In-situ FT-IR spectroscopy and kinetic study of methanol synthesis from CO/H_2 over $ZnAl_2O_4$ and $Cu–ZnAl_2O_4$ catalysts

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Abstract

The CO/H_2 reaction over $ZnAl_2O_4$ (support) and $Cu–ZnAl_2O_4$ (catalyst) performed at 250°C up to 0.3 MPa, was studied by combining in-situ FT-IR experiments and kinetic investigations. The obtained results showed the existence of two reaction mechanisms for methanol formation involving formate species (mainly on $ZnAl_2O_4$) and carbonyl species (on $Cu–ZnAl_2O_4$), as key reaction intermediates. Inactive formate species were also evidenced. Carbon dioxide, which is the initial major product formed on the $ZnAl_2O_4$ support, is produced through the partial reduction of the latter.

1. Introduction

Methanol synthesis from $CO/CO_2/H_2$ mixtures using $Cu–ZnOAl_2O_3$ catalysts is an important industrial process [1,2]. Although this reaction has been subject to numerous investigations, the nature of the active site, the involved reaction steps and the role of carbon oxides (CO or CO_2) continue to be discussed in the literature [3–9]. Some aspects of the reaction mechanism are still not fully understood and are subject to considerable controversy [6–9].

Several investigations have provided evidence that methanol is formed predominantly from carbon dioxide [10–15]. Recent studies have shown that carbon monoxide can act as a methanol precursor under specific conditions [10,16–18] and it was concluded that carbon dioxide hydrogenation occurs via a route independent of that for carbon monoxide hydrogenation [10,19,20]. While different workers have reported a direct proportionality between methanol synthesis activity and the measured copper surface area [12–14,21–25], it has been recently shown that the choice of the support affects the activity of copper in the methanol synthesis reaction [2,26–28]. However, a correlation between activity and copper surface area has been observed for families of related catalysts on the same support [10,26–29].

As to the reaction intermediates, several surface species have been identified during the course of the hydrogenation of CO, CO_2 and CO/CO_2 mixture, mainly by FT-IR spectroscopic, TPD and chemical trapping methods [30–44].

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Formate species have been observed for the CO/H_2 reaction on ZnO [30,31], $ZnAl_2O_4$ [32,33], Cu–ZnO [34,35] and $Cu–ZnOAl_2O_3$ [32,36,37] catalysts and it was claimed that they resulted from CO insertion into surface hydroxyl groups [31]. In the case of the CO_2/H_2 reaction the formate species, identified on ZnO [38–40] and $Cu–ZnOAl_2O_3$ [32,33] catalysts, are probably formed either by insertion of CO_2 into a surface metal hydride or via carbonate or hydrogen-carbonate species [36].

Methoxy species have been analyzed on $Cu–ZnOCr_2O_3$ [40], $Cu–ZnOAl_2O_3$ [32] and $ZnAl_2O_4$ [33] catalysts during the CO/H_2 reaction and relations seem to exist between the surface formate species and the surface methoxy formation [32,33]. Zinc methoxy species were claimed to be the active intermediates of methanol synthesis for the CO_2/H_2 reaction on Cu–ZnO catalysts, whereas copper and zinc formate species were not [42]. Contrastingly, for the same reaction but on Cu, Zn, Cr, Al mixed oxides catalysts, formate species were observed and considered as the active intermediates whereas no methoxy species were detected [41].

Formyl species have been found to mainly occur in the CO/H_2 reaction [30–32,43,44]. They have been observed on ZnO catalysts [30,31] and seemed to be more reactive on copper based catalysts [32,43]. On the other hand, their presence was reported to be related to that of methoxy species on ZnO [30,44] or $ZnAl_2O_4$ [32] catalysts but not in the case of copper based catalysts [32].

These apparently contrasting results show that the reaction mechanisms of methanol synthesis from carbon oxides on copper-based catalysts strongly depend on the catalysts structure and on the reaction conditions. It also appears that the role of the detected surface species is still not well clearly established. This prompted us to reinvestigate methanol synthesis from CO/H_2, CO_2 and $CO/CO_2/H_2$ mixtures over $ZnAl_2O_4$ and $Cu–ZnAl_2O_4$ catalysts by combining kinetic, TPD and FT-IR spectroscopy studies. We aimed to obtain more insight about

the nature of the active sites and of the active intermediates and about the respective roles of the carbon oxides. The present paper reports FT-IR spectroscopy investigations concerning the CO/H_2 reaction performed over $ZnAl_2O_4$ and $Cu–ZnAl_2O_4$ catalysts.

