

In situ FT-IR and kinetic study of methanol synthesis from CO_2/H_2 over ZnAl_2O_4 and $\text{Cu-ZnAl}_2\text{O}_4$ catalysts

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Abstract

The kinetics of the CO_2/H_2 reaction over ZnAl_2O_4 and $\text{Cu-ZnAl}_2\text{O}_4$ catalysts at 250°C up to 0.3 MPa have been followed by in situ FT-IR spectroscopy. Both methanol and carbon monoxide formation were enhanced in presence of copper. They were also produced by independent routes through different adsorbed species. Formate (type I, I' and II), methoxy and carbonate species were identified on the support and, in addition, copper formate and copper carbonyl species when copper was present. The hydrogenation of carbonate species to copper formate species was found rate determining in methanol synthesis over the $\text{Cu-ZnAl}_2\text{O}_4$ catalyst whereas type I formate species were shown to be the active intermediate for this reaction over the ZnAl_2O_4 support. Carbon monoxide resulted from the water gas shift reaction probably through the same species as methanol formed over the $\text{Cu-ZnAl}_2\text{O}_4$ catalyst whereas it seemed to stem from formate species of type II in the case of the ZnAl_2O_4 support. Type II formate species were shown inactive in presence of copper whereas the methoxy species adsorbed on the support were found inactive in presence and in absence of copper. The comparison of these results with those previously obtained with the CO/H_2 mixture showed that the nature and the role of the detected species strongly depended on the reactive atmosphere and on the presence or not of copper in the catalyst composition. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Methanol synthesis from $\text{CO}/\text{CO}_2/\text{H}_2$ mixtures using $\text{Cu-ZnAl}_2\text{O}_4$ catalysts is an important reaction from both industrial and fundamental point of view [1–10]. Though a great number of studies have been devoted to this reaction, its

mechanism is still not well understood [6–9]. Particularly the role of each carbon oxide in relation with the detected reaction intermediates is still debated [10–26].

We previously reported [27] the results of the CO/H_2 reaction over a $\text{Cu-ZnAl}_2\text{O}_4$ catalyst at 250°C up to 0.3 MPa using an in situ FT-IR method. We observed the formation of several adsorbed species: four formate species (three on the support and one on copper), methoxy and carbonate species adsorbed on the support and carbonyl species adsorbed on copper. The study

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of species reactivity and kinetic investigations showed the existence of two reaction paths for methanol synthesis, involving as key reaction intermediate formate species (on the ZnAl_2O_4 support) and copper carbonyl species respectively. Inactive formate species adsorbed on the support have been also evidenced. Carbon dioxide, also formed during the reaction, resulted from the partial reduction of the support.

The present paper deals with the CO_2/H_2 reaction on ZnAl_2O_4 and $\text{Cu-ZnAl}_2\text{O}_4$ catalysts at 250°C which is investigated by an in situ FT-IR method. The observed reaction rates and evidenced adsorbed species throw some light on the involved chemical paths. The obtained results are compared to those reported for the CO/H_2 reaction on the same catalysts [27].

2. Experimental

The catalyst preparation and characterization, the in situ FT-IR device and the method used were described previously [27]. The operating conditions were as following: before FT-IR experiments the catalysts were reduced in situ at 250°C under a hydrogen flow (0.9 l/h) at atmospheric pressure; the CO_2/H_2 mixture was then introduced. The pressure variation ranges were 0.01–0.3 MPa for CO_2 and 0.2–0.9 MPa for H_2 .

3. Results

3.1. Characterization of the adsorbed species

The IR spectra of the catalysts under CO_2/H_2 flow show the characteristic bands of the following species [28]:

- Carbonates species ($1510, 1410\text{ cm}^{-1}$).
- Carbonyl species adsorbed on copper (2100 cm^{-1}). Its wavenumber allowed one to follow the copper oxidation state as a function of P_{CO_2} (Fig. 1).

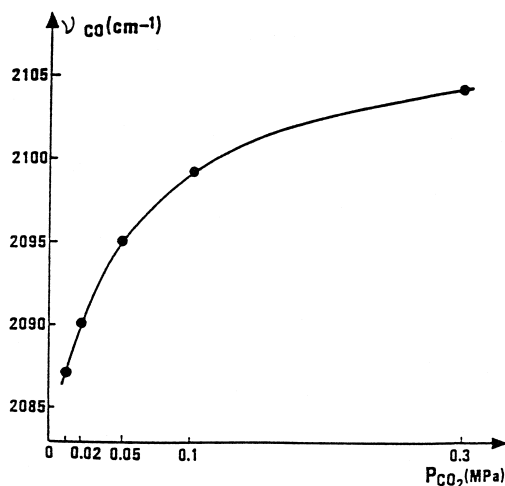


Fig. 1. Variations of the wavenumber of the surface carbonyl species as a function of the partial pressure of CO_2 in the case of the $\text{Cu-ZnAl}_2\text{O}_4$ catalyst. $P_{\text{H}_2} = 0.7\text{ MPa}$, $T = 250^\circ\text{C}$.

