Influence of titania on zirconia promoted Cu/SiO_2 catalysts for methanol synthesis from CO/H_2 and CO_2/H_2

Tobin C. Schilke, Ian A. Fisher and Alexis T. Bell

Chemical Sciences Division, Lawrence Berkeley National Laboratory and Department of Chemical Engineering, University of California, Berkeley, CA 94720, USA

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The effects of adding mixtures of titania and zirconia on the methanol synthesis activity and selectivity of Cu/SiO_2 were investigated. The synthesis of methanol from both CO/H_2 and CO_2/H_2 mixtures was examined at 0.65 MPa and temperatures between 448 and 573 K. For CO hydrogenation, the addition of ZrO_2 alone increased the methanol synthesis activity of Cu/SiO_2 by up to three-fold. Substitution of a portion of the ZrO_2 by TiO_2 decreased the methanol synthesis activity of the catalyst relative to that observed when only ZrO_2 is added. ZrO_2 addition also enhanced the methane synthesis activity by as much as seven-fold. In the case of CO_2 hydrogenation, the maximum methanol synthesis activity is achieved when a 50/50 wt% mixture of ZrO_2 and TiO_2 is added to Cu/SiO_2. Neither the presence of the oxide additive nor its composition had any effect on the activity of the reverse water–gas-shift reaction, which suggests that this reaction proceeds only on Cu. The observed effects of ZrO_2 and TiO_2 on the catalytic activity of methanol synthesis from CO and CO_2, and methane synthesis from CO, are interpreted in terms of the strength and concentration of acidic and basic groups on the surface of the dispersed oxide.

Keywords: methanol, copper, titania, zirconia

1. Introduction

Recent studies have demonstrated that zirconia present either as a support or an additive strongly enhances the activity of Cu for the synthesis of methanol from either CO or CO_2 [1–13]. *In situ* infrared investigations of the effects of zirconia indicate that zirconia is more effective than Cu for the adsorption of CO and CO_2, and that in both cases the synthesis of methanol occurs on the surface of zirconia, with hydrogen supplied by spillover from Cu [11–13]. In the case of CO, the first adsorbed species are formate (HCOO) groups formed by the reaction of CO with hydroxyl groups present on the surface of zirconia [12]. Infrared spectroscopy shows that the formate groups undergo hydrogenation to form methylenebisoxy (CH_2OO) groups and then methoxy (CH_3O) groups, all bound to the surface of zirconia [12]. The last of the species is the precursor to methanol. In the case of CO_2, the first species formed are bicarbonate (HCO_3) groups [13]. These species react with hydrogen to form formate groups, which then undergo hydrogenation to form methanol in a manner similar to that observed during CO hydrogenation [13]. The only significant difference is that in the case of CO_2 hydrogenation, methanol is produced by hydrolysis of methoxy groups, rather than by reductive elimination of these groups [13].

The mechanistic studies described above suggest that the enhanced activity of zirconia-containing catalysts is attributable to the amphoteric character of zirconia, which possesses both weak Brønsted acidic and basic sites [14]. CO, a weak Lewis base, [15] would be expected to interact with the Brønsted acidic sites of zirconia, whereas CO_2, being a Lewis acid, [16] would be expected to interact with Brønsted basic sites. Each of these interactions would serve to increase the adsorption of CO or CO_2 over that observed on Cu alone. If this interpretation is correct then even higher methanol synthesis activity might be achieved by increasing the concentration and strength of the Brønsted acidic and basic sites on the surface of zirconia. This objective might be achieved by making a mixed metal oxide containing titania and zirconia, since it has been observed that the concentrations of both acidic and basic sites pass through a maximum as the proportions of ZrO_2 and TiO_2 are varied, the highest concentration occurring for 50/50 mol% mixture [17]. Using similar logic, it has been argued that Cu supported on ZrO_2 and TiO_2 should be more active than Cu supported on SiO_2, since both ZrO_2 and TiO_2 are amphoteric [14]. In the present study, we have examined the effects of adding ZrO_2/TiO_2 mixtures to Cu/SiO_2 on the activity and selectivity of the catalyst for methanol synthesis from both CO and CO_2, to determine if the above hypothesis is valid.

