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Lewis acidic supports promote the selective hydrogenation of carbon dioxide to methyl formate in the presence of methanol over Ag catalysts

Juan José Corral-Pérez [a], Christophe Copéret [b], Atsushi Urakawa [a,c,*]

[a] Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, 43007 Tarragona, Spain
[b] Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich, Switzerland
[c] Catalysis Engineering, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, the Netherlands

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ABSTRACT

Silica-supported silver nanoparticles exhibit outstanding efficiency in the CO_2 hydrogenation to methyl formate in the presence of methanol under high pressure. Here, we show that ZrO_2 and Al_2O_3 supports significantly increase the catalyst activity, in line with their higher Lewis acidity. The weight time yield of methyl formate over Ag/ZrO_2 is up to 16.2 $g_{MF}\,g_{Ag}\,h^{-1}$ without detectable side-products, 25 times higher compared to Ag/SiO_2 at the same temperature. Transient *in situ* and *operando* DRIFTS studies uncover spillover processes of formate species from Ag onto the acidic support materials and show that the surface formates can further react with adsorbed methanol at the sites near the perimeter between Ag and the support to yield methyl formate.

1. Introduction

Methyl formate (MF) is an important intermediate in C_1 chemistry [1] as well as a potential intermediate in the continuous synthesis of thermodynamically-unstable formic acid through hydrolysis of MF [2]. In industry, it is also used as a blowing agent for foams [3] and as an agricultural fumigant [4]. The most common commercial route to synthesize MF is the base-catalysed reaction of methanol and carbon monoxide at 80 °C and 40 bar (Eq. (1)) [5].

$$CO + CH_3OH \rightleftarrows HCOOCH_3 \qquad (1)$$

Although high MF selectivity is achieved in this process, methanol conversion is only about 30% and the use of sodium methoxide as a catalyst presents some disadvantages such as equipment corrosion, the need of high purity reactants, and low process efficiency due to difficulty in separating the product and the catalyst, an intrinsic problem for most homogeneous production processes [5]. Therefore, synthesizing MF via a heterogeneous catalytic continuous process would be highly desirable. Metal-based heterogeneous catalysts have been proven active in alternative synthetic routes of MF such as methanol dehydrogenation [6,7], oxidative dehydrogenation of methanol [8,9] and carbon dioxide (CO_2) hydrogenation in the presence of methanol (Eq. (2)) [10–12].

$$CO_2 + H_2 + CH_3OH \rightleftarrows HCOOCH_3 + H_2O \qquad (2)$$

Of them, the last route is particularly appealing because it valorizes CO_2 in the context of climate change mitigation [13]. However, efficient catalysts and processes are required to convert highly stable CO_2 to MF [14]; a reaction that still suffers from low catalytic activities. Methanol conversion up to 5% has been achieved by gold nanoparticles supported on ZrO_2 at 160 bar under batch operation (maximum TOF of 534 h^{-1}) [10]. In our recent work, we demonstrated that SiO_2-supported Ag nanoparticles outperform Cu and Au counterparts in the continuous selective catalytic hydrogenation of CO_2 to methyl formate in the presence of methanol [15]. A detailed mechanistic study showed that adsorbed methanol reacts with formate species or formic acid, initially formed over Ag sites, at the perimeter sites of Ag on SiO_2 to yield MF [15]. Since even SiO_2, generally considered as a neutral and catalytically innocent support, plays key roles in the reaction, it is anticipated that the reaction performance and mechanism can be influenced by the nature of the support material. Indeed, materials such as Al_2O_3 and ZrO_2 with strong acido-basic properties [16,17] can activate CO_2 and methanol, and they may potentially stabilise reaction intermediates promoting MF formation [18,19]. In fact, support effect for this reaction has been discussed, for supported gold nanoparticles, albeit not investigated in details [10,20].

Therefore, we reasoned that investigating alternative supports for silver nanoparticles could help improving MF yield. Towards this goal, Ag nanoparticles are supported on selected metal oxide

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[*] Corresponding author.
E-mail address: A.Urakawa@tudelft.nl (A. Urakawa).

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materials via wetness impregnation method and evaluated in the MF synthesis. In order to compare the various supports without additional interference of metallic particle size, we have also used Surface Organometallic Chemistry (SOMC) to prepare supported Ag nanoparticles with a narrow particle size distribution and similar size on various supports [21]. Process parameters such as temperature, gas hourly space velocity (GHSV) and molar ratio of reactants are studied to achieve the highest MF yield and to gather information on reaction mechanisms. Finally, transient *in situ* and *operando* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies in combination with multivariate spectral analysis [15,22,23] are performed to elucidate the origin of support effects in relation to the formation of reactive intermediate species, their dynamics and the location of active surface species in MF synthesis.

