Topics in Catalysis 2 (1995) 103–116

On the mechanism of the methanol synthesis involving a catalyst based on zirconia support

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The nature of the pivotal intermediate during the synthesis of methanol from CO_2/H_2, in the presence of ZnO/ZrO_2 aerogel catalyst is envisaged. The kinetic studies performed using in situ FTIR spectroscopy of the species formed on the surface of the catalyst in the absence and in the presence of hydrogen show that the initial reactive adsorbed species formed from CO_2 gas is the unidentate carbonate species. Its hydrogenation into the formate species is much faster than the hydrogenation of the formate species into methoxyl species. The comparison is based on a quantitative measurement of the rate constant of the hydrogenation of the various species. The results explain that during the CO_2/H_2 reaction only formate and methoxyl species are observed.

Keywords: surface FTIR; methanol synthesis; zinc based catalyst; zirconia

1. Introduction

Methanol synthesis from syngas mixtures ($CO/CO_2/H_2$) over copper/zinc-based catalysts [1] has been the subject of controversies concerning various fundamental aspects of the mechanism as the nature of the active sites, the effective role of CO and CO_2 and the nature of the pivotal intermediate species which lead to methanol. Some authors attribute this pivotal function to the formate species [2–6], whereas others deny this role of formate and consider carbonates [7–10] for this function. Most of the experimental data which support the two interpretations are based on the characterisation using FTIR spectroscopy of the adsorbed species formed during the reaction of hydrogenation of either CO or CO_2. Usually, only a qualitative interpretation of the spectrum recorded is advanced. For example, the observation of the well characteristic IR bands of the formate species during the methanol synthesis leads to the conclusion that this species is the pivotal intermediate [6].

To give more accuracy to such interpretations the present study gives a quantitative comparison of the reactivity in the hydrogenation of the formate and carbo-

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nate species formed on a ZnO/ZrO_2 catalyst after an interaction with CO_2/He and CO_2/H_2. The comparison is based on the measurement of the rate of hydrogenation of these species by the quantitative exploitation of their FTIR spectrum recorded under various experimental conditions.

2. Experimental

The catalyst studied, 5 wt% ZnO/ZrO_2, and the support ZrO_2 are aerogel solids and their preparations have been described elsewhere [11]. Briefly, the zirconia support is obtained by the hydrolysis, with a stoichiometric amount of water, of zirconium propylate, dissolved in propanol. The solvent is evacuated in an autoclave under hypercritical conditions. The ZnO/ZrO_2 solid is obtained similarly by hydrolysis of zinc acetate dissolved in methanol, containing a dispersion of ZrO_2, followed by the evacuation of the solvent in an autoclave. Before the contact with the gaseous reactants, the aerogel solids are heated in O_2 at 440°C (2 h) and 10 min in helium, in order to remove the adsorbed carbonaceous species coming from the preparation. The surface areas of the solids, which present a very good IR transmission, are in the range 200–220 m^2/g. For the FTIR study the solids are compressed in pellets of 2 cm diameter with a weight in the range of 50–70 mg. At 300°C and 3.2 MPa total pressure, the ZrO_2 solid is slightly active in the methanol production from CO/H_2 and CO_2/H_2 mixtures compared to the solids containing CuO [12] which are very active. It has also been observed that ZnO deposited on inactive support (Al_2O_3) leads to low activity catalyst [12]. In the present experimental conditions (1 atm total pressure and 250°C) the activity of the ZnO/ZrO_2 catalyst is fairly low (see below).

The stainless-steel IR cell of 1 cm^3 dead volume allows in situ studies under 1 atm total pressure in a flow of gas (range 150 cm^3/min and higher) and at temperatures in the range 25–600°C. During the temperature programmed process a linear heating rate of 15°C/min is used. The gas flow control system permits transient studies as for example: 5% $CO_2/H_2(t_1) \rightarrow He(t_2) \rightarrow H_2(t_3)$ with t_1, t_2 and t_3 time of the treatment of the solid pellet in the reactive mixture.

3. Results and discussion

3.1. EFFECT OF THE PRESENCE OF H_2 ON THE NATURE OF THE ADSORBED SPECIES FORMED WITH CO_2 ON ZrO_2 AND ON ZnO/ZrO_2

Fig. 1 compares the FTIR spectrum recorded at 250°C under 5% CO_2/He on the ZrO_2 support alone (spectrum b) and on the ZnO/ZrO_2 catalyst (spectrum a). The bands recorded on ZrO_2 have been interpreted (refs. [13,14] and references therein) as due to the presence on the surface of an ionic carbonate CO_3^{2-}