2. Experimental

2.1. Catalysts preparation and characterization

Mixed Cu–Zn–Al oxides catalysts were prepared by the coprecipitation technique already described [45–47]. Metal nitrates of copper, zinc and aluminum were coprecipitated by sodium carbonate in 0.5–1.5 M aqueous solutions under controlled and constant pH conditions at temperatures between 333 and 363 K. The precipitates were subsequently washed, dried at 383 K and calcined under flowing air at 623 K.

Two samples were prepared in these conditions, the zinc aluminate support $(ZnAl_2O_4)$ and a copper based catalyst containing 15 weight percent of copper $(Cu_{0.6}Zn_1Al_2O_4)$. Due to their stoichiometry, which corresponds to that of the spinel phase, these two samples do not contain any free zinc oxide phase. In addition, the copper content of the Cu–Zn–Al catalyst is low. This particular composition allowed us to perform FT-IR experiments on reduced samples and under a syngas atmosphere with only a slight loss of transparency to the infrared radiation due to zinc oxide reduction.

The metal surface area of the catalyst was determined by N_2O titration at room temperature after reduction at 280°C; it was found to be 9.4 m^2/g.

2.2. FT-IR analysis

The in-situ FT-IR device used in the present study was already described [36]. The operating conditions were the following: before FT-IR experiments the catalysts were reduced in situ at 250°C under a hydrogen flow (0.9 l/h) at atmo-

spheric pressure. Hydrogen partial pressure was then increased and maintained at 0.7 MPa, CO partial pressure was varied between 0.01 and 0.3 MPa at 250°C.

3. Results

3.1. Characterization of the adsorbed species

The IR spectra of catalysts under the CO/H_2 flow show the appearance of characteristic bands of carbonate, carbonyl, methoxy and formate species:

(i) carbonate species have been identified by broad bands appearing at 1510 and 1410 cm^{-1} similar to those observed on zinc carbonate [48];

(ii) the band arising at 2080–2120 cm^{-1} is characteristic of a carbonyl group adsorbed on copper [36]; the $\nu(CO)$ wavenumber allowed one to determine the copper oxidation state as a function of the carbon monoxide partial pressure P_{CO} [36];

(iii) methoxy species adsorbed on the support have been identified by bands at 2943, 2835 and 1100 cm^{-1} [36]; the intensity of the 1100 cm^{-1} band was chosen to follow the surface methoxy concentration;

Methoxy species adsorbed on copper, generally identified by a set of IR bands at 2907, 2861, 2787 and 990 cm^{-1} [49,50], were not detected under the conditions used.

(iv) four types of formate species can be distinguished, the characteristic bands of which are reported in Table 1; one is adsorbed on copper and the three others (type I, I' and II) on the support. Formate I and I' species are symmetrically and unsymmetrically adsorbed species. As to formate II species, its spectrum is similar to that of formate species adsorbed on alumina [51].

The bands used for the determination of the relative amount of the formate formed are underlined in Table 1. No peculiar band allowed us to dose formate I' surface species.

3.2. ZnAl$_2$O$_4$ support

The spectrum of the ZnAl$_2$O$_4$ sample activated under hydrogen (Fig. 1A), presents bands characteristic of surface hydroxyl (3680 cm^{-1}), carbonate (1510 and 1410 cm^{-1}) and residual formate (2900, 1600, 1390 and 1370 cm^{-1}) species.

Under CO/H_2 flow (Fig. 1B), the stationary state is rapidly reached (within 20 min). The IR spectrum (Fig. 1C) presents bands characteristic of formates (I, I' and II) and methoxy species.