2. Results and discussion

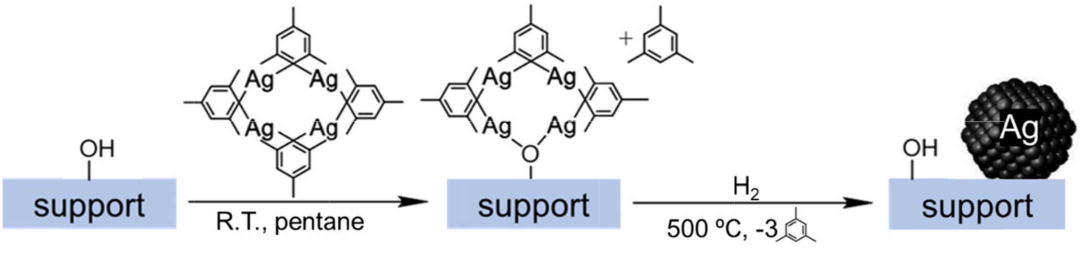
2.1. Catalyst synthesis and catalytic performance

Preliminary screening of selected support materials (ZrO_2, γ-Al_2O_3, CeO_2, pumice versus SiO_2, Table S1) was carried out using Ag as the active metal for MF synthesis from CO_2 and H_2 in the presence of CH_3OH. These catalysts are synthesized via incipient wetness impregnation using silver nitrate as precursor and subsequently calcined in air at 400 °C for 4 h. The nominal silver loading is kept constant at 1 wt% (actual Ag loading is 1–2 wt% according to EDX, Table S2). These Ag catalysts are evaluated in the continuous MF synthesis at high pressure (300 bar) because of the beneficial effect of pressure for that reaction [15]. The experimental details are described in the Supporting Information (S1). At low temperatures, all Ag catalysts with the various supports exhibit full selectivity to MF at our detection limit, and importantly those supported on ZrO_2 and γ-Al_2O_3 (Table S1), that are known Lewis acidic supports, display superior catalytic activity (Fig. S1). According to Aspen HYSYS (V8.6) simulations of the reaction mixture using the Soave–Redlich–Kwong (SRK) equation of state (EOS), the reactants are in one (gaseous/supercritical) state at the examined temperatures (higher than 152 °C, Fig. S10). Therefore, in this study, the effects of phase separation on the catalytic performance are assumed negligible, and thus we attribute the superior catalytic activity mostly to the support effect.

Besides the clear influence of the type of support used for the Ag catalysts on MF yield, the Ag particle size may also affect the catalytic performance. In order to discern if the superior MF yield arises from the support or Ag particle size, comparative Ag catalysts supported on ZrO_2, γ-Al_2O_3 and SiO_2 are synthesized via the SOMC approach [21,24–27]. While Ag/ZrO_2 and Ag/γ-Al_2O_3 are chosen because of their high activity (vide supra), Ag/SiO_2 is used as a benchmark because of its previously reported activity in this particular reaction [15]. Thanks to SOMC, narrowly dispersed Ag nanoparticles of similar sizes (2.6 ± 0.6 nm) are obtained on all supports by grafting silver mesityl on the surface hydroxyl groups of the respective support (partially dehydroxylated at 500 °C), followed by reduction under H_2 at 500 °C for 5 h (Scheme 1, Table S3 and Figure S2). The formation of Ag particle with virtually identical size (Table S3) for the three catalysts allows interrogating the support effects on the hydrogenation of CO_2 in the presence of methanol.

The supported Ag catalysts prepared via SOMC (Fig. 1, dashed line) are evaluated in the CO_2 hydrogenation to MF in the presence of methanol and compared to the counterparts prepared via impregnation (Fig. 1, solid line) by means of weight time yield of MF (WTY_{MF}) and selectivity to MF (S_{MF}). As depicted in Fig. 1, there are no significant differences between the catalytic activities of the materials prepared by the two different methods for the same type of support material. γ-Al_2O_3 and ZrO_2 supported Ag catalysts show similar catalytic trends. Both support materials facilitate MF formation at lower temperatures when compared to SiO_2. MF is exclusively formed over Ag/SiO_2 in the whole evaluated temperature range (Fig. 1) [15] while DME and CO are the predominant products for Ag/Al_2O_3 and Ag/ZrO_2, respectively, at higher temperatures (Fig. 2c, Supporting Information, Figs. S3 and S4). Note that in the absence of Ag nanoparticles over γ-Al_2O_3 and ZrO_2, only DME is observed as product at temperatures higher than 200 °C (Fig. S5). Hence, Ag nanoparticles promote the formation of MF and CO, but effects of its particle size are not evidently observed, thus highlighting the dominant effects of support material on the MF synthesis. This is also indicated by the formation of side-products since the selectivity to MF is strongly affected by the nature of support material at high temperatures.

A more detailed study regarding the effect of the gas hourly space velocity (GHSV) over the most reactive catalyst, i.e. Ag/ZrO_2 prepared by the impregnation method, is performed in a wider range of reaction temperatures to gather information on what is limiting the MF formation rate. In this case, lower temperatures (120 and 140 °C) are studied. As mentioned above, at 120 and 140 °C, phase separation is expected for the reaction mixture itself, where the vapour phase fraction is 0.86 and 0.93, respectively. Fig. 2a shows that upon increasing GHSV from 9000 to 24000 h^{-1}, i.e. decreasing the residence time of the reactants in the catalytic reactor, MF yield (methanol conversion basis) drops with the similar reactivity trend with the maximum at 180 °C. On the other hand, MF yield increases drastically at 4000 h^{-1} in the lower temperature range (120–160 °C), reaching close to 10% MF yield and without showing a maximum MF yield in the temperature range examined. This may be due to phase separation (i.e. liquid and gas/supercritical phases) that can take place at temperatures below ca. 150 °C (Fig. S10), where catalytic activity could be enhanced by surface wetting, although no conclusive statement can be made solely based on this study. It is interesting to note that the MF yield drops more rapidly towards higher temperatures at 4000 h^{-1} in comparison to the higher GHSV cases (Fig. 2). This drop in MF yield is obviously related to the amount of CO formed, which is more pronounced at lower GHSV (Fig. 2b). A closer look into MF yield (Fig. 2a) upon increasing reaction temperatures shows that



Scheme 1. Schematic representation of the grafting-reduction sequence for supported Ag nanoparticles catalysts prepared via the SOMC approach.