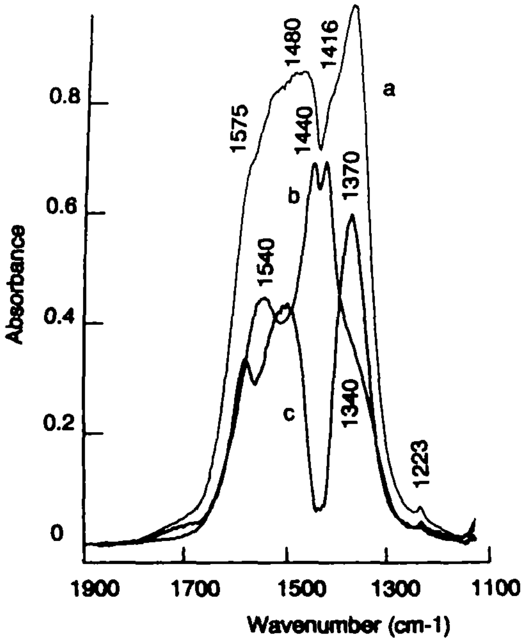

Fig. 1. Comparison of the adsorbed species formed on the ZrO_2 support and on the ZnO/ZrO_2 catalyst after 80 s in a 5% CO_2/He flow at 250°C. (a) On ZnO/ZrO_2, (b) on ZrO_2, (c) = a − xb (see the text).

(1440 cm^{-1}), a bidentate carbonate (1540 and 1340 cm^{-1}) and a carboxylate (1416 and 1340 cm^{-1}). The small 1223 cm^{-1} IR band is due to the bicarbonate species which are present with a low coverage at 250°C. At 25°C the spectrum of this latter species (3615, 1616, 1430 and 1223 cm^{-1}) dominates the recorded spectrum [14]. On the ZnO/ZrO_2 solid the same species are observed but new IR bands indicate the formation of other carbonate species: an unidentate carbonate with intense IR bands at 1480 and 1370 cm^{-1} and a second bidentate species with lower intensity band at 1575 cm^{-1} and a contribution to the band at 1370 cm^{-1} [14].

Under 5% CO_2/H_2 the spectrum recorded on the ZrO_2 support at 250°C is the same as spectrum b of fig. 1 and this indicates that the presence of hydrogen does not produce any modification in the nature and quantities of the adsorbed species formed from the CO_2/He mixture. On ZnO/ZrO_2, at 250°C, the 5% CO_2/H_2 mixture (fig. 2, spectrum b) leads to major changes in the adsorbed species compared to those formed with 5% CO_2/He (fig. 2, spectrum a). In the presence of H_2, the quantity of the unidentate carbonate (1480 and 1370 cm^{-1}) is strongly decreased. The ionic carbonate (1440 cm^{-1}) and the carboxylate (1416 cm^{-1}) formed on the support are still well detected. New IR bands are observed indicating the formation of the formate species: 2967, 2882, 2740, 1575, 1382, 1367 cm^{-1} (ref. [13] and references therein). For a longer time on stream (30 min versus 80 s, fig. 2 spectrum c),

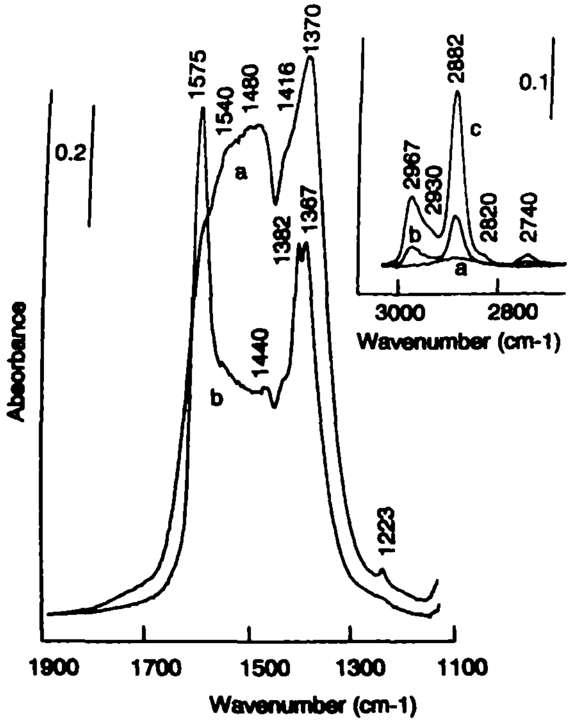

Fig. 2. Comparison of the adsorbed species formed on the ZnO/ZrO_2 catalyst in the presence and without hydrogen at 250°C. (a) 80 s in 5% CO_2/He, (b) 80 s in 5% CO_2/H_2, (c) 30 min in 5% CO_2/H_2.

methoxyl groups are detected by the IR bands at 2930 and 2820 cm^{-1} (ref. [13] and references therein). The IR bands of the bidentate species are now overlapped by those of the formate. The slow increase of the bands of the methoxyl with time on stream reveals the low activity of the catalyst in the present experimental conditions.

