

A Versatile Ambient-to-High-Pressure Reaction Transmission Cell for *in situ/operando* Infrared Spectroscopic Investigations

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Design and applications of an in-house developed high pressure/high temperature transmission FTIR reaction cell are presented. By coupling with a mass spectrometer online analysis of product formation is possible enabling *operando* FTIR spectroscopic studies. The cell, made of stainless-steel, has been designed to be operable at pressures up to 30 bar and temperatures between 22°C and 300°C. Long-time tests, with no signs of damage of the cell and windows have been

1. Introduction

In situ infrared (IR) spectroscopy is undoubtedly one of the most important tools in catalysis research to gain detailed insights into structure-activity relationships.^[11] Thus, infrared spectroscopy in transmission mode (FTIR) is well suited to study changes of gas composition (with detection of early reaction products) as well as adsorbate formation simultaneously, also at low concentrations. In order to obtain a realistic picture of the working catalyst, specific spectroscopic reaction cells have been developed, which allow *in situ* or *operando* investigations of different types of catalytic reactions under real reaction conditions.^[2] While a large variety of established cell designs was applied for *in situ* studies at ambient pressure,^[3] respective reaction cells applicable for *in situ* and particularly for *operando* studies under higher pressure and temperature are rare.

A selection of commercial and home-made high pressure and high temperature *in situ* FTIR reaction cells, their specifics and applications is presented in Table 1. For detailed information it is referred to the respective citations.

It is advantageous to combine *in situ* FTIR spectroscopy with simultaneous analysis of product composition such as mass

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/cmtd.202100024

conducted at 15 bar and 250 °C. The performance of the cell was tested by studying three types of CO_2 hydrogenation reactions (CO_2 Fischer-Tropsch synthesis, CO_2 methanation, CO_2 conversion to dimethyl ether) on selected catalyst systems by varying temperature and pressure. The *operando* spectroscopic measurements revealed reliable data which reflect the same trends as found by respective catalytic tests.

spectrometry or gas chromatography. Such *operando technique enables* comprehensive spectroscopic as well as catalytic activity information.^[4]

However, the availability of high-pressure cells from commercial suppliers is limited and, in many cases an in-house development of a customized cell setup is necessary either due to scientific, technical, or economic reasons. Especially the convenience regarding the way of cell assembly is one important aspect.

Herein we present a versatile transmission infrared cell for *in situ* and *operando* spectroscopic studies of gas/solid catalytic reactions at higher pressures. The aim was to provide versatile application of this cell regarding reaction conditions, ensuring low dead volume to enable simultaneous product analysis and easy handling. Due to the great interest in using CO₂ as a feedstock for chemical production and synthesis of fuels, the CO₂-hydrogenation was chosen as a model reaction to evaluate the performance of the new reaction cell.

2. Results and Discussion

2.1. Heatable High-Pressure FTIR-Transmission Cell

The heatable high pressure FTIR-reaction unit consists of three main components, namely two window assemblies, surrounding a heating block with the reaction cell in a sandwich-like manner held together with four long screws (Figure 1). The cell components consist of V4 stainless steel. Due to its compact design and reduced size (Length: 80 mm, width: 60 mm, height: 55 mm, weight: 1700 g) this cell can be easily implemented into the sample compartment of the IR spectrometer without special instrument modification. By using a respective holder system, the cell can be adjusted in the optical path of the spectrometer.

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Table 1. Selected in situ high pressure FTIR reaction cells and application.								
Cell type	Investigated reaction	Specifics	Ref.					
ISRI HPL-TC-13-1, Harrick Scientific home-made Specac home-made	Alcohol synthesis from CO_2 , H_2 and olefins Reverse water gas shift reaction at supercritical conditions CO adsorption on MeOH catalysts CO Fischer-Tropsch reaction Methanol synthesis	250°C, 10 bar 60°C, 138 bar 200°C, 50 bar 225°C, 10 bar 230°C, 100 bar	[5] [6] [7] [8] [9]					

For loading the sample, one of the window assemblies (Figure 1a) has to be removed completely from the heating block by loosening the screws. Generally, 50 mg of the sample powder is pressed into a wafer (diameter = 20 mm) which is inserted into the sample holder and placed in the heating block. To fix the sample holder a mounting ring is screwed in and the window assembly is attached again. After adjusting the cell on the baseplate in the spectrometer compartment, it is connected to the gas dosing and cooling system.