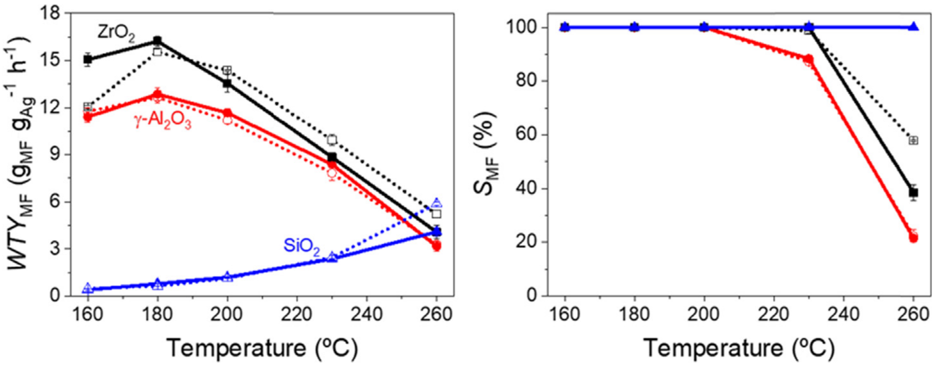


Fig. 1. Effects of reaction temperature on weight time yield of MF (WTY_{MF}) and selectivity to MF (S_{MF}) over silica- (blue), γ-alumina- (red) and zirconia- (black) supported Ag catalysts. Catalysts prepared via the impregnation method (solid line) and the SOMC approach (dashed line). Reaction conditions: CO_2:H_2:CH_3OH = 4:4:1 (molar ratio), 300 bar, GHSV = 9000 h^{-1}.

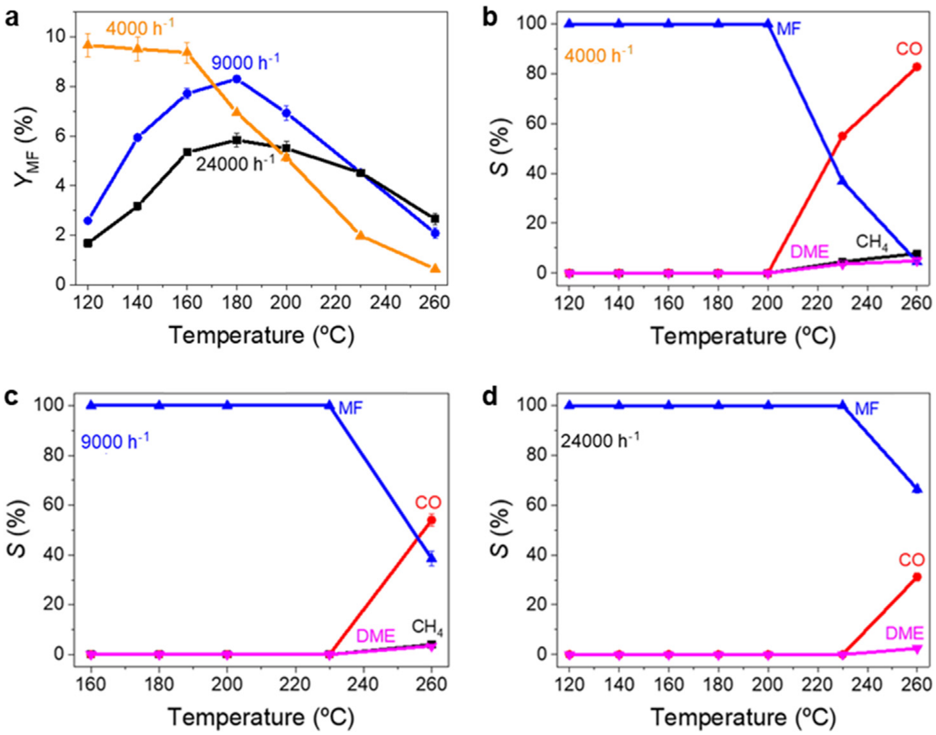


Fig. 2. (a) Effects of GHSV on MF yield (Y_{MF}) and selectivity (S) to MF, DME, CO and CH_4 at (b) 4000, (c) 9000 and (d) 24000 h^{-1} over zirconia-supported Ag catalyst prepared via impregnation method. Reaction conditions: CO_2:H_2:CH_3OH = 4:4:1 (molar ratio) and 300 bar.

the onset temperature of CO formation (Fig. 2b-c) and the maximum temperature where MF yield drops are highly related. These results imply that the reaction is kinetically more limited at the higher GHSV due to the short residence time. The observed correlation between the MF drop and CO formation suggests that CO is formed through the decomposition of MF possibly over the acidic sites [28,29], although we cannot fully exclude the possibility of reverse water-gas shift reaction through a surface intermediate for CO formation since this reaction is favoured at higher temperatures [30]. Possible effects of phase separation (i.e. liquid and gas/supercritical phases) are neglected here since the reaction mixture exists in one phase within the temperature range where the catalytic activity is high (ca. above 150 °C, Figure S10).