On ZrO_2 support, the absence of any modification of the bands of the carbonates in the presence of H_2 comes from the fact that this solid, in the range 25–350°C and under 1 atm total pressure, has no chemisorption properties for hydrogen [11]. In contrast, the ZnO/ZrO_2 catalyst chemisorbs H_2 [11] with a saturation value of 10 μmol of H_2/g of catalyst, after chemisorption at 100°C. This property explains that the presence of H_2 with CO_2 on this solid leads to the formation of hydrogenated carbonaceous adsorbed species: the formate and the methoxyl detected after 15 min of reaction in CO_2/H_2.

Considering the above remarks, and in relation to the pivotal species of the methanol synthesis, we have studied the nature of the carbonate, formed on the ZnO/ZrO_2, which is hydrogenated into formate with the fastest rate. We have also compared the rates of hydrogenation of this species and of the formate. To support the conclusions we worked on a quantitative (or semi-quantitative) exploitation of the data using preliminary treatments of the FTIR spectrum.

On the other hand, as the adsorbed species are not thermally stable in an inert gas at $T > 200°C$, their rates of desorption/decomposition and of hydrogenation have been compared.

3.2. TREATMENT OF THE FTIR SPECTRUM FOR A QUANTITATIVE ANALYSIS

The quantitative exploitation of the recorded spectra of an adsorbed species i is based on the assumption that the value I_i, of the integration of a FTIR spectrum in the absorbance mode between two wavenumbers where i absorbs the IR beam, is proportional to the adsorbed quantity Q_i ($I_i \propto Q_i$). This means that if the rate of disappearance (e.g. by desorption) of the species i is of first order with a rate constant k, then $\ln(I_i/I_i^0) = -kt$. Using the experimental values of I_i and I_i^0 for time t and time 0 of the reaction, the value of k can be determined if an experimental straight line is observed for the curve: $\ln(I_i/I_i^0) = f(t)$.

In the present study, a spectral region where only one adsorbed species absorbs the IR beam is not found and in the range 1800–1200 cm^{-1} (figs. 1 and 2), the absorbance recorded is the result of the additive contribution of various adsorbed species. For the objectives of the present study this imposes an initial treatment of the recorded spectrum in order to evaluate as precisely as possible the contribution of the individual adsorbed species.

With a FTIR spectrometer, it is easy to realise in absorbance mode the subtraction of two spectra with the objective to found the spectrum of a specific compound. For example, from the spectrum of a mixture (A + B) of two gases A and B, it is possible to obtain the spectrum of the gas A if the spectrum of a concentration of B in an inactive IR gas is known and used as reference. Usually, a parameter x in the subtraction: spectrum (A + B) – x spectrum B, is adjusted in order to lead to the disappearance of the IR bands of B in the initial spectrum (A + B). The value of x (higher or lower than 1) depends on the relative concentration of B in the two mixtures. This treatment can be applied in our case, but the main difficulty is to specify the reference spectrum used. For example, in fig. 1, spectrum a, the contribution of the adsorbed carbonate species formed in the presence of ZnO can be obtained considering that the species formed on ZrO_2 (spectrum b) are not modified by the presence of ZnO. Note that the ionic carbonate and the carboxylate have the same IR bands on the two solids (respectively 1440 and 1416 cm^{-1}) and this supports the previous assumption. Spectrum c of fig. 1 is thus obtained according to the previous procedure a – xb. The coefficient x is determined when the characteristic IR bands (1440 and 1416 cm^{-1}) of spectra b have disappeared from the initial spectrum a. The spectrum c confirms (assuming the same order of magnitude for the IR absorption coefficients of the various carbonates) that the carbonates correlated with the presence of ZnO, are mainly the unidentate carbonate (IR band at 1480 and 1370 cm^{-1}) with a very small presence of a bidentate carbonate (1575 cm^{-1}).

A similar treatment is presented in fig. 3 in order to evaluate the contribution of the carbonate species in the spectrum recorded, at 250°C, on the ZnO/ZrO_2 solid after 80 s in CO_2/H_2 flow (spectrum a). Spectrum b which is used as reference spectrum is obtained according to the following procedure. A helium flow (200 cm^3/min) saturated at 10°C with methanol is introduced on the ZnO/ZrO_2 solid at 250°C during 10 min followed by a purge in He during 15 min. This latter treatment leads to the total transformation of the methoxyl groups, observed after the methanol adsorption, into formate groups as it is observed in spectrum b of fig. 3 (IR bands at 1575, 1382, and 1367 cm^{-1}). Note the absence of IR bands of the carbonates in spectrum b. The spectrum of c of fig. 3 is obtained according to the subtraction a $- y$b). The value of the coefficient y is determined by the disappearance in the initial spectrum a of the 1575 cm^{-1} IR band of the formate. The spectrum c gives the contribution of the various carbonate species to spectrum a. This latter spectrum may also be treated in fig. 4 as in fig. 1, using the same reference spectrum b to reveal the contribution of the unidentate carbonate as shown in fig. 4 spectrum c (a $- x'$b). After two successive subtractions it is apparent that the profile of the spectrum of the unidentate carbonate (1480 and 1370 cm^{-1}) is not so well defined as on the spectrum c of fig. 1, obtained after only one subtraction. The above proce-