- Methoxy species adsorbed on the support ($2943, 2835, 1100\text{ cm}^{-1}$). No copper methoxy species were detected.

- Three types of formate species (type I, I', II) adsorbed on the support: type I (F_{I}) ($2881, 2744, 1595, 1375\text{ cm}^{-1}$) and type I' ($F_{\text{I}'}$) ($1650, 1320\text{ cm}^{-1}$). Type II species (F_{II}) ($2895, 2767, 1590, 1390, 1370\text{ cm}^{-1}$) was similar to that detected on alumina.

- Formate species adsorbed on copper (F_{Cu}) ($2925, 2847, 2692, 1352\text{ cm}^{-1}$).

The reference bands for quantitative FT-IR analysis are those underlined above [27].

3.2. ZnAl_2O_4 catalyst

The spectrum of the $\text{ZnAl}_2\mathbf{O}_4$ sample activated under H_2 at atmospheric pressure shows characteristic bands of surface hydroxyl species (free OH at 3680 cm^{-1} and associated OH at 3500 cm^{-1}). An important amount of carbonate and residual formate species is also present. This spectrum has always been subtracted from those obtained in the following experiments under CO_2/H_2 flow in order to follow the apparition of new bands due to the adsorbed species formed. Under CO_2/H_2 flow a stationary state

is rapidly reached. The IR spectra present bands characteristic of the three types of formate species (type I, I', II) and of methoxy species.

Fig. 2 shows as a function of P_{CO_2} , the amount variations of the adsorbed species and of the reaction products in the gas phase respectively.

The formate I species concentration increases rapidly up to 0.1 MPa of CO_2 and then much more slowly (Fig. 2A). The amount of these species is greater than that obtained under CO/H_2 atmosphere [27]. Contrarily, formate II species formation seems to be independent of P_{CO_2} (Fig. 2A) as it was for P_{CO} [27]. As to the carbonate species, Fig. 2A suggests that they arise at the expense of the methoxy species when P_{CO_2} is higher than 0.1 MPa whereas they were not detected at all in the presence of CO/H_2 mixture [27]. We may speculate that a

competitive adsorption occurs between carbonate and methoxy species under CO_2/H_2 over the ZnAl_2O_4 support.

From the analysis of the gas phase (Fig. 2B) it appears that methanol and carbon monoxide formation are quasi-independent of P_{CO_2} in almost the whole pressure range studied. The amount of methanol formed (Fig. 2B) is greater than that obtained from the CO/H_2 mixture [27].

In order to study the surface species reactivity, transient experiments were performed by switching off the CO_2 flow after the stationary state was reached and by maintaining the H_2 partial pressure (P_{H_2}). The spectra recorded with 10 min intervals (Fig. 3) show the progressive disappearance of formate I and I' species accompanied by a sensible increase of the methoxy species amount. As to formate II species concentration it seemed unchanged.

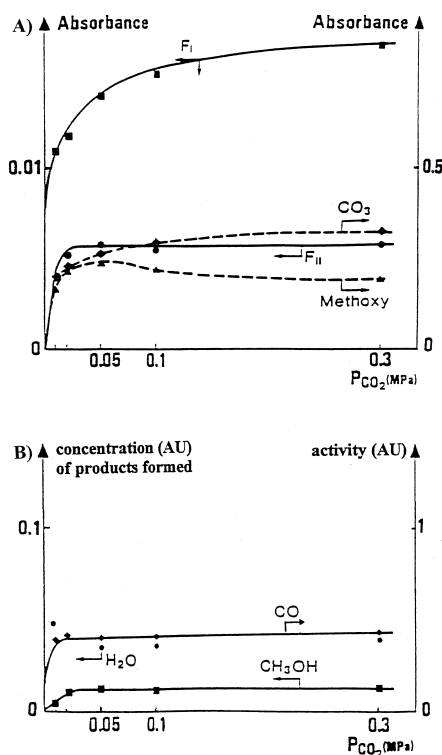


Fig. 2. Variation as a function of the partial pressure of CO_2 in the case of the ZnAl_2O_4 catalyst ($P_{\text{H}_2} = 0.7$ MPa, $T = 250^\circ\text{C}$) of: (A) the intensity of the characteristic bands of the adsorbed species formed; (B) the relative amount of products formed.

