In-situ and operando infrared spectroscopy study on SiO_2-supported inverse ZrO_2/Cu catalysts for CO_2 hydrogenation to methanol

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Resumo/Abstract

RESUMO – Esta contribuição traz dados de testes catalíticos em alta pressão e experimentos de espectroscopia no infravermelho in-situ e operando de catalisadores inversos ZrO_2/Cu supportados em SiO_2 para a hidrogenação de CO_2 a metanol. A razão Zr/Cu ótima para a produção de metanol encontrada é de 0,5, alcançando seletividade de 35%. Os experimentos de DRIFTS in-situ mostraram que o principal mecanismo é a rota do formiato. Experimentos de Modulação Excitação com Detecção Sensitiva de Fases revelaram que metóxido e formiato ligados à Zr e Cu são intermediários na síntese de metanol, confirmando que o Cu tem o papel de formar compostos intermediários, além de ativar o H_2. O aumento da carga de Zr para 20 wt% causou maior exposição da SiO_2, formando metóxido inativo ligado à sílica, inibindo a produção de metanol. Essas descobertas são corroboradas pelas caracterizações por DRX e TPR-N_2O, mostrando o Cu altamente disperso na superfície do suporte. As análises de FTIR operando em alta pressão sugerem modificação nas propriedades eletrônicas do Cu e Zr, resultando na presença de novas espécies superficiais, sendo algumas delas como o carbonato (CO_3-Cu) possivelmente contribuído para a síntese de metanol.
Palavras-chave: hidrogenação de CO_2, ZrO_2/Cu, espectroscopia in-situ, modulação excitação

ABSTRACT – This contribution brings high pressure catalytic tests data and in-situ and operando infrared spectroscopy experiments on inverse ZrO_2/Cu catalysts supported on SiO_2 for CO_2 hydrogenation to methanol. The optimal Zr/Cu ratio found for methanol production was 0.5, reaching selectivity of 35%. In-situ DRIFTS experiments showed the main mechanism is the formate pathway. Modulation Excitation-Phase Sensitive Detection experiments revealed Zr and Cu-bound formate and methoxy are intermediates in the methanol synthesis, confirming Cu also plays the role of forming intermediates, besides activating H_2. Increasing the Zr loading to 20 wt% caused SiO_2 to be more exposed forming inactive silica-bound methoxy, hindering methanol production. The findings are supported by XRD and TPR-N_2O characterization, showing Cu highly dispersed over the support surface. High pressure operando FTIR experiments suggest a modification in the electronic properties of Cu and Zr, with the appearance of new surface species, some of which such as carbonate (CO_3-Cu) may also contribute in the methanol synthesis.
Keywords: CO_2 hydrogenation, ZrO_2/Cu, in-situ spectroscopy, modulation excitation

Introduction

Recent studies on inverse catalysts for CO_2 hydrogenation, such as ZnO/Cu and ZrO_2/Cu, have shown the possibility of enhancing methanol selectivity through optimization of the metal-support interface, achieved by dispersing the oxides on a continuous Cu structure, in contrast to the conventional systems of oxide-supported metal nanoparticles (1). From a mechanistic standpoint, the superior activity of the inverse configuration has been ascribed mainly to the formation of copper-bound formate and its faster conversion to methoxy (2,3).

In this contribution we employed in-situ and operando infrared spectroscopy with Modulation Excitation-Phase Sensitive Detection on SiO_2-supported ZrO_2/Cu catalysts, aiming to investigate the mechanism of methanol synthesis and the reaction intermediates.

Experimental

Catalysts synthesis.