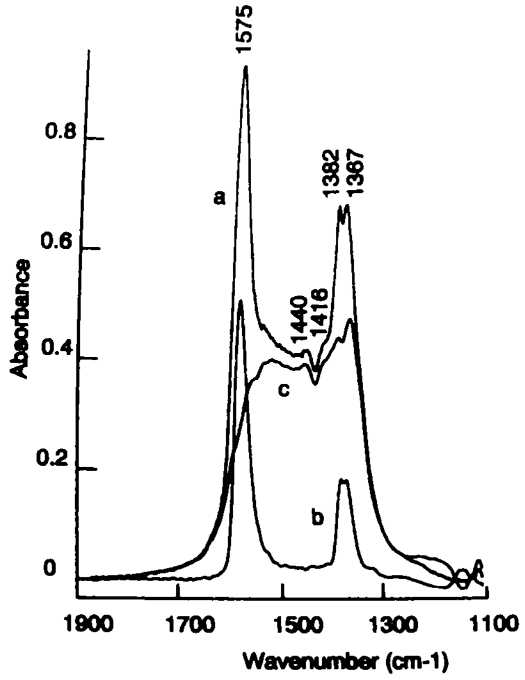

Fig. 3. Treatment of the spectrum recorded at 250°C on ZnO/ZrO_2 under 5% CO_2/H_2 (a) after 80 s in CO_2/H_2, (b) after methanol adsorption followed by 15 min desorption at 250°C, (c) = a $- y$b (see the text).

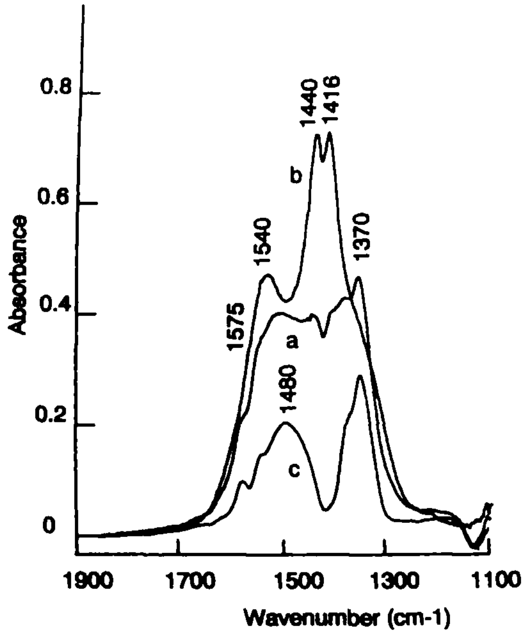

Fig. 4. Treatment of the spectrum recorded at 250°C on ZnO/ZrO_2 under 5% CO_2/H_2 (a) as spectrum c of fig. 3, (b) under 5% CO_2/He on ZrO_2, (c) = a – x'b (see the text).

dure was applied for series of spectra recorded during either a desorption or a hydrogenation process.

It must be noted that the treatments of the FTIR spectra described above lead to the spectrum representative of the adsorbed species because no significant shifts, in the IR bands, are observed between the unitial spectrum and the reference spectrum, althrough they are recorded in different experimental conditions. For example, in fig. 1, the presence of ZnO does not modify the IR bands of the species adsorbed on ZrO_2 alone and, in fig. 2, the formate bands are similar after the two experimental procedures. This situation is not often observed in catalysis.

Assuming that the IR absorption coefficients of the various carbonates are of the same order of magnitude, the integration I_{1c} of the absorbance of spectrum c of fig. 1 in the range 1800–1200 cm^{-1} is mainly related to the surface quantity (noted Q_{uni}) of the unidentate carbonate: $I_{1c} = I_{uni} \propto Q_{uni}$ (the contribution of the bidentate carbonate (1575 cm^{-1}) in the presence of ZnO is negligible. The subtraction of I_{1c} from the integration I_{1a} of spectrum a (in the same range 1800–1200 cm^{-1}) gives the contribution, to spectrum a, of the carbonate species (ionic, bidentate and carboxylate) formed on the support alone. The value $I_{1a} - I_{1c}$ is proportional to the quantity, noted Q_{car} of these carbonates ($I_{1a} - I_{1c} = I_{car} \propto Q_{car}$). These species cannot be individually differentiated and will be considered together.

