Catalysis Letters Vol. 80, Nos. 1–2, May 2002 (© 2002)

Effects of zirconia phase on the synthesis of methanol over zirconia-supported copper

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Received 21 November 2001; accepted 24 January 2002

A study has been conducted to identify the influence of zirconia phase and copper to zirconia surface area on the activity of Cu/ZrO_2 catalysts for the synthesis of methanol from either CO/H_2 or CO_2/H_2. To determine the effects of zirconia phase, a pair of Cu/ZrO_2 catalysts was prepared on tetragonal (t-) and monoclinic (m-) zirconia. The zirconia surface area and the Cu dispersion were essentially identical for these two catalysts. At 548 K, 0.65 MPa, and $H_2/CO_x = 3$ ($x = 1, 2$), the catalyst prepared on m-ZrO_2 was 4.5 times more active for methanol synthesis from CO_2/H_2 than that prepared on t-ZrO_2, and 7.5 times more active when CO/H_2 was used as the feed. Increasing the surface area of m-ZrO_2 and the ratio of Cu to ZrO_2 surface areas further increased the methanol synthesis activity. *In situ* infrared spectroscopy and transient-response experiments indicate that the higher rate of methanol synthesis from CO_2/H_2 over Cu/m-ZrO_2 is due solely to the higher concentration of active intermediates. By contrast, the higher rate of methanol synthesis from CO/H_2 is due to both a higher concentration of surface intermediates and the more rapid dynamics of their transformation over Cu/ZrO_2.

KEY WORDS: methanol synthesis; zirconia; copper.

1. Introduction

Zirconia-supported copper catalysts exhibit a high activity for the synthesis of methanol from both CO/H_2 and CO_2/H_2 [1–18]. Mechanistic studies of methanol synthesis have demonstrated that zirconia plays an active role in the formation of methanol when either CO_2 or CO is used as the source of carbon [14–18]. In the case of CO_2 hydrogenation, CO_2 adsorbs on the zirconia forming a bicarbonate species, which undergoes hydrogenation to produce formate, methylenebisoxy, and finally methoxide species [17]. The hydrogen required for the progressive hydrogenation of the zirconia-bound species is provided by the spillover of H atoms produced by the dissociative adsorption of H_2 on Cu [19]. In the case of CO hydrogenation, CO adsorption on zirconia produces formate species, which then undergo sequential hydrogenation to form methoxy species [18]. The methoxy species derived from either CO or CO_2 hydrogenation are converted to methanol either by reductive elimination or by hydrolysis, the latter process being significantly more rapid than the former.

Since CO_x ($x = 1, 2$) adsorbs on zirconia, the question arises as to the effect of the zirconia phase on the strength of CO_x adsorption and the activity of zirconia-supported Cu catalysts for the synthesis of methanol. Recent studies have shown that tetragonal and monoclinic phases of ZrO_2 show dramatically different adsorption capacities for CO and CO_2 [20–30]. For example, the adsorption capacity of CO_2 is more than an order of magnitude higher on monoclinic ZrO_2 (m-ZrO_2) than tetragonal ZrO_2 (t-ZrO_2) and the adsorption capacity for CO is 5–10 times higher on m-ZrO_2 [30]. These differences have been attributed to the higher Lewis acidity/basicity of Zr^{4+}/O^{2-} pairs present on the surface of m-ZrO_2.

The objective of the present investigation was to establish the influence of ZrO_2 phase on the steady-rate of methanol synthesis from CO/H_2 and CO_2/H_2. For this purpose, t-ZrO_2 and m-ZrO_2 were prepared with nearly identical surface areas and Cu was introduced onto each of these supports so as to obtain Cu particles of nearly the same dispersion. The effects of ZrO_2 surface area and Cu loading were also investigated. *In situ* infrared spectroscopy and transient-response experiments were conducted in order to obtain insights into the origin of the observed differences in catalyst activity.

2. Experimental

The supports used for this study, t-ZrO_2 and m-ZrO_2, were prepared using techniques described previously [30,31]. Both phases were prepared in a low and high surface area modification. Cu was introduced from a solution of $Cu(NO_3)_2$ by incipient wetness impregnation. The freshly impregnated material was dried and then calcined at 548 K for 8 h, after which it was reduced in

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1011-372X/02/0500-0063/0

H_2 for 2 h at 548 K. Transmission electron microscopy was used to determine the particle size distribution of Cu.