The SiO_2 support was prepared by treatment of TEOS with HNO_3 and NH_4OH, followed by drying at 100 ºC and calcining under air flow at 500 ºC for 5h. The catalysts were synthesized by consecutive incipient wetness impregnations. Initially, $Cu(NO_3)_2$*xH_2O aqueous solutions were added dropwise to SiO_2, homogenizing the mixture after each drop to obtain the Cu/SiO_2 catalysts, which were then dried at 100 ºC and calcined under air flow at 450 ºC. After determining the pore volume of the new samples, $ZrO(NO_3)_2$*xH_2O was impregnated on the Cu/SiO_2 material using the same methodology described, resulting in the Zr/Cu/SiO_2 bimetallic catalysts. The Cu/SiO_2 samples are denoted as x-CS where x is the Cu loading (wt%)

incorporated on SiO_2 and the Zr/Cu/SiO_2 catalysts y-ZCS, where y is the Zr/Cu ratio impregnated.

Characterization.

X-Ray Diffraction (XRD) analyses were performed in a Rigaku Miniflex 600 diffractometer using CuKα radiation with 2θ = 8 – 90º (0.07 step).

Temperature Programmed Reduction experiments followed by N_2O chemisorption (TPR-N_2O) were conducted to analyse the reduction profile and determine the surface Cu area. The equipment employed was a Micromeritics Autochem II 2920. The experiment details are reported elsewhere (4).

Catalytic activity tests.

The activity was measured in a FlowCat (H.E.L) reaction system. Initially 400 mg of catalyst were loaded in a stainless steel tubular reactor (i.d. = 12mm) and reduced under H_2 flow (25 mL.min-1) for 1h at 300 ºC. The flow was then switched to a $H_2/CO_2/N_2$ (27/9/4 $mL.min^{-1}$) commercial mixture and the reaction was carried out at 30 bar and 250 ºC for 8h. Products were analyzed by on-line Gas Chromatography (GC Agilent 8860) equipped with FID and TCD.

Modulation Excitation-Phase Sensitive Detection-DRIFTS.

The ME-PSD experiments were carried out in diffuse reflectance mode (DRIFTS) using a Nicolet-iS50 (Thermo-Scientific) infrared spectrometer equipped with a High-Temperature reaction cell and a Praying Mantis (Harrick) optical system. The sample was reduced under H_2/He flow at 300 ºC for 1h, then the reaction cell was cooled to 250 ºC and the flow switched to CO_2 : $3H_2$. Spectra were collected until steady-state (64 scans, 8 cm^{-1} resolution). Afterwards, CO_2 was switched to He and then back to CO_2 periodically every 60s using an automated multiposition Vici valve (Valco). Throughout the reactant modulation, spectra were collected rapidly with 8 scans and 8 cm^{-1} resolution during 90 min. The resulting spectra were treated using a Fourier Transform and Inverse Fourier Transform methodology described elsewhere (5).

Operando high pressure FTIR.

The Operando FTIR experiments were performed in transmission mode. Approximately 15 mg of catalyst were pelletized into a self-supported wafer and loaded in a homemade low dead-volume reaction cell. The sample was reduced under H_2/Ar flow at 300 ºC for 1h. Then CO_2 hydrogenation was carried out at 4 bar and 250 ºC under CO_2 : $3H_2$ flow. Spectra were collected until steady-state was reached (64 scans, 4 cm^{-1} resolution). Methanol production was monitored by on-line Mass Spectrometry (MS).

Results and Discussion

Characterization

XRD results are presented in Figure 1. For the SiO_2 support only a broad feature was observed at 22.0º, which is characteristic of an amorphous material. When impregnating 10 or 20 wt% Cu on SiO_2, diffraction lines corresponding to monoclinic CuO (ICDD 00-045-1548) were detected, while the amorphous characteristic is progressively lost, denoting the crystallization of the sample. The incorporation of Zr did not cause significant changes to the diffractograms, with no visible ZrO_2 lines, indicating the oxide is highly dispersed over the SiO_2 structure.

Interestingly, when increasing Zr loading to 20 wt% (2-ZCS), the amorphous aspect of the sample is recovered, suggesting Zr may act as a spacer between CuO particles. With this sample it was also observed another broad feature at 2θ = 32.2º, which may indicate Zr is also incorporated as an amorphous solid.

