains difficult to assess whether methanol synthesis start from CO or CO_2. Anyhow, the support of zirconia is by itself a catalyst for the synthesis of methanol in contrast to silica or alumina support thanks to its capacity to store hydrogen [11] and it provides adsorption sites for the surface reaction intermediates.

Moreover, it is generally assumed that either a formate or a carbonate type species could be the pivotal intermediates. For example, Bowker *et al.* [12] demonstrated that the coadsorption of hydrogen and carbon dioxide on copper resulted in the formation of formate species, even if, on the contrary, Burch et al. [6] suggested that under typical methanol synthesis conditions (230°C, 5-10 MPa), formate species may not actually be involved in the synthesis mechanism.

For this purpose, operando FT-IR measurements have been exploited as a suitable tool to identify and quantify the catalyst active sites and so to correlate the catalytic behavior with the surface properties of the investigated system. Specifically, in this study, the interaction of CO_2/H_2 mixtures with Cu-ZnO/ZrO₂ (CZZ) and hybrid catalysts (CZZ-Fer), at different reaction temperature and 9.3 bar was studied using operando FT-IR spectroscopy.

1.2 Operando FT-IR study

Operando Infrared Spectroscopy is a methodology that allows the investigation of a material during its working conditions. The Latin term operando derives from the field of heterogeneous catalysis, in which the spectroscopic characterization of a catalytic material takes place during the reaction with the simultaneous measurement of catalytic activity/selectivity. The goal is a qualitative and quantitative characterization of the surface species correlated with the catalytic performances of the material [13]. It is often used qualitatively to elucidate reaction mechanism thanks to the observation of the catalyst under actual operating conditions. Besides in principle such technique can also provide quantitative information that can be used to describe detailed chemical kinetics (spectrokinetic approach).

The operando methodology consists in a real-time spectroscopic survey of a reaction coupled to simultaneous activity measurements in kinetically relevant cell [14]. Due to its potentiality to carry out surface and gas phase analyze under actual reaction conditions, this technique is able to provide, in principle, significant insight for a knowledge-based catalyst description and enhancement.

In particular, spectroscopic techniques operating under actual reaction conditions uncover how a catalytic surface behaves, and may provide insights on the relevant catalytic steps, active sites and reaction intermediates during a given process. In such a way, a catalytic process can be finely described, and information can be obtained on the elementary steps and/or the rate determining processes.

On this account, as proved by many papers, the research team of LCS laboratory has long tradition in operando IR cell design and manufacturing [14 and reference therein].

2. EXPERIMENTAL SET-UP

2.1 Catalyst preparation

Cu-ZnO-ZrO₂ catalyst. CZZ catalyst has been prepared by gel oxalate coprecipitation method [17]. The precursors (nitrate of Cu, Zn, Zr) were solubilized in ethanol and coprecipitated by oxalic acid at room temperature under vigorous stirring. The precipitated was dried at 110°C for 16h and then calcined at 350°C for 4h.

Cu-ZnO-ZrO₂FER catalyst. $Cu(NO_3)_2*2.5H_2O$, $Zn(NO_3)_2*6H_2O$ and $ZrO(NO_3)_2*nH_2O$ (in a Cu/Zn/Zr atomic ratio of 60/30/10) were solubilized in ethanol and coprecipitated by oxalate acid (gel oxalate coprecipitation) at room temperature under vigorous stirring in a solution containing the zeolite finely dispersed (particle size<100 nm) with a final CuZnZr:zeolite weight ratio of 1:2 and 2:1. They were labelled CZZ-FER0.5 and CZZ-FER2 respectively. The solids were stirred for 3 h, aged overnight, then filtered, dried at 110°C for 16h and calcined at 350°C for 4h according to [3-5].

The atomic composition (evaluated by EDX measurements) and porous information are reported in Table 1. The average copper particle size is 11 nm for the CZZ catalyst and about 8 nm for the hybrid systems.

Table 1. Chemical composition and textural properties of the investigated samples.

Catalyst	Atomic composition* (wt%)					SA (m²/g)	PV (cm³/g)	APD (Å)	d_{Cu} nm
	CuO	ZnO	ZrO₂	SiO₂	Al₂O₃				
CZZ	56.8	27.7	15.5	-	-	145	0.228	63	11
CZZ-FER0.5	14.6	8.4	5.2	65.1	6.7	293	0.256	35	8
CZZ-FER2	35.0	18.8	10.9	31.7	3.6	182	0.335	73	8

* evaluated by EDX measurements.

2.2 FT-IR operando system

IR operando system. The IR operando system, which was used for this study, is schematized in Figure 2 and shown in Figure 3.
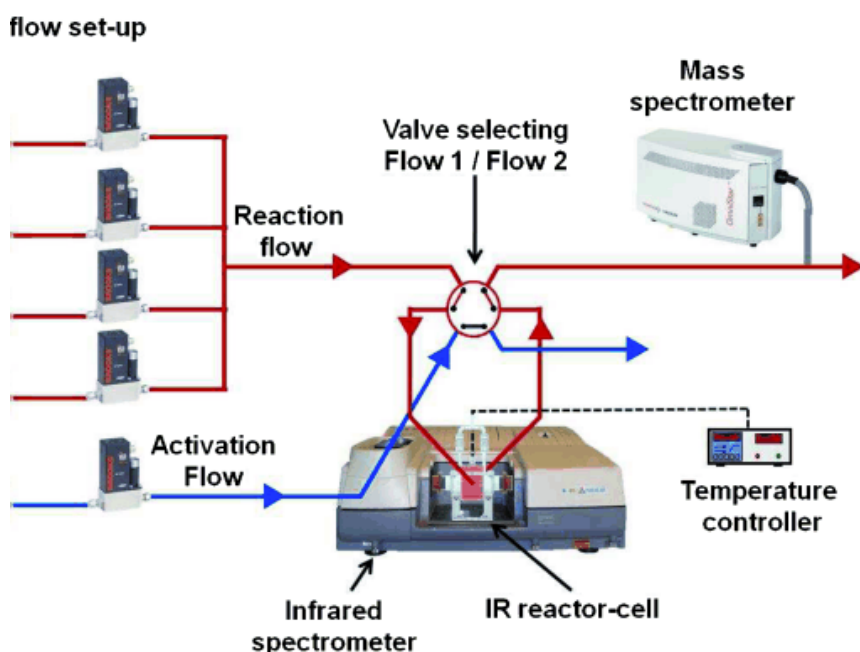

Figure 2. General scheme of the IR operando system.

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This system is composed of four main parts: *i)* the infrared spectrometer, *ii)* the IR reactor cell, *iii)* the gas flow set-up and *iv)* the exhaust gas analyzers. The cell was connected to the operando gas-system including mass flow controllers for the introduction of gases into the lines. The two gas mixtures (for the activation and for the reaction) can be prepared and sent independently to the reactor cell. The system allows investigating the exhaust gases (reactive and/or reaction products) by a quadrupole mass spectrometer (Pfeiffer Oministar GSD 301). IR spectra (64 Scans per spectrum) are collected with a Thermo Scientific Nicolet 6700 spectrometer, equipped with a MTC detector.
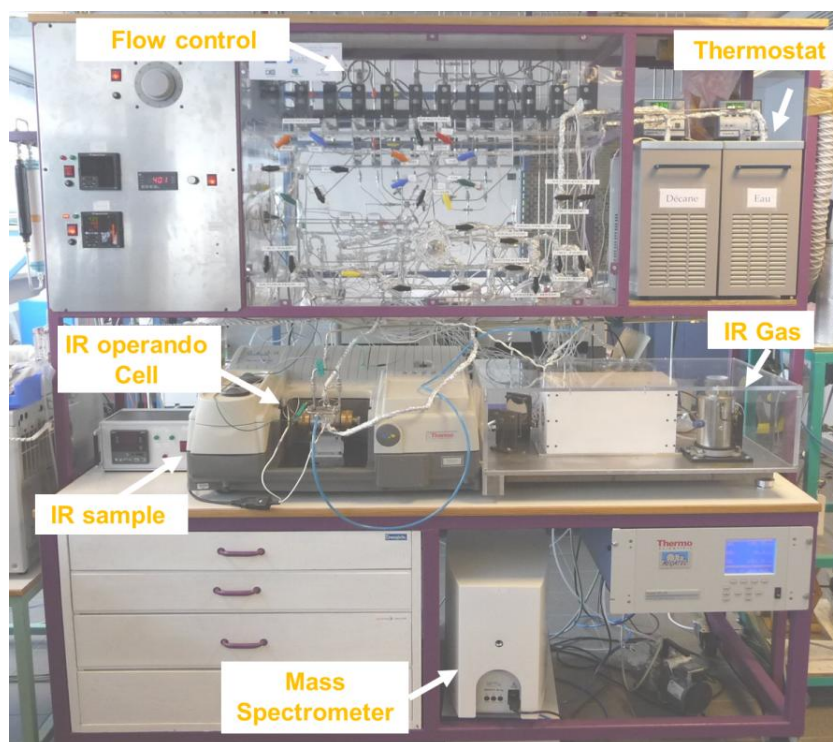

Figure 3. Picture of the IR operando system.