The steady-state rate of methanol formation from H_2/CO_2 or H_2/CO was determined using a glass microreactor with product analysis done by mass spectrometry. Transient-response experiments were carried out in an infrared cell. Two types of experiment were conducted. For the first, a flow of H_2 in He was switched to an equivalent flow of D_2 in He and the substitution of O–H groups on the surface of ZrO_2 by deuterium was monitored by infrared spectroscopy [19]. These experiments were used to determine the effects of ZrO_2 phase on the dynamics of H spillover onto ZrO_2. The second set of experiments involved switching from a flow of CO_x to a flow of CO_x/H_2 at a constant CO_x partial pressure. The transient formation of HCOO and CH_3O species adsorbed on the surface of ZrO_2 was monitored via infrared spectroscopy [17,18].

2. Results and discussion

The distribution of Cu particle sizes is shown in figure 1 for each of the catalysts investigated. The corresponding average particle size and degree of metal dispersion is given in table 1. Very similar particle size distributions and average particle sizes were observed for 5-Cu/t-ZrO_2(20) and 5-Cu/m-ZrO_2(19). In both cases, the average particle size is 3.1–3.3 nm and the ratio of Cu surface area to unexposed ZrO_2 surface area is 0.11. An increase in the surface area of m-ZrO_2 to 110 m^2/g increases the average particle size of Cu to 4.5 nm for 5-Cu/m-ZrO_2(110) and the ratio of Cu to ZrO_2 surface areas decreases to 0.04. The Cu particle size increases to 5.5 nm when the Cu loading is increased to 15 wt% and increases further to 9.8 nm when the Cu loading is increased to 25 wt% Cu. The corresponding ratios of Cu to ZrO_2 surface areas are 0.03 and 0.02.

Table 1
Particle size and BET surface area of Cu/ZrO_2 system

Sample	d_{Cu} [a] (Å)	Dispersion (%)	S_{Cu} [b] (m^2/g Cu)	S_{Cu}/S_{ZrO_2}
5 wt% Cu/t-ZrO_2(20)	31.0	29.0	40.5	0.11
5 wt% Cu/m-ZrO_2(19)	32.7	27.5	47.8	0.11
5 wt% Cu/m-ZrO_2(110)	45.0	20.0	35.2	0.02
15 wt% Cu/m-ZrO_2(110)	54.7	16.5	25.4	0.04
25 wt% Cu/m-ZrO_2(110)	98.3	9.2	12.7	0.03

[a] Average particle size of copper observed by TEM.
[b] Surface area of Cu.

The steady-state activities of the ZrO_2-supported Cu catalysts for methanol synthesis from CO_2/H_2 and CO/H_2 were determined at 548 K, a total pressure of 0.65 MPa, and a H_2/CO_x ratio of 3. The weight of catalyst used for these experiments was 0.2 g and the total feed flow rate was 60 cm^3/min. Table 2 shows that the rate of methanol synthesis from H_2/CO_2 over 5-Cu/m-ZrO_2(19) is nearly 4.5 times higher than that measured over 5-Cu/t-ZrO_2(20) and for methanol synthesis from H_2/CO, the activity of 5-Cu/m-ZrO_2(19) is 7.5 times higher than that of 5-Cu/t-ZrO_2(20). Since the ratio of Cu to ZrO_2 surface areas is identical for these two