2. Experimental

The catalysts used in these investigations were prepared in two steps. In the first step Cu (5 wt%) was dispersed onto SiO_2 by deposition-precipitation [18]. Materials used were copper(II) nitrate ($Cu(NO_3)_2{\cdot}6H_2O$, Alfa Products, 99.999%), urea (NH_2CONH_2, Fluka, 99.9%), nitric acid (HNO_3, Mallinckrodt, 70.5%), fumed silica (SiO_2, CAB-O-SIL M-5, 99.99%), and distilled water. The silica was

Table 1
Compositions of catalysts used in this study.

Catalyst designation[a]	Cu loading (wt%)	ZrO_2 loading (wt%)	TiO_2 loading (wt%)	Proportion of ZrO_2 to TiO_2 (wt%)
Zr(0)/Ti(0)	5.2	0.0	0.0	NA
Zr(0)/Ti(100)	5.2	0.0	5.2	0
Zr(25)/Ti(75)	5.2	1.3	3.8	25
Zr(50)/Ti(50)	5.2	2.5	2.5	50
Zr(75)/Ti(25)	5.2	3.8	1.2	75
Zr(100)/Ti(0)	5.2	5.0	0.0	100

[a] All catalysts contain 5.2 wt% Cu, the weight balance in all cases is due to SiO_2.

doubly washed in nitric acid to ensure the removal of ppm levels of trace metals. Adding urea to the silica containing copper nitrate solution and then gradually raising the temperature to 363 K, causes the urea to decompose and thereby raise the pH of the solution, resulting in the precipitation of copper onto the silica. A final pH of 6.7 was observed. Following Cu precipitation, the solid was filtered, washed, and dried in a vacuum oven at 393 K for 24 h. The dried catalyst precursor was then calcined at 473 K for 1 h, at 573 K for 1 h, and finally at 723 K for 17 h in air flowing at 60 cm^3 (STP)/min. The preparation procedure just described has been shown to produce Cu/SiO_2 catalysts with higher methanol synthesis activities than catalysts prepared by other techniques [19].

The second step in catalyst preparation involved the deposition of zirconia and titania by slow hydrolysis of the isopropoxides of zirconium and titanium. Zirconium isopropoxide ($Zr(OC_3H_7)_4{\cdot}C_3H_7OH$, Alfa Products 99.9%) and titanium isopropoxide ($Ti(OC_3H_7)_4$, Alfa Products 99.999%) were dissolved in toluene in a nitrogen atmosphere to avoid premature hydrolysis of the isopropoxides. The resulting solutions were mixed with Cu/SiO_2 in a nitrogen atmosphere using the incipient wetness technique. The catalysts were then exposed to atmospheric water vapor for 24 h, to initiate the hydrolysis of the isopropoxides and the condensation of the resulting M–OH groups to produce M–O–M linkages. Since silica is hygroscopic (picking up 2% water by weight at equilibrium under typical laboratory humidity conditions) [20], it adsorbs atmospheric water. This slow adsorption of water promotes the condensation of the M–OH groups and reaction with the hydroxyl groups on the surface of the silica, resulting in significant branching and crosslinking of the resulting metal oxide gel. The dominance of condensation over hydrolysis enhances the structural stability of the deposited metal oxide after calcination [21]. After deposition of the zirconium/titanium oxide, the catalyst was calcined in air flowing at 60 cm^3 (STP)/min, while the temperature was increased from 273 to 698 K at 10 K/min, after which the temperature was held at 698 K for 5 h. The compositions of the catalysts used in this study are shown in table 1. The weight loadings of Cu, Zr, Ti on the catalysts were determined by ICP analysis. Measurement of the exposed Cu surface area by N_2O decomposition after reaction and catalyst reduction gave an average value of 0.61 m^2/g with a spread in values of $\pm$ 0.05 m^2/g, independent of whether or not Cu/SiO_2 had been promoted and independent of the composition of the added oxide.