The same type of calculation (integration in the range 1800–1200 cm^{-1}) applied to fig. 3 leads, using the integration I_{3c} of spectrum c, to the contribution of the total quantity (noted Q_{tcar}) of the carbonate species adsorbed on the ZnO/ZrO_2 solid (unidentate + other carbonates) to spectrum a ($I_{3c} = I_{tcar} \propto Q_{tcar}$). The value I_{3c} subtracted from the integration I_{3a} of spectrum a of fig. 3, gives the contribution to this spectrum of the quantity (noted Q_f) of the formate species ($I_{3a} - I_{3c} = I_f \propto Q_f$). The integration I_{4c} of spectrum c of fig. 4 reveals the contribution of the quantity of the unidentate carbonate (Q_{uni}) to the spectrum a of fig. 4, representative of all carbonates ($I_{4c} = I_{uni} \propto Q_{uni}$). According to the treatment procedure this gives also the contribution of the unidentate carbonate to spectrum a of fig. 3, recorded during the hydrogenation process. The contribution of the quantity, Q_{car}, of other carbonates detected on ZrO_2 (ionic, bidentate and carboxylate) is obtained by the subtraction: $I_{4a} - I_{4c} = I_{car} \propto Q_{car}$.

3.3. RATE CONSTANTS OF DESORPTION AND OF HYDROGENATION OF THE CARBONATE SPECIES

Fig. 5 gives the spectra recorded on the ZnO/ZrO_2 catalyst at 250°C after 80 s adsorption in CO_2/He during the increasing time in He. It is observed that all the IR bands decrease but only a quantitative treatment of the recorded spectra according to section 3.2 can indicate the rate order of disappearance of the unidentate car-

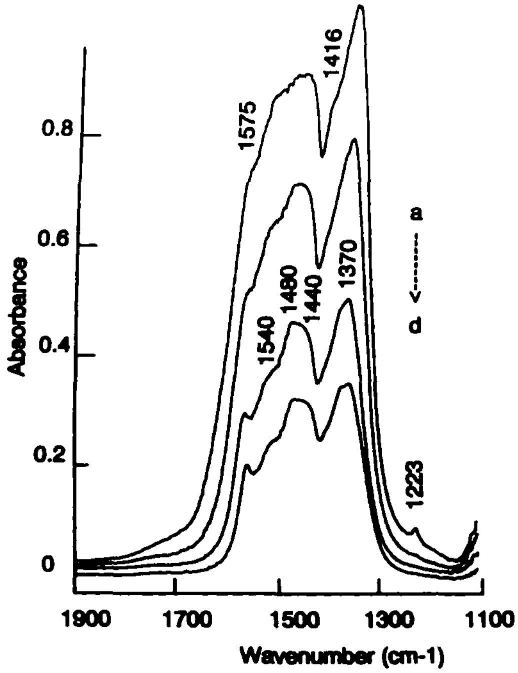

Fig. 5. Desorption of the carbonate species at 250°C under a helium flow (a) under 5% CO_2/He, (b) 1 min in helium, (c) 5 min in helium, (d) 15 min in helium.

bonate and of other carbonates. Fig. 6 corresponds to the hydrogenation at 250°C of the adsorbed carbonates formed on ZnO/ZrO_2 after 80 s in CO_2/He according to the experimental sequence $CO_2//He$ (80 s) $\rightarrow H_2$ (1 atm). A fast formation of the formate species is observed (2967, 2882, 2740, 1575, 1382, 1367 cm^{-1}), while the IR bands of the carbonate decrease. This decrease may be related to the hydrogenation of some carbonate species but also to their desorption according to the experiment of fig. 5. The IR bands at 2882 and 2967 cm^{-1} show that the amount of formate increases during the first 3 min of hydrogenation (spectra b and c) and then decreases slowly (spectra d and e), whereas the quantity of the methoxyl group (2930 and 2820 cm^{-1}) increases continuously. Only the quantitative treatment of the spectra would indicate which type of carbonates is hydrogenated into formate with the fastest rate.

Each spectrum of figs. 5 and 6 can be treated according to the procedure described in section 3.2 to obtain the value of the parameter I_i, proportional to the adsorbed quantity Q_i, of the adsorbed following i species: unidentate carbonate, formate and other carbonates. The same reference spectra as in fig. 1 and 3 are used and the values of x and y change with the time on stream of the experiment (either desorption or hydrogenation). Fig. 5 leads (not shown) to the decrease, with the time of desorption, of I_{uni} and I_{car} respectively, proportional to the quantities of