There is a small temperature window where MF yield drops upon increasing reaction temperatures while only MF is observed (e.g. 160–200 °C at 4000 h^{-1}, Fig. 2a,b). This drop is more pronounced at lower GHSV and hence at longer reaction time in the catalytic reactor. These observations indicate that prior to CO formation, MF decomposition to CO_2, H_2 and methanol may become prominent at longer residence time. This as well as the higher MF yield at lower GHSV and temperatures (Fig. 2a) imply that the MF formation is kinetically controlled through a delicate balance between its formation and decomposition. The thermodynamic analysis shows that the equilibrium yield of MF is low (Table S4) and the observed values can only be explained by kinetically controlled reactions. Furthermore, while DME is observed at elevated temperatures when CO is also present (Fig. 2b,c), DME is likely formed through dehydration of methanol over the acidic sites of the support because Ag/A_2O_3 (Figure S4) shows high DME selectivity and Al_2O_3 is a well-known active catalyst for methanol dehydration [13].

With the implication of MF formation being kinetically limited, attempts are made to increase MF yield by varying the molar ratios of the reactants at low GHSV (4000 h^{-1}) over Ag/ZrO_2 prepared by the impregnation method (Fig. 3). When the partial pressure of CO_2 and H_2 is roughly halved by increasing the methanol concentration (CO_2:H_2:CH_3OH = 2:2:1 M ratio), MF yield drops (Fig. 3). In sharp contrast, when the partial pressure of CO_2 and H_2 is drastically increased (CO_2:H_2:CH_3OH = 30:30:1 M ratio), the MF yield increases to values up to 22%. The practically identical WTYs at 4:4:1 and 2:2:1 M ratios indicate that at constant GHSV, hence residence time, the conversion rates of methanol per unit time do not change significantly. However, WTY drops greatly at 30:30:1 M ratio. This is a clear indication that at this ratio, the amount of methanol on the catalyst surface is rate-limiting due to lower methanol partial pressure and/or abundant coverage of formates/formic acid on the catalyst surface, thus highlighting how critical the formation of formate species or methanol adsorption is for this reaction. Under this limiting condition, higher portion of methanol can be reacted compared to CO_2 and H_2, hence the highest achieved MF yield.

2.2. Surface species involved in CO_2 hydrogenation

Aside from the mechanistic hints provided by the catalytic data, *in situ* DRIFTS is performed to gain chemical insights into the surface chemical species formed over the different catalysts prepared via the impregnation method under reaction conditions, thus allowing molecular understanding of support effects observed when comparing the improved catalytic activity for ZrO_2 and Al_2O_3 vs. SiO_2 [15]. The general challenge of such spectroscopic methodology lies in the complexity of spectra due to the presence of spectator species which are not directly involved in the reaction and to the overlapping signals arising from several chemical species that coexist on the catalyst surface. Transient response techniques together with multivariate spectral analysis allows a selective and sensitive monitoring of the dynamic behaviour of the active species involved in the complex catalytic system [31]. However, such approach cannot establish relationships among surface intermediates and catalytic performance. That is why *operando* methodology [32–34], through simultaneous reactivity evaluation, is further employed in combination with transient techniques to elucidate surface species responsible for the target product formation.

As noted previously, MF is formed only when Ag is present on the metal oxide support materials. *In situ* DRIFTS measurements reveal that only carbonates are formed over pure ZrO_2 under the mixture of CO_2 and H_2 (1:1 M ratio) at 230 °C and 5 bar (Fig. S6) [35]. The experimental condition is identical to that used in our previous study on Ag/SiO_2, hence the results can be directly compared [15]. The characteristic bands in the ν(C—H) region assigned to formate species are observed only when Ag is present on the support surface (Fig. S6). To learn more about the nature of these surface species, a transient *in situ* DRIFTS study is performed by passing alternatingly the reactant gas (CO_2:H_2 at 1:1 M ratio) and an inert gas (Ar) over Ag/ZrO_2 catalyst at 230 °C and 5 bar (Fig. 4a). The IR spectra of "kinetically separable" surface species (Fig. 4b) and their concentration profiles (Fig. 5) are obtained by multivariate spectral analysis.

In the ν(C—H) region (Fig. 4), the presence of two distinct surface species, whose concentrations respond to the partial pressure of CO_2 and H_2, is confirmed (Fig. 5, solid line). In the ν(C—O) region, there are three distinguishable species and their concentration profiles are shown in Fig. 5 (dashed line). One of them show characteristic bands of carbonates over ZrO_2 (Fig. 4, black line) [23,24]. The other two species behave kinetically identical to those observed in the ν(C—H) region (shown in the same line colour in Figs. 4 and 5). These two species are assigned to formate species since their characteristic features are simultaneously observed in the ν(C—H) and ν(C—O) regions and are consistent with literature data [17,19,35,36]. Thus, two kinds of formate species are formed over the catalyst surface. The bands at 2940, 2838, 2723, 1648, 1394 and 1286 cm^{-1} (Fig. 4, orange line) are assigned to formates on Ag as previously proposed [15], while these at 2969, 2923, 2877, 2815, 2753, 1733 and 1639 cm^{-1} (Fig. 4, green line) can be assigned to formates adsorbed over ZrO_2 support [19,36] or possibly at the perimeter sites of Ag and ZrO_2.