The cell is heated by two heating cartridges (60 mm, 500 W), which are placed above and below the catalyst sample holder in the heating block, to ensure uniform heat distribution. The temperature is measured and controlled by a thermocouple fixed in the vicinity of the sample holder (Figure 1b). Additionally, the temperature is adjusted by a thermostat. The window assemblies are equipped with a water-cooling system to avoid high-temperature window seals and to prevent any excessive



Figure 1. Disassembled high pressure FTIR cell (a) and cross-section of the FTIR cell (b): (1) Cooling; (2) Heating block; (3) Heating cartridge; (4) Window fixing ring; (5) CaF_2 window; (6) Mounting ring; (7) Sample holder; (8) Gas inlet (Gas outlet is hidden); (9) Hole for thermocouple.

heating of the spectrometer sample compartment. For further details of the FTIR cell the interested reader is referred to additional information giving in the Supporting Information.

The infrared transparent window material and the seals are key features in this setup in terms of the needed temperatures and pressures. Because of its high stability and good resistance to water, CaF₂ as a windows material has been chosen. Besides its material properties, further crucial parameters in terms of pressure stability are the unsupported diameter D and the thickness of the windows. For practical reasons an outer diameter of 20 mm of the windows and O-rings with a diameter of 18 mm and a cross section thickness of 1 mm were selected. This results in an unsupported free diameter of the windows of 19 mm. The thickness of 6 mm was found to be suitable for our cell design, resulting in an upper limit for the operable pressure of ca. 30 bar. For the calculation of respective parameters, the following Equation (1) has been used, in which T is the window thickness, D is the unsupported diameter, p is the maximum operable pressure and F_a is the apparent elastic limit for CaF₂ (365 bar).^[10,11] The factor 1.06 was determined considering a safety factor (4) and an empirical constant K (1.125), that depends on the method of support, on the force introduced in clamping and on the brittle and ductile character of window material involved.[12,13]

$$\frac{T}{D} = 1.06\sqrt{\frac{p}{F_a}} \tag{1}$$

Since effects of higher temperatures and temperature gradients on the upper pressure limit are more difficult to determine, we integrated an active water cooling for the windows in the cell. Nevertheless, we must notice that it is possible that strains on the CaF_2 might result from the combination of pressurization and temperature gradients (due to simultaneous heating of the cell and active cooling of the windows). Safety measures such as operation only in a shielded hood suitable for pressure reactions are a requirement.

Due to their chemical inertness and high temperature resistance (320 °C), O-Rings consisting of perfluoroelastomers (FFKM) have been utilized to seal the reaction cell, while the CaF₂ windows were sealed with fluoroelastomer O-rings. Repeated long-time tests at reaction conditions (T \leq 250 °C, p \leq 15 bar) did not show any damage of the windows or seals.

The reaction cell is connected to a gas supplying system, by which the reactants are dosed along both sides of the wafer, and to a quadrupole mass spectrometer (MS) (OmniStar, Pfeiffer Vacuum) for product analysis (Figure 2).





Figure 2. Schematic diagram of the experimental setup.

The gases CO_2 , H_2 and He as well as the gas mixture Ne/He (20%) were dosed by using high pressure (<30 bar) mass flow controllers (Bronkhorst). Neon was used as reference gas for normalization of the mass spectrometric signals of educts and products. The desired pressure was adjusted by means of a backpressure regulator and it took approximately 15 min to achieve a pressure of 15 bar.

2.2. High-Pressure FTIR Cell Performance

The development of processes for CO_2 conversion into valuable chemicals is highly desired for both environmental and economic reasons.^[14] Therefore, three types of CO_2 hydrogenation reactions (CO_2 Fischer-Tropsch synthesis, CO_2 methanation, CO_2 conversion to dimethyl ether) were selected to demonstrate the FTIR cell operation by varying temperature and pressure. It has to be mentioned, that aspects such as gas flow dynamics, effects of temperature gradients, catalyst pelletizing and thus mass transfer as well as heat transfer have not been studied in detail and would go beyond the scope of the present paper.^[4,15] The main aim was to investigate the general impact of increasing the partial pressures of reactants on observable spectroscopic features and the performance of the catalysts applied for the respective reactions.

The reader should keep the following aspects in mind. The cell has been designed for the detection of adsorbed species and gaseous components at higher pressures and temperatures. With an optical pathlength of 2.8 cm, band intensities of gases (such as CO₂, CO, CH₄) can become considerably large at higher pressures. Nevertheless, the spectral region between 1000-2000 cm⁻¹ remains open for the analysis of important adsorbates (such as carbonates, formates, etc.). Subtraction of background spectra of the same gas phase measured with an empty cell or inert material at identical conditions might be very helpful when band superpositions of gas and adsorbate components occur.^[16] But the pressure broadening effect on band linewidths of gases leads to larger band intensities at increasing overall pressures.^[17] Thus, no linear relation between the partial pressure and band intensity can be observed, especially within large relative pressure changes.