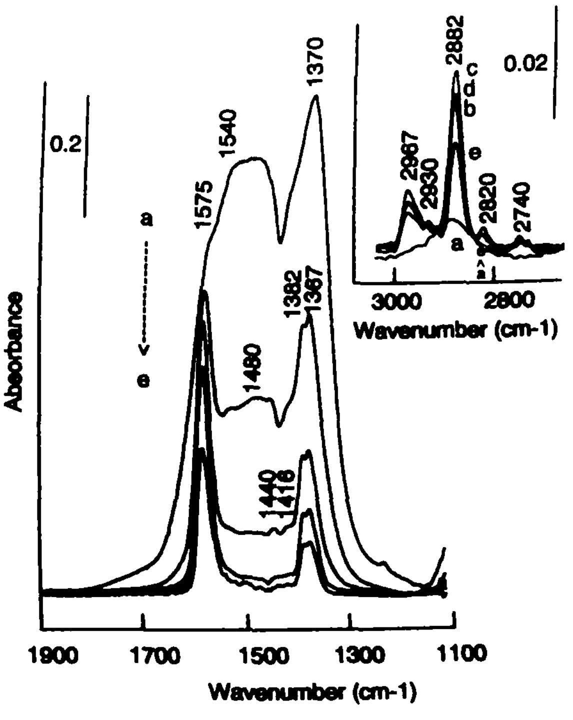

Fig. 6. Hydrogenation of the carbonate species at 250°C under a hydrogen flow at 1 atm (a) after 80 s in CO_2/He, (b)–(e) in hydrogen flow; (b) 1 min, (c) 3 min, (d) 30 min, (e) 90 min.

unidentate carbonate (Q_{uni}) and of other carbonates (Q_{car}). Fig. 7 gives, according to the treatment of fig. 3 (the carbonates are considered together: unidentate + other carbonates), the change of various $I_i \propto Q_i$, with the time of hydrogenation. The evolution of the quantity of the methoxyl groups is obtained, according to a procedure similar to figs. 1 and 3, using the formate spectrum of fig. 3, in the range 3100–2700 cm^{-1}, as a reference spectrum. The contribution of the unidentate carbonate to curve b of fig. 7 is obtained according to the procedure of fig. 4.

The kinetic exploitation of the experimental results is based on the following remarks:

Desorption experiment. During a TPD experiment in He, after the adsorption of CO_2 at 25°C on ZnO/ZrO_2, using a mass spectrometer as detector, it has been observed that only CO_2 is desorbed giving a TPD spectrum with an overlap of desorption peaks [14]. This permits to consider that the rate of desorption of the various carbonate species is of first order. The change of the surface quantity Q_i of one carbonate, noted i, with time on stream is: $Q_i = Q_i^0 \exp(-k_{di}t)$ with k_{di} the rate constant of desorption of i. As Q_i is proportional to I_i (as defined above) the plot of $\ln(I_i/I_i^0)$ versus the time of desorption must lead to a straight line (I_i^0 at time 0 of the desorption).

Hydrogenation experiment. For the hydrogenation, the rate of disappearance of the carbonate species like the unidentate carbonate (noted C_{uni}) may be considered as following the mechanism:

H_2 chemisorption : $H_2g \rightleftharpoons 2H_{\text{ads}}$ (0)

C_{uni} desorption : $C_{\text{uni}} \rightarrow CO_2$ gas (1)

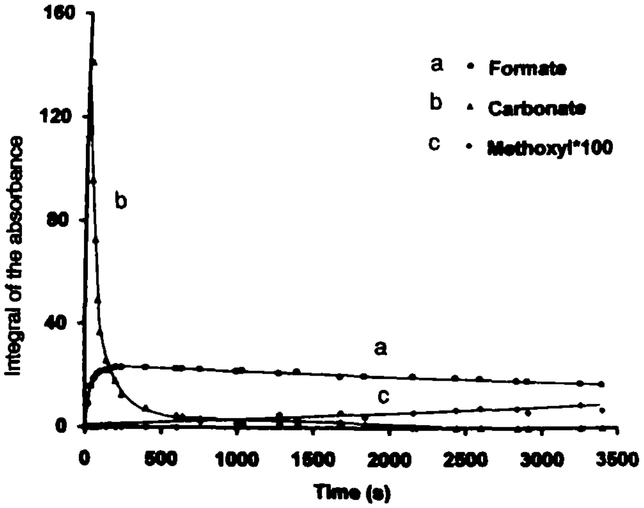

Fig. 7. Evolution of the integral of the absorbance of various adsorbed species formed under CO_2/He during the hydrogenation process.

C_{uni} hydrogenation : $C_{uni} + H_{ads} \rightarrow I_1$ (I_1 intermediate like formate). (2)

The rate of disappearance of the adsorbed quantity Q_{uni} is therefore:

$$-dQ_{uni}/dt = k_2 Q_{uni} Q_H + k_1 Q_{uni}$$

with k_1 and k_2 the rate constants of the steps (1) and (2) and Q_H the quantity of H_{ads} adsorbed. Assuming that the equilibrium (0) is rapidly obtained and that Q_H is constant, and noting $K_{uni} = k_2 Q_H + k_1$, the change of the quantity of Q_{uni} with the time of hydrogenation is: $\ln(Q_{uni}/Q^0_{uni}) = -K_{uni}t$. Similar expressions are obtained for the other carbonate species. As Q_{uni} is proportional to I_{uni} (as defined above) the plot of $\ln(I_{uni}/I^0_{uni})$ versus the time of hydrogenation must lead to a straight line.