3.3. $\text{Cu-ZnAl}_2\text{O}_4$ catalyst

On the H_2 -activated $\text{Cu-ZnAl}_2\text{O}_4$ catalyst spectrum, the intensity of the OH band at 3500 cm^{-1} is much more important than that observed in the case of the ZnAl_2O_4 catalyst. The amount of residual carbonate species is nearly the same but that of residual formates is clearly lower.

Under CO_2/H_2 flow stationary states are rapidly reached. The IR spectra of the catalyst under flow (Fig. 4) show the appearance of the characteristic bands of carbonate, formate and methoxy species adsorbed on the support and of formate species adsorbed on copper. Formate I and I' adsorbed on the support, which were not detected under CO/H_2 atmosphere [27], are here observed. In addition, the carbonate species are in a higher amount than under CO/H_2 flow [27].

The variation of the amount of these adsorbed species with increasing P_{CO_2} is reported in Fig. 5A where it can be seen that, as for the ZnAl_2O_4 catalyst, the amount of formate II species appears to be independent of P_{CO_2} . Sim-

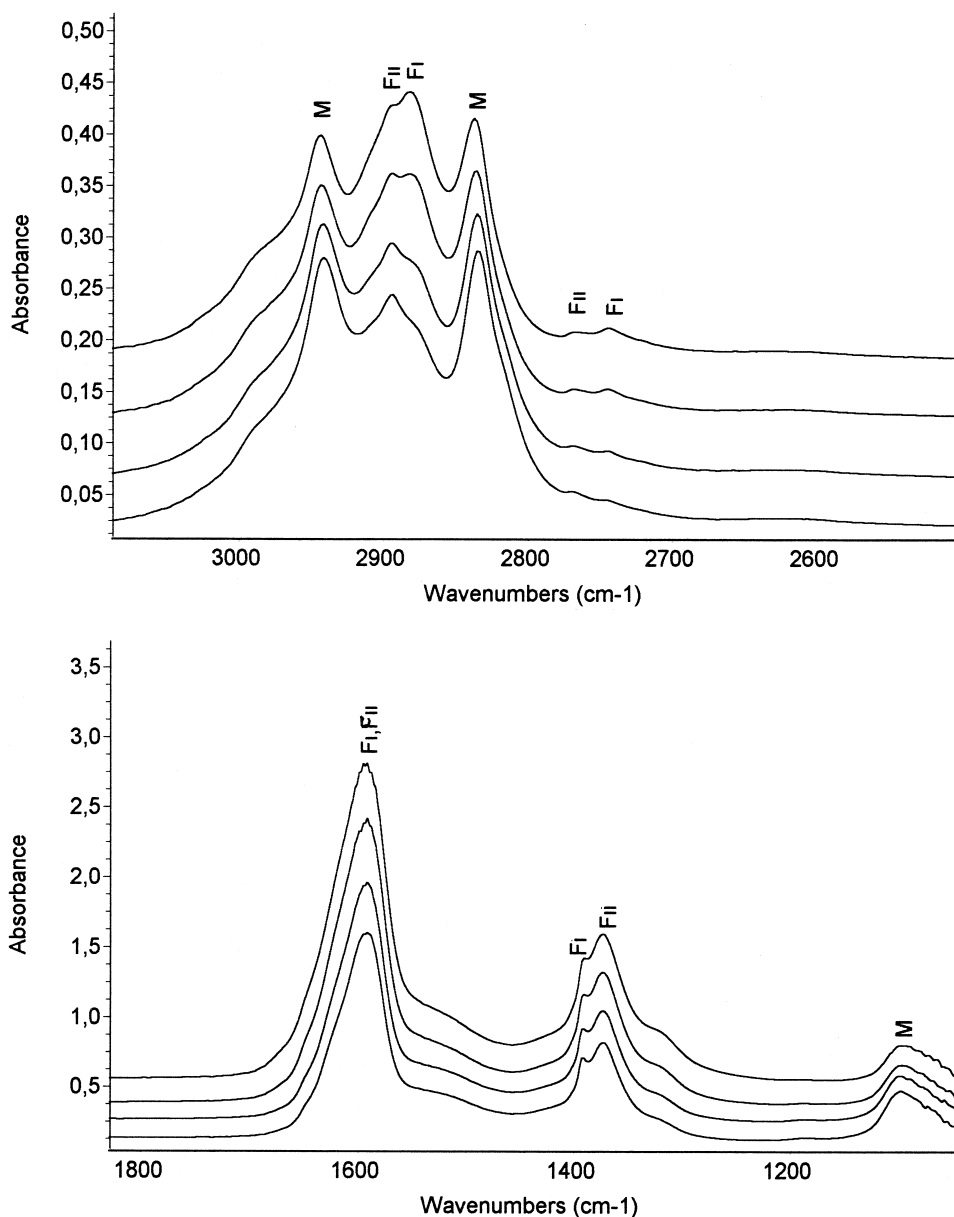


Fig. 3. Variation of the intensity of the characteristic bands of the adsorbed species formed with time on stream under H₂ atmosphere in the case of the ZnAl₂O₄ catalyst after switching off the flow of CO₂. *T* = 250°C.

ilar formation amounts are observed for formate I species (F_I) and copper formate species (F_{Cu}) and these amounts increase in parallel to that of methanol (Fig. 5B).

The carbonate species amount increases with *P*_{CO₂}, contrarily to what happened on the

ZnAl₂O₄ support. This fact suggests either the formation of carbonate species directly adsorbed on copper which, in addition, increases their concentration, or the copper promoting effect on carbonate species formed on the support. In addition, the increase of the amount of the

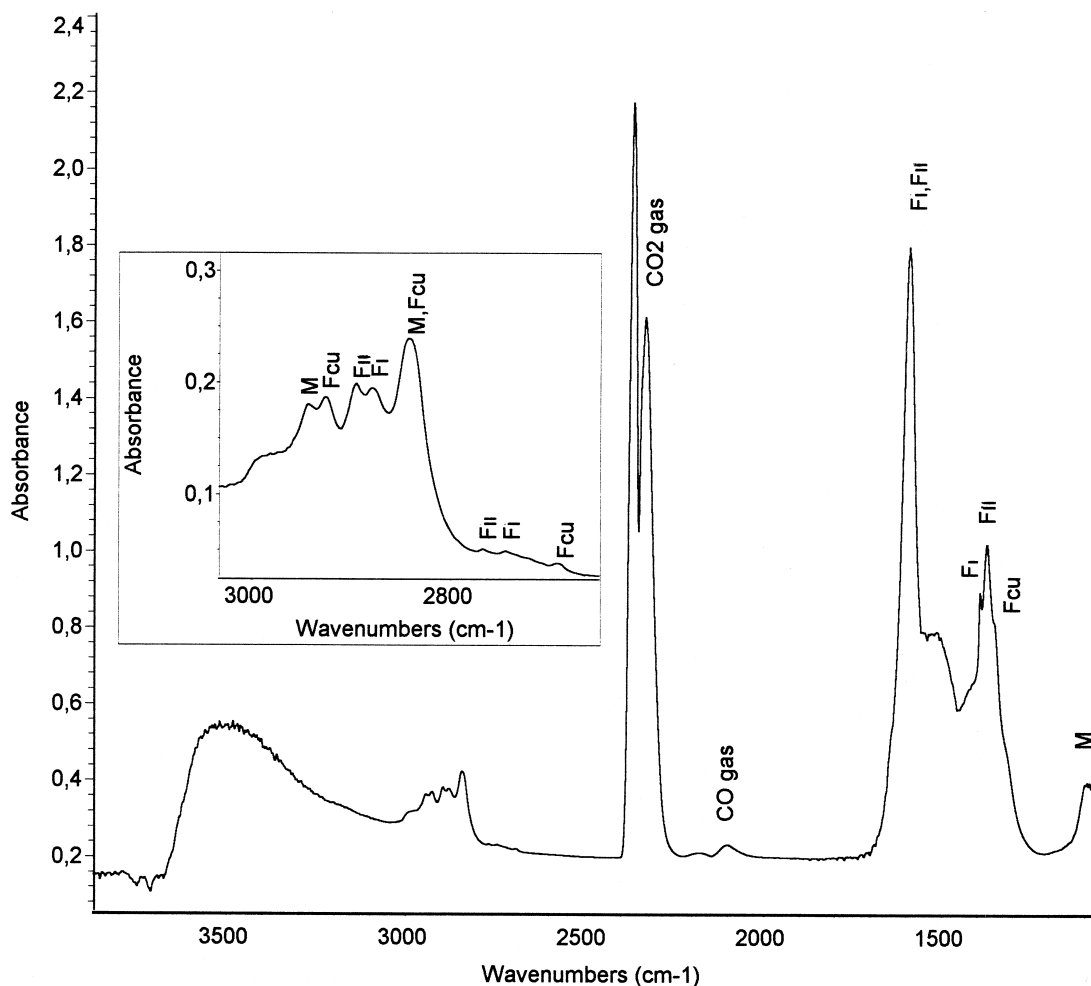


Fig. 4. Spectrum of the Cu-ZnAl₂O₄ catalyst under CO₂/H₂ flow at 250°C.

carbonate species on the catalyst surface (Fig. 5A) is parallel to that of methanol in the gas phase (Fig. 5B).