Figs. 2 and 3, respectively, present the variation of the relative amount of the different adsorbed species and that of the reaction products formed as a function of carbon monoxide pressure P_{CO}. It can be seen that the quantity of formates I and methoxy species increases gradu-

Table 1

Characteristic IR wavenumbers of the surface formate species identified under the CO/H_2 atmosphere over the Cu–ZnAl$_2$O$_4$ catalyst and the ZnAl$_2$O$_4$ support. $T = 250$°C

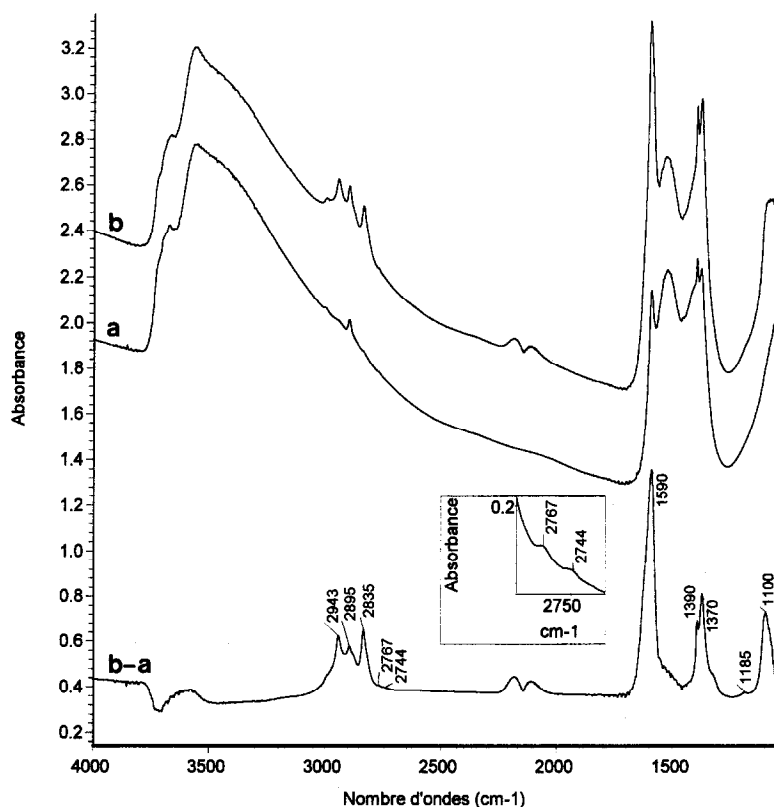| Formate I	Formate I'	Formate II	Copper formate
		2990 $\nu_a(CO_2^-)$ + δ(CH)	
2881 $\nu(CH)$		2895 $\nu(CH)$	2925
			2847 $\nu(CH)$
2744 $2\nu_s(CO_2^-)$		2767 $\nu_s(CO_2^-)$ + δ(CH)	2692 $2\nu_s(CO_2^-)$
1595 $\nu_a(CO_2^-)$	1650 $\nu_a(CO_2^-)$	1590 $\nu_a(CO_2^-)$	
		1390 δ(CH)	
1375 $\nu_s(CO_2^-)$	1320 $\nu_s(CO_2^-)$	1370 $\nu_s (CO_2^-)$	1352 $\nu_s(CO_2^-)$

Fig. 1. Infra-red spectra of $ZnAl_2O_4$ at 250°C: (A) after activation under H_2 flow at 250°C. (B) Under CO/H_2 flow. $T = 250°C$, $P_{H_2} = 0.7$ MPa; $P_{CO} = 0.1$ MPa. (C) Subtracted spectra (spectrum B minus spectrum A).

ally when P_{CO} is increased, the relative amount of the latter species being particularly important. In parallel, the quantity of surface hydroxyl

species strongly decreases (not represented). On the other hand, the concentration of formate II species appears to be independent of the CO
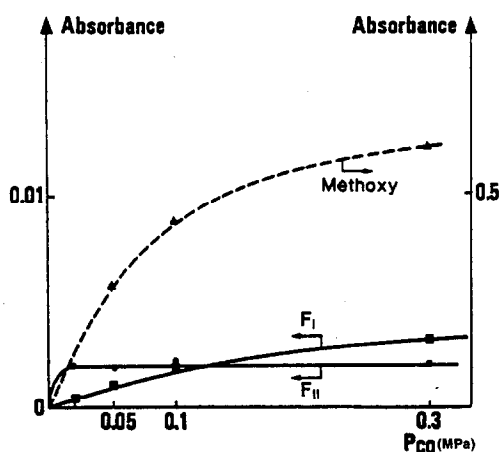