Sandwich IR reactor cell. The "sandwich" reactor-cell used in this study is shown in Figure 4 in 3D view and Figure 5 [A-C]. The shape of the mail part is cylinder made of stainless steel that carries a spherical sample holder in its centre. That is where the sample is placed in the form of a self-supported water of 16 mm of diameter [Figure 5B]. The heating system allows a maximum temperature of 600°C for the sample, whereas the air cooling system keeps the two ends of the cell below 300°C. The required tightness of the cell can be obtained by using Kalrez *O*-ring between the terminal KBr windows and the extremities of the cell. The rest of the space is filled by KBr windows which limit the dead volume to 0.12 cm³. The experiment was carried out at 9.4 bar; gases are introduced onto the sample by a 1/8'' OD pipe and collected on the opposite side of the sample older.
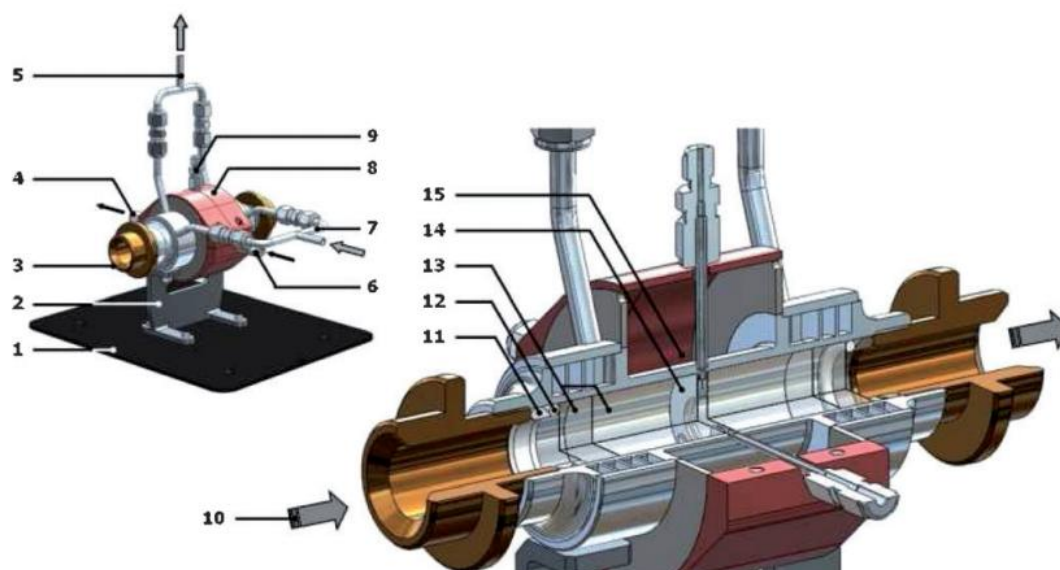
Figure 4. *General and detailed views of the "sandwich" reactor-cell. 1=Spectrometer base-plate; 2= IR cell support; 3= adjusting nut for air tightness; 4=gas outlet; 5=air cooling outlet; 6=gas inlet; 7=air cooling inlet; 8=external shell; 9=thermocouple location; 10=IR beam; 11=stainless steel ring; 12=Kalrez O-ring; 13=KBr windows; 14 =wafer holder; 15=oven location [13].*
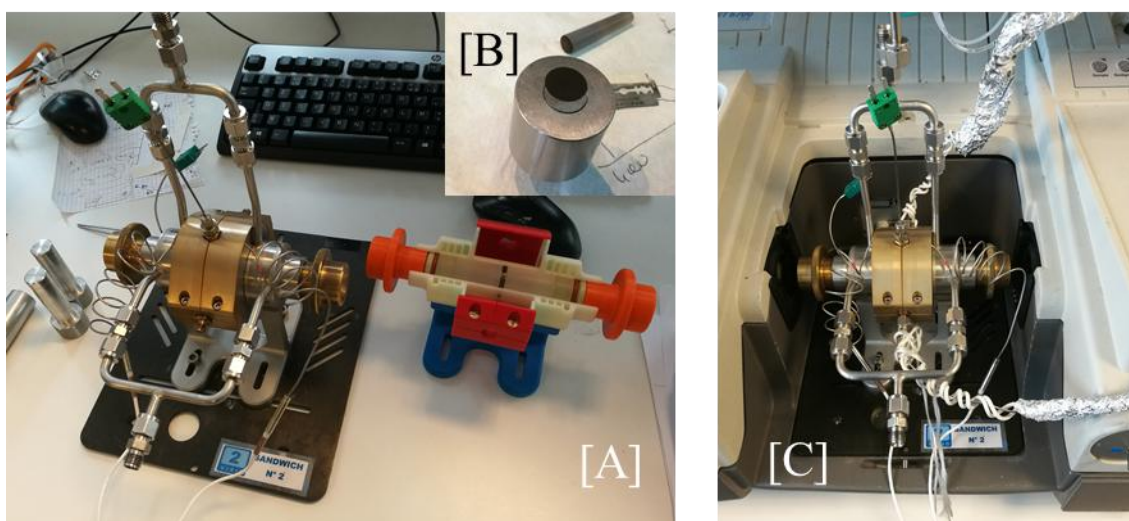

Figure 5. *Picture of the sandwich reactor-cell [A-C] and of the sample [B].*

Gas composition and experimental description. The gas compositions were the following: activation flow, H$_2$ – total flow 10 cm^{3}min^{-1} and reaction flow, mixture of H$_2$, CO$_2$ and Ar in 9/3/1 ratio – total flow 14 cm^{3}min^{-1}. Considering that the reactions have been carried out under different conditions, they will be better explained in the corresponding paragraphs.

As regards the mass spectroscopy analysis, the species followed were CO$_2$, CO, H$_2$, Ar, CH$_3$OH, O$_2$, CH$_3$OCH$_3$, O$_2$ and the H$_2$O by considering the *m/e* ratio = 44, 28, 2, 40, 31, 32, 45, 18. Such analyses allowed following the reaction profiles and understanding when it was possible to change or not the reaction temperature investigated.

Conversion-selectivity data were calculated after calibration measurements of each product under the same reaction conditions.

3. RESULTS AND DISCUSSION

3.1 CO₂ hydrogenation reaction in operando conditions

The CO_2 hydrogenation was carried out at a reaction temperature ranging from 180 to 280°C with a flow ratio$_{CO2/H2/Ar}$ of 3:9:1 . Prior to each test, the catalyst was reduced *in situ* at 300°C for 1h30' in pure hydrogen at atmospheric pressure, with a flow of 10 cm^{3}min^{-1}. Then, the temperature was reduced to 160°C whereas the pressure was raised up to 9.3 bar. The reaction at each temperature was stopped only after stabilization of the signals (about 2h). Under such reaction conditions, catalysts investigated were CZZ and CZZ-FER2.