2.2.1. CO₂ Fischer–Tropsch Synthesis (CO₂-FT) over Fe-based Catalysts

Generally, CO_2 -FT comprises two reaction steps *i*) the reduction of CO_2 to CO via the reversed water-gas shift (RWGS) reaction (Eq. (2)) and *ii*) the subsequent hydrogenation of CO via the classical FT reaction (Eq. (3) and (4)).^[18]

$$\mathrm{CO}_2 + \mathrm{H}_2 \to \mathrm{CO} + \mathrm{H}_2 \mathrm{O} \tag{2}$$

$$n \operatorname{CO} + (2n+1) \operatorname{H}_2 \to \operatorname{C}_n \operatorname{H}_{2n+2} + n \operatorname{H}_2 \operatorname{O}$$
 (3)

$$n \operatorname{CO} + (2n) \operatorname{H}_2 \to \operatorname{C}_n \operatorname{H}_{2n} + n \operatorname{H}_2 \operatorname{O}$$
(4)

It is well known, that Fe-based catalysts possess the ability to catalyze both the RWGS and the FT reaction.^[19] While Fe₃O₄ is responsible for the RWGS reaction, iron carbides are suggested to catalyze the hydrogenation of CO to hydrocarbons.^[20] The reaction behavior of a selected Fe₃O₄ catalyst in CO₂ hydrogenation at 250 °C in dependence on pressure is shown in Figure 3.

Already at one bar CO_2 is reduced by H_2 to CO (RWGS reaction), the characteristic gas-phase-spectrum of which is seen by the band centered at 2143 cm⁻¹ (Figure 3a). With increasing pressure, the intensity of the CO band rises and characteristic bands of gaseous water (1300–1900 cm⁻¹, 3500–4000 cm⁻¹) appear.

Interestingly, no features resulting from adsorbed CO or CO_2 (*e.g.* carbonates, formates) have been observed, which might be due to a weak adsorption ability of this catalyst.^[21] This is in line with previous studies in which also no adsorbed carbonate species could be detected on magnetite under any conditions.^[22] It must be noted that the signals of adsorbed CO may be superimposed by gas-phase CO, which becomes quite



Figure 3. FTIR-spectra recorded after 60 min exposure of Fe_3O_4 to the $CO_2/H_2/He/Ne$ feed (20/60/18/2; 50 ml/min) at 250 °C and different pressures (a), intensity of selected bands depending on pressure (b), relative MS signal intensity of fragment m/z = 59 (C₄₊) and m/z = 41 (C₃₊) recorded after 60 min time on feed at different pressures (c).



intense especially at higher pressures. As already mentioned a correction of gas-phase CO signal can be obtained by collecting a subtrahend spectrum under identical conditions in an empty cell or over an inert material.^[16] But this method is not applicable here, because the presence of other gaseous components with changing concentrations complicates a proper modeling of respective gas compositions.

Starting from a pressure of five bar the formation of methane is clearly seen by means of its typical gas phase spectrum with main bands centered at 3016/1305 cm⁻¹^[23] the intensity of which growths with increasing pressure. The bands at 2959/2854 and 2927 cm⁻¹, well observable in particular at 10 bar, can be assigned to CH₃ and CH₂ containing species.^[8] It needs to be noticed that with increasing pressure not only the band intensities increase, the intensity ratio of characteristic bands of CH₃ and CH₂ changes, too (Figure 3b). Thus, the band, characteristic for CH₂, grows stronger than the band that reflects CH₃, which is an indication of chain growth. Therefore, an increase of total pressure resulted in longer chains which opens the possibility to monitor the amount and the changes of chain length of formed hydrocarbons during FT synthesis by FTIR spectroscopy.^[24] This observation agrees with results of simultaneous mass spectrometric analysis, showing the evolution of higher hydrocarbons with increasing pressure (Figure 3c).

For comparison, also a Fe₂O₃ catalyst, pre-reduced in the FTIR reaction cell with H₂/He at 300 °C for 2 h at 15 bar, was tested in CO₂-FT. In Figure 4 the spectrum of this catalyst obtained after exposure to the CO₂/H₂ feed for 120 min at 240 °C and 19 bar is compared with that of Fe₃O₄, obtained after 60 min reaction at 250 °C and 15 bar (*cf.* Figure 3a).