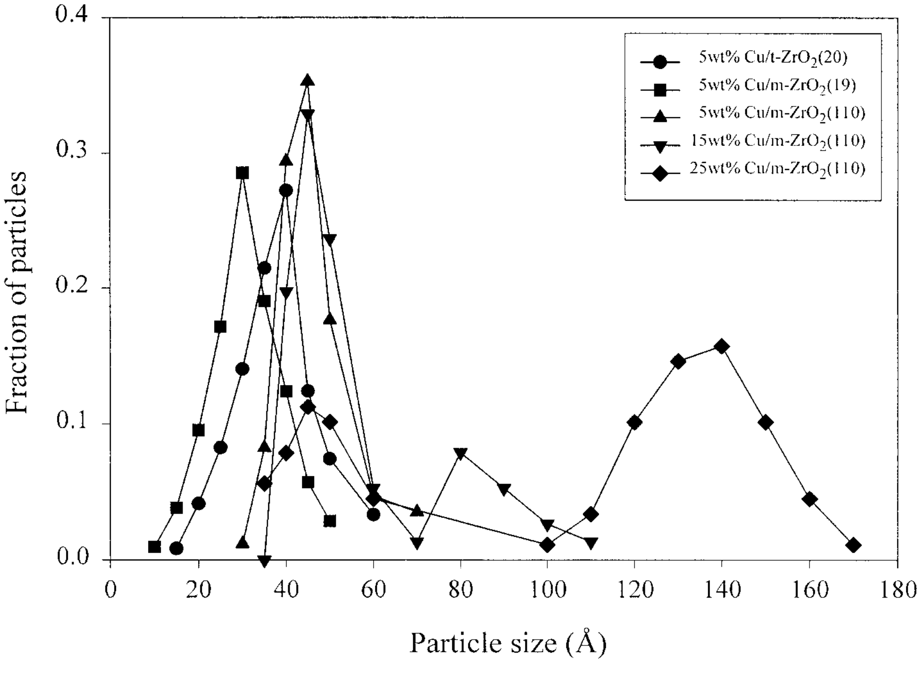

Figure 1. Particle size distribution of copper on zirconia observed by TEM.

Table 2
Effect of zirconia phase on methanol synthesis activity

Sample	S_{Cu} [a]/S_{ZrO_2}	Activity of CO_2/H_2 (μmol/s-gcat)	Activity of CO/H_2 (μmol/s-gcat)
5 wt% Cu/t-ZrO_2(20)	0.11	0.014	0.004
5 wt% Cu/m-ZrO_2(19)	0.11	0.06	0.03
5 wt% Cu/m-ZrO_2(110)	0.02	0.11	0.13
15 wt% Cu/m-ZrO_2(110)	0.04	0.34	0.16
25 wt% Cu/m-ZrO_2(110)	0.03	0.28	0.13

[a] Surface area of Cu.

[b] Reaction conditions: $T = 548$ K, $P = 0.65$ MPa, $H_2/CO_x = 3$, flow rate = 60 cm^3/min, catalyst mass = 0.2 g.

catalysts, the higher rate of methanol synthesis over the catalyst based on m-ZrO_2 is directly attributable to the phase of the support. Increasing the surface area of the support to 110 m^2/g while holding the Cu loading at 5 wt% increases the methanol synthesis activity from H_2/CO_2 by 1.8 and by 4.3 for methanol synthesis from H_2/CO, relative to 5-Cu/t-ZrO_2(20). These results show that methanol synthesis activity is more sensitive to the surface area of m-ZrO_2 than to the ratio of Cu to ZrO_2 surface areas. On the other hand, when this ratio is doubled the rate of methanol synthesis increases by a factor of 3 when H_2/CO_2 is used as the feed and by 1.3 when H_2/CO is used as the feed. These results indicate that the ratio of Cu to ZrO_2 surface area is also important. Consistent with this finding, the methanol synthesis activity from both H_2/CO_2 and H_2/CO decreases when the Cu loading is increased to 25 wt% because of the corresponding decrease in the ratio of Cu to ZrO_2 surface areas.

The steady-state observations presented in table 2 clearly demonstrate that the phase of ZrO_2, the surface of ZrO_2, and the ratio of Cu to ZrO_2 surface areas are important parameters in determining the methanol synthesis activity of ZrO_2-supported Cu catalysts. Left unanswered are the following two questions. Does the phase of ZrO_2 affect the spillover of H atoms from Cu to ZrO_2, an important step in the proposed mechanism of methanol synthesis as noted in table 1? Does the phase of ZrO_2 affect the dynamics of CO and CO_2 hydrogenation to methanol? To address these questions, appropriate transient-response isotopic tracer experiments were conducted.