A) Pretreatment step.
For all systems, during the reduction step, the intensity of signals decreases progressively as it is possible to see in Figure 6A. Moreover, at about 140°C, the catalyst becomes semiconductive and less transparent to the IR beam. Unfortunately, this causes a further decrease in the signals with very poor profiles (B-C).
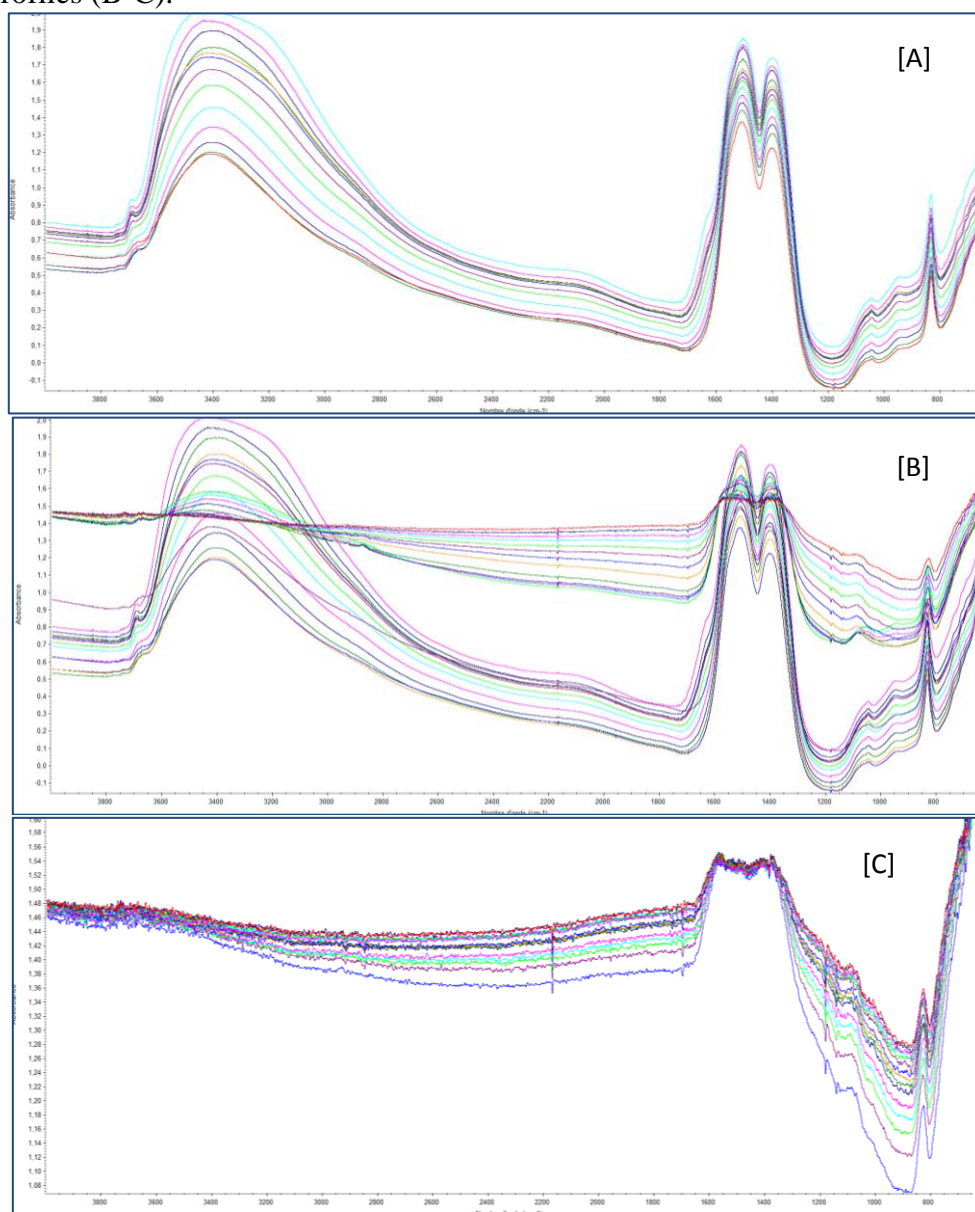

Figure 6. *CZZ catalyst [A] Reduction step in pure H₂ from 20°C to 140°C; [B] Reduction step in pure H₂ from 20°C to 300°C; [C] Reduction step in pure H₂ at 300°C (1h30').*
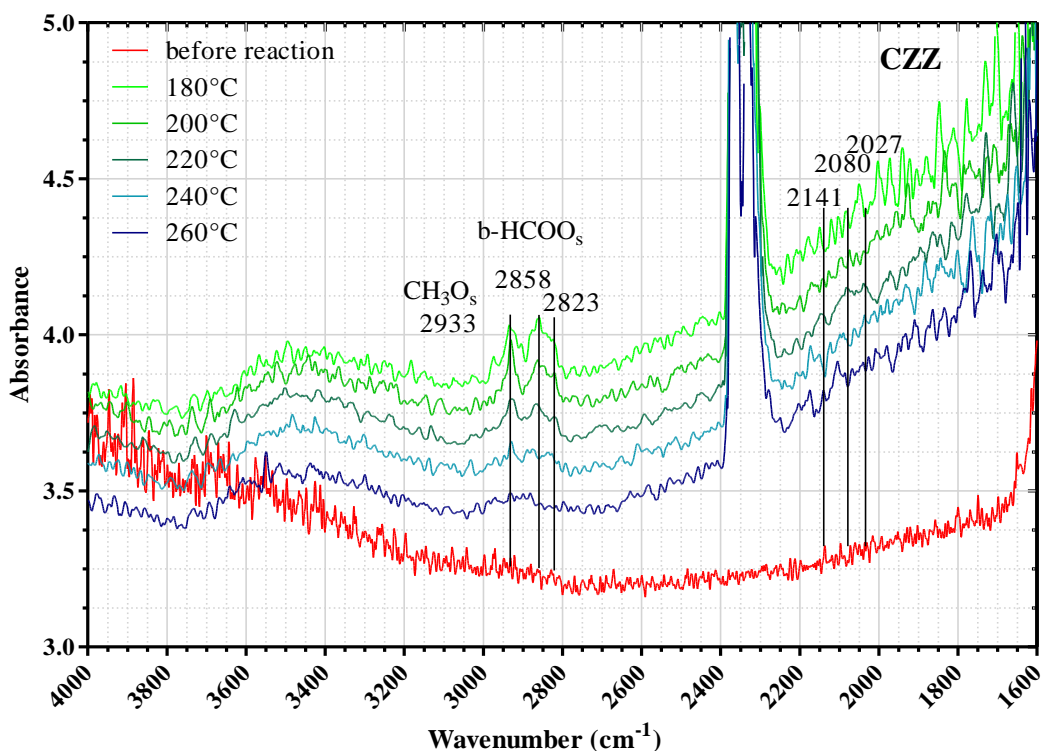
B) Hydrogenation from 180 to 280°C.

Figure 7. *Spectra recorded during CO₂ hydrogenation reaction from 180°C to 260°C on CZZ catalyst.*
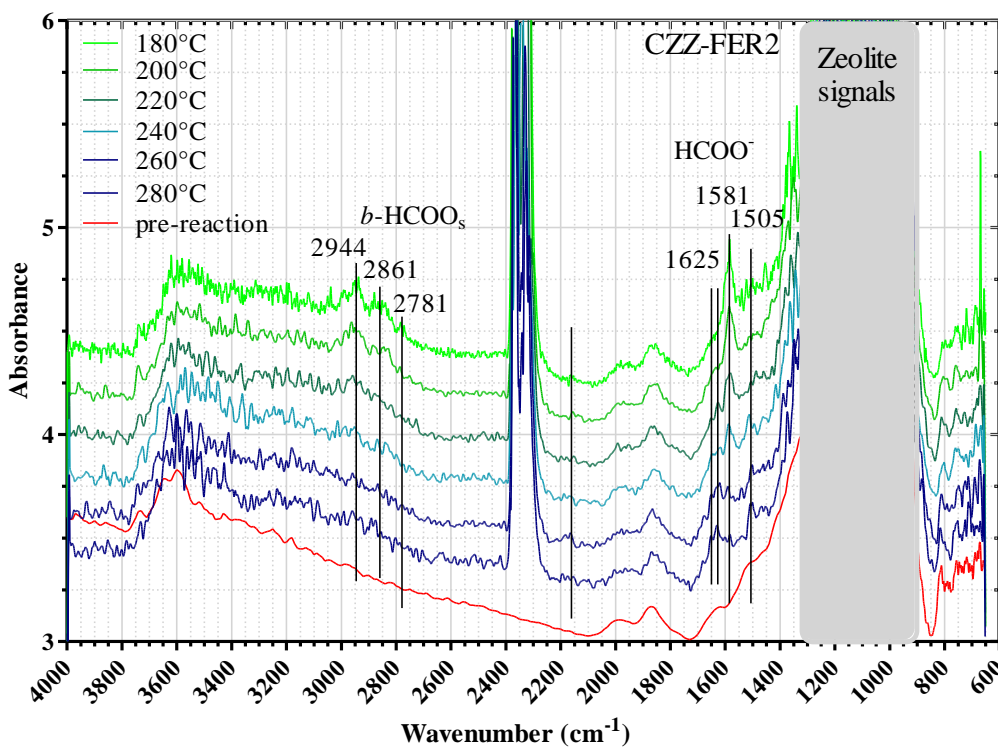

Figure 8. *Spectra recorded during CO₂ hydrogenation reaction from 180°C to 280°C on CZZ-FER2 hybrid catalyst.*

In Figure 7 and 8, the spectra obtained after a contact time of 2h at different temperature (from 180 °C to 280°C) for samples CZZ and CZZ-FER2 are shown in comparison with the profile recorded before the hydrogenation reaction.