In order to further confirm the nature of the two kinds of formates discussed above, i.e. formates on Ag and formates on ZrO_2, the concentration profiles of these kinetically distinct species are more carefully examined. When the catalyst is exposed to $CO_2 + H_2$, carbonates (Fig. 5, black line) and formates on Ag (Fig. 5, orange line) are immediately formed reaching a stable concentration relatively quickly while formates on ZrO_2 slightly increase. After switching the reactant gas to argon, carbonates depletion is instantaneous while the decrease in the concentration of the formates on Ag (Fig. 5, orange line) is accompanied by the compensating formation of formates on ZrO_2 (Fig. 5, green line). The reversed concentration profiles of the two kinds of formates (Fig. 5) indicates a spillover process of the formates formed on Ag under $CO_2 + H_2$ towards the support or possibly at the perimeter sites of Ag and ZrO_2. Such spillover process takes place more slowly under $CO_2 + H_2$ (Fig. 5a,b) than argon (Fig. 5c,d), most likely due to the presence of carbonates over the support (Fig. 5a,b) that compete with formates for the same adsorption sites on ZrO_2, thus hindering the spillover process.

It should be noted that in the case of Ag/SiO_2, formates on Ag are removed under argon while on SiO_2 they are not observed [15]. Hence, the stable formation of formates on support and the possibility of spillover from Ag are ascribed to the (Lewis acidic) properties of ZrO_2 support [19]. Importantly, this spillover phenomenon is also observed for Ag/Al_2O_3 (Fig. S7), confirming the

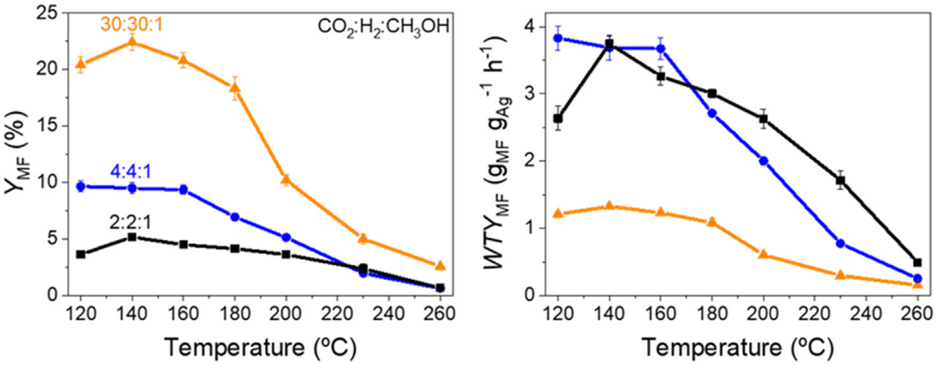


Fig. 3. Effects of CO_2:H_2:CH_3OH molar ratio on (left) MF yield (Y_{MF}) and (right) weight time yield of MF (WTY_{MF}) over zirconia-supported Ag catalyst. Catalyst prepared via the impregnation method. Reaction conditions: GHSV = 4000 h^{-1} and 300 bar.