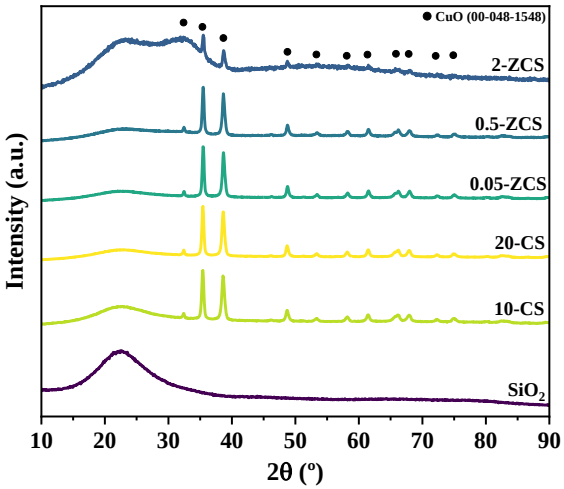

Figure 1. X-Ray Diffractograms obtained for the support and x-CS and y-ZCS catalysts, where x is the Cu loading and y is the Zr/Cu ratio in weight.

Figure 2 exhibits the first reduction profile obtained during the TPR-N_2O experiments for the representative samples 0.5-ZCS and 2-ZCS. Calculated Cu surface area (S_{Cu}) and dispersion (D_{Cu}) are also shown. The 0.5-ZCS catalyst presented a broad signal centered at 243 ºC with shouldering at 209 ºC, while in the 2-ZCS profile there are two distinct features, at 203 and 237 ºC. It has been reported previously that small Cu particles reduce at lower temperatures than larger ones (4,6), so the TPR profiles are in accordance with XRD results, in a sense that Zr may favor Cu dispersion and enhance its reducibility. Thus, the 2-ZCS catalyst possesses higher Cu dispersion (36.38%) and metallic surface area (50.68 m^2/g) than the 0.5-ZCS (11.53% and 32.12 m^2/g, respectively), as determined after oxiding

the catalysts' surface with N_2O and then performing a second reduction with H_2.

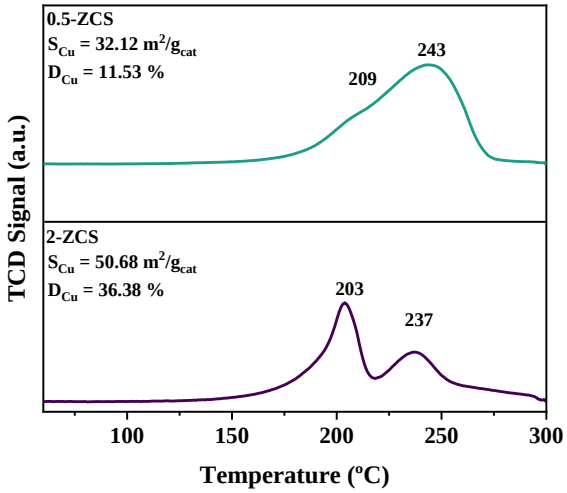

Figure 2. TPR-N_2O profiles of the y-ZCS catalysts, where y is the Zr/Cu ratio in weight. Metallic surface and Cu dipersion are indicated.

Overall, the TPR profiles are significantly different from the conventional $Cu/Zr/SiO_2$ catalysts, reported by Yang et al., in which the authors observed a progressive shift of the main peak to higher temperatures when increasing Zr loading (10), indicating the inverse configuration may result in Cu particles with relatively weaker metal-support interaction, facilitating CuO reduction to Cu^0.

Catalytic activity tests

Regarding the catalytic tests, CO_2 conversion was kept at 8% or below in order to avoid the thermodynamic limitation of the reaction, the results are presented in Figure 3 in terms of CO_2 conversion and CH_3OH and CO selectivities. The results are shown in Figure 3.