In the CZZ sample, the presence of formate species on Cu was observed at 180°C with their characteristic peaks at 2933 and 2858 cm^{-1}. They completely disappear at 260°C. Peaks at 1591 and 1353 cm^{-1} are hidden below the carbonate area [6,15].

Also on the CZZ-FER2 sample, new peaks at 2944, 2861 and 1581cm^{-1} are evident. Then they completely disappear at 260°C. At such temperature, a peak at 1625 increased, likely indicative of the presence of molecular water.

The region 1950-2200 cm^{-1} is phenomenally informative. It is the region of the C-O stretch of CO adsorbed on Cu and this stretch is structure sensitive. The peak at about 2070 is characteristic of CO adsorbed on metal copper, whereas that a 2126-2132 cm^{-1} can be assigned to linear CO adsorption on oxidized copper sites [6]. The detection of some bands at about 2180 and 2113 cm^{-1} attributed to gas-phase carbon monoxide demonstrated that the reverse water-gas shift reaction occurred too.

In the following Figures 9 and 10, the gas phase analyses are reported in the range 800-2300 cm^{-1}. The main difference between the two systems is that by using the hybrid system CZZ-FER2, the DME is formed already at 180°C to disadvantage of MeOH. The identification of methane as a minor reaction product was in agreement with literature results [16]. In both cases, CO is the main product at all reaction temperature. However, a selectivity pattern is reported afterwards in the Table 2 and further discussed.
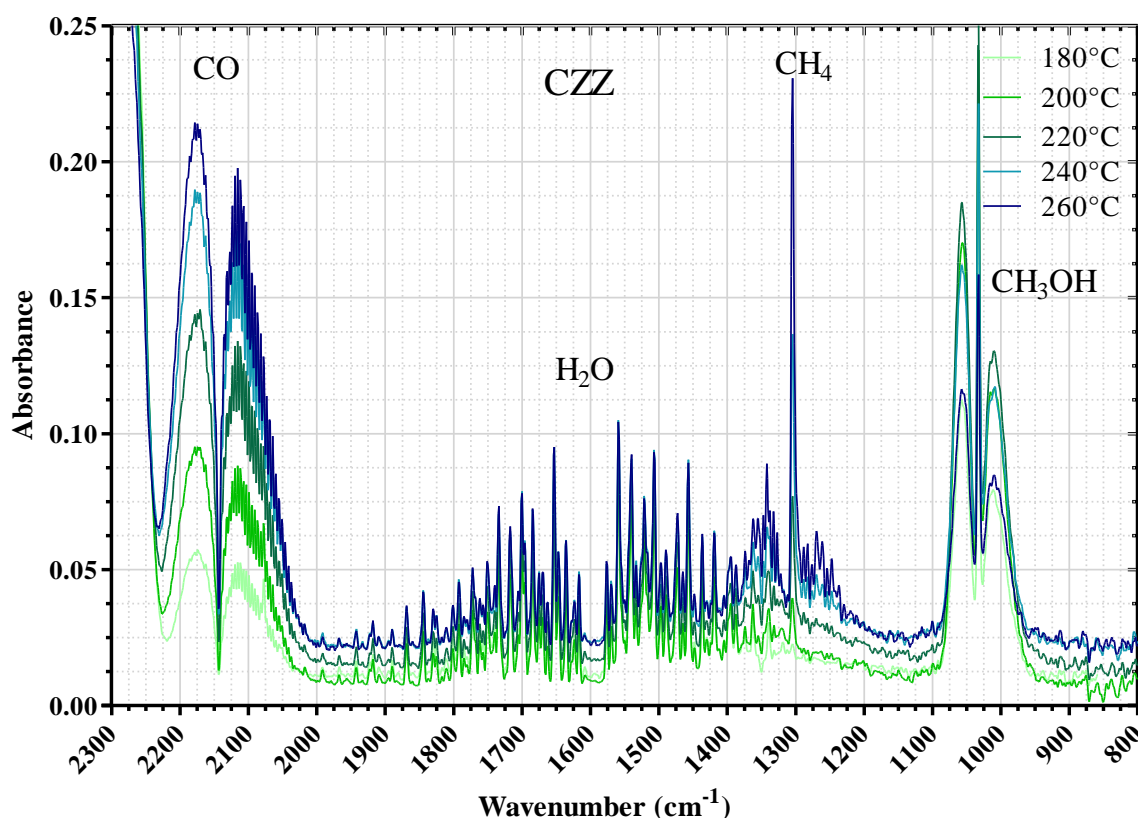

Figure 9. *Spectra recorded during CO₂ hydrogenation reaction from 180°C to 260°C on CZZ catalyst.*
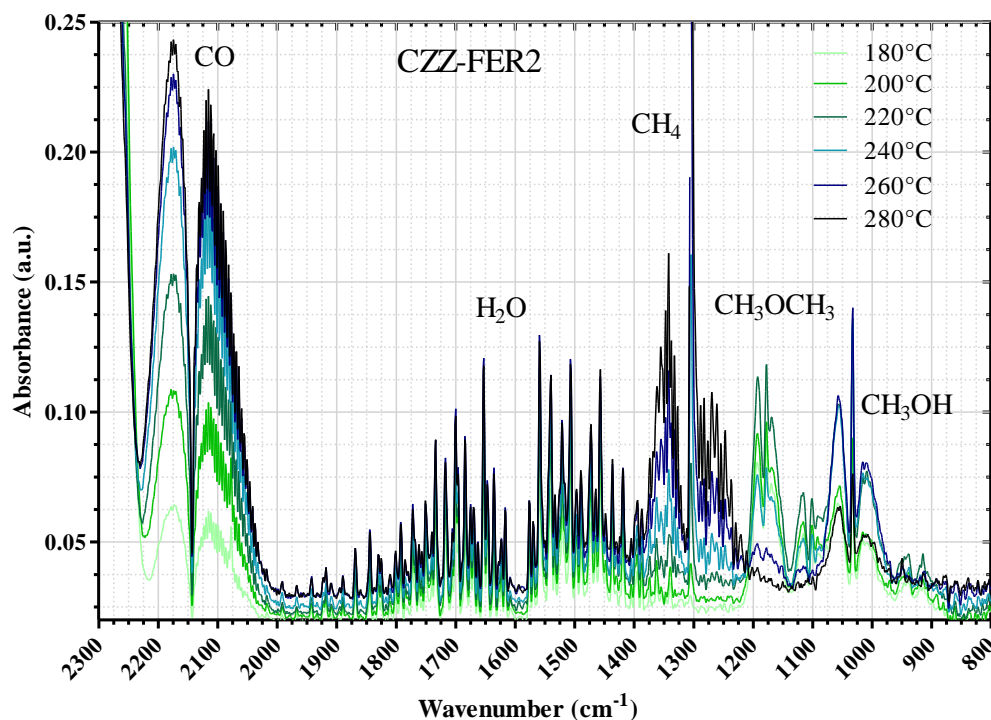
***Figure 10**. Gaseous phase recorded during CO_2 hydrogenation reaction from 180°C to 280°C on CZZ-FER2 catalyst.*

3.2 CO₂ hydrogenation reaction and Ar cleaning at each temperature

Considering the difficulties in identifying the adsorbed species in operando conditions due to the very low signals, new experiments have been carried out with a new procedure. Specifically, after the reduction in hydrogen at 300°C, the catalyst has been cooled down at 160°C in Ar in order to clean the surface and then pressure was raised up to 9,3 bar. Thus, the CO_2 hydrogenation reaction was started by using the same flow gas of 14 cm^3min^{-1} and a flow ratio$_{CO2/H2/Ar}$ of 3:9:1. The reaction at each temperature was stopped only after stabilization of the signals and then the surface had been cleaned with an Ar flow in order to individuate the adsorbed species. The spectra had been recorded both under flow reaction than under Argon flow. Under such reaction conditions, the two catalysts investigated were CZZ and CZZ-Fer0.5.