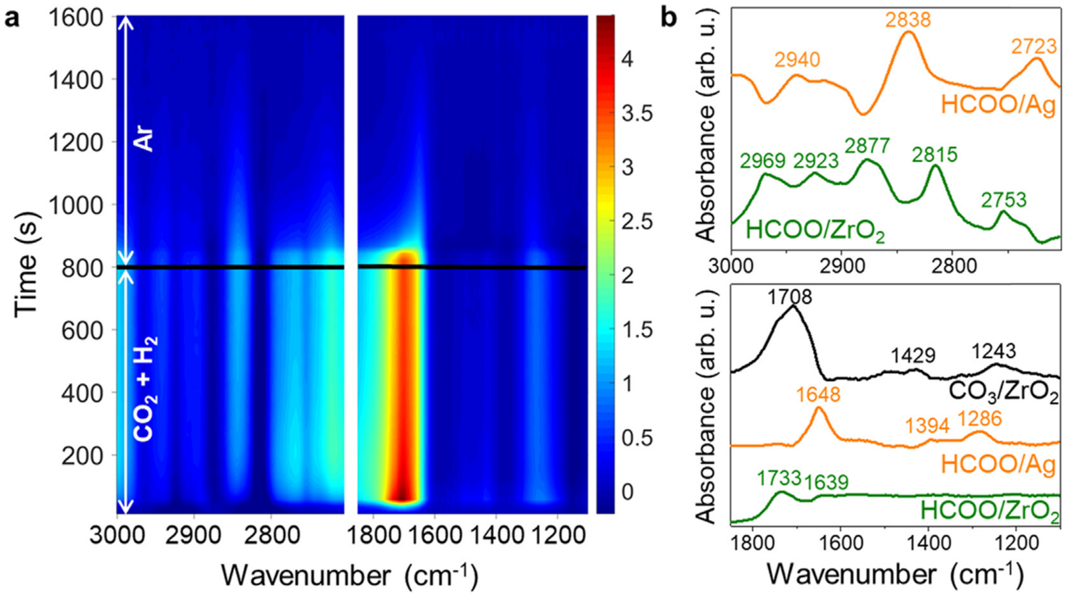


Fig. 4. Transient DRIFTS study on CO_2 hydrogenation over Ag/ZrO_2 catalyst prepared via the impregnation method. (a) Time-resolved DRIFT spectra upon exposure to CO_2: H_2 = 1:1 M ratio (the first half period) and then to Ar (the second half period), concentration perturbation experiment at 230 °C and 5 bar. The DRIFT spectra are shown in milli-absorbance unit taking the last spectrum in the Ar atmosphere as background. (b) Components spectra obtained by multivariate spectral analysis applied on the depicted time-resolved DRIFT spectra.

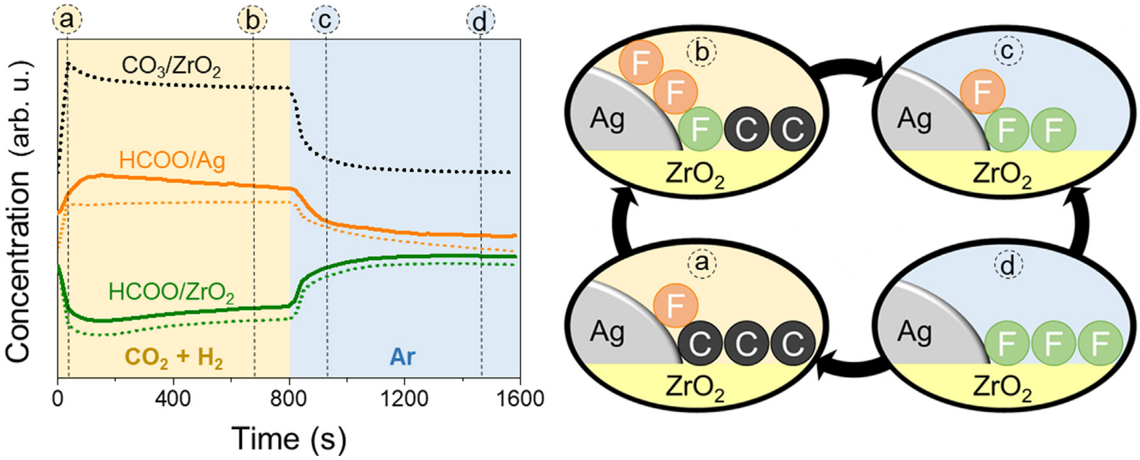


Fig. 5. (left) Concentration profiles of the components spectra in the ν(C—O) (dashed line) and ν(C—H) (solid line) regions shown in Fig. 4, obtained by the multivariate spectral analysis. (right) A scheme of the surface species, i.e. carbonates (C) and formates (F), involved in CO_2 hydrogenation over Ag/ZrO_2 catalyst under transient conditions (a–d).

stable formation/presence of formates on both support materials and explaining why acidic supports like ZrO_2 and Al_2O_3 exhibit better catalytic performance than SiO_2 in MF formation (Fig. 1). However, it should be underlined that the acidity of these support materials also induces the formation of DME at high temperature and facilitates CO formation through the decomposition of MF (Fig. 2) [29,37].

2.3. Mechanistic insights into MF formation

In order to understand how the formate species spillover from the Ag surface to the support affects the MF yield, transient DRIFTS measurements were performed under *operando* conditions (i.e., simultaneous reactivity measurements by mass spectrometry (MS)) over the catalysts prepared via the impregnation method. Despite the lower pressure (5 bar) used in these experiments due to technical limitations (methanol saturator), pressure is not expected to alter significantly the reaction mechanism as evidenced by the observation of similar reactivity trends according to MS analysis. Thus, the resulting insights can be transferable to higher pressure conditions. The major aim of this study is to evaluate and differentiate the reactivity induced by different support materials to firmly establish relationships among the nature of the support materials, surface intermediates and catalytic activity.

The MS signals of MF observed for Ag/ZrO_2 are depicted and compared to those of Ag/SiO_2 in Fig. 6. In the first experiment, Ag/ZrO_2 is initially exposed to the gas flow of $CO_2 + H_2 + CH_3OH$ (vapor), followed by exposure to CH_3OH and then switched back to $CO_2 + H_2 + CH_3OH$ (Fig. 6a). The two gas atmospheres are switched repeatedly and periodically. The IR spectra of "kinetically separable" species (Supporting Information, Fig. S8), i.e. adsorbed CH_3OH (or methoxy), formates on Ag and formates on ZrO_2, and their concentration profiles (Fig. 6a) are obtained by the multivariate spectral analysis.

