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Characterization of the sites involved in the adsorption of CO on ZrO_2 and ZnO/ZrO_2 methanol synthesis aerogel catalysts

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Abstract

The interaction of CO with two aerogel solids have been investigated by in situ FTIR spectroscopy in order to obtain experimental data on the mechanism of formation of the formate species which can be considered as the intermediate adsorbed species in the methanol synthesis from CO/H_2. The adsorption of CO on ZrO_2 and ZnO/ZrO_2 aerogel solids was studied in the temperature range 298–623 K. At temperatures lower than 373 K, CO is mainly reversibly adsorbed on a cationic site M_1, leading to an IR band at 2192 cm^{-1} on ZrO_2 and 2183 cm^{-1} on ZnO/ZrO_2. It is shown that this adsorption follows the Langmuir's model on both solids. At higher temperatures (T>400 K) formate species are detected characterized on ZrO_2 by IR bands at 2967, 2882, 1576 1382 and 1367 cm^{-1}. It is shown that the formation of this species: (a) decreases the number of cationic sites M_1 which adsorb CO at temperatures lower than 373 K and (b) creates a new cationic site M_2. This is interpreted by a mechanism of formation of the formate species involving two sites of the surface: an OH group and a cationic site M_1. The CO is first adsorbed on the cationic site M_1, followed by a reaction with an OH group to produce a formate species. This last species is adsorbed on the cationic site M_1 and a new cationic site M_2 is formed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Aerogels; ZnO_2; Methanol synthesis; FTIR spectroscopy

1. Introduction

The nature of the adsorbed intermediate species of the reactions with syngas mixtures: $CO/CO_2/H_2$ (WGSR and methanol synthesis) over catalysts containing copper and zinc [1] has been the subject of controversy. The debate is focused on the nature of the first adsorbed intermediate species which is considered either as a carbonate or as a formate species [2–8]. Most of the experimental data which support these interpretations are based on the characterization using FTIR spectroscopy of the adsorbed species formed during the reaction of hydrogenation of either CO or CO_2 or CO/CO_2 mixtures. Several studies ([5,9–19] and references therein) have shown that during those reactions, a formate entity is formed and that this species appears as one of the possible intermediate of the methanol synthesis. In previous works [13–15] we have shown that during the CO_2/H_2 reaction on a ZnO/ZrO_2 aerogel catalyst, the formate species is formed by the hydrogenation of a unidentate carbonate produced by the adsorption of CO_2 on sites

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involving the ZnO part of the catalyst. The formate species is then hydrogenated into methoxyl groups via an adsorbed intermediate not yet identified [15]. Using the same experimental conditions, the formate species is not detected on ZrO_2 alone. In the present paper, we study the mechanism of the formation of the formate species not from the hydrogenation of CO_2 but from the adsorption of CO on two aerogel solids: ZrO_2 and ZnO/ZrO_2 which present an activity in the methanol synthesis at high pressure [15,18]. It is well known that the formate is formed by the reaction between CO and an OH group of the metal oxide surface. The objective of the present work is to obtain more insight into the elementary steps of formation of the formate species. In particular, the number of superficial steps as well as the number of sites involved in the formation of the formate species are considered.

2. Experimental

2.1. Catalysts

The preparation of the ZrO_2 and ZnO/ZrO_2 aerogel solids has been described in a previous work [19]. Briefly, the zirconia aerogel is obtained by the hydrolysis of zirconium propylate dissolved in propanol by a stoichiometric amount of water. The solvent is then evacuated in an autoclave under hypercritical conditions. The 5 wt% ZnO/ZrO_2 solid is obtained by the hydrolysis of zinc acetate dissolved in methanol containing a suspension of zirconia as initially prepared [19]. The solvent is evacuated in hypercritical conditions. After this preparation the solids are treated in O_2 at 713 K (2 h) in order to remove the adsorbed carbonaceous species coming from the preparation. The BET areas of both solids are in the range 200–220 m^2/g.