The same amounts of methoxy species are found on both ZnAl₂O₄ and Cu-ZnAl₂O₄ catalysts (Fig. 2A and Fig. 5A) under CO₂/H₂ flow. However, in presence of copper, the methoxy species amount is lower under CO₂/H₂ (Fig. 5A) than under CO/H₂ flow [27].

As to the carbonyl species, its corresponding wavenumber increases from 2087 to 2104 cm⁻¹ when P_{CO_2} increases from 0.01 to 0.3 MPa (Fig. 1). The observed wavenumber range is

attributed to relatively reduced state of copper. Indeed, according to Ghiotti et al. [29] ν_{CO} varies in the range 2125–2115 cm⁻¹ when CO is adsorbed on Cu⁺ species and in the range 2100–2090 cm⁻¹ when CO is coordinated on metal copper Cu⁰.

Fig. 5B shows that methanol and carbon monoxide appear simultaneously and their formation rates rapidly and similarly increase with P_{CO_2} up to 0.3 MPa and then seem to reach a plateau. The CO formation rate is an order of magnitude higher (multiplied by 40 at $P_{\text{CO}_2} = 0.3$ MPa) on Cu-ZnAl₂O₄ (Fig. 5B) than on

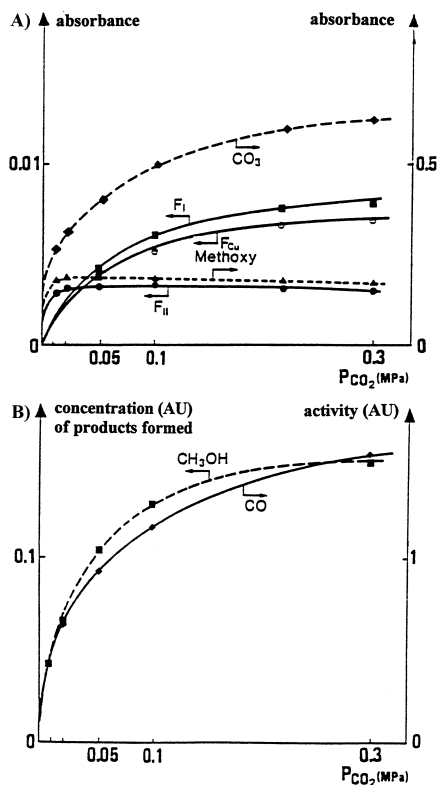


Fig. 5. Variation as a function of the partial pressure of CO₂ in the case of the Cu–ZnAl₂O₄ catalyst ($P_{H_2} = 0.7$ MPa, $T = 250^\circ\text{C}$) of: (A) the intensity of the characteristic bands of the adsorbed species formed; (B) the relative amount of products formed.

ZnAl₂O₄ (Fig. 2B). The presence of copper then substantially modifies the CO formation rate since no rate variation is observed on ZnAl₂O₄. Moreover, the amount of water formed on Cu–ZnAl₂O₄ fits well with that expected to be produced in both the reverse water gas shift and methanol synthesis reactions. Thus copper is really involved in the reverse water gas shift reaction as well as in methanol synthesis reaction.

Transient experiments, performed in the same conditions as for the ZnAl₂O₄ support, show that under H₂ atmosphere the formate II species concentration remained almost constant whereas formate I and copper formate species rapidly and simultaneously disappeared.

We have also studied the variation of the amount of the adsorbed species (Fig. 6A) and of the reaction products formed in the gas phase (Fig. 6B) as a function of P_{H_2} at $P_{CO_2} = 0.1$ MPa. In the adsorbed phase, relatively little variations are observed (Fig. 6A): a slight decrease of the amount of F_I and F_{Cu} species and, apparently, of carbonate species accompanied by a sensible increase of that of the methoxy species. Contrastingly, the variations observed in the gas phase are clearly more important (Fig. 6B). The rate of formation of methanol was very sensitive to P_{H_2} : its concentration sharply increased when P_{H_2} increased. Carbon monoxide formation was also sensitive to P_{H_2} , although to a lesser extent: its concentration sensibly decreased when P_{H_2} increased.