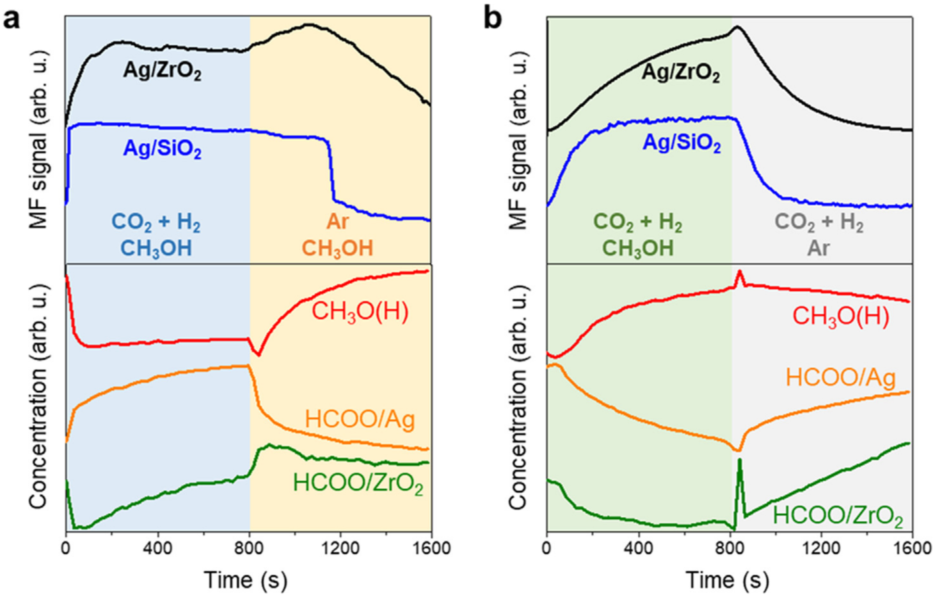


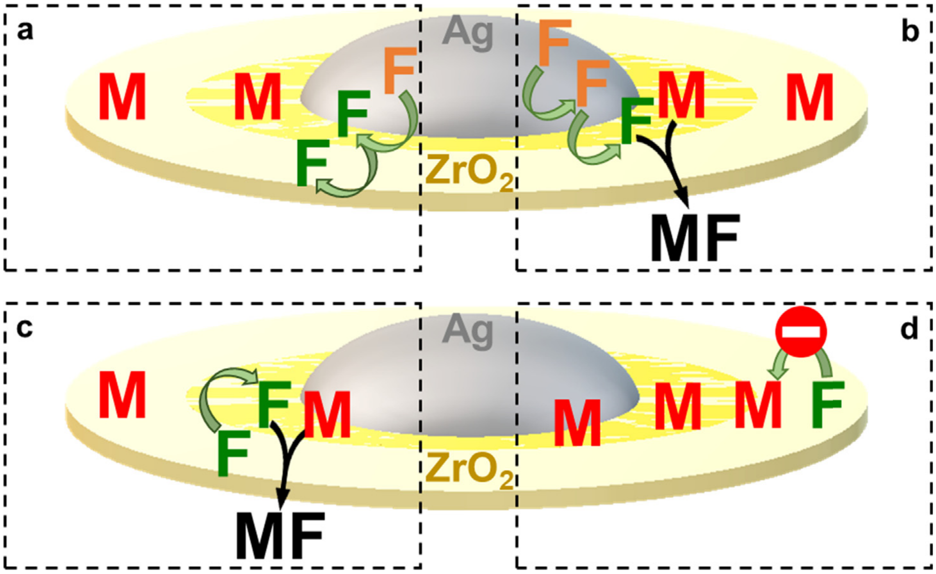
Fig. 6. Transient *operando* DRIFTS studies on the esterification of formates with CH_3OH to MF over Ag/ZrO_2. MS signal of MF ($m/z = 60$, top graphs) and concentration profiles of adsorbed CH_3OH and formates obtained by the multivariate spectral analysis (bottom graphs). MS signal of MF over Ag/SiO_2 as a reference [15]. The analysis was applied on the time-resolved DRIFT spectra of Ag/ZrO_2 upon exposure to (a) $CO_2 + H_2 + CH_3OH$ (the first half) vs Ar + CH_3OH (the second half period), and (b) $CO_2 + H_2 + CH_3OH$ (the first half) vs $CO_2 + H_2$ + Ar (the second half period) at 230 °C and 5 bar (total pressure).

When the reactant gas is changed from CH_3OH (the second half period of Fig. 6a) to $CO_2 + H_2 + CH_3OH$ (the first half period), MF is instantly produced, and its increasing formation profile is similar to that of formates over Ag but inversely correlated with that of adsorbed CH_3OH (Fig. 6a). Upon switching the atmosphere to CH_3OH (the second half period), a slight enhancement in the production of MF is observed, which is apparently linked with the concentration change of formates on ZrO_2 (Fig. 6a). After the initial increase in the concentration of formates on ZrO_2, their concentration decreases only slightly, indicating that they are not decomposed and can be stably present in the CH_3OH atmosphere. At the same time, the MF production rate decreases over time as methanol is increasingly adsorbed on the catalyst. Unlike for Ag/SiO_2, the initial increase in the concentrations of gaseous MF and surface formates on ZrO_2 upon switching to CH_3OH implies that the specific transient condition creates highly reactive environment between surface formates/formic acid with adsorbed methanol to enhance MF yield.