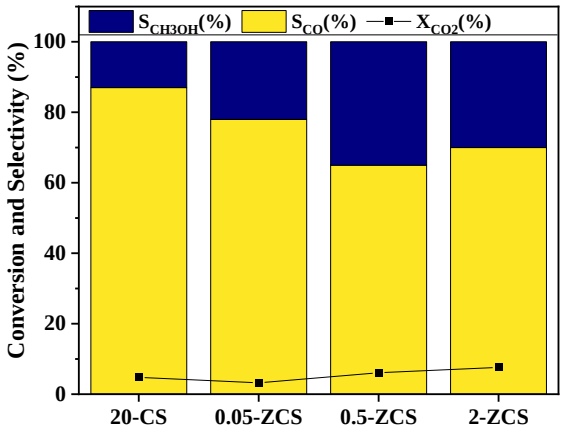

Figure 3. Catalytic activity of the y-ZCS samples, y is the Zr/Cu ratio in weight. The blue bar and yellow bar denote CH3OH and CO selectivity, respectively. CO2 conversion is represented by the black squares. Conditions: T = 250 ºC, P = 30 bar, GHSV = 6000 mL.h-1.gcat-1, t = 8h.

The 20-CS catalyst showed very low CH_3OH selectivity (13%), highlighting the importance of Zr to methanol production, as even with 1 wt% Zr loading (0.05-ZCS) it was possible to observe a significant increase in selectivity (22%), which was further enhanced when incorporating Zr up to 10 wt% (0.5-ZCS), reaching the highest CH_3OH selectivity among the samples, 35%.

When increasing Zr content to 20 wt% (2-ZCS), even though the catalyst was slightly more active (X_{CO2} = 8%) than the samples with lower Zr loading, CH_3OH selectivity dropped to 30%, suggesting a delicate balance between Cu and Zr loadings is required to optimize methanol production.

In the case of inverse ZrO_2/Cu catalyst, Wu et al., observed a maximum methanol selectivity at around 10 – 20 wt% Zr, reaching 75%.

Overall, the catalytic tests data shows that Zr is fundamental for promoting CH_3OH formation, possibly inhibiting the reverse-water-gas-shift reaction to some extent. Nevertheless, the ZCS catalysts are less selective to methanol than the previously reported ZrO_2/Cu (2,3).

Modulation Excitation-Phase Sensitive Detection-DRIFTS

Using data from TPR-N_2O and the catalytic tests results, the Turnover Frequency (TOF) determined for the 0.5 and 2-ZCS samples was 0.0028 and 0.0022 s^{-1}, respectively. Therefore, the CO_2 modulation cycle period was set to 120 s (60 s for CO_2 then 60 s for He), that is, a frequency of 0.0083 s^{-1}, which is in the same order of the TOF values. While modulating the reactant, approximately 8 scans were collected every second. The dataset obtained was the variation of the intensities of all wavenumbers with time, then the Fourier transform was applied to return a new set on the frequencies domain, which was then filtered to remove signals that did not respond to the modulation with a similar frequency, that is, infrared signals corresponding to spectators or background noise. In this sense, the resulting spectra after an inverse Fourier transform showing only active intermediates obtained for the 0.5 and 2-ZCS catalysts are exhibited in Figures 4 – 6A. For direct comparison, Figures 4 – 6B present the conventional in-situ DRIFTS spectra collected for the samples until steady-state was reached, before starting the modulation excitation procedure. The regions shown in all spectra are from 1700 to 1300 cm^{-1} and 3000 to 2800 cm^{-1}.

For the 0.5-ZCS sample (Figs. 4 and 5), the reaction intermediates observed were formates, mainly on Zr (b-HCOO-Zr at 1371, 1387, 1575, 2891 and 2974 cm^{-1} (1,2,7-10), but also HCOO-Cu (1350 cm^{-1}) and CH_3OH-Zr (2846 and 2934 cm^{-1}), which are characteristic of the formate

pathway of CO_2 hydrogenation to methanol, also reported in previous works regarding Cu/ZrO_2 catalysts.