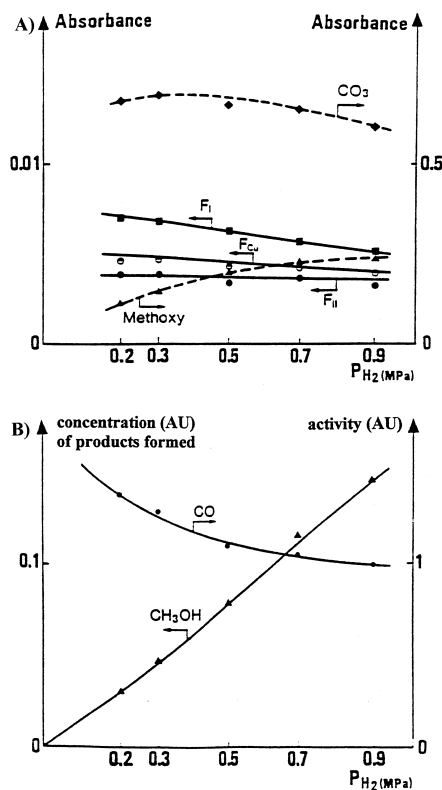
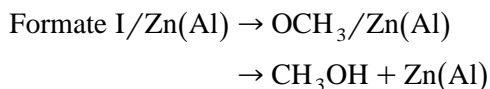


Fig. 6. Variation as a function of the partial pressure of H₂ in the case of the Cu–ZnAl₂O₄ catalyst ($P_{CO_2} = 0.1$ MPa, $T = 250^\circ\text{C}$) of: (A) the intensity of the characteristic bands of the adsorbed species formed; (B) the relative amount of formed products.

4. Discussion

4.1. $ZnAl_2O_4$ catalyst

Fig. 2A shows that the amount of formate I species increases with P_{CO_2} . Since these species are reduced to methoxy species under H_2 atmosphere (Fig. 3) they can be considered as methanol precursor:



As to formate II species, they seem to be not reducible under H_2 atmosphere (Fig. 3) and it may be concluded that they are not directly involved in the methanol synthesis under CO_2/H_2 flow. They were also shown to be inactive under CO/H_2 flow [27]. However, they should be intermediate species in the formation of CO as proposed in literature for the reverse water gas shift reaction [21,23,30,31]. In the present case, formate II species formation (Fig. 2A) as well as CO formation (Fig. 2B) are both independent of P_{CO_2} , suggesting that the former could be indeed the precursor of the latter.

4.2. $Cu-ZnAl_2O_4$ catalyst

When considering the behavior of the carbonate, F_I and F_{Cu} surface species (Fig. 5A) it seems that their amount increases in parallel to that of methanol and carbon monoxide (Fig. 5B). This result indicates that all these species are good candidate as surface precursor of the products formed. Let us discuss in more detail the observed trends during the CO_2/H_2 reaction course.

4.3. Carbonate species adsorbed on the support

The curves for methanol presented in Fig. 5B and Fig. 6B seem to indicate that its rate of formation follows a kinetic mechanism of Eley–Rideal type where CO_2 adsorbed species

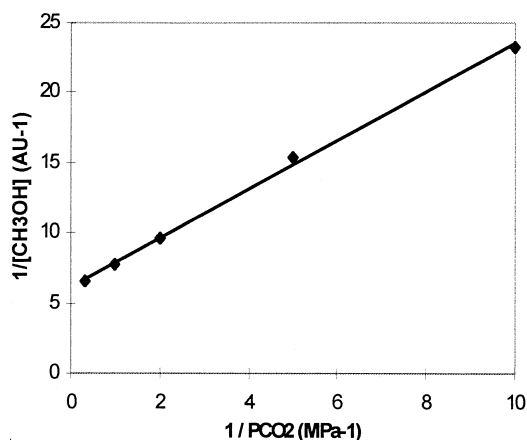


Fig. 7. Variation of $1/r_{CH_3OH}$ as a function of $1/P_{CO_2}$ in the case of the $Cu-ZnAl_2O_4$ catalyst. $P_{CO_2} = 0.1$ MPa, $T = 250^\circ\text{C}$.

should be reduced by molecular hydrogen in the slow step of the reaction. The reaction rate should be then expressed as below:

$$r_{CH_3OH} = k \frac{K_{CO_2} P_{CO_2}}{1 + K_{CO_2} P_{CO_2}} P_{H_2}$$

where k is the rate constant and K_{CO_2} the adsorption constant for CO_2 . Indeed, a linear curve is obtained for r_{CH_3OH} as a function of P_{H_2} at constant P_{CO_2} (Fig. 6B) as well as for $1/r_{CH_3OH}$ as a function of $1/P_{CO_2}$ at constant P_{H_2} (Fig. 7).