Fig. 2. Variation of the intensity of the bands characteristic of the different adsorbed species formed as a function of P_{CO} in the case of the $ZnAl_2O_4$ support. $T = 250°C$, $P_{H_2} = 0.7$ MPa.
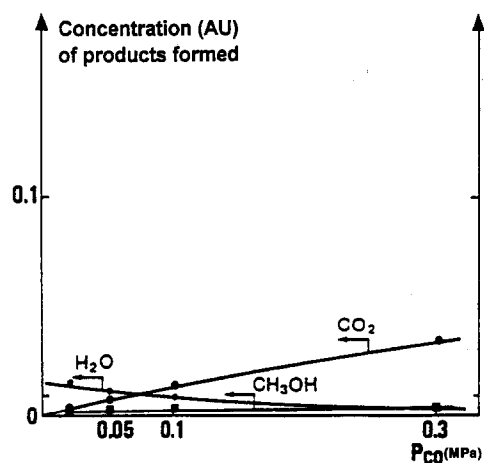

Fig. 3. Variation of the relative amount of products formed as a function of P_{CO} in the case of the $ZnAl_2O_4$ support. $T = 250°C$, $P_{H_2} = 0.7$ MPa.

partial pressure. In the gas phase, the increase of P_{CO} leads to the formation of a very low amount of methanol, and a much higher amount of CO_2. The H_2O concentration decreases in parallel.

3.3. Cu–ZnAl₂O₄ catalyst

The spectrum of the reduced $Cu-ZnAl_2O_4$ catalyst has already been reported [36]. The intensity of the OH band at 3500 cm^{-1} is much more important than in the case of the $ZnAl_2O_4$ support activated under hydrogen. The amount of carbonate species is nearly the same but the quantity of residual formate species is clearly lower. Spectra obtained under $H_2 + CO$ flow have been reported in [36]. In steady-state conditions they mainly present bands due to formate II, $ZnAl_2O_4$ methoxy and copper CO species, the latter being situated at about 2080 cm^{-1} [36].

The variation of the adsorbed species amount with increasing CO partial pressure is reported in Fig. 4. It appears that the amount of:

– the only one formate species (II) which appears is independent of P_{CO} as already observed in the case of the $ZnAl_2O_4$ support. An important point is the absence of formate I species formed when comparing to the support results.
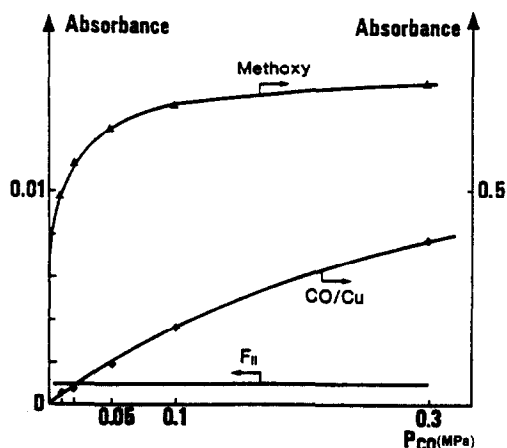

Fig. 4. Variation of the intensity of the bands characteristic of the different adsorbed species as a function of P_{CO} in the case of the Cu–ZnAl₂O₄ catalyst.
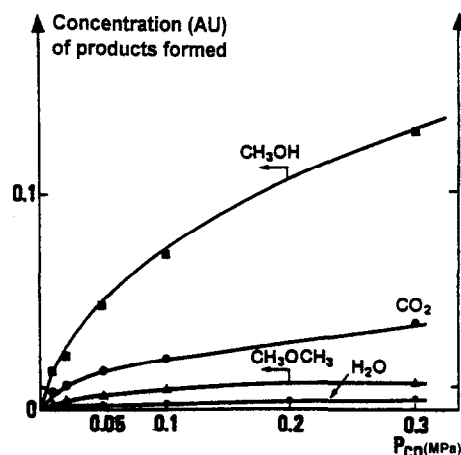

Fig. 5. Variation of the relative amount of products formed as a function of P_{CO} in the case of the Cu ZnAl₂O₄ catalyst. $T = 250°C$, $P_{H_2} = 0.7$ MPa.