Fig. 8 gives the plot of the above expression for the hydrogenation of the unidentate carbonate. A straight line is observed in agreement with the above kinetic model. The slope gives a rate constant of disappearance by desorption and hydrogenation of $K_{uni} = 1.6 \times 10^{-2}$ s^{-1}. The same treatment for other carbonates leads also to a straight line and the value $K_{car} = 2 \times 10^{-4}$ s^{-1}. The plot of the $\ln(I_{uni}/I^0_{uni})$, during the desorption process (from fig. 5) gives also a straight line. The rate constant of desorption obtained from the slope is $k_1 = 3 \times 10^{-3}$ s^{-1}. This value is smaller than the rate constant measured during the hydrogenation process ($K_{uni} = k_2 Q_H + k_1 = 1.6 \times 10^{-2}$ s^{-1}). This means that the value of $k_2 Q_H$ is 1.3×10^{-2} s^{-1} and that it is the hydrogenation which mainly affects the disappearance of C_{uni} during the hydrogenation and not its desorption. The same treatment for other carbonates (which are not differentiated) during the desorption process gives a rate constant of desorption of 5×10^{-4} s^{-1}. Taking into account the approximation linked to the procedure described in section 3.2, this value is of the same order of magnitude as the rate constant measured during the hydrogenation (K_{car}

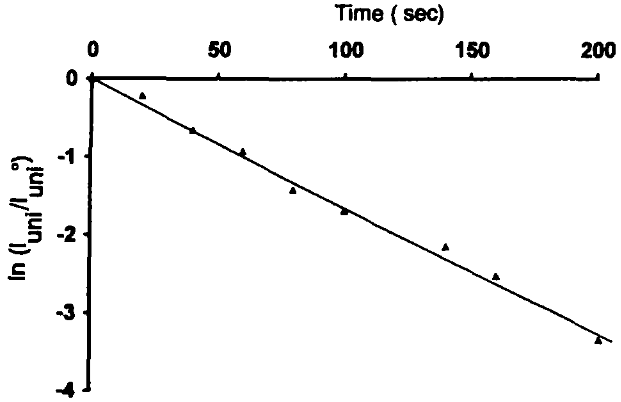

Fig. 8. Kinetic exploitation of the experimental data recorded during the hydrogenation of the unidentate carbonate species: $\ln(I_{uni}/I^0_{uni}) = f(t)$.

$= 2 \times 10^{-4}$ s^{-1}). For these carbonates, the rate of disappearance during the hydrogenation is strongly controlled by the desorption.

The above rate constant values show that (i) the unidentate carbonate is hydrogenated faster than the other carbonate species (ionic, bidentate and carboxylate) and (ii) the rate of hydrogenation of the unidentate carbonate is higher than the rate of desorption.

3.4. RATE CONSTANTS OF DESORPTION AND OF HYDROGENATION OF THE FORMATE

The desorption of the formate species (not shown) is studied after the total hydrogenation at 250°C of the unidentate carbonate as shown in fig. 6, spectrum e. Hydrogen is replaced by helium and the disappearance of the formate is recorded. The hydrogenation is studied from the experiment of fig. 7 when carbonates are no longer detected ($t > 2500$ s). This means that the rate of formation of the formate may be considered as negligible.

The kinetic exploitation of the data of fig. 7 is based on the following remarks. During a TPD experiment, using a mass spectrometer as detector, it has been observed that the formate species (noted F) decomposes/desorbs into three compounds H_2, CO, CO_2 [13]. According to the literature [15,16] this is explained by the existence of two processes:

$$F \rightarrow CO_2g + \tfrac{1}{2}H_2g \tag{4}$$

$$F \rightarrow COg + OH_{ads}\,. \tag{5}$$

The rate of desorption is therefore: $-dQ_f/dt = (k_4 + k_5)Q_f$, and $\ln(Q_f/Q_f^0) = -(k_4 + k_5)t$.

From the experimental results during the desorption the plot $\ln(I_f/I_f^0) = f(t)$ gives a straight line (not shown) and the slope leads to $k_4 + k_5 = 1.2 \times 10^{-4}$ s^{-1}.

For the hydrogenation of the formate, another step (6) must be added with the chemisorption equilibrium (0):

$$\text{hydrogenation of F:}\quad F + H_{ads} \rightarrow I_2 \ (I_2 \text{ intermediate like oxymethylene})\,. \tag{6}$$

Assuming as previously, Q_H as constant, the rate of disappearance of F during the hydrogenation is of first order in F with a rate constant $K_f = k_6 Q_H + k_5 + k_4$. The plot of $\ln(I_f/I_f^0) = f(t)$ using the experimental data of fig. 7 (for $T > 2500$ s) gives a straight line (fig. 9). The rate constant of disappearance of the formate during the hydrogenation process is determined by the slope: $K_f = 1.4 \times 10^{-4}$ s^{-1}. This value is of the same order of magnitude as the rate constant of desorption $k_5 + k_4 = 1.2 \times 10^{-4}$ s^{-1}. This means that the rate constant of hydrogenation of the formate $k_6 Q_H$ is of the range (or smaller) of the rate of desorption. This indicates that the rate of hydrogenation of the unidentate carbonate (1.3×10^{-2} s^{-1}) is faster than the rate of hydrogenation of the formate.