2.2. Analytical procedure

The experimental data are obtained by in situ FTIR analysis of the adsorbed species. The two solids compressed as a pellet of 2 cm diameter with a weight in the 50–70 mg range, present a very good IR transmission. The pellet is introduced in a stainless steel IR cell of 1 cm^3 dead volume which allows in situ studies under 1 atm total pressure in a flow of gas (100–200 cm^3/min) and in a temperature range 298–873 K.

The catalyst is initially treated in situ in O_2 at 713 K (15 min) then in helium (10 min). After cooling down in helium to the adsorption temperature, CO is introduced using the switch: He→x%CO/He (with x in the range 1–40%) and the FTIR spectra are recorded with time on stream.

3. Results and discussion

3.1. Adsorption of CO on ZrO_2

3.1.1. Adsorption at room temperature

The adsorption of CO (5%CO/He) at 298 K on a treated ZrO_2 pellet leads to the detection of a single IR band at 2192 cm^{-1}, with a constant intensity against time on stream, indicating a linear adsorbed CO species [13,20] on a cationic site M_l (either Zr^{4+} or Zr^{3+}). During the switch 5%CO/He→He, this IR band disappears (reversible chemisorption). Fig. 1 gives the change of the intensity of this IR band with the partial pressure of CO from 0.049 to 0.3 atm using various CO/He mixtures. The position of the IR band slightly shifts from 2192 cm^{-1} at the lower CO pressure used, to 2188 cm^{-1} at the higher partial pressure. The change of the surface area of this IR band with the partial pressure of CO is similar to the one expected for an adsorption which obeys the Langmuir's model.

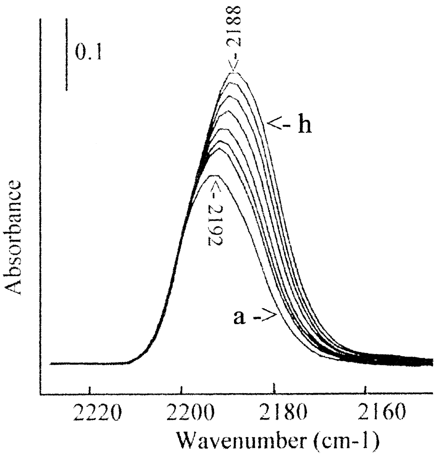

Fig. 1. Adsorption of CO on ZrO_2 at 298 K using increasing partial pressures of CO in helium from (a) 0.049 up to (h) 0.3 atm.

This can be verified using the procedure described by Kohler et al. [21] on a Cu/SiO_2 catalyst. The coverage θ of the sites according to the Langmuir's model is given by

$$\theta = \lambda P/(1+\lambda P), \tag{I}$$

with λ the adsorption coefficient and P the partial pressure of CO. The coverage θ is obtained experimentally using $\theta=(A/A_\infty)$ with A the surface area of the IR band at the partial pressure P and A_∞ the surface area of this IR band at the full coverage of the surface. As the full coverage is not obtained experimentally at the higher partial pressure used, relationship (I) can be expressed as

$$(P/A) = (1/\lambda A_\infty) + (P/A_\infty). \tag{II}$$

The plot of (P/A) versus P must give a straight line to validate the Langmuir's model. Using the experimental data of Fig. 1, Fig. 2 shows that the expected straight line is observed leading to an adsorption coefficient $\lambda_1=2.3\times10^{-4}$ Pa^{-1} and $A_{1\infty}=10$. This last value allows to calculate the coverage of the sites at a given partial pressure of CO using $\theta=A/A_\infty$. For instance with a 20%CO/He mixture the coverage of the sites is $\theta=0.8$.