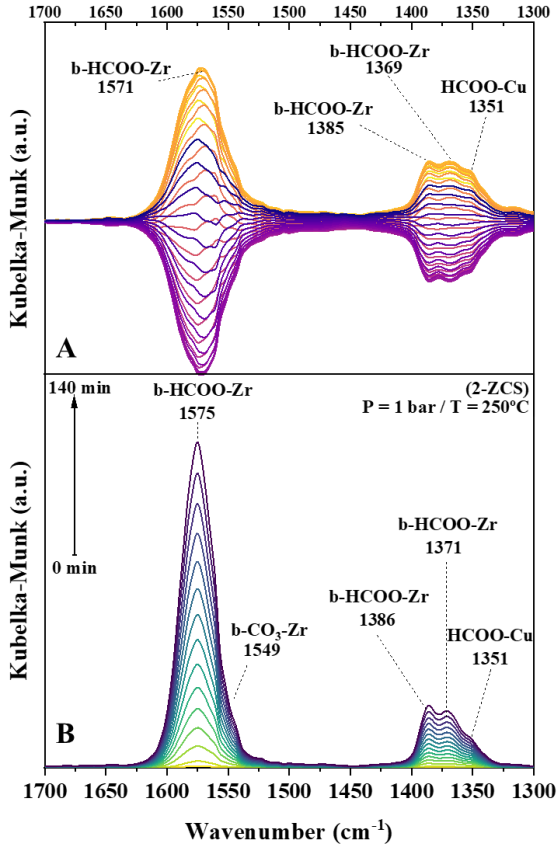

Figure 4. (A) ME-PSD-DRIFTS spectra in the region between 1700 and 1300 cm-1 obtained for the 0.5-ZCS catalyst (Zr/Cu = 0.5). **(B)** In-situ DRIFTS specta collected until steady-state. Conditions: T = 250 ºC, P = 1bar.

Additionally, the ME-PSD spectra revealed the formation of formic acid b-CH_2OO-Zr (2867 cm^{-1}), which is rarely observed (6) but is expected to intermediate the HCOO hydrogenation to CH_3OH (10,11). The absence of the b-CH_2OO-Zr in the steady-state spectra may be explained in terms of the compound being highly active, quickly hydrogenated to methoxy, which is relatively more stable, as reported by DFT studies (9).

HCOO-Cu was observed previously specifically on the inverse ZrO_2/Cu and not on the traditional Cu/ZrO_2 catalysts (2), being highly active during transient studies and improving methanol production when compared to the conventional system. The data presented here further corroborates the generation of the formate intermediate on Cu species, that is, the role of Cu in CO_2 hydrogenation catalysts is not only activating H_2 but also producing actual reaction intermediates.

Furthermore, the steady-state in-situ DRIFTS spectra also presented a negative Zr-OH band at 3852 cm^{-1} (not shown), possibly participating in CO_2 activation, as it responded to the reactant modulation substantially. The ME-PSD spectra also revealed the CO-Cu^+ signal at 2143 cm^{-1}, suggesting Cu is not fully reduced to Cu^0 at the reaction conditions and the oxide may contribute to CO formation.

For the 2-ZCS sample, the region between 1700 and 1300 cm^{-1} showed very similar behavior to the 0.5-ZCS catalyst (Fig. 4), therefore it is now shown, with the appearance of formates bound to Zr and Cu, all of which are active in the reaction, as confirmed by ME-PSD-DRIFTS.

In the C-H stretching region (3000 – 2800 cm^{-1}) (Fig. 6), however, the in-situ DRIFTS spectra presented along with the aforeseen intermediates (b-HCOO-Zr, CH_3O-Zr and b-CH_2OO-Zr), bands related to CH_3OH-Si as well (Fig. 7A) at 2825 and 2983 cm^{-1} (7,8) . This may be explained in terms of higher Cu dispersion in this sample (Fig. 2), that is, the SiO_2 surface is less covered with Cu particles, presenting more sites for CH_3O adsorption, when compared to the 0.5-ZCS catalyst, as observed with the TPR-N_2O experiments.