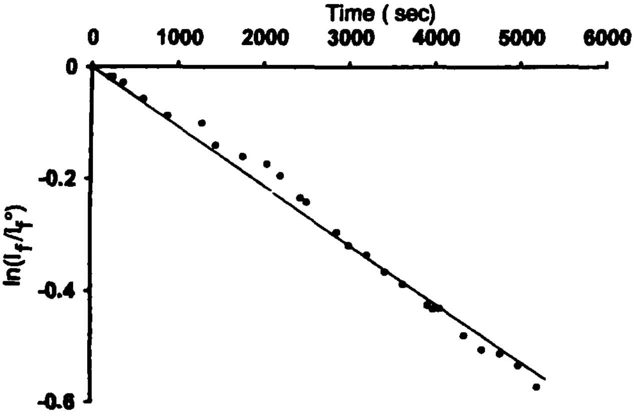

Fig. 9. Kinetic exploitation of the experimental data recorded during the hydrogenation of the formate species: $\ln(I_f/I_f^0)=f(t)$.

Assuming that the intermediate I_1 (see above) is the formate and taking into account the steps (0)–(6) one can write:

$$\mathrm{d}Q_{\mathrm{uni}}/\mathrm{d}Q_f=(k_1+k_2Q_H)Q_{\mathrm{uni}}/(k_2Q_HQ_{\mathrm{uni}}-K_fQ_f)\,.$$

During the three first minutes of hydrogenation of the unidentate carbonate (figs. 5 and 7) and considering the respective values of $K_f=1.1\times10^{-4}\ \mathrm{s}^{-1}$ and $k_2Q_H=1.3\times10^{-2}\ \mathrm{s}^{-1}$, the term K_fQ_f is negligible. This leads to a linear relation between Q_{uni} and Q_f which is well observed experimentally in fig. 10 using the proportional parameter I_{uni} and I_f obtained from the data of fig. 7. This confirms that the formate species is mainly formed by the hydrogenation of the unidentate carbonate. The other carbonates may lead also to the formate species but with a smaller rate.

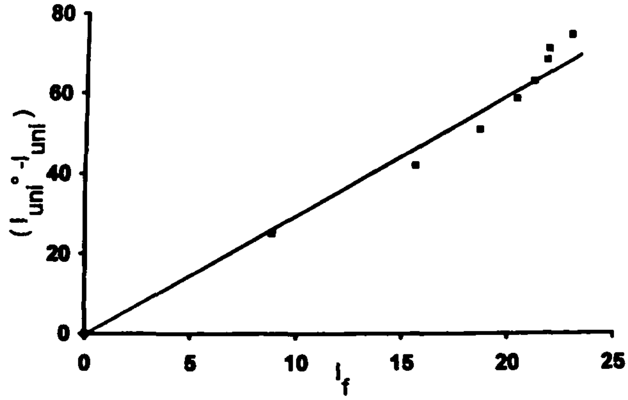

Fig. 10. Kinetic exploitation of the experimental data recorded during the formation of the formate by hydrogenation the unidentate carbonate $(I_{\mathrm{uni}}^0-I_{\mathrm{uni}})=f(I_f)$.

4. Conclusion

The present study shows that on a ZnO/ZrO_2 catalyst and at 250°C under 1 atm total pressure, the rate of hydrogenation of a unidentate carbonate, formed by interaction with CO_2, into formate species, is around ten times higher than the rate of the hydrogenation of the formate itself. The other carbonates present on the surface are hydrogenated more slowly than the unidentate carbonate. This permits to interpret the fact that during the CO_2/H_2 reaction mainly formate species is observed: the unidentate carbonate may be formed, but is hydrogenated rapidly and only the less reactive adsorbed intermediate is detected. As during the hydrogenation process no other IR bands were detected which could be attributed to hydrocarbon species other than formate and to the methoxyl groups, this means that the intermediate I_2 (like oxymethylene) is not detectable because of a high rate of hydrogenation.

Concerning the pivotal intermediate species of the methanol synthesis it may be considered that on the ZnO/ZrO_2 catalyst the unidentate carbonate and the species I_2 (not identified) are hydrogenated faster than the formate and the methoxyl. It is the rate of transformation of these species which controls the overall process. It should be observed that this order of reactivity may be changed with the nature of the catalyst used and this point may be the basis of the controversy concerning the pivotal intermediate species of the methanol synthesis.

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