3.1.2. *Adsorption at high temperature*

When the temperature of adsorption is linearly increased (15 K/min) under a 5%CO/He mixture, initially a decrease of the intensity of the 2192 cm^{-1} IR band without modification of its position is observed, followed by its disappearance at around 400 K. At 423 K, some new IR bands are observed which increase with the temperature until 623 K. Fig. 3 gives the spectrum observed at 623 K (spectrum a). The IR bands at 2967, 2882, 1567, 1382 and 1367 cm^{-1} can be attributed to formate species ($HCOO_{ads}$), combination band, νCH, ν_{as}OCO, δCH, ν_sOCO, respectively ([13] and references therein). The two small bands at 1440 and 1416 cm^{-1} may correspond to ionic carbonate and carboxylate, respectively [14]. The symmetrical band of this last species usually observed in the range 1540–1560 cm^{-1} is superimposed with the intense formate band at 1567 cm^{-1}. One of the objective of the present paper is to determine the modification of the ZrO_2 surface after the formation of the formate, but Fig. 3 shows that two other species are present on the surface under 5%CO/He. However, spectrum b in Fig. 3, recorded after 3 min in helium at 637 K after a switch 5%CO/He→He, shows that the ionic carbonate and the carboxylate desorb and that only formate species remain on the surface. This procedure allows to study the surface of ZrO_2 with only the adsorbed formate species. Fig. 4 gives the change of the OH groups of ZrO_2 during the adsorption of CO. At room temperature, the IR bands at 3770 and 3680 cm^{-1}, characteristic of the OH groups on ZrO_2, are not modified by the reversible adsorption of CO (spectrum a). When the temperature increases the intensities of both the IR bands decrease but the νOH bands at 3770 cm^{-1} are more affected by the formate formation (spectra b and c, Fig. 4). The decrease of the OH groups confirms that the formation of the formate species involves a reaction between OH groups and CO. However, this interaction can follow various mechanisms.

For instance, it can be considered that the gaseous CO reacts with an OH group in one step and that the

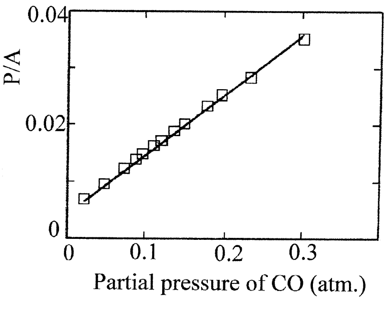

Fig. 2. Langmuir's transform for the linearly adsorbed CO species.

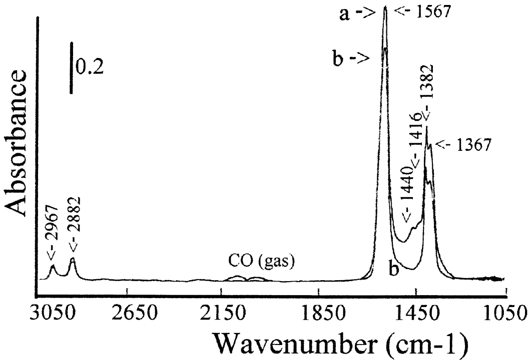

Fig. 3. Adsorption of CO on ZrO_2 at 623 K: (a) after 30 min in 5%CO/He; (b) 3 min in He after (a).

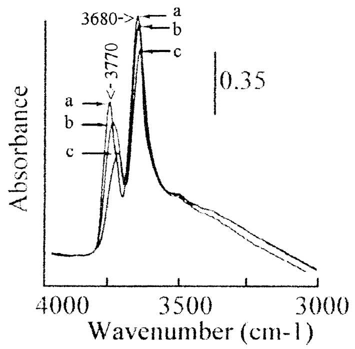

Fig. 4. Evolution of the OH groups of ZrO_2 during the adsorption of CO (5%CO/He): (a) before and after adsorption of CO at 298 K, (b) adsorption of CO at 473 K and (c) adsorption of CO at 673 K.