Reactions were carried out in a stainless steel microreactor (7.7 mm ID) heated by a small furnace. Catalyst samples weighing 0.25 g were used in all cases. A type K thermocouple in the center of the catalyst bed was used to measure the catalyst temperature and the temperature was controlled by an Omega series CN-2010 programmable temperature controller. Purified gases were delivered to the reactor via Tylan model FC-280 mass flow controllers and the reactor effluent composition was analyzed with a quadrupole mass spectrometer (UTI model 100C). Bay Airgas UHP H_2 and He, and Matheson UHP CO and CO_2 were purified prior to use. Hydrogen was passed through a Deoxo unit (Engelhard) to remove O_2 impurities by forming water which was subsequently removed by a molecular sieve trap (3A Davison grade 564). Helium was passed through a molecular sieve trap for water removal. Carbon monoxide was passed through an ascarite trap for CO_2 removal and a molecular sieve trap for water removal. Carbon dioxide was passed through a hopcalite trap (80% MnO_2 + 20% CuO) to remove CO and a molecular sieve to remove water.

Freshly prepared catalysts were reduced initially in 10% H_2 in He flowing at 55 cm^3 (STP)/min as the temperature was raised from 298 to 523 K at 2 K/min. Additional reduction was carried out in pure H_2 (40 cm^3 (STP)/min) at 523 for 24 h. Catalyst activities were determined at a total gas pressure of 0.65 MPa and temperatures between 448 and 573 K. The reactor feed consisted of a mixture of H_2/CO or H_2/CO_2 ($H_2/CO_x = 3$) flowing at 60 cm^3 (STP)/min. Product composition measurements were made after the catalysts had been on stream for 2 h at 448 K, after which the reactor temperature was increased by 25 K increments and measurements were taken after 2 h following each 25 K temperature increase.

3. Results

Over all catalysts, during the hydrogenation of CO, the only products observed were methanol and methane. The temperature dependence of CO conversion to methanol and methane are presented in figures 1 and 2, respectively, for each of the catalysts listed in table 1. Since the equilibrium conversion of CO to methanol is five times greater than that of the most active catalyst at 573 K, the curve of equilibrium conversion versus temperature is not shown in figure 1. Apparent activation energies for CO hydrogenation to methanol and to methane are listed in table 2.

It is evident from figures 1 and 2 that Cu/SiO_2 free of either zirconia or titania is the least active catalyst for methanol synthesis. The addition of zirconia alone, the catalyst designated as Zr(100)/Ti(0), increases the methanol synthesis activity by up to three-fold. Substitution of a portion of the zirconia by titania reduces the methanol synthesis activity. As seen in figure 3a, the methanol synthesis

Table 2
Apparent activation energies for CO and CO_2 hydrogenation.[a]

Catalyst designation	E_a for CO hydrogenation to CH_3OH (kcal/mol)[b]	E_a for CO hydrogenation to CH_4 (kcal/mol)[c]	E_a for CO_2 hydrogenation to CH_3OH (kcal/mol)[d]
Zr(0)/Ti(0)	20	31	9
Zr(0)/Ti(100)	20	29	11
Zr(25)/Ti(75)	16	35	10
Zr(50)/Ti(50)	15	26	11
Zr(75)/Ti(25)	19	33	14
Zr(100)/Ti(0)	18	36	14

[a]Reaction conditions: $P = 0.65$ Mpa, $H_2/CO_x = 3$, total flow = 60 cm^3 (STP)/min, catalyst mass = 0.25 g.
[b]Temperatures used 498–573 K.
[c]Temperatures used 523–573 K.
[d]Temperatures used 448–523 K.

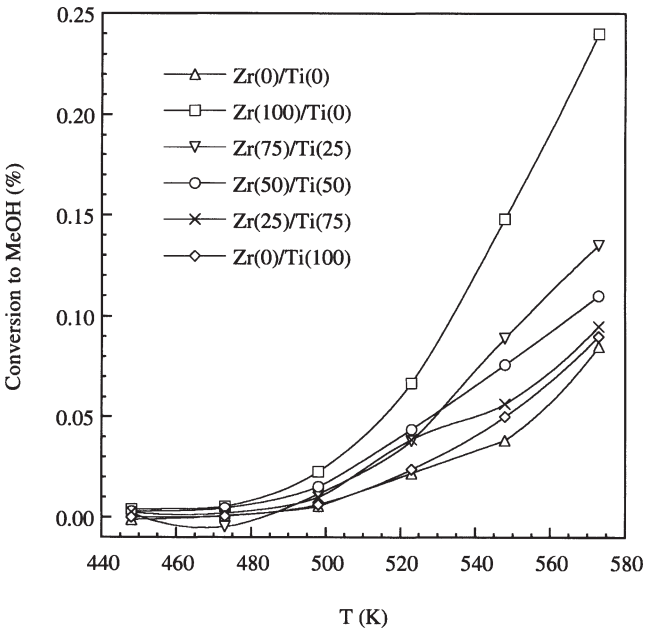

Figure 1. Effect of temperature on the conversion of CO to methanol during CO hydrogenation from $T = 448$ to 573 K: Catalyst mass = 0.25 g; $P = 0.65$ MPa; $H_2/CO = 3$; total flow rate = 60 cm^3 (STP)/min.