While no features resulting from adsorbed CO or CO_2 (carbonates, formates) are observable on Fe_3O_4 , mainly adsorbed monodentate carbonate (1502/1334/1060 cm⁻¹) besides formate species (2821/1598/1390 cm⁻¹)^[25,26] are detectable on

the Fe₂O₃ catalyst, which points to a stronger adsorption ability of the latter. However, this is in turn associated with an essentially lower hydrogenation activity as indicated by particularly significant lower CO and CH₄ formation compared to that observed for Fe₃O₄. On the other hand, this example shows that surface adsorbates can be observed when they exist or formed during reaction besides high concentrations of gaseous components.

2.2.2. CO₂ Methanation over Ni-based Catalysts

Ni-sepiolite has been proved as efficient CO_2 methanation catalyst being essentially more active as a Ni/Al₂O₃ reference catalyst.^[27] *Operando* DRIFTS studies have shown a dissociative adsorption of CO_2 in the presence of H₂, activated by dissociation into H atoms on Ni⁰ particles. As a consequence, linearly and bridged bonded CO on Ni⁰ were detected, while preferentially linearly bound CO was hydrogenated to methane.^[27]

While DRIFT spectroscopy is advantageous for examining adsorbates on the surface, measurements performed in transmission mode are beneficial to monitor changes of gas composition (with detection of early reaction products) and adsorbate formation simultaneously. This is demonstrated in Figure 5 by comparing the respective DRIFT and FTIR spectra of 5Ni-Sep(P) measured under the same reaction conditions.

Both spectra are dominated by the intense bands of gaseous CO_2 around 2350 cm⁻¹. While the main bands for methane at 3016/1305 cm⁻¹ are more intense in the transmission spectrum, the bands assigned to linearly and bridged bound CO on Ni⁰ around 2050 and 1922 cm⁻¹, respectively, can be more clearly seen in the DRIFT spectrum.^[27] This is also true for the bands of adsorbed formate species (2882/2873, 1598, 1393 cm⁻¹), formed by direct reaction of CO₂ with activated H₂ on Ni⁰ or by the reaction of adsorbed CO with neighbored OH groups of the support. These formate bands are hardly seen in



Figure 4. FTIR-spectra recorded for pre-reduced Fe₂O₃ (H₂/He, 2 h, 300 °C, 15 bar) after 120 min and for Fe₃O₄ after 60 min exposure to the CO₂/H₂/He/ Ne feed (20/60/18/2; 50 ml/min).



Figure 5. Transmission vs. DRIFT spectra, recorded after 30 min exposure of pre-reduced 5Ni-Sep(P) to methanation feed (20 vol% $CO_2/60$ vol% $H_2/20$ vol% He) at 250 °C, 1 bar.

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the transmission spectrum at these conditions and are partly overlaid by the rotational bands of water in the range of 1200–1800 cm⁻¹. The band at 1634 cm⁻¹ in the DRIFT spectrum is related to $\delta H_2 O$ of adsorbed water.

The previous DRIFTS studies of CO₂ methanation have been carried out at ambient pressure.^[27] To demonstrate the influence of the total pressure, additional measurements in transmission mode on the same catalyst have been carried out. The spectra collected during CO₂/H₂/He dosage at 250 °C in dependence on pressure are depicted in Figure 6.

By comparing the spectra recorded at different pressure, an essentially higher amount of formed methane with characteristic bands at 3016, 1345 and 1305 cm⁻¹ is observed at elevated pressure. While the band intensity in the gas spectra depends on the total pressure,^[17a] the simultaneously recorded MS signals (inset) also indicate the stronger methane formation with increasing pressure. Consequently, an enhanced formation of water is seen too. Because of the dominating methane bands at higher pressures, those of adsorbed formate species cannot unequivocally assigned, and merely very weak bands of adsorbed CO around 2050 cm⁻¹ are detectable.

2.2.3. CO₂ Conversion to Dimethyl Ether (DME)

Catalysts for the direct conversion of CO_2 to DME have to meet two requirements. They must efficiently catalyze the methanol synthesis (Eq. (5)) as well as the methanol dehydration reaction to DME (Eq. (6)).