The CO_2 adsorbed surface species are most probably carbonate species here evidenced and the parallel increase of concentration of both the carbonate species (Fig. 5A) and methanol (Fig. 5B) strengthens this assumption. In addition, the carbonate species concentration sensibly decreased when the partial pressure of H_2 increased at constant partial pressure of CO_2 (Fig. 6A), showing it is an active reaction intermediate in methanol synthesis.

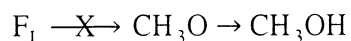
4.4. F_{Cu} and F_I formate species

It has to be said that the same rate law for methanol formation as above was reported by other authors in the case of the 5%Cu–2.2%ZnO– Al_2O_3 catalyst [32], but the rate de-

termining step proposed was the hydrogenation of surface copper formate species by gaseous hydrogen [32]. Thus, the hydrogenation of F_{Cu} as rate determining step in the case of methanol synthesis over $Cu-ZnAl_2O_4$ catalyst should also be considered. The parallel increase of the F_{Cu} concentration on the surface of the catalyst (Fig. 5A) and that of methanol in the gas phase (Fig. 5B) confirms they are indeed potential intermediates in the formation of methanol as it was suggested in the case of the CO/H_2 reaction [28]. In addition, these species are reduced under H_2 atmosphere as demonstrated by the transient experiments and their concentration decreases (although slightly) when P_{H_2} increases (Fig. 6A).

However, for a better fitting of the rate equation to the experimental curves in the hypothesis of the hydrogenation of formate species as rate determining step, it has to be assumed that, in one hand, a strong hydrogen adsorption occurs for the formation of the formate species and, in the other hand, that gaseous hydrogen is involved for the hydrogenation of the formate species [32]. If the latter assumption is experimentally justified — a quite linear curve is obtained for the rate law of methanol formation as a function of P_{H_2} ([32], this study) — the former is rather speculative, more especially the adsorption of hydrogen on copper materials is complex [1,2,33]. Also we conclude that the simplest kinetic model which explains our results is the Eley–Rideal mechanism involving the hydrogenation of carbonate species in the rate determining step. In such a case, formate species are expected to be produced through the hydrogenation of surface carbonate in the rate determining step of the reaction and to react in the faster subsequent steps. This conclusion is in good agreement with previous work on the same catalytic system [34] showing that carbonate species, besides their role in the dispersion of the active copper phase, participate to the overall mechanism of methanol formation via their hydrogenation into formate species and subsequently methoxide species.

Moreover, it is worth to note the similar behavior of F_{Cu} and F_I species: (i) their concentration increases in parallel to methanol formation in the gas phase (Fig. 5), (ii) it decreases during the transient experiments under H_2 atmosphere, (iii) or when P_{H_2} is increased (Fig. 6A). These trends indicate that both species should be associated in methanol formation. However, the analysis of the results shows that the role of F_I species in methanol synthesis is probably more complex. Indeed, if these species adsorbed on the support were directly involved in methanol synthesis, the reaction route should, in turn, involve methoxy species also adsorbed on the support: the concentration of the latter should vary in the same way as that of the former or as that of the rate of methanol appearance. This seems to be not the case (Fig. 5) and we conclude that the route:



is not the main reaction path to methanol. The desorption of methoxy species as gaseous methanol is likely blocked: they accumulate on the surface of the support where they seem to be stable and then behave as spectator species. In other words, the $Cu-ZnAl_2O_4$ catalyst most probably catalyses the transformation of F_I species to methanol but this route should be blocked. A possibility to overcome this blocking is the spillover of F_I species onto copper, thus explaining the parallel behavior of F_{Cu} and F_I species.