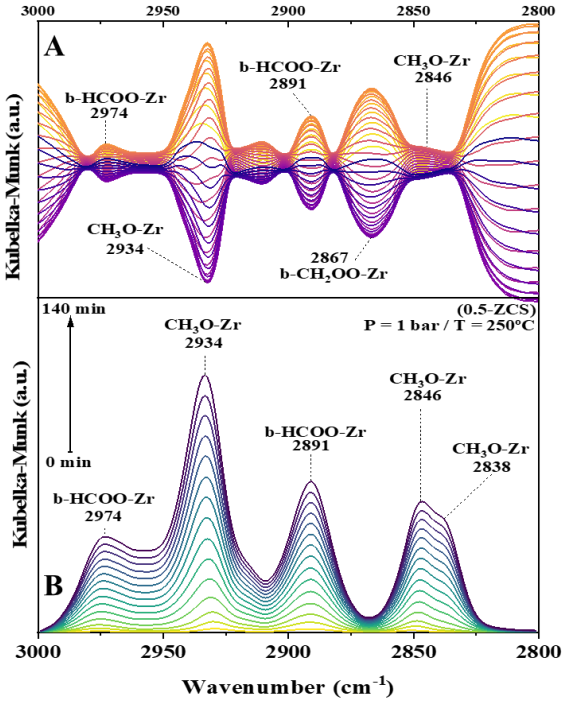

Figure 5. (A) ME-PSD-DRIFTS spectra in the region between 3000 and 2800 cm-1 obtained for the 0.5-ZCS catalyst (Zr/Cu = 0.5). **(B)** In-situ DRIFTS specta collected until steady-state. Conditions: T = 250 ºC, P = 1bar.

Differently from the CH_3O-Zr intermediate, however, when modulating CO_2 the SiO_2-bound methoxy did not respond in the same frequency and the signal was filtered out in the ME-PSD spectra (Fig. 6A), suggesting that this species is not active in the CO_2 hydrogenation to methanol. This may be explained either in terms of spillover of the

CH_3O-Zr species to Si, generating stable CH_3O-Si compounds that are hardly hydrogenated and desorbed as methanol, or methanol is actually desorbed but quickly adsorbed back on the SiO_2 surface.

Nonetheless, the spectra suggest that the formation of stable and inactive methoxy species bound to SiO_2 hinders CH_3OH formation, possibly being the reason the 2-ZCS catalyst was less selective thant the 0.5-ZCS material (Fig. 3). Therefore, even though Zr is fundamental for the reaction in order to form active HCOO, CH_2OO and CH_3O compounds, it also act as spacer, increasing Cu dispersion over the SiO_2 surface, leaving more exposed SiO_2 sites for generating inactive CH_3O-Si spectators. This is also corroborated by the XRD experiments (Fig. 1), as the 2-ZCS sample diffractogram presented broad signals, denoting an amorphous material, typical of a SiO_2 structure.