 $\mathrm{CO}_2 + 3 \,\,\mathrm{H}_2 \rightarrow \mathrm{CH}_3\mathrm{OH} + \mathrm{H}_2\mathrm{O} \tag{5}$

 $2 \text{ CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \tag{6}$

The amount of CO produced by the RWGS reaction should be minimized.^[28] Therefore, multifunctional catalysts such as Cu–ZnO– Al_2O_3 /H-ZSM-5 are used which possess basic sites for



Figure 6. FTIR spectra, recorded after 60 min exposure of pre-reduced 5Ni-Sep(P) to methanation feed ($CO_2/H_2/He/Ne = 20/60/18/2$; 50 ml/min) at 250 °C and at different pressures. Inset: relative MS signal intensity of fragment m/z = 16 (CH₄) recorded at steady state at different pressure.

 CO_2 adsorption, metal sites for H_2 activation and acid sites for methanol dehydration. The basic properties of the oxide support can be modified for example with La or Zr. For optimizing the catalyst design, knowledge concerning the mode of catalyst action under reaction conditions is needed, which requires *in situ* studies at higher pressures.

We have studied the reaction exemplarily on two catalysts consisting of a mixture of a commercial MeOH catalyst Cu–ZnO–Al₂O₃ with H-ZSM-5 (CZA/Z). One of them was modified by impregnating the CZA component with Zr (Zr-CZA/Z).

Catalytic test results obtained at 250 °C and 20 bar on prereduced catalysts are summarized in Table 2, were only the selectivities for CO, MeOH, and DME are given. The selectivities for CH₄ and other products are low and comparable for both catalysts. The FTIR spectra measured on Zr-CZA/Z after exposing the pre-reduced catalyst to the CO₂/H₂/He feed at 250 °C at different pressures are depicted in Figure 7.

Starting from 5 bar, bands in the region 3100–2800 cm⁻¹ appear, which are related to vC–H modes. Characteristic bands of gaseous CO at 2143 cm⁻¹ and gaseous water around 1650 cm⁻¹ are also observable. Additional bands around 1185 cm⁻¹ emerge at 10 bar, which stem from vC–O–C modes of DME^[29] as can also be concluded from comparison with the respective reference gas phase spectrum of DME.^[23]

Because of the superimposed features, particularly in the vC-H region, a clear distinction between methanol and DME

Table 2. Cataly $(CO_2/H_2/N_2 = 1/2)$	ble 2. Catalytic test results of CZA/Z and Zr-CZA/Z at 250 °C and 20 bar $O_2/H_2/N_2 = 1/3/0.3$).					
Catalyst	X(CO ₂)	S(CO)	S(MeOH)	S(DME)		
	%	%	%	%		
CZA/Z	12.7	80.8	17.1	0.0		
Zr-CZA/Z	17.8	55.4	11.1	32.1		



Figure 7. FTIR spectra, recorded after 60 min exposure of pre-reduced catalyst Zr-CZA/ZSM-5 to CO_2/H_2 /He/Ne feed (20/60/18/2; 50 ml/min) at 250 °C and different pressures. The gas spectra of DME and methanol⁽²³⁾ are shown for comparison.



based on the band position is difficult. It seems that both, methanol and DME are formed at higher pressures, while a significant quantity of CO is also produced, which is however in accordance with the catalytic test results.

Comparing the FTIR spectra of Zr-CZA/Z with those of CZA/Z measured at 10 and 15 bar, respectively, (Figure 8) the different behavior becomes obvious. Thus, an essentially higher amount of CO is formed over CZA/Z, particularly at 15 bar, which is in accordance with the catalytic test results (compare Table 2). Furthermore, a different pressure dependence of CO formation is seen. Because the spectral region below 1300 cm⁻¹ is optically dense for CZA/Z, the comparative inspection of the characteristic vC–O–C modes of DME is not possible. But, looking at the catalytic test results, the formation of DME over CZA/Z is not expected. Otherwise, the intense bands in the vC–H region at 3100–2800 cm⁻¹ in the case of CZA/Z point to a stronger MeOH formation compared to Zr-CZA/Z which is also reflected by the catalytic test results.

The experiments performed with the whole gas mixture revealed that general information about catalyst performance at elevated pressures are available. However, for gaining mechanistic insights concerning CO_2 activation as well as methanol formation and dehydration additional transient experiments are necessary.

3. Conclusion

A new FTIR transmission cell was developed, which enables operation under increased pressures, changing gas atmospheres and temperatures up to 300 °C. The combination with a mass spectrometer allows for the simultaneous monitoring of product formation. The cell is small, compact, easy to handle and can be adjusted in the optical path of each type of FTIR spectrometer by using a respective holder system.