As it is possible to see in the Figure 11, the intensity of gaseous CO_2 during the reaction is very high and, at the same time, the intensity of carbonaceous species decreases immediately. Anyhow, after cleaning the surface with Ar flow, under the same pressure, the carbonaceous species are still visible and adsorbed species on the surface become detectable. The figure shows this behavior for CZZ catalyst at 160°C but this is true for each temperature. On the contrary, on the CZZ-FER0.5, carbonaceous species are not present, so the spectra appear fairly neat, even if there are the intense signals of the zeolite.
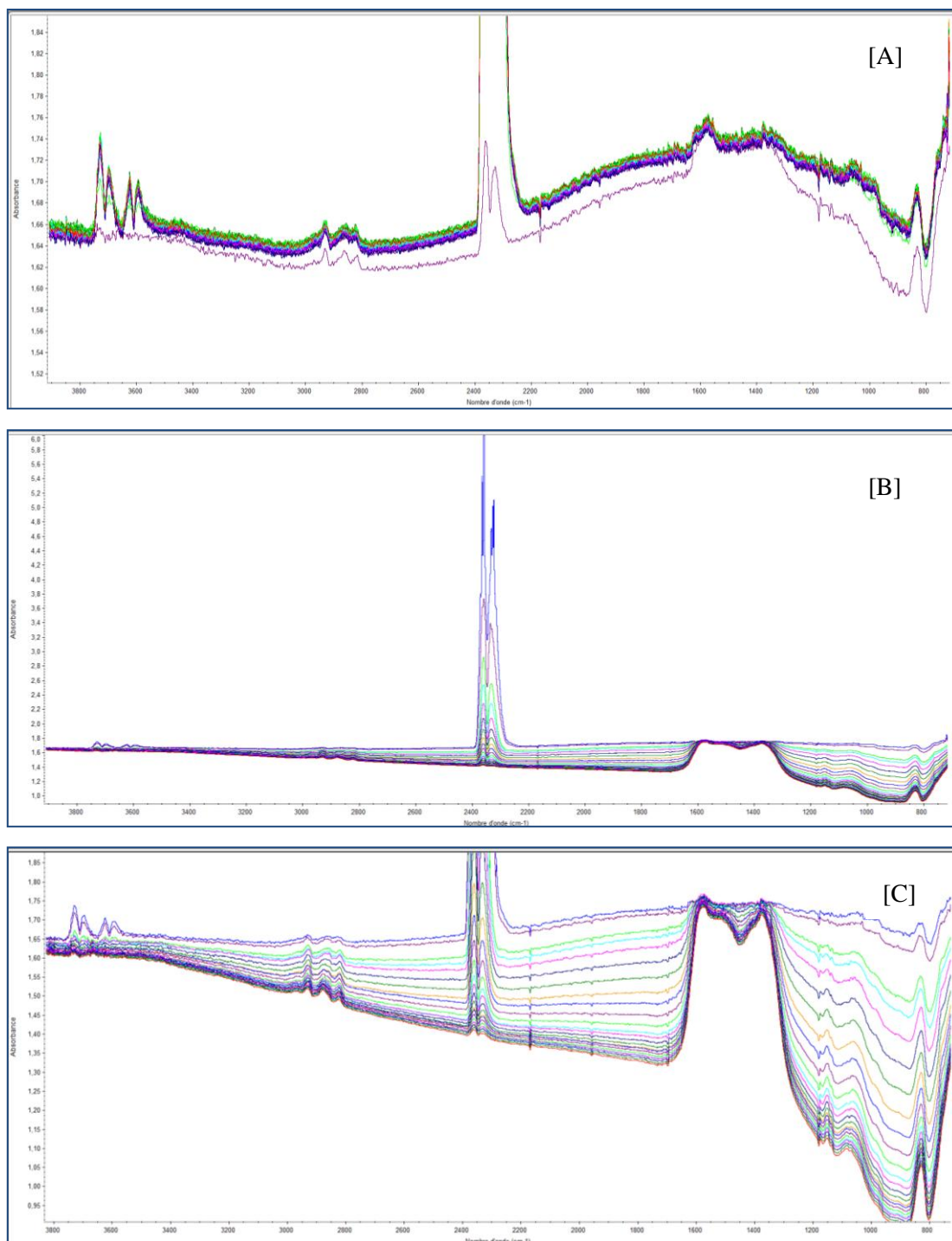
Figure 11. *[A] Reaction at 160°C with CO$_2$/H$_2$/Ar (3:9:1) on CZZ catalyst. [B] Cleaning of the surface in Ar at 160°C. [C] Zoom of cleaning of the surface in Ar at 160°C.*

So, in the Figure 12 and 13, the infrared spectra indicative of the adsorbates species which exist at a steady state on a Cu/ZnO/ZrO$_2$ catalyst and the hybrid CZZ-FER0.5 system at 160°C, 180°, 200, 220 and 240°C are reported. It is possible to see that already at 160°C, new species are present on the surface of both samples.

As already mentioned, on CZZ, the region 1300-1600 cm^{-1} contains the C-O stretches of the carbonate species. However, a new peak is evident at 1604 cm^{-1} due to formate specie adsorbed on the copper (HCOO-Cu). The maximum height of the composite peak of carbonate and formate species is at about 1465 cm^{-1}, it decreasing with increasing temperature. This indicates that their

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formation is a thermodynamic function and not a kinetic one [17]. The corollary of this argument is that the adsorption and decomposition of CO$_2$ to form the carbonate on copper is only weakly activated. The peak at 1151 is assigned to a methoxy species adsorbed on the ZrO$_2$ component of the catalyst.

At 160°C, π-bound formaldehyde and surface bound methylate could be observed too (2930, 2830, 1150 and 1050 cm^{-1}) [16]. Bands at 2928, 1560 and 1351 cm^{-1} could be generally assigned to bringing formate on copper [6] too.

On CZZ-FER0.5, instead, thanks to the absence of carbonaceous compounds, the peaks at 1590 and 1372 cm^{-1} are well visible from 160°C to 220°C.
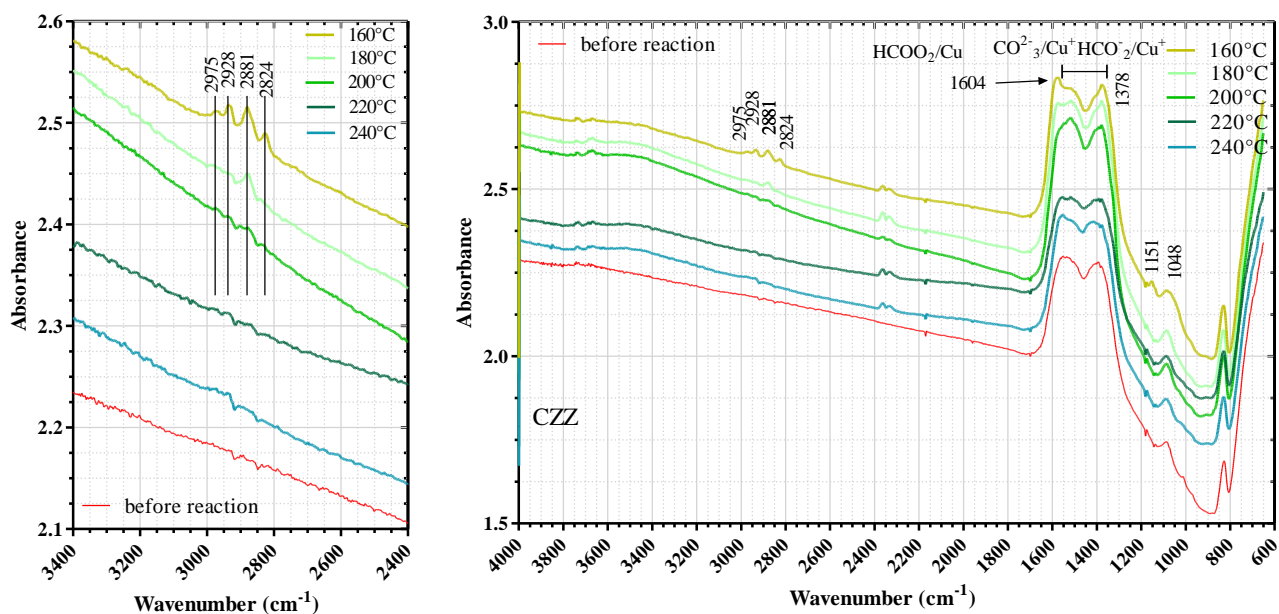