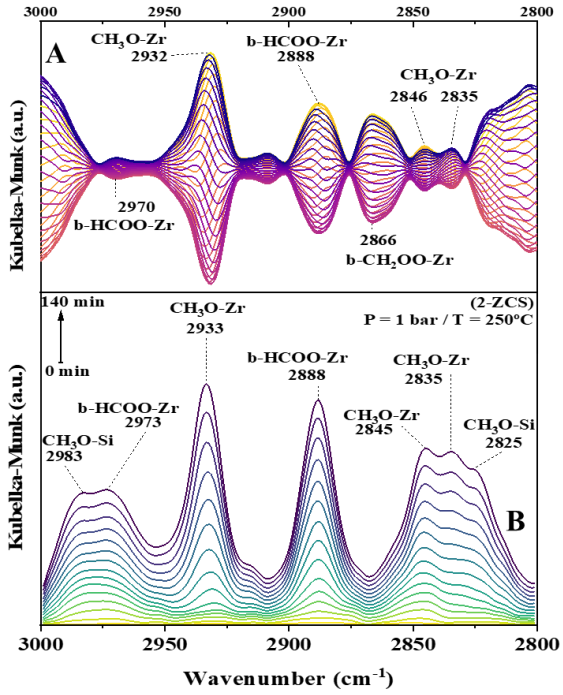

Figure 6. (A) ME-PSD-DRIFTS spectra in the region between 3000 and 2800 cm-1 obtained for the 2-ZCS catalyst (Zr/Cu = 2). **(B)** In-situ DRIFTS specta collected until steady-state. Conditions: T = 250 ºC, P = 1bar.

Moreover, the presence of CH_3O-Si on the 0.5-ZCS catalyst cannot be completely discarded, as the signal may be hidden by the highly intense b-HCOO-Zr bands and was filtered out by ME-PSD just like with the 2-ZCS sample.

Operando high pressure FTIR

Using transmission mode and a low dead volume reaction cell, high pressure operando FTIR experiments were carried out to track the reaction intermediates at more realistic reaction conditions, the results obtained for the 0.5-ZCS and 2-ZCS catalysts are presented in Figures 7 and 8, respectively. The inset shows the MS methanol signal (m/z = 31) during time on stream. The C-H stretching region presented very similar behavior than the experiments at ambient pressure and therefore are not shown.

For the 0.5-ZCS catalyst, when operating at high pressure (4 bar), after approximately 50min on stream, several new species can be observed in the spectra, Zr-bound ionic and bidentate carbonates (i-CO_3-Zr and b-CO_2-Zr) at 1450 and 1549 cm^{-1}, respectively, bidentate bicarbonate (b-HCO_3-Zr) at 1610 cm^{-1} and Cu-bound carbonate (CO_3-Cu) at 1421 cm^{-1} (7,8). The b-HCOO-Zr and HCOO-Cu identified in the in-situ DRIFTS experiments are present as well. Also, both the IR spectra and the methanol MS signal did not reach steady-state until 140 min on stream, indicating in high CO_2/H_2 pressure the catalyst may undergo a period of induction time, possibly having an effect on the electronic properties of Cu and Zr, facilitating the formation of these new surface compounds. Likewise, the carbonate and bicarbonate species observed here were reported by Fisher and Bell (7) during high pressure in-situ infrared experiments.

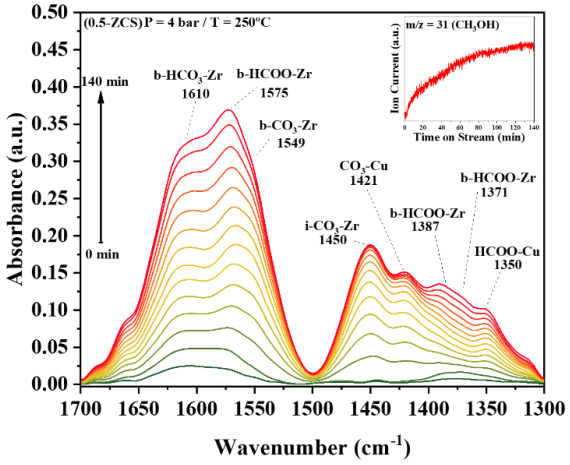

Figure 7. Operando FTIR spectra in the region between 1700 and 1300 collected for the 0.5-ZCS catalyst (Zr/Cu = 0.5). The inset shows the CH_3OH signal obtained by MS (m/z = 31) during the test. Conditions: T = 250 ºC, P = 4 bar.