– the methoxy species adsorbed on the support increases for low CO partial pressures ($P_{CO} < 0.1$ MPa), this increase being clearly more pronounced than in the case of the $ZnAl_2O_4$ support. A stabilization of the methoxy surface concentration is noticed at higher partial pressures.

– the carbonyl species adsorbed on copper atoms (CO–Cu) gradually increases. The variation of their wavenumber from 2081 to 2078 cm^{-1} when P_{CO} increases from 0.01 to 0.3 MPa indicates that only a reduced state of copper is present.

The presence of copper leads to an important modification of the product composition in the gas phase (Fig. 5) since an increase by a factor of 30 of the methanol content is obtained. On the other hand the variation of the CO_2 amount with P_{CO} is nearly the same as that reported above for the $ZnAl_2O_4$ support.

4. Discussion

4.1. ZnAl₂O₄ support

The support activity in methanol was quite low (Fig. 3) as expected [1,2]. The main product observed was CO_2, accompanied by few amount of H_2O. In addition, catalyst deactivation with

time on stream was expected, but was not been observed, probably because of the low conversions obtained and of the short time on stream studied. Nevertheless, the FTIR spectra examination showed interesting information on the surface species formed in the CO/H_2 reaction conditions.

Formates II species are practically the same as those detected on alumina [51]. On the other hand their amount is independent from the CO partial pressure (Fig. 2) and, moreover, they are not reducible under hydrogen atmosphere as shown elsewhere [36]. It may be concluded that these species are not active intermediates and thus they are probably not directly involved in methanol synthesis.

Contrastingly, the amount of formate I species increases with the CO partial pressure and it has been reported elsewhere [36] that these species are reduced into methoxy species under a hydrogen flow at 250°C [36]. It can be seen that the amounts of surface formate I species and of surface methoxy species increase quite similarly with the CO partial pressure (Fig. 2). However, the very small amounts of methanol obtained in the considered experiments (Fig. 3) cannot allow us to conclude about the exact nature of its precursors. These methoxy species should be considered as spectator species.

Carbon dioxide is the main product obtained and necessarily results from the oxidation of CO. The hypothesis of the occurrence of the Boudouard reaction:

$$2CO \rightarrow CO_2 + C$$

may be excluded since no carbon deposits have been observed in the used catalysts. Carbon dioxide may then result from the support partial reduction by carbon monoxide:

$$ZnOZn(Al) + CO \rightarrow Zn \square Zn(Al) + CO_2$$
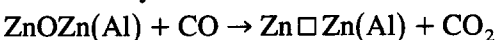
or by H_2 (producing water observed in the gas phase)and then through the water–gas shift reaction:

ZnOZn(Al) +H₂ ⇌ ZnOHZnH(Al) ⇌ Zn ☐ Zn(Al) + H₂O

CO ↑↓

ZnHCOOZnH(Al) ⇌ CO₂ + H₂ + Zn ☐ Zn(Al)
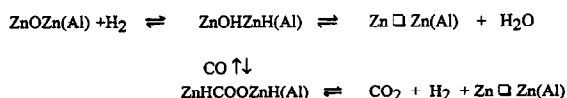
There is a competition between the reduction of the support to water and its reduction to carbon dioxide through the water–gas shift reaction. The latter reaction is favored thermodynamically and explains most probably the formation of CO_2 at the expense of H_2O when the partial pressure of CO was increased (Fig. 3). In addition, the parallelism between the formation rates of formate I species (Fig. 2) and of CO_2 (Fig. 3) is striking.

4.2. Cu–ZnAl₂O₄ catalyst

Methanol activity for the Cu–ZnAl₂O₄ catalyst was by far higher than for the ZnAl₂O₄ catalyst and the discussion of the FT-IR spectra allowed us to establish correlations between methanol formation and the detected surface species.

Formates I and I′ species are no longer detected on the Cu–ZnAl₂O₄ catalyst working under a H_2/CO atmosphere whereas the amount of methoxy species (Fig. 4) increases much more quickly than on the ZnAl₂O₄ support. Methanol formation is also much greater on the copper catalyst. These results could suggest that copper may, on one hand, reduce these formates I to methoxy species and on the other hand facilitate the desorption of these methoxy species into methanol. However, carbonyl species CO–Cu are also detected in these conditions. It is therefore necessary to consider both species as intermediates of two different pathways. These two possibilities have been examined through a kinetic approach.