Figure 8. Comparison of the FTIR spectra of CZA/Z and Zr-CZA/Z, recorded after 60 min exposure of the pre-reduced catalysts to $CO_2/H_2/He/Ne$ feed (20/60/18/2; 50 ml/min) at 250 °C and different pressures.

The performance of the cell has been successfully proved by investigating different CO_2 hydrogenation reactions over representative catalysts as model. The formation of varying amounts of gaseous products (CO, CH_4 , C_xH_{yr} DME) in dependence on pressure could nicely be observed. Simultaneous mass spectrometric gas analysis revealed the same trends as observed in catalytic tests. Thus, the obtained spectroscopic results are directly related to the catalytic performance which is important particularly for mechanistic studies.

Particularly at higher pressures and under exposure of the catalyst to the whole gas feed (CO_2 and H_2) the intense bands of the gaseous products can be dominant in the spectra. Even though the spectral region between 1000–2000 cm⁻¹ remain open, the observation of surface adsorbates *e.g.* carbonates, formates, metal carbonyls might become difficult, when their concentrations are low. This might be a drawback for mechanistic studies. To overcome this problem, transient experiments could be helpful, in which CO_2 is pre-adsorbed and the subsequent reaction with H_2 is followed. In this way, the activation of CO_2 as well as the reactivity of possible adsorbed intermediate species towards H_2 can be studied. Such studies were however not a subject of the present work.

Experimental Section

The catalyst Fe₃O₄ was prepared by decomposition of FeC₂O₄·2H₂O at 330 °C in a 20 ml/min flow of Ar for 24 h and subsequent calcination at 500 °C in a 20 ml/min flow of Ar for 5 h. The final composition is 76.4% Fe₃O₄, 23,6% Fe. For comparison a catalyst consisting of Fe₂O₃ was prepared by precipitation from an aqueous solution of Fe(NO₃)₃·9H₂O with ammonia solution at pH 9.5. After filtration of the precipitate, washing with water and drying at 100 °C, the precursor was calcined at 400 °C for 6 h.

5Ni-Sep (P) was prepared by precipitation method,^[27] in which a solution with required amount of Ni(NO₃)₂·6H₂O to obtain 5 wt%Ni was added to a suspension of sepiolite in water under agitation. Afterwards, Ni was precipitated using a NaOH (1 M) solution, washed with distilled water until pH 7, dried at 100 °C and finally calcined at 450 °C for 3 h.

Commercial Cu–ZnO–Al₂O₃ and H-ZSM-5 (Zeolyst, Si/Al ration = 80) were physically mixed in 1:1 wt ratio to get CZA/Z. For preparing Zr-CZA/Z, CZA was initially impregnated with aqueous zirconium (IV) oxynitrate hydrate to give 1 wt% of Zr. After evaporation of water, the obtained powder catalyst was dried for 12 followed by calcination in static air at 400 °C for 4 h. Then, Zr-CZA and H-ZSM-5 were physically admixed in 1:1 wt ratio.

The catalysts 5Ni-Sep (P), CZA/Z and Zr-CZA/Z were externally reduced in H_2 (1 bar, 50 ml/min) at 400 °C for 2 h immediately before the material has been used for the FTIR experiments.

FTIR Measurements

The measurements were performed on a Nicolet iS10 spectrometer (Thermo Scientific) equipped with an MCT-detector. The spectra were recorded in transmission mode at 4 cm^{-1} resolution and 64 scans. After heating up to 250 °C in a He flow (40 ml) and holding for 30 min the samples were exposed to a gas mixture containing 20% CO₂, 60% H₂, 18% He and 2% Ne (all Air Liquide) with a total gas flow rate of 50 ml/min. The pressure was hold on



15 bar. Spectra were collected at various time points throughout the reaction. An initial spectrum was collected after the sample pretreatment, but before the introduction of the reactants. This spectrum was subtracted from all subsequently collected spectra during the reaction to obtain difference spectra. During the whole time MS signals of selected fragments (m/z = 18, 41, 44, 56) were recorded and normalized to the Ne signal.

Acknowledgements

This study was financially funded by the Deutsche Forschungsgemeinschaft (DFG) in the framework of the Schwerpunktprogramm SPP 2080. The authors thank Vijay Kumar Velisoju for providing the CZA/Z catalysts and respective catalytic data.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Infrared spectroscopy · in situ/*operando* studies · heterogeneous catalysis · high-pressure · cell design

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Manuscript received: March 15, 2021