formate is adsorbed on the site where the OH group was initially present, according to mechanism A:

$$CO_g + HO\text{-}M_2 \rightarrow HCOO\text{-}M_2$$

Another possibility is to consider that CO is first adsorbed on a cationic site M_1 and then reacts with an OH group, according to the following two-step mechanism B:

$$CO_g + M_1 - (1) \rightarrow CO_{ads}\text{-}M_1$$

$$CO_{ads}\text{-}M_1 + HO\text{-}M_2 - (2) \rightarrow \text{formate}$$

The formate species can be adsorbed on the surface according to three possibilities:

- On the site M_2 where the OH group was initially adsorbed:

  $-(2) \rightarrow M_1 + HCOO\text{-}M_2$ (mechanism B_1)

- On the M_1 which initially adsorbs linearly CO:

  $-(2) \rightarrow HCOO\text{-}M_1 + M_2$ (mechanism B_2)

- On both sites (mechanism B_3).

To make a choice between those various possibilities we have studied the change of the number of cationic sites M_1 which adsorb linearly CO at room temperature after the formation of the formate species.

This is realized according to the following procedure. After the initial treatment at 713 K in O_2 followed by 10 min in helium, the adsorption of CO, at room temperature, is performed with a 20%CO/He mixture (Fig. 5, spectrum a). The surface area of the 2192 cm^{-1} IR band is determined (the coverage is θ=0.8). After desorption of CO at room temperature, the temperature is increased to 573 K and the 20%CO/He mixture is introduced during 30 min. In Fig. 6, part A gives the formation of the formate species following the IR bands at 2967 and 2882 cm^{-1} while part B reports the change of the intensity of those bands with time on stream. It can be observed that even after 30 min at 573 K, the formate species are still formed. The catalyst is then treated in He to desorb the ionic carbonate and the carboxylate species according to the results already shown in Fig. 3. The pellet of catalyst is then cooled down in helium to room temperature and the adsorption of 20%CO/He mixture is achieved. Fig. 5 (spectrum b) shows the IR bands observed in

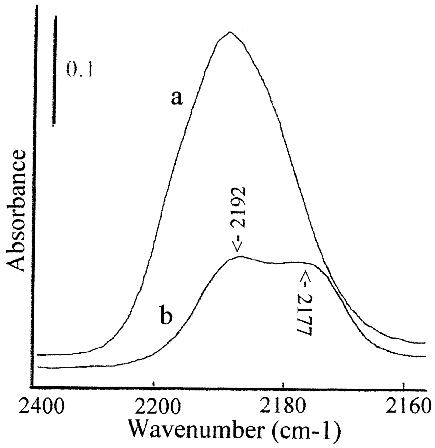

Fig. 5. Adsorption of CO (20%CO/He) at 298 K on ZrO_2: (a) after the initial treatment and (b) after the formation of the formate species (30 min at 573 K in 20%CO/He).

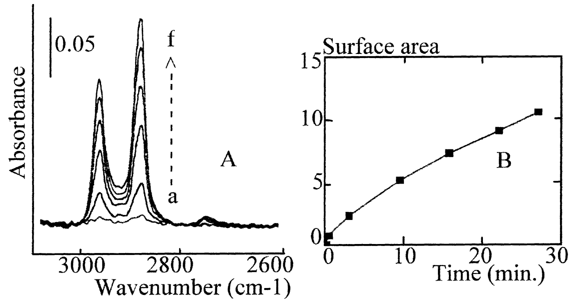

Fig. 6. Formation of the formate species at 573 K in 20%CO/He. Part A: Evolution of the FTIR spectra in the 3100–2600 cm^{-1} range with time on stream (min) in 20%CO/He: (a) 0.5, (b) 5, (c) 9.5, (d) 15, (e) 22, and (f) 27. Part B: Evolution of the surface area of the IR bands of part A with time on stream in 20%CO/He.

the range characteristic of the linear adsorbed CO species. The comparison of the spectra a and b shows that the presence of the formate species on the surface leads to two modifications: (a) the intensity of the 2192 cm^{-1} IR band decreases and (b) a new band is detected at 2177 cm^{-1}. The formation of the formate species decreases the number of cationic sites M_1 (which reversibly adsorb CO at room temperature) without modification of the position of the IR band and creates a new cationic site which also adsorbs reversibly CO (new IR band at 2177 cm^{-1}). This is in agreement with a formation of the formate species according to mechanism B_2. The new cationic site is the one where the OH group was located. The mechanisms A, B_1 and B_3 cannot explain the formation of this new cationic site.