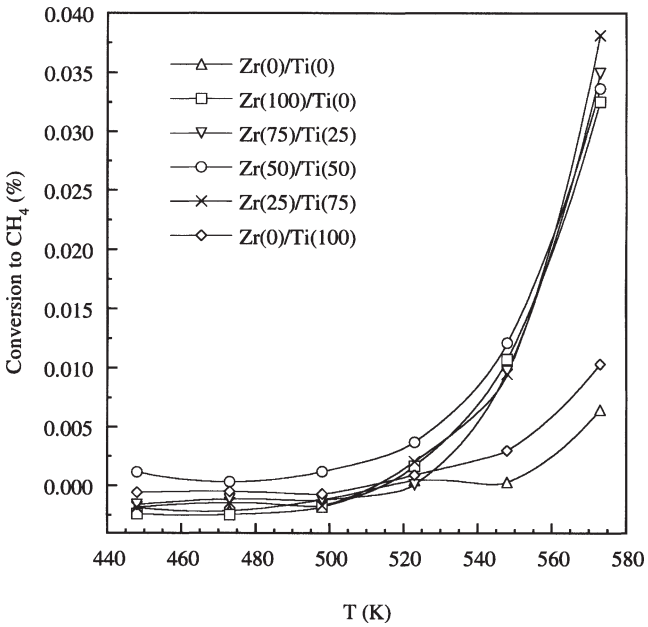

Figure 2. Effect of temperature on the conversion of CO to CH_4 during CO hydrogenation from $T = 448$ to 573 K: Catalyst mass = 0.25 g; $P = 0.65$ MPa; $H_2/CO = 3$; total flow rate = 60 cm^3 (STP)/min.

activity declines monotonically as the composition of the oxide additive changes from Zr(100)/Ti(0) to Zr(0)/Ti(100), and, in fact, the latter catalyst exhibits an activity not much different from that of Cu/SiO_2 alone. As can be seen in table 2, the apparent activation energy for methanol synthesis passes through a minimum as the composition of the oxide additive changes from Zr(100)/Ti(0) to Zr(0)/Ti(100). At both extremes the activation energy is very close to that for Cu/SiO_2, 20.1 kcal/mol.

The effects of zirconia and titania addition on the methane synthesis activity are more complex than those observed for methanol synthesis. As seen in figures 2 and 3b, Cu/SiO_2 exhibits the lowest methane synthesis activity. Addition of zirconia alone [Zr(100)/Ti(0)] increases the rate of methane synthesis about seven-fold. Surprisingly, substitution of titania for zirconia has little further effect on the methane synthesis activity until the proportion of titania rises above that of the catalyst designated as Zr(25)/Ti(75). When titania alone is added to the catalyst [Zr(0)/Ti(100)], the methane synthesis activity is only slightly greater than that observed for Cu/SiO_2. The apparent activation energy for methane synthesis varies in a non-systematic fashion as the composition of the added oxide changes from Zr(100)/Ti(0) to Zr(0)/Ti(100). The highest value of the activation energy is for the case of zirconia alone [Zr(100)/Ti(0)] and the lowest value is for the composition Zr(50)/Ti(50).