The dynamics of H atom spillover were investigated at 323 K using 5-Cu/t-ZrO_2(20) and 5-Cu/m-ZrO_2(19). For these experiments, the catalyst was first exposed to a stream of H_2 and then switched to one containing an equivalent concentration of D_2. Figure 2 shows the observed disappearance of the infrared band for OH groups and the increase in the band for OD as functions of time. The rate of H/D of exchange of hydroxyl groups associated with ZrO_2 is 100-fold faster on 5-Cu/m-ZrO_2(19) than on 5-Cu/t-ZrO_2(20). While not shown, similar experiments were conducted on each of the supports in the absence of Cu. In that case the rate of H/D exchange was more than a factor of 10 slower than that shown in figure 2, indicating the importance of Cu for the dissociative adsorption of H_2, a necessary first step for H/D exchange [19].

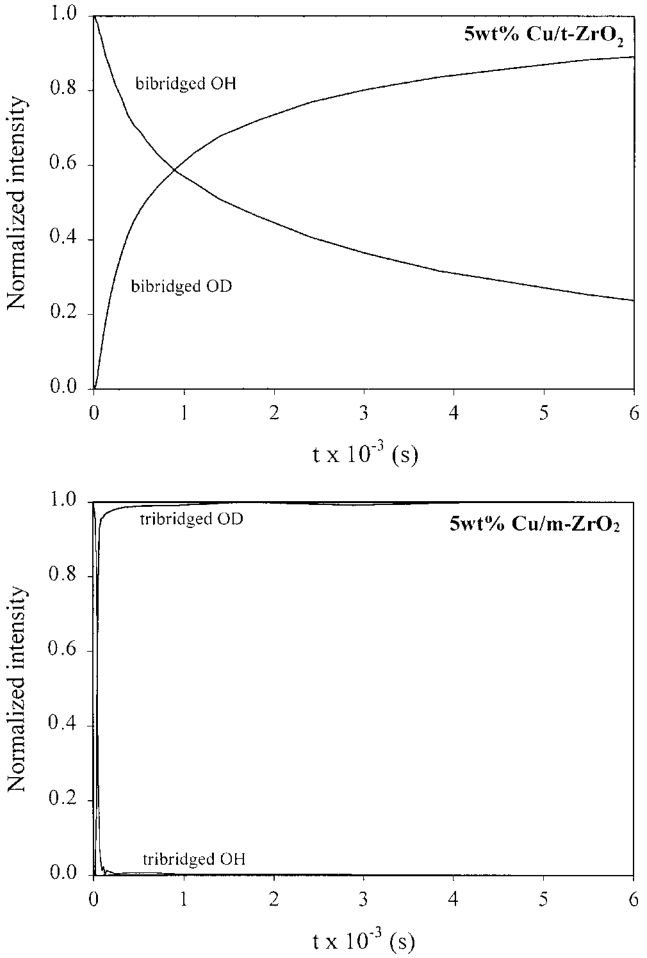

Figure 2. Intensities of OH and OD features taken during exposure of 5 wt% Cu/t-ZrO_2 and 5 wt% Cu/m-ZrO_2 to 0.49 MPa D_2 and 0.16 MPa He flow at a total rate of 60 cm^3/min at 523 K. Spectra referenced to the same zirconia under 0.65 MPa He flow at 523 K. Intensities normalized to those observed at the beginning of the transient for OHs, and to the value observed at the end of the transient for ODs.

Transient-response experiments were carried out to determine whether the effect of the phase of zirconia on the rate of methanol synthesis is due solely to the number of active sites or, additionally, to the influence of the zirconia phase on the rate of CO_x hydrogenation. For these experiments, CO_x in He was passed over the catalyst for 100 min to establish a steady state. The gas stream was then switched to one containing a H_2/CO_x mixture in which the concentration of CO_x was identical to that contained in the gas phase before the switch in gas composition was made. As discussed below, the result of these experiments depended upon whether CO or CO_2 was used in the feed.