Regarding the 2-ZCS catalyst, the spectra (Fig. 8) show the species already observed in the ambient pressure in-situ DRIFTS tests and the additional compounds formed at high pressure seen on the 0.5-ZCS spectra, but also a feature at 1471 cm^{-1} ascribed to CH_3O-Si spectator (7,8), corroborating the results obtained in the ME-PSD experiments. It is noteworthy that the overall intensity of the 2-ZCS signals is significantly higher than the 0.5-ZCS spectra, which is expected specially for the Zr-bound compounds, as the sample possesses double the amount of Zr in weight. The appearance of a CH_3O-Si feature in the fingerprint region suggests high pressure favors the generation of intermediates like b-HCOO-Zr and HCOO-Cu

but also facilitates the supposed spillover of CH_3O to Si, which is in accordance with the catalytic data, as the 2-ZCS is less selective to methanol at 30 bar.

Once again, it is not possible to completely discard the formation of CH_3O-Si on the 0.5-ZCS catalyst, however, given the data obtained in both types of in-situ experiments performed, it is safe to assume that this effect is much more pronounced in the 2-ZCS sample, which is accordance with the XRD and TPR-N_2O characterizations and the catalytic tests results.

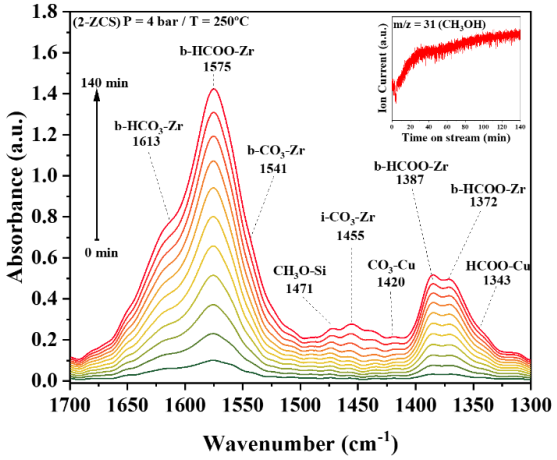

Figure 8. Operando FTIR spectra in the region between 1700 and 1300 collected for the 2-ZCS catalyst (Zr/Cu = 2). The inset shows the CH_3OH signal obtained by MS (m/z = 31) during the test. Conditions: T = 250 ºC, P = 4 bar.

Given that the "high pressure species" only start to appear after about 50 min on stream and the overall spectra and methanol signal take around 140 min to reach steady-state, it is implied that at least some of these species are intermediates in methanol production. After reaching steady-state in the operando experiments, CO_2 was switched to Ar and spectra were collected (not shown) during the transient hydrogenation of adsorbed species. The intermediates b-HCOO-Zr and HCOO-Cu signals quickly vanish as is expected for active compounds. However, among the species observed specifically at high pressure, only CO_3-Cu presented a similar behavior, so it may be a reaction intermediate, while the other surface species are still present even after 30 min under H_2 flow, indicating these may be spectators.

Conclusions

The activity of the inverse ZrO_2/Cu catalysts supported on SiO_2 in CO_2 hydrogenation to methanol was investigated by catalytic tests at high pressure and in-situ and operando infrared spectroscopy. It was found that Zr is fundamental for increasing methanol production, causing a significant enhancement in selectivity, reaching a maximum of 35% with the catalyst containing 10 wt% Zr. With ME-PSD-DRIFTS it was possible to observe the formate pathway as the main mechanism of methanol synthesis from CO_2 over the catalysts studied. Also, the identification of the short-lived formic acid intermediate highlight the potential of the technique. The in situ data also corroborates the recent idea of Cu adsorbing active compounds, besides its role of dissociating H_2. The low selectivity to methanol in comparison with previously reported ZrO_2/Cu catalysts was ascribed to the formation of inactive CH_3O-Si, caused by a largely exposed SiO_2 surface resulting from highly dispersed Cu over a material majoritarily amorphous, as suggested by XRD and TPR. Therefore, it may be necessary to cover the SiO_2 surface to some extent in order to enhance methanol productivity. Finally, operando infrared experiments at high pressure revealed extra signals, whose activity has yet to be completely understood in future investigations. The data provided here contribute to better understanding the activity and behavior of spectators and intermediates formed over the inverse ZrO_2/Cu catalyst for CO_2 conversion.

Acknowledgements

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