The deconvolution of spectrum b assuming two symmetric IR bands leads to the surface area of the 2192 cm^{-1} band after the formation of the formate. Taking into account the initial surface area of the IR band (spectrum a) it was found that the number of M_1 remaining cationic sites after the formation of the formate represents 30% of the initial sites (considering a coverage of θ=0.8). The intensity of the band at 2177 cm^{-1} on the new cationic sites depends of the adsorption coefficient of this new CO species which is not determined in the present paper.

3.2. Adsorption of CO on the 5%ZnO/ZrO_2 catalyst

3.2.1. Adsorption at room temperature

The adsorption of CO (20%CO/He) at 25°C on a treated 5%ZnO/ZrO_2 leads to a spectrum with a single IR band at 2183 cm^{-1} with a constant intensity against time on stream. This band is assigned to CO linearly and reversible adsorbed on a cationic site. Fig. 7 compares the spectra after adsorption of CO (20%CO/He) at room temperature on ZrO_2 and on 5%ZnO/ZrO_2 (pellets of same weights). The small shift observed can be attributed to the presence of ZnO in the catalyst. The lower intensity on the ZnO/ZrO_2 sample suggests the coverage of a fraction of the ZrO_2 cationic sites by ZnO. Fig. 8 shows that the intensity of this IR band increases with the partial pressure of CO from 0.021 up to 0.2 atm as observed on ZrO_2. After the measurement of the surface area, A, of the IR band in function of the various CO pressures (P), the plot of $(P/A)=f(P)$ (as described above) gives a straight line (Fig. 9) confirming that the adsorption again follows the Langmuir's model. The adsorption coefficient is $\lambda_2=1.3\times10^{-4}$ Pa^{-1} and the intensity at full coverage is $A_{2\infty}=5.4$. The value of λ_2 is very close to the one found on ZrO_2 alone (λ_1) and confirms that

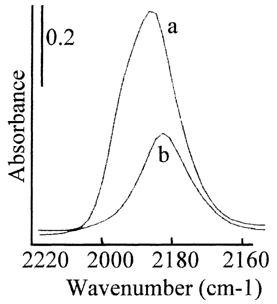

Fig. 7. Comparison of the adsorptions of CO at 298 K on (a) ZrO_2 and (b) ZnO/ZrO_2.

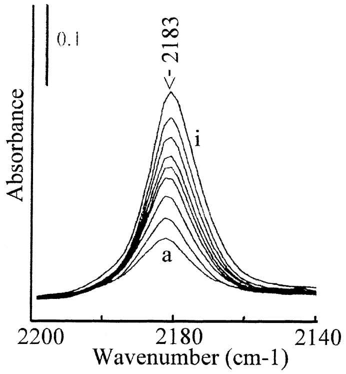

Fig. 8. Adsorption of CO on ZnO/ZrO_2 at 298 K using increasing partial pressures of CO in helium from (a) 0.021 up to (h) 0.2 atm.

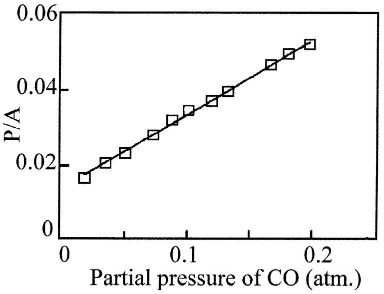

Fig. 9. Langmuir's transform for the linearly adsorbed CO species on ZnO/ZrO_2.