Because of the distinctly different manners in which the oxide additives affect the activities for methanol and methane synthesis, the selectivity for methanol synthesis is a function of both oxide composition and temperature, as illustrated in figure 4. At 520 K, all the catalysts exhibit a methanol selectivity in excess of 0.92. As the temperature rises, the methanol selectivity decreases, the degree

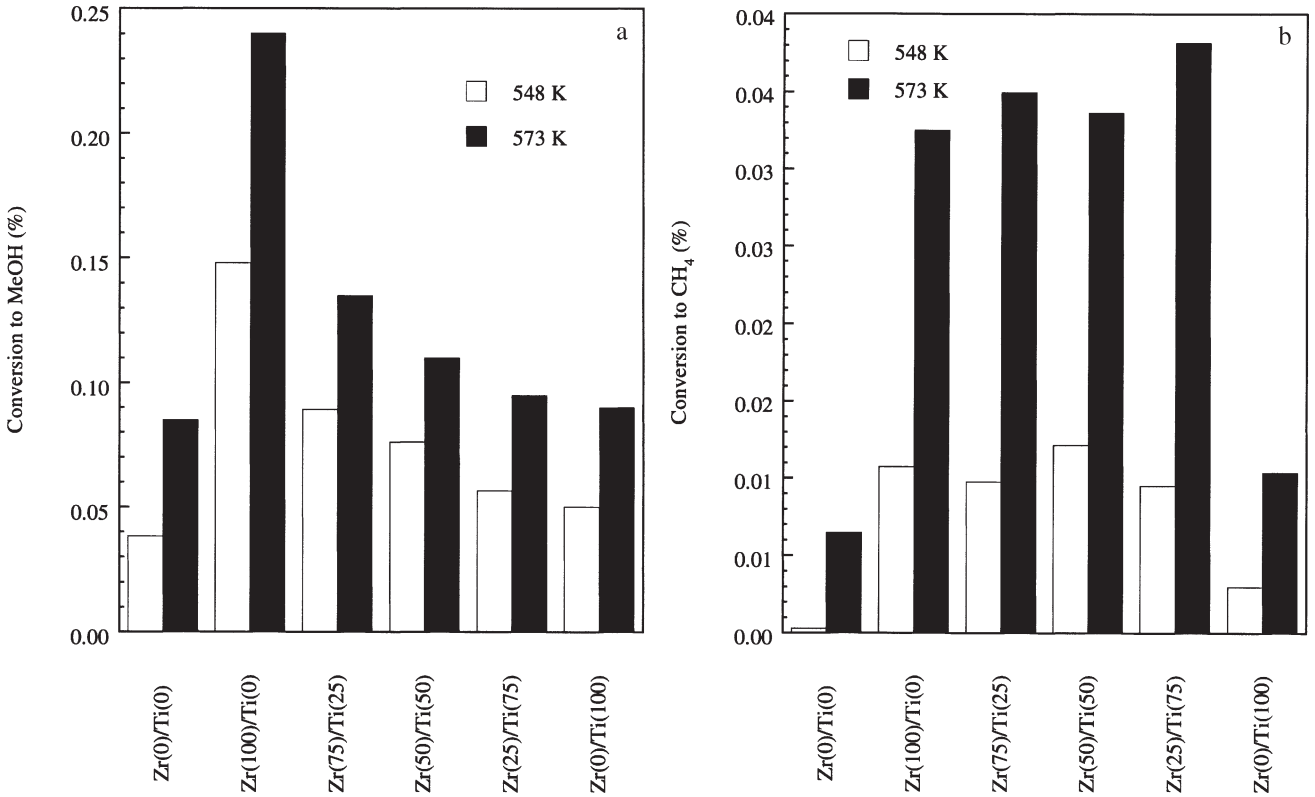

Figure 3. (a) Effect of catalyst composition on the conversion of CO to methanol during CO hydrogenation at $T = 548$ and 573 K: Catalyst mass = 0.25 g; $P = 0.65$ MPa; $H_2/CO = 3$; total flow rate = 60 cm^3 (STP)/min. (b) Effect of catalyst composition on the conversion of CO to methane during CO hydrogenation at $T = 548$ and 573 K: Catalyst mass = 0.25 g; $P = 0.65$ MPa; $H_2/CO = 3$; total flow rate = 60 cm^3 (STP)/min.

depending on the composition of the oxide additive and reflecting the differences in the apparent activation energies for methanol and methane synthesis. At 573 K, Cu/SiO_2 exhibits a selectivity of 0.93. Addition of zirconia alone reduces the selectivity to 0.88. Substitution of titania for zirconia further reduces the methanol selectivity until it reaches a minimum of 0.71 for the oxide composition designated Zr(25)/Ti(75). Interestingly, the addition of titania alone raises the methanol selectivity back up to 0.90.