Figure 12. *Spectra recorded during CO$_2$ hydrogenation after cleaning surface in Argon on CZZ catalyst.*
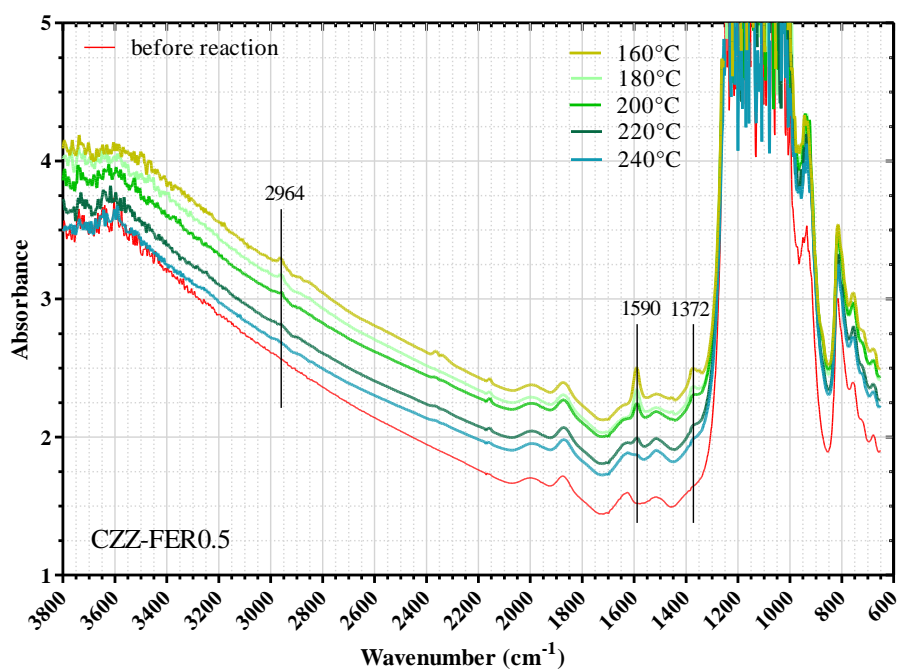

Figure 13. *Spectra recorded during CO$_2$ hydrogenation after cleaning surface in Argon on CZZ-FER0.5 catalyst*

In the Table 2, the results obtained in the CO_2 hydrogenation in terms of CO_2 conversion and products selectivity are reported for CZZ and CZZ-FER0.5 catalysts. Specifically, for the CZZ system, the results of the two reactions under different experimental conditions after the reduction pretreatment (without Argon cleaning* and with Ar surface cleaning**) are compared. In general, as foreseen, the CO_2 conversion increases during the reaction with the temperature, by passing from about 9.8% at 160°C up to 33% at a temperature as high as 260°C. As regards the products selectivity, it is possible to see that by increasing the temperature, the CO increases too along with a lower amount of CH_4. On the contrary, the methanol selectivity decreases to advantage of CO from 45.45% at 160°C to about 3% under 240°C. The methanol storing in the first reaction condition without no cleaning of the surface likely justifies the higher values of methanol produced at 220°C and 240°C in respect to the amount recorded after the Ar treatment.

The hybrid system shows a different trend in terms of product selectivity. In this case, in fact the CO selectivity is very high already at lower temperature (>80-90%) with a correspondent very low selectivity to methanol which is only 8.53% at 160°C instead of the 45.45% value obtained with CZZ. However, a certain amount of DME is formed to, even if, as expected from thermodynamic studies, it decreases with the temperature.

***Table 2.** CO₂ hydrogenation reaction: CO₂ conversion and products selectivity.*

Catalyst	T (°C)	X_{CO2} (%)		Selectivity (%)							
				CH₄		CO		MeOH		DME	
CZZ	160	-*	9.83**	-*	0.96**	-*	53.59**	-*	45.45**	-*	-**
	180	11.86	20,22	2.11	2.08	69.79	64.13	28.10	33.79	-	-
	200	16.41	21.06	2.94	2.42	79.79	79.63	17.28	17.95	-	-
	220	20.98	25.65	3.81	3.13	86.00	87.98	10.20	8.88	-	-
	240	27.70	31.27	5.63	4.53	88.80	91.85	5.57	3.62	-	-
	260	33.11	-	9.50	-	87.59	-	2.90	-	-	-
CZZ-FER0.5	160	19.11	9.80	-	4.04	-	83.48	-	8.53	-	3.95
	180	19.26	17.27	-	5.15	92.11	81.74	3.76	6.63	4.14	6.48
	200	20.31	20.14	2.38	5.10	90.86	87.63	2.64	3.60	4.12	3.68
	220	21.80	24.46	4.16	6.66	86.34	89.56	4.08	2.30	5.42	1.48
	240	25.58	28.00	4.80	8.51	88.55	89.50	3.23	1.38	3.42	0.61
	260	30.05	-	7.56	-	88.53	-	2.53	-	1.39	-

*operando reaction (first condition); ** operando reaction with cleaning in Ar

It is interesting to observe the products concentration trend in terms of ppm obtained during the two reactions on CZZ catalyst (with and without surface cleaning with Ar). The results are shown in Figure 14. CO and CH_4 concentrations almost linearly increase with the temperature, but the methanol shows a volcano-like trend with a maximum peak at 220°C during the operando reaction and at 200°C by stopping the reaction at each temperature and then cleaning with Ar. This could indicate the initial formation of MeOH and then its decomposition to CO (see eq. 6).
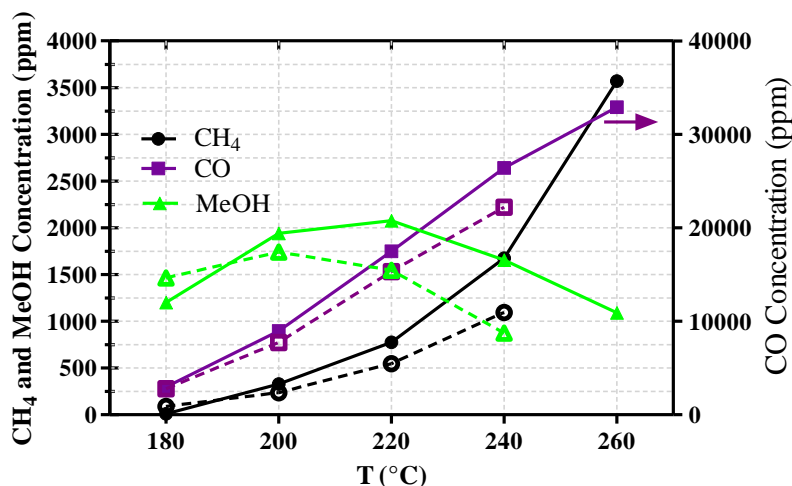
Figure 14. *Conversion and selectivity as a function of temperature on CZZ catalyst. Broken line (- - -) is referred to CO₂ hydrogenation and Ar cleaning at each temperature.*

3.3 Temperature Programmed Surface Reaction (TPSR)

At this point, a new kind of experiments was carried out in order to further investigate the behavior of the CO_2 on the three systems without the preliminary reduction step. Specifically, the reaction flow was maintained 14 cm³min⁻¹ with a flow ratio$_{CO2/H2/Ar}$ of 3:9:1. The pressure was raised up to 9.3 bar at room temperature and then a TPSR was followed with a β=1°Cmin⁻¹ from 20°C up to 260°C. This study was carried out on all three catalysts, but only some of most interesting results are here shown.

Specifically, from Figure 15, it is possible to see that, already at room temperature and pressure, carbon dioxide is adsorbed on all three investigated systems as linear specie [18], Specifically, two linear CO_2 species are evident at 2361 and 2336 (sh) cm⁻¹. However, a different profile is observed for the systems, thus indicating that CO_2 likely adsorbs in a different way. Further investigations must be done to highlight this aspects which could be an important key of CO_2 activation on Cu-based catalysts and hybrid systems containing the acid zeolite.