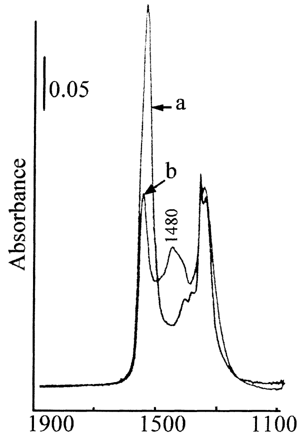

Fig. 10. Comparison of the adsorptions of CO at 673 K (5%CO/He, 15 min) on (a) ZrO_2 and (b) ZnO/ZrO_2.

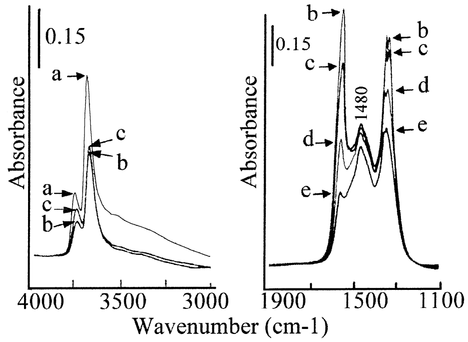

Fig. 11. IR bands of the OH groups and of the formate species adsorbed on ZnO/ZrO_2 during the isothermal desorption at 623 K: (a) before adsorption, (b) 30 min in 5%CO/He, (c)–(e) desorption in helium (c) 3, (d) 6, and (e) 15 min.

the same cationic sites M_I adsorb CO linearly on both ZrO_2 and ZnO/ZrO_2. The lower value of $A_{2\infty}$ on the $5\%ZnO/ZrO_2$ solid compared to $A_{1\infty}$ on ZrO_2 alone indicates that ZnO covers around 50% of the M_I sites previously found on ZrO_2. It can be also observed that the value $A_{2\infty}$ on ZnO/ZrO_2 leads to a coverage of the sites of θ=0.8 with a 20%CO/He mixture in agreement with the value found on ZrO_2 alone.

3.2.2. *Adsorption of CO at high temperature*

When the temperature of adsorption is linearly increased (15 K/min) under a 5%CO/He mixture, the intensity of the 2183 cm^{-1} band initially decreased and the band disappears at around 400 K. Some new IR bands are also detected, as on ZrO_2, at 1440 and 1416 cm^{-1} which are, respectively, attributed to ionic carbonate and carboxylate species, and at 1367, 1382, 1575, 2882 and 2967 cm^{-1} due to formate species. The main differences with the ZrO_2 solid (Fig. 10) are the detection of an IR band at 1480 cm^{-1} attributed to a unidentate carbonate species [13,14]. This is probably due to the fact that, on the ZnO/ZrO_2 solid, the formate species is less stable than on ZrO_2 (see below) and decomposes mainly into CO_2 and H_2, while on ZrO_2, the formate species decomposes into CO and an OH group [13]. On ZnO/ZrO_2, a fraction of CO_2 formed is adsorbed as carbonates groups [14].

Fig. 11 gives the spectra observed during a switch 5%CO/He→He at 623 K. It can be observed that: (a) the formate species disappear (they are less stable than on ZrO_2), (b) the OH groups are not regenerated (the formate species are decomposed into CO_2 and H_2) and (c) the unidentate carbonate is stable. This shows that it is not possible to use the same procedure than the one described above on ZrO_2 to study the surface of the catalyst with only the formate species. To study the change of the ZnO/ZrO_2 surface after the formation of the formate the following procedure is realized: after the initial treatment of the catalyst at 673 K, CO is adsorbed at room temperature using a 20%CO/He mixture and the area of the IR band at 2183 cm^{-1} (Fig. 12, spectrum a) is determined (coverage of the sites of θ=0.8). After heating in helium to 573 K, the 20%CO/He mixture is introduced to yield the formate species (as observed on ZrO_2 alone). After 40 min, the temperature is decreased in CO/He to 523 K and