Figure 5 shows a plot of CO_2 conversion to methanol versus temperature for the six catalysts listed in table 1. Also included is the equilibrium conversion to methanol for the reaction conditions used in this study. The equilibrium curve was adjusted to account for the decreasing partial pressure of CO_2 and H_2 due to the reverse water–gas-shift (RWGS) reaction by using the experimentally determined conversions of the RWGS reaction. Apparent activation energies for CO_2 hydrogenation to methanol are listed in table 2. For all catalysts, conversion rises with increasing temperature, until the equilibrium curve is approached. The effect of temperature on the conversion of CO_2 to CO via the RWGS reaction is illustrated in figure 6. The conversion of CO_2 to CO begins at ~523 K and the conversion of CO_2 to CO remains more than an order of magnitude below equilibrium at all temperatures. It can be seen from figure 6 that catalyst composition has little effect on the RWGS reaction.

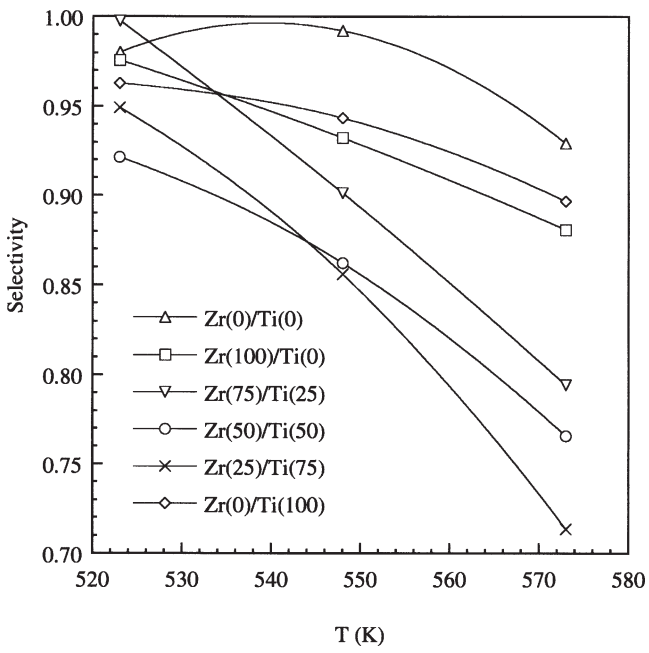

Figure 4. Effect of temperature on the methanol selectivity for CO hydrogenation from $T = 523$ to 573 K: Catalyst mass = 0.25 g; $P = 0.65$ MPa; $H_2/CO = 3$; total flow rate = 60 cm^3 (STP)/min. Selectivity = conversion of CO to CH_3OH / (conversion of CO to CH_3OH + conversion of CO to CH_4).

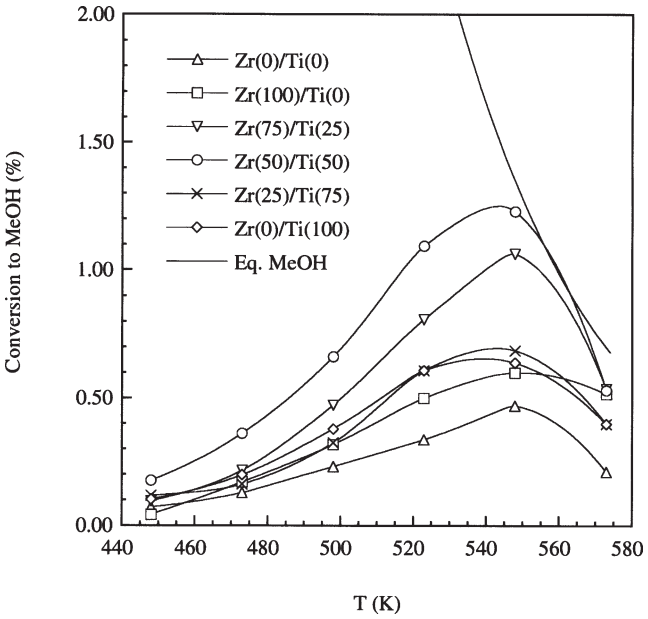

Figure 5. Effect of temperature on the conversion of CO_2 to methanol during CO_2 hydrogenation from $T = 448$ to 573 K: Catalyst mass = 0.25 g; $P = 0.65$ MPa; $H_2/CO_2 = 3$; total flow rate = 60 cm^3 (STP)/min.