4.2.1. Pathway through adsorbed formate I and methoxy species

Since methoxy species are the only intermediates of this pathway which are detected on the catalytic surface, the desorption of adsorbed methoxy species into methanol can be proposed as the rate determining step. In this hypothesis the methanol formation rate in the gas phase can be represented by the following equation rate:

$$V_{CH_3OH} = k[\mu_{OCH_3}] \cdot [\mu_H]$$

where $[\mu_{OCH_3}]$ and $[\mu_H]$ are the concentration of methoxy and hydrogen species adsorbed on the catalytic surface respectively. The infrared study shows that methoxy species are adsorbed on the support. As for hydrogen species, it is generally admitted that they are adsorbed on copper [1,2,52,53]. Therefore, hydrogen and methoxy species are not adsorbed on the same sites. For a constant H_2 partial pressure value, the $[\mu_H]$ term remains constant; therefore the methanol concentration in the gas phase is directly proportional to the amount of adsorbed methoxy species. Comparison of Figs. 4 and 5 shows that the rate of appearance of adsorbed methoxy species does not follow the rate of methanol formation in the gas phase, especially for the higher partial pressures ($P_{CO} > 0.1$ MPa): the methanol formation rate increases whereas the concentration of methoxy species tends to stabilize. Thus, we have to consider the second hypothesis to explain the obtained results.

It has to be noted that the above considered adsorbed hydrogen species may be either adsorbed hydride (methoxy hydrogenolysis) or adsorbed OH groups (methoxy hydrolysis), as far as heterolytic H_2 dissociation occurs on the catalyst surface [52,53]. For both considered species the above equation remains valid. Moreover, in the case of methoxy hydrolysis, an enhancement of the methanol formation was expected in presence of water [42]. In our conditions the amount of water produced during the reaction is quite low and does not seem to be related to the methanol formation rate (Fig. 5). Furthermore, kinetic results, reported elsewhere, showed that methanol and water are produced by independent pathways under experimental conditions similar to the present ones [54].

4.2.2. Pathway through carbonyl species adsorbed on copper

The hydrogenation of carbonyl species (CO–Cu) is then considered as the rate determining step. The corresponding rate equation is:

$$V_{CH_3OH} = k[\mu CO{-}Cu] \times [\mu H]$$

where k is the kinetic rate constant and $[\mu_{CO{-}Cu}]$ the concentration of adsorbed carbonyl species on copper. Following the formalism of Langmuir–Hinshelwood for a non competitive adsorption between CO and hydrogen, the rate equation is:

$$V_{CH_3OH} = k\frac{K_{CO}P_{CO}}{(1 + K_{CO}P_{CO})}\frac{K_{H_2}P_{H_2}^{1/2}}{\left(1 + K_{H_2}P_{H_2}^{1/2}\right)}$$

where K_{CO} and K_{H_2} are respectively the adsorption constant for CO adsorbed on a copper site and hydrogen dissociated on a different site. For a constant hydrogen partial pressure the following equation is obtained:

$$V_{CH_3OH} = k'\frac{K_{CO}P_{CO}}{(1 + K_{CO}P_{CO})}$$

In the same way, for a competitive adsorption of CO and hydrogen on a metal copper site and a constant hydrogen partial pressure the resulting rate is:

$$V_{CH_3OH} = k''\frac{K_{CO}P_{CO}}{(1 + K_{CO}P_{CO})^2}$$

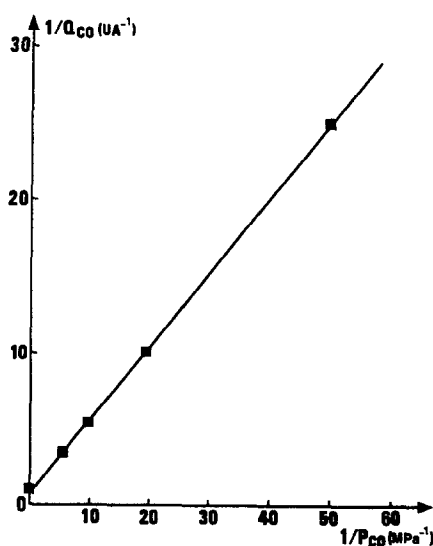The quantity of CO adsorbed on copper is directly proportional to the intensity of the CO–