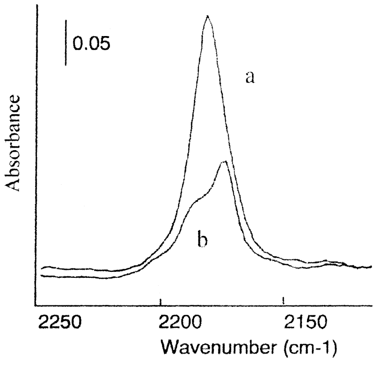

Fig. 12. Adsorption of CO (20%CO/He) at 298 K on ZnO/ZrO_2: (a) after the initial treatment and (b) after the formation of the formate species (40 min at 573 K in 20%CO/He).

helium is introduced. The decrease of the temperature limits the decomposition of the formate species. After cooling down to room temperature, the 20%CO/He mixture is introduced and spectrum b in Fig. 12 is recorded. It can be observed that, as on the ZrO_2 support, the intensity of the IR band at 2180 cm^{-1} decreases and that a new site is formed able to adsorb linearly CO with an IR band at 2173 cm^{-1}. This indicates that the formation of the formate species follows a similar mechanism on the two solids (mechanism B_2). However, it cannot be excluded that the unidentate carbonate coming from the decomposition of the formate is also adsorbed on a fraction of the M_1 sites.

3.3. Remarks

1. Mechanism B_2 for the formation of the formate species involves the adsorption on CO on the cationic sites M_1. However, at temperature higher than 400 K, the linear CO species on the M_1 site is not detected. This can be explained taking into account the fact that the adsorption follows the Langmuir's model. Considering the value determined for the adsorption coefficients, the coverage of the sites by CO must be low at high temperature and therefore the linear CO species cannot be detected. A low coverage of the M_1 sites is in agreement with the time needed to obtain a high quantity of formate species on the surfaces. After 30 min at 573 K in 20%CO/He, the superficial concentration of the formate species is still increasing (see Fig. 6).
2. The results presented here can be connected with the methanol synthesis from CO/H_2. The ZrO_2 solid presents a very low activity in the methanol synthesis while the ZnO/ZrO_2 is much more active. The present study shows that at high temperatures, on both solids, CO is adsorbed mainly as a formate species on the same cationic sites (either Zr^{4+} or Zr^{3+}). The difference of the stability of the formate species (lower on ZnO/ZrO_2) may explain the higher activity of the ZnO/ZrO_2 solid. However, in a previous study [19] it has been shown that hydrogen is adsorbed on the ZnO part of the catalyst. It seems that it is the ZrO_2 part of the catalyst which activates CO while the ZnO part activates hydrogen. A hydrogen spill-over from ZnO to ZrO_2 can also be considered [12,15,17,22].
3. The lower stability of the formate species on the ZnO/ZrO_2 catalyst is associated with the ZnO fraction of the catalyst. This interaction is revealed by some differences in the FTIR spectra of the formate species on ZrO_2 and ZnO/ZrO_2. Fig. 10 reveals a slight shift of the ν_{as}OCO IR band and a lower intensity of this IR band on ZnO/ZrO_2. However, in a previous work [13], it has been shown that the surface concentration of the OH groups which may react with CO, is higher on ZnO/ZrO_2 (factor of 10). It can be considered that the ZnO influences the reactivity of the OH groups and that it is this parameter which may explain the higher reactivity of the formate to form CO_2 and H_2 on ZnO/ZrO_2.

4. Conclusion

The adsorption of CO at room temperature on the two aerogel solids leads to a reversible adsorption following the Langmuir's model and involving the same cationic sites M_1 (Zr^{4+} or Zr^{3+}). At a higher temperature the adsorption of CO gives formate species according to a two-step mechanism: adsorption of CO on a cationic site M_1 followed by the reaction with surface OH group. The formate is adsorbed on the cationic sites M_1 and the removal of the OH groups creates new cationic sites M_2.

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