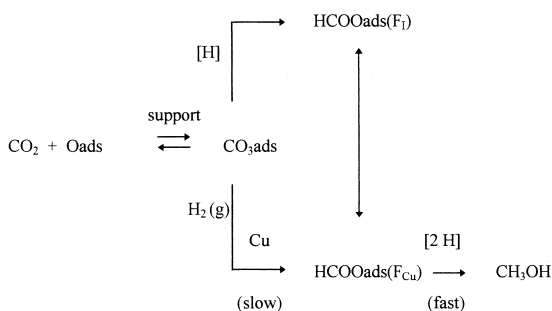
4.5. Other adsorbed species

The amount of formate II species is constant in the whole range of P_{CO_2} (Fig. 5A) whereas the rate of methanol formation increased (Fig. 5B). In addition, formate II species do not seem reducible under H_2 atmosphere as shown by transient experiments. These results led us to conclude that these surface species are not methanol precursors. As to the carbonyl CO/Cu species, no correlation was found between the

variation of their concentration and that of methanol (Fig. 6B).

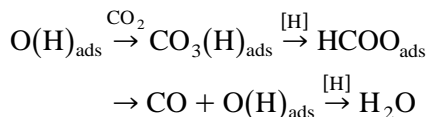
4.6. Reaction paths for methanol and carbon monoxide

The kinetic results have shown that the slow step of the reaction is the reduction of chemisorbed CO_2 by one H_2 gaseous molecule whereas the IR spectra revealed the intervention of carbonate and formate species as active intermediates in methanol formation. The discussion allows us to propose the following mechanism for the methanol synthesis from the CO_2/H_2 mixture over the $\text{Cu-ZnAl}_2\text{O}_4$ catalyst:



As to carbon monoxide, calculations have shown that its formation reaction is at equilibrium in our conditions. Also no kinetic equations can be drawn from the activity curves (Fig. 5B and Fig. 6B). However, these curves compared to that obtained from the IR spectroscopic study (Fig. 5A and Fig. 6A) throws some light on the involved reaction paths. Indeed, the trends of curves in Fig. 5A and B seem to indicate that carbonate, F_I and F_{Cu} species are also reaction intermediates of CO formation. Since copper enhanced CO formation (compare Fig. 2B and Fig. 5B) mainly surface copper species have to be considered. Also, it is tempting to consider not only copper formate species [21,23,30,31] but also carbonate species as in-

termediates in the reverse water gas shift reaction:



However, further work is needed to determine the real route(s).

5. Conclusions

The study of the CO_2/H_2 reaction at 250°C over ZnAl_2O_4 and $\text{Cu-ZnAl}_2\text{O}_4$ catalysts showed the formation of methanol and carbon monoxide by independent chemical paths. Both methanol and carbon monoxide formation rates were enhanced in presence of copper. The use of in situ IR spectroscopy permitted to detect adsorbed species and to determine their reactivity and role in the formation of both methanol and carbon monoxide. The species evidenced on the support (ZnAl_2O_4) are symmetric (F_I) and unsymmetric (F_{II}) formates, formates adsorbed on alumina sites (F_{II}), carbonate and methoxy species. In presence of copper ($\text{Cu-ZnAl}_2\text{O}_4$), copper formates and carbonyl species have been detected in addition to the above species.

Carbonate species should be involved in methanol synthesis and their hydrogenation is most probably the rate determining step of the reaction in the case of the $\text{Cu-ZnAl}_2\text{O}_4$ catalyst. Both F_{Cu} and F_I formate species should be associated in methanol synthesis and the spillover of F_I from the support onto copper is suggested. Formate II and methoxy species were found to be inactive under H_2 atmosphere in presence or in absence of copper.

In the case of the ZnAl_2O_4 catalyst, the carbon monoxide formation seemed to be linked to the decomposition of formate species of type II. In the case of the $\text{Cu-ZnAl}_2\text{O}_4$ catalyst copper participates to the CO formation through the reverse water gas shift reaction where both carbonate and formate species should be involved.

If we now compare the above results obtained with the CO_2/H_2 mixture to those previously obtained with the CO/H_2 mixture in the same reaction conditions, it appears that the nature and the role of the detected surface species depend strongly on both the reactive atmosphere and on the catalyst nature. For the methanol synthesis on the ZnAl_2O_4 support the active intermediates seemed to be formate I species in both CO/H_2 and CO_2/H_2 atmospheres. In the case of the $\text{Cu-ZnAl}_2\text{O}_4$ catalyst copper carbonyl species was the reactive intermediates under CO/H_2 atmosphere, whereas under CO_2/H_2 atmosphere the reaction mechanism involved both carbonate and formate (F_{Cu} and F_1) species. The reduction of the former species should be the rate determining step of the reaction. In the CO/H_2 reaction, carbon dioxide is formed in large amount probably due to some support reduction whereas carbon monoxide is formed in the CO_2/H_2 reaction through the reverse water gas shift reaction.

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