Fig. 6. Representation of $1/Q_{CO} = f(1/P_{CO})$ in the case of the Cu–ZnAl$_2$O$_4$ catalyst. $T = 250°C$, $P_{H_2} = 0.7$ MPa. (Q_{CO} is the intensity band of CO–Cu adsorbed species).
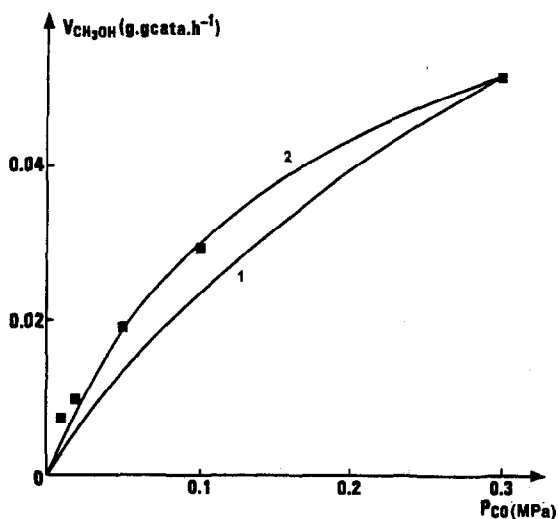
Fig. 7. Calculated (−) and experimental (■) rates of methanol formation as a function of P_{CO} in the case of the Cu–ZnAl$_2$O$_4$ catalyst. $T = 250°C$, $P_{H_2} = 0.7$ MPa. Curve 1 assuming a non-competitive adsorption between CO and H$_2$. Curve 2 assuming a competitive adsorption between CO and H$_2$.

Cu band (Q_{CO}). The linear transformation of the variation of Q_{CO} as a function of P_{CO} (Fig. 6) leads to the direct measure of K_{CO}: a value of 2 MPa^{-1} is obtained, in good agreement with values found in the literature [55,56]. The values of k' and k'' are deduced from this direct measure of K_{CO} and from the experimental data of the methanol formation rate at a P_{CO} value of 0.3 MPa. The comparison of the calculated and experimental rate of methanol formation in all the range of the CO partial pressure studied (Fig. 7) shows that the equation derived from a competitive adsorption between CO and H$_2$ fits well the experimental data.

Thus, the results of the spectroscopic and kinetic experiments, presented here above, show that methanol synthesis from a CO/H$_2$ feed-stock involves carbonyl and hydrogen species adsorbed on metal copper particles as reactive intermediates on Cu–ZnAl$_2$O$_4$ catalysts. The proposed mechanism is in good agreement with several literature data showing that methanol activity in the CO/H$_2$ reaction is proportional to copper surface area [12–14,21–25]. As to the reaction path, CO–Cu species hydrogenation

may lead either to formyl species or to formate species by attack of adsorbed hydride or adsorbed OH groups respectively. The present results cannot discriminate between the two mechanisms.

Concerning the CO$_2$ formation (Fig. 5), its rate is strikingly similar to that obtained with the ZnAl$_2$O$_4$ catalyst (Fig. 3), suggesting similar reaction mechanisms on the same sites.

5. Conclusions

The combined kinetic and FT-IR spectroscopic approach presented here has given more insight into the mechanism of CO hydrogenation over Cu–ZnAl$_2$O$_4$ catalysts. From the study of adsorbed species, two reaction pathways for methanol formation are proposed. The first mechanism involves the successive hydrogenation of active formate species into methoxy species and then methanol, it mainly occurs on the ZnAl$_2$O$_4$ support. The second reaction pathway consists in the hydrogenation of CO adsorbed species on metal copper. Indeed, in the latter case, a good fit was obtained between the corresponding rate equation and the experimental data. Furthermore, the intervention of metal copper as an active site in the proposed mechanism is in good agreement with several reported literature data showing the proportionality between methanol activity and copper surface area. Inactive formate species have also been evidenced on both catalysts. Carbon dioxide formation is also observed, mainly on the ZnAl$_2$O$_4$ catalyst, as a result of the partial reduction of the support.

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