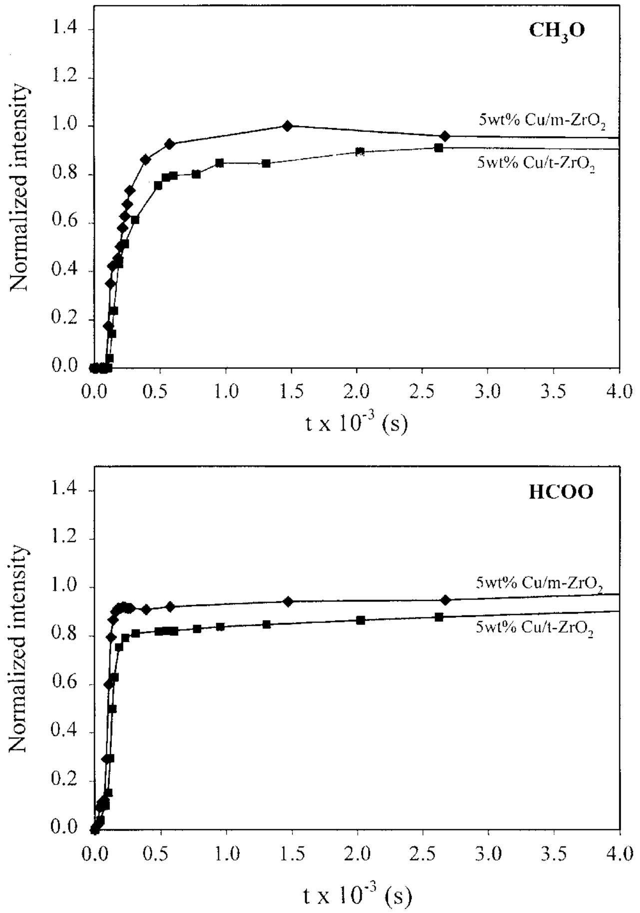

Figure 3. Intensities of b-HCOO-Zr and CH_3O-Zr features for 5 wt% Cu/t-ZrO_2 and 5 wt% Cu/m-ZrO_2 during CO_2 hydrogenation reaction ($T = 523$ K, $P = 0.65$ MPa, $H_2/CO_2 = 3/1$, flow rate = 60 cm^3/min). Intensities normalized to those observed at the end of the transient.

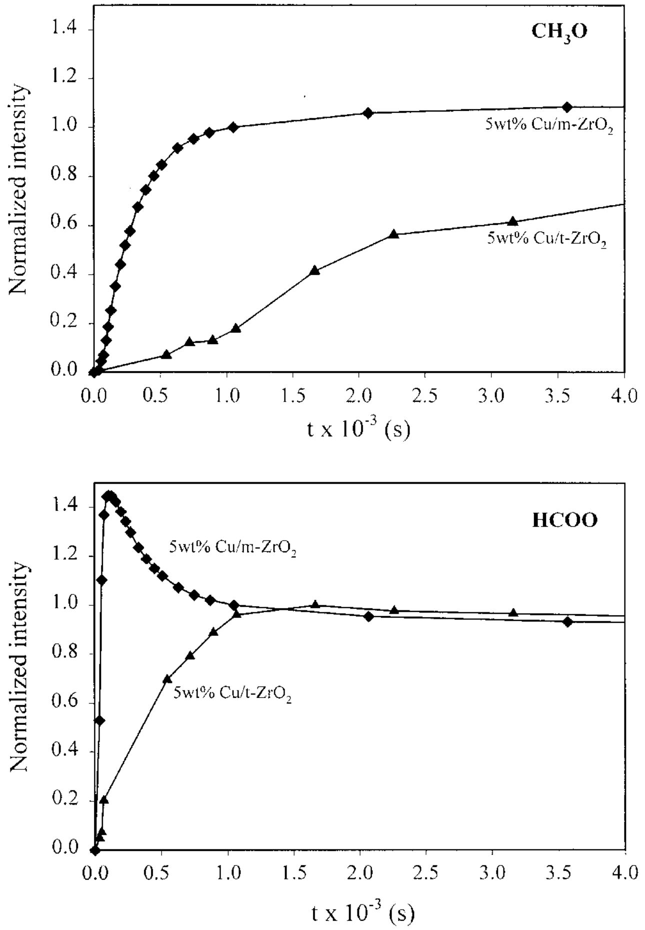

Figure 4. Intensities of b-HCOO-Zr and CH_3O-Zr features for 5 wt% Cu/t-ZrO_2 and 5 wt% Cu/m-ZrO_2 during CO hydrogenation reaction ($T = 523$ K, $P = 0.65$ MPa, $H_2/CO = 3/1$, flow rate = 60 cm^3/min). Intensities normalized to those observed at the end of the transient.