Moreover, on CZZ sample, carbonate species already present on the surface of the catalyst are modified. Various types of carbonate species on ZrO_2 have been characterized by Monterra and Orio [19] with their nature depending on the dehydration and sintering state of the support. In particular, a hydrogen carbonate species CO_2OH^- is reported to have a υ_{OH} vibration at ≈ 3600 cm⁻¹, δ_{OH} at 1227 cm⁻¹ and υ_{CO2} asymmetric and symmetric at 1620 and 1453 cm⁻¹ [18].
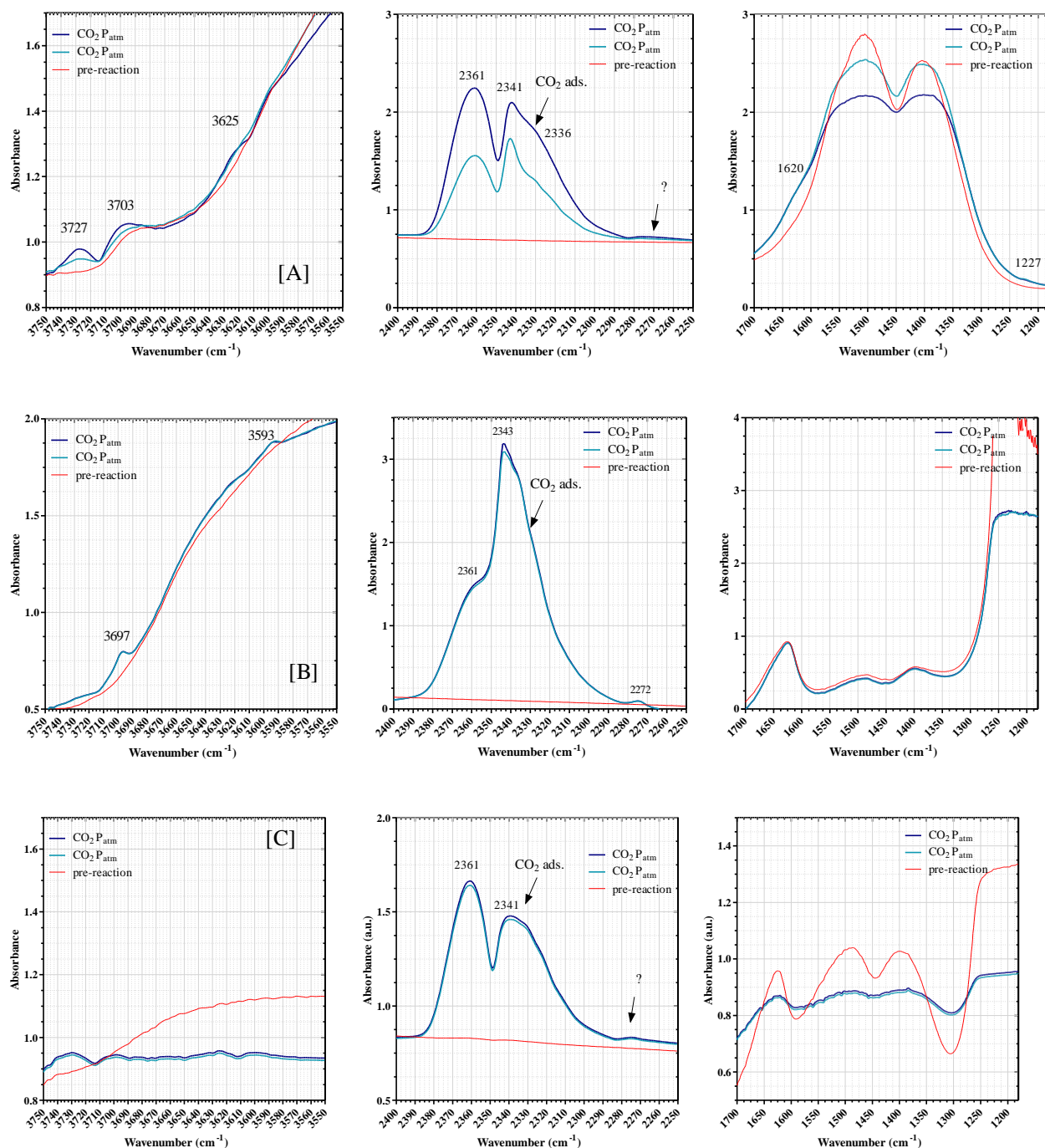
Figure 15. *CO₂ adsorption on unreduced [A] CZZ, [B] CZZ-FER0.5 and [C] CZZ-FER2 catalysts under atmospheric pressure.*

In Table 3, the results obtained on unreduced catalysts are reported in terms of CO_2 conversion and product selectivity. Such data are compared with previously results obtained with CZZ and CZZ-FER0.5 in CO_2 hydrogenation on reduced catalysts and following cleaning of the surface at each temperature (**).

It is noteworthy the high CO_2 conversion obtained also under such reaction condition, likely due to the progressive reduction of copper oxide to metallic Cu with the hydrogen present in the mixture. By focusing on CZZ, for example, even if the selectivity of products is a little different in the two tests, about the same CO_2 conversion is reached at each temperature, apart from 160°C. Then, a greater amount of CO is quickly produced at lower temperature to disadvantage of MeOH,

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however, methanol production could be considered higher at temperature higher that 200°C. Regarding the hybrid catalysts, an higher amount of zeolite contributes to obtain an higher amount of DME, above all at lower temperature (8.78% at 200°C). By using such systems, the MeOH selectivity doesn't follow a linear decrease as in case of CZZ, rather a volcano trend allows to reach a maximum value at 220 and 200°C for CZZ.FER0.5 and CZZ-FER2 catalysts respectively in agreement with the maxima values of DME selectivity.

***Table 3.** CO$_2$ hydrogenation reaction: CO$_2$ conversion and products selectivity.*

Catalyst	T (°C)	X$_{CO2}$ (%)		Selectivity (%)							
				CH$_4$		CO		MeOH		DME	
CZZ	160	19.44*	9.83**	-*	0.96**	84.85*	53.59**	15.15*	45.45**	-*	-**
	180	21.17	20.22	0.61	2.08	77.44	64.13	21.95	33.79	-	-
	200	20.85	21.06	2.29	2.42	77.06	79.63	20.64	17.95	-	-
	220	22.62	25.65	3.10	3.13	83.38	87.98	13.52	8.88	-	-
	240	27.05	31.27	4.58	4.53	86.72	91.85	8.70	3.62	-	-
	260	31.30	-	8.03	-	86.65	-	5.33		-	-
CZZ-FER0.5	160	19.11	9.80	-	4.04	-	83.48	-	8.53	-	3.95
	180	19.26	17.27	-	5.15	92.11	81.74	3.76	6.63	4.14	6.48
	200	20.31	20.14	2.38	5.10	90.86	87.63	2.64	3.60	4.12	3.68
	220	21.80	24.46	4.16	6.66	86.34	89.56	4.08	2.30	5.42	1.48
	240	25.58	28.00	4.80	8.51	88.55	89.50	3.23	1.38	3.42	0.61
	260	30.05	-	7.56	-	88.53	-	2.53	-	1.39	-
CZZ-FER2	160	19.90	-	-	-	85.41	-	5.34	-	9.25	-
	180	20.55	-	0.75	-	86.70	-	6.73	-	5.83	-
	200	21.45	-	2.99	-	77.05	-	11.18	-	8.78	-
	220	23.66	-	3.20	-	81.28	-	8.59	-	6.93	-
	240	27.46	-	4.03	-	86.43	-	5.55	-	3.99	-
	260	32.56	-	4.26	-	85.81	-	5.98	-	3.96	-

*TPRS on unreduced catalysts ** operando reaction with cleaning in Ar

During the TPSR, on the surface catalysts new bands appeared and some disappeared as shown in the following Figures 16-18.

By increasing the temperature, the development of the band at 2929 cm^{-1} on CZZ sample is characteristic of surface-bound methylate which reaches a maximum at 120°C. Remarkably, on this catalyst surface there is no evidence for a formate species under the present reaction conditions, contrarily to that previously observed on the reduced catalyst. However, although formate species are not present, as reported in Table 3, MeOH is formed already at 160°C. This result could indicate that more than a single mechanism could be involved into the CO$_2$ hydrogenation reaction, which could be characterized by the formate intermediate or not.