According to the concentration profiles of formates on Ag and ZrO_2 upon switching to the CH_3OH atmosphere (Fig. 6a), the sudden increase in gaseous CH_3OH concentration induces an increase in the concentration of formates on ZrO_2 that promotes the formation of MF. This indicates a rapid migration of formates on Ag toward the perimeter sites and further over ZrO_2 (Scheme 2a). Most likely this is due to the reaction of surface species with methanol to yield MF, thus creating vacant sites on ZrO_2 that accelerates the spillover process. This hypothesis is supported by the fact that the spillover of formates to ZrO_2 is slower under CO_2 and H_2 ($HCOO/ZrO_2$ in Fig. 5 vs Fig. 6a), since the surface species cannot be consumed in the absence of methanol.

Another important observation is that the MF formation gradually decreases along the CH_3OH atmosphere (Fig. 6a) despite the stable presence of formates on ZrO_2 and increasing amount of adsorbed CH_3OH. This indicates that the actual MF formation sites is highly location-sensitive; the formates that react with methanol to yield MF are likely those present close, i.e. at the interface between Ag and ZrO_2 (Scheme 2b). In any case, formates on ZrO_2 could function as a sink to provide active formates reacting with CH_3OH at the perimeter sites through reverse-spillover (Scheme 2c). However, if the distance from the formates on ZrO_2 to Ag is too large, the reverse-spillover and consequently the reaction toward MF formation seem prohibited by the blockage of near-perimeter sites on ZrO_2 by methanol (Scheme 2d). This would explain the concentration profiles of the transient *operando* study, where both formates and adsorbed methanol coexist on ZrO_2 with reduced formation of MF.

To elucidate further how the reactive surface species interplay, methanol is discontinuously fed by alternatingly exposing the catalyst to the gas flows of $CO_2 + H_2 + CH_3OH$ and $CO_2 + H_2$ and the reaction monitored under operando conditions (Fig. 6b and Supporting Information, Figure S9). In this case, MF concentration follows a similar profile of gaseous and adsorbed CH_3OH but inversely with that of adsorbed formates on Ag. After switching from $CO_2 + H_2 + CH_3OH$ (the first half period of Fig. 6b) to $CO_2 + H_2$ (the second half period), adsorbed methanol is present on the catalyst at a high concentration whereas both formates on Ag and ZrO_2 gradually increase with time. Despite the presence of both adsorbed methanol and formates on the catalyst, MF formation drops progressively. This further supports the fact that the reaction between formates and CH_3OH only takes place at specific sites/location (Scheme 2b,c). Since MF formation apparently responds to the concentrations of gaseous methanol and the adsorbed methanol, the adsorption and diffusion of CH_3OH on the catalyst surface are likely rate-limiting. This may be due not only to the strong binding of CH_3OH on ZrO_2 [38,39] but also to the surface interaction of pre-adsorbed formates, competing with the adsorption and diffusion of CH_3OH over ZrO_2. The abrupt and then gradual formation of formates on ZrO_2 in the absence of CH_3OH (Fig. 6b, the second half period) evidences the initially enhanced spillover of formates from Ag to ZrO_2, leading to enhanced MF formation, followed by a gradual spillover competing for the adsorption site with surface $CH_3O(H)$. In contrast to the Ag/SiO_2 case, the MF formation rate decreases more gradually, most likely due to the presence of stable formates over support which were not observed over SiO_2 [15]. The adsorbed CH_3OH can therefore be depleted in the vicinity of Ag through MF formation (Scheme 2b,c) or through formates spillover



Scheme 2. Suggested mechanisms for the formation of MF from CO_2, H_2 and CH_3OH over Ag/ZrO_2 catalyst by the *operando* studies shown in Fig. 6. Surface species: methanol (M) and formates (F).

(Scheme 2a), which is why the access of CH_3OH to the perimeter sites affects more critically the MF formation rate. Another interesting observation is that the MF yield is not much influenced by the particle size of Ag according to the catalytic results (Fig. 1). This implies that the rate-determining step under the steady-state condition is not the reaction at the perimeter sites. Rather it could be adsorption of reactants and/or diffusion of methanol/formates on the support surface thus determining the catalytic activity.

3. Conclusions

We show that silver nanoparticles supported on ZrO_2 and Al_2O_3 are highly active for the continuous and catalytic formation of methyl formate from CO_2, H_2 and CH_3OH. MF yield can reach a value of up to 16.2 $g_{MF}\,g_{Ag}\,h^{-1}$ over Ag/ZrO_2 at 180 °C without the detection of side-products. Transient *operando* vibrational spectroscopy studies together with multivariate spectral analysis show that Al_2O_3 and ZrO_2, two Lewis acidic supports, promote the spillover of formates from Ag to the support in contrast to SiO_2; these formates can then react with adsorbed CH_3OH at the perimeter sites to yield MF. The rate-determining step under steady-state condition is likely the adsorption of reactants and/or diffusion of methanol/formates on the support surface rather than reaction at the perimeter sites. The current catalytic system presents a great step forward from the conventional homogeneous CO_2 reduction catalysts since MF can be formed in the gas phase without the addition of basic additives, thus avoiding post-synthetic work-up of the formate salts generated in the homogeneously catalysed processes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.10.013.

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