Figure 3 shows that for CO_2 hydrogenation, the dynamics of forming HCOO and CH_3O on the surface of ZrO_2 are identical, independent of the phase of the oxide. However, the steady-state concentration of both species is higher on m-ZrO_2, as shown in table 3. In the case of HCOO, the concentration ratio is 4.0 in favor of m-ZrO_2 and in the case of CH_3O, the ratio is 2.0 in favor of this phase. A very different picture is found for CO hydrogenation. As seen in figure 4, the rates of HCOO and CH_3O formation are considerably faster on m-ZrO_2 than t-ZrO_2. Here too, the concentrations of both species are higher on m-ZrO_2 (see table 3). In the case of HCOO, the ratio of concentrations is 4-fold higher on m-ZrO_2 and in the case of CH_3O the ratio of concentrations is 2.5-fold higher on m-ZrO_2. These results suggest that the factors contributing to the higher rate of methanol formation over Cu/m-ZrO_2, as compared with Cu/t-ZrO_2, are different for CO_2 and CO hydrogenation. When CO_2 is the source of carbon for the synthesis of methanol, the 5-fold higher rate of methanol formation is attributed to the higher concentration of adsorbed intermediates, *i.e.* HCOO and CH_3O. For methanol synthesis from CO, the higher rate observed over Cu/m-ZrO_2 is attributed to a combination of higher concentrations of surface intermediates and their higher rate of hydrogenation (see figure 3). While the rate of H-atom spillover was higher for Cu/m-ZrO_2 than Cu/t-ZrO_2, the absolute rate of H-atom spillover at 548 K is roughly an order of magnitude faster than the rate of methanol synthesis on both catalysts for either CO or CO_2 hydrogenation. Thus, the rate of H-atom spillover does not appear to limit the rate of methanol synthesis. This conclusion is consistent with the findings of Jung and Bell [19].

Table 3
Effect of crystalline structure on the absolute intensity (a.u.) of the b-HCOO and CH_3O during hydrogenation reaction at 523 K under 0.65 MPa

Sample	H_2/CO_2		H_2/CO	
	b-HCOO	CH_3O	b-HCOO	CH_3O
5 wt% Cu/t-ZrO_2	0.24	0.07	0.11	0.09
5 wt% Cu/m-ZrO_2	0.94	0.14	0.42	0.25

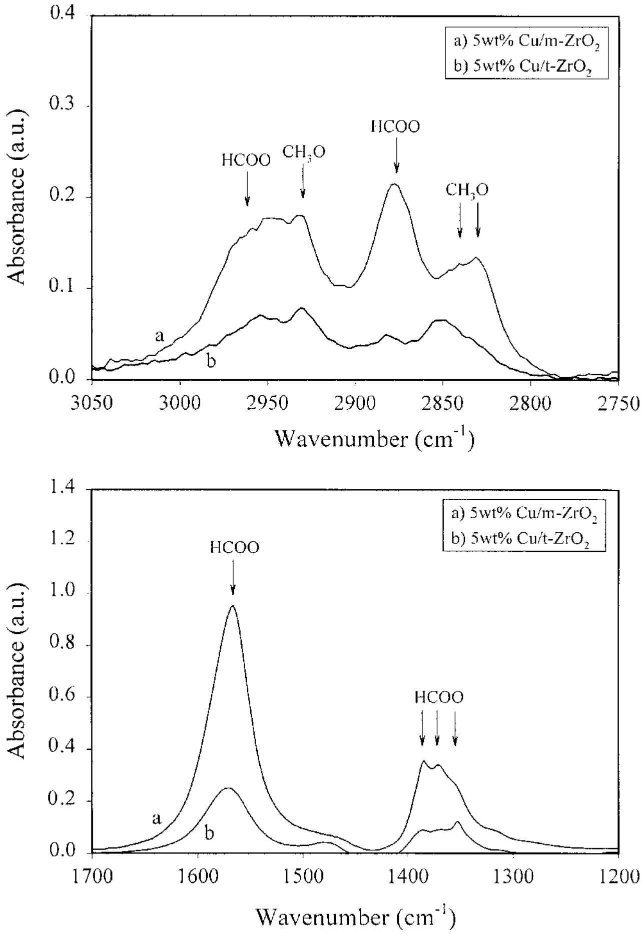

Figure 5. Infrared spectra taken for 5 wt% Cu/t-ZrO_2 and 5 wt% Cu/m-ZrO_2 at 523 K after switching feed from 0.65 MPa H_2 to 0.16 MPa CO_2 and 0.49 MPa H_2 at a total rate of 60 cm^3/min. Spectra referenced to the same zirconia reduced under 0.65 MPa H_2 flow at 523 K.