The profiles of CZZ-FER0.5 are reported in Figure 16 and some interesting signals could be individuated. Specifically, the peak at 1590 cm^{-1} which appeared at 120°C could be ascribed to zinc formate species [6] as already seen in the Figure 13, related to the experiment on the reduced catalyst. As time elapsed, maxima developed at 2935 and 2848 cm^{-1} which are characteristic of copper formate. A band at 2848 cm^{-1} could be assigned to methoxy groups on zinc oxide, whereas the 2137 cm^{-1} peak could derive from CO adsorbed on Cu$^+$ site on the copper.
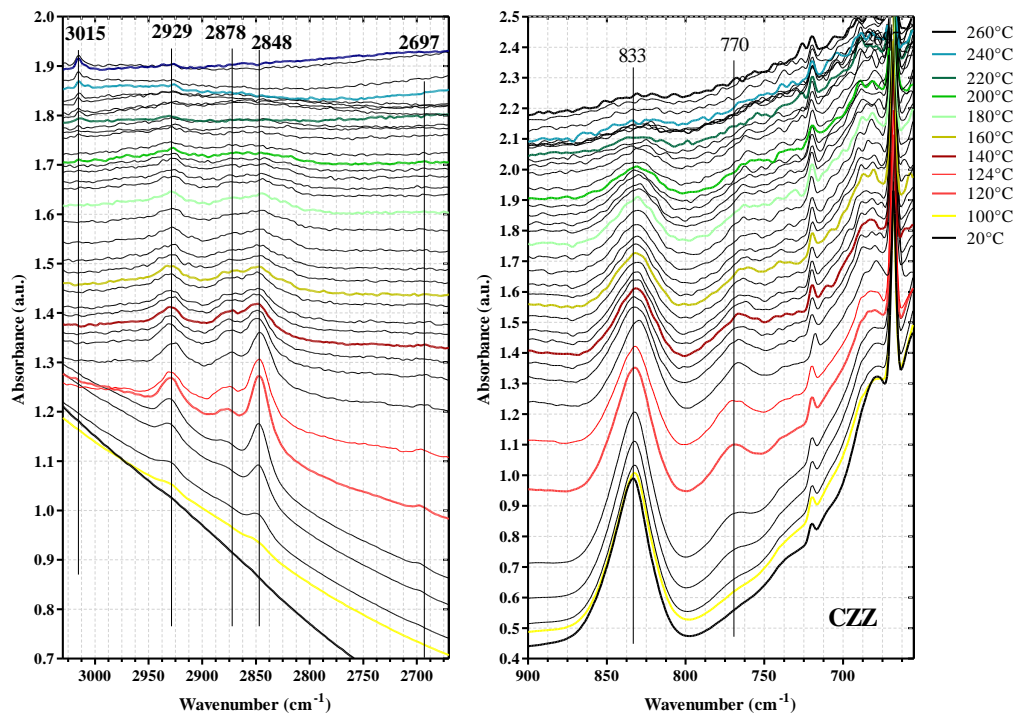
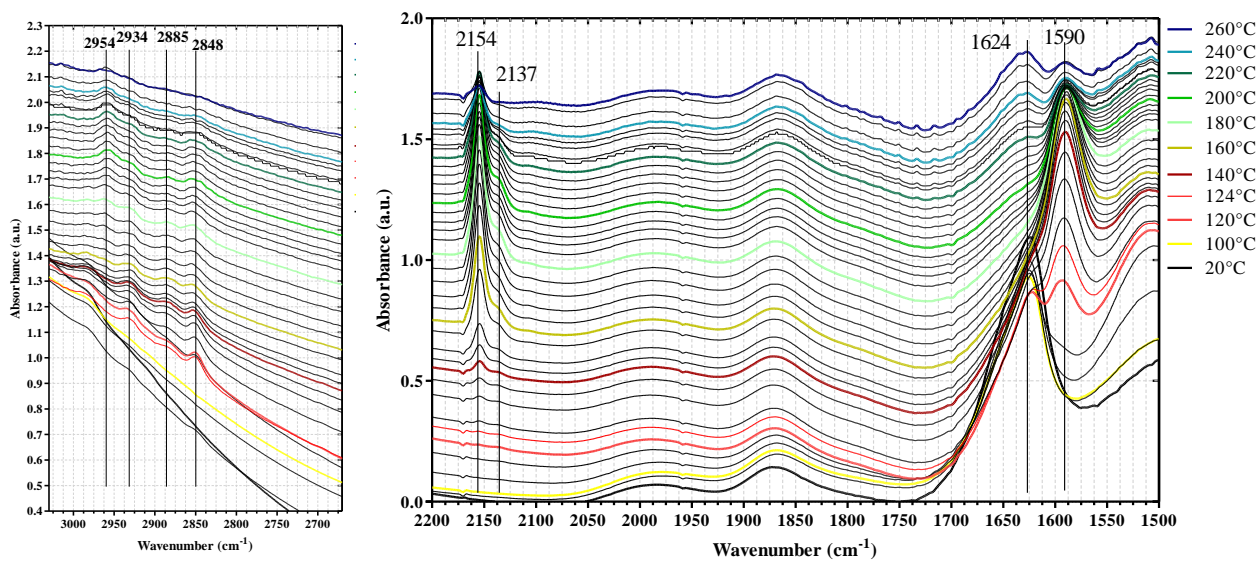*Figure 16. TPSR on CZZ unreduced catalyst from 20 to 260°C.*

Figure 17. TPSR on CZZ-FER0.5 unreduced catalyst from 20 to 260°C.

Surprising, very few signals are observable on CZZ-FER2 catalyst during the TPSR reaction, thus indicating the need to further investigate on this aspect. The spectra recorded from 20 to 260°C are reported in Figure 18.
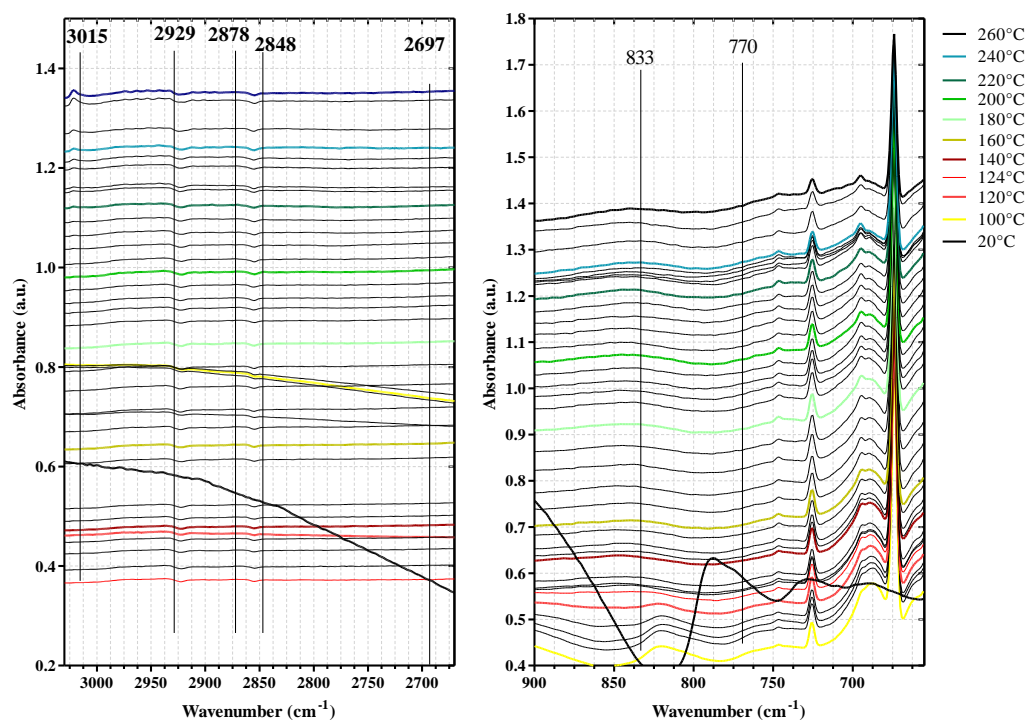
Figure 18. *TPSR on CZZ-FER2 unreduced catalyst from 20 to 260°C.*

4. CONCLUSIONS

During the CO$_2$ hydrogenation experiments on Cu-based catalysts, several reaction intermediates could be observed, depending on reactants, reaction conditions and the state of the catalyst, reduced or not. The hydration state of the support plays an important role in providing adsorption sites for the reaction intermediates observed in methanol synthesis over copper/zinc/zirconia catalysts and dimethylether on hybrid systems containing acid zeolites. For example, if formate species are evident upon CZZ reduced catalysts, there is no spectroscopic evidence of their formation under the unreduced CZZ sample. However, the situation is different when CZZ-FER0.5 is used, considering that formate species are evident both on reduced and unreduced samples.

In general, on reduced catalysts, formate species were initially formed which were subsequently hydrogenated to methanol on Cu-ZnO-ZrO$_2$ catalyst and then converted to dimethyl ether on Cu-ZnO-ZrO$_2$/ferrierite system. During the reaction, a steady state concentration of formate species persisted on the copper so copper formate could be really considered the pivotal intermediate for methanol synthesis. Anyhow, it is not easy to say the same on unreduced CZZ and CZZ-FER2 catalysts. This results could indicate that also a different pathway of reaction should be take into consideration too.

Some literature papers deals about the study of the mechanism of CO$_2$ hydrogenation on different Cu-based catalysts but it is the first time that hybrid catalysts used for DME are studied by operando FT-IR measurements. Even if, at moment, many aspects need to be deepened, it is possible to confirm that the collaboration between LCS and CNR-ITAE allowed obtaining important preliminary results regarding the mechanism of the reaction of one of the most attractive route for converting CO$_2$ into fuels, MeOH and DME, and above all to lay the bases for future project finalized to develop new processes for large scale production of alternative fuels from CO$_2$.

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