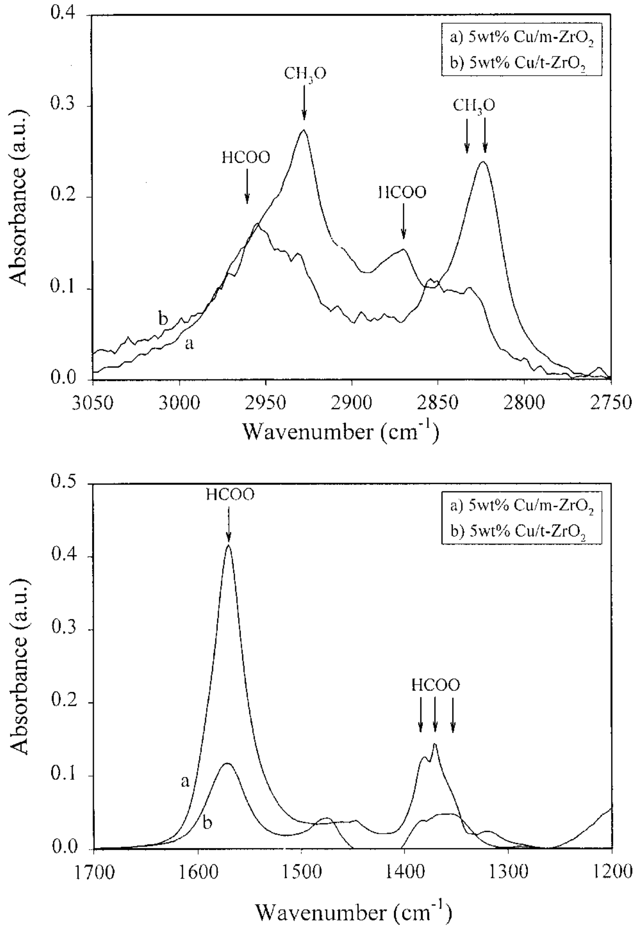

Figure 6. Infrared spectra taken for 5 wt% Cu/t-ZrO_2 and 5 wt% Cu/m-ZrO_2 at 523 K after switching feed from 0.65 MPa H_2 to 0.16 MPa CO and 0.49 MPa H_2 at a total rate of 60 cm^3/min. Spectra referenced to the same zirconia reduced under 0.65 MPa H_2 flow at 523 K.

4. Conclusions

The present investigation has shown that the methanol synthesis activity of Cu/ZrO_2 is strongly influenced by the phase of the ZrO_2. For constant ZrO_2 surface area and Cu dispersion, the methanol synthesis activity is significantly higher for m-ZrO_2 than t-ZrO_2, independent of whether CO_2/H_2 or CO/H_2 is used as the feed. For Cu/m-ZrO_2, the methanol synthesis activity can be increased by increasing the surface area of m-ZrO_2 and the ratio of the surface area of Cu to that of ZrO_2. The cause of the higher activity of m-ZrO_2-supported Cu appears to depend on the composition of the feed. For CO_2/H_2, the concentration of adsorbed formate and methoxide species is higher on m-ZrO_2 than t-ZrO_2, but the dynamics of the formation and consumption of these species are the same on both phases. Thus, the higher methanol synthesis activity of Cu/m-ZrO_2 is attributed to the higher concentration of the intermediates to methanol. For CO/H_2, both the surface concentrations of formate and methoxide species and their dynamics of formation and consumption are higher when Cu is supported on m-ZrO_2. While the dynamics of H-atom spillover from Cu to ZrO_2 are faster for Cu/m-ZrO_2 than for Cu/t-ZrO_2, this process occurs at a rate that is an order of magnitude faster than that of methanol synthesis. Consequently, while H-atom spillover is an essential part of the reaction mechanism, it is not rate determining.

Acknowledgments

This work was supported by the Director, Office of Basic Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

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