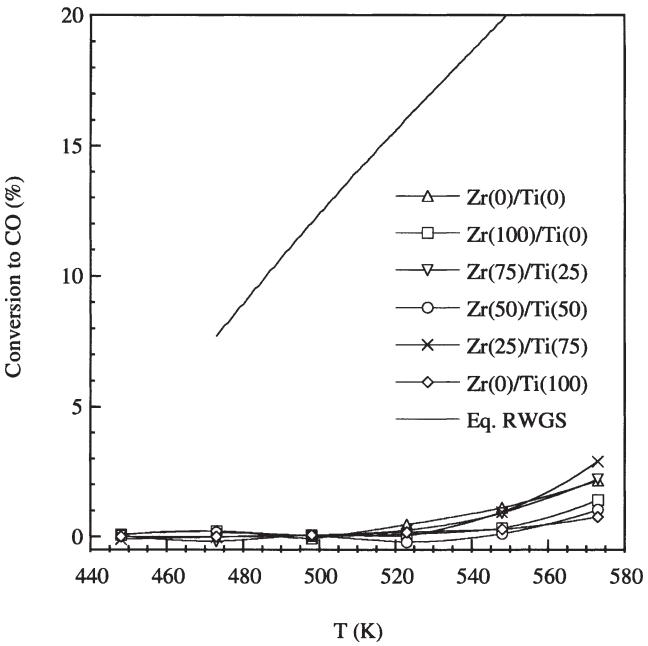

Figure 6. Effect of temperature on the conversion of CO_2 to CO during CO_2 hydrogenation from $T = 448$ to 573 K: Catalyst mass = 0.25 g; $P = 0.65$ MPa; $H_2/CO_2 = 3$; total flow rate = 60 cm^3 (STP)/min.

The effect of catalyst composition on the conversion of CO_2 to methanol is shown in figure 7. In contrast to CO hydrogenation, both titania and zirconia enhance the methanol synthesis activity. Mixtures of zirconia and titania appear to have a synergistic effect and the highest methanol synthesis activity is achieved when the oxide composition is Zr(50)/Ti(50). The effect of catalyst composition on the selectivity to methanol is shown in figure 8. For all catalysts and at all temperatures the selectivity to methane is

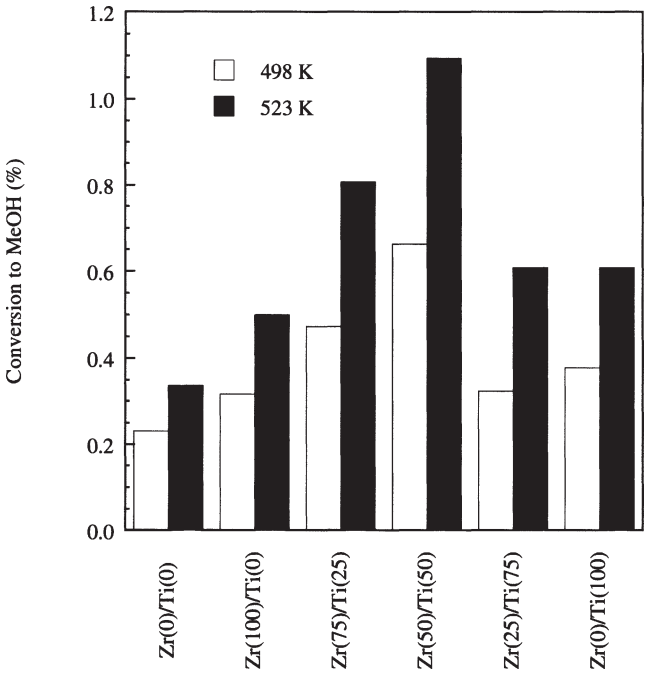

Figure 7. Effect of catalyst composition on the conversion of CO_2 to methanol during CO_2 hydrogenation from $T = 448$ to 523 K: Catalyst mass = 0.25 g; $P = 0.65$ MPa; $H_2/CO_2 = 3$; total flow rate = 60 cm^3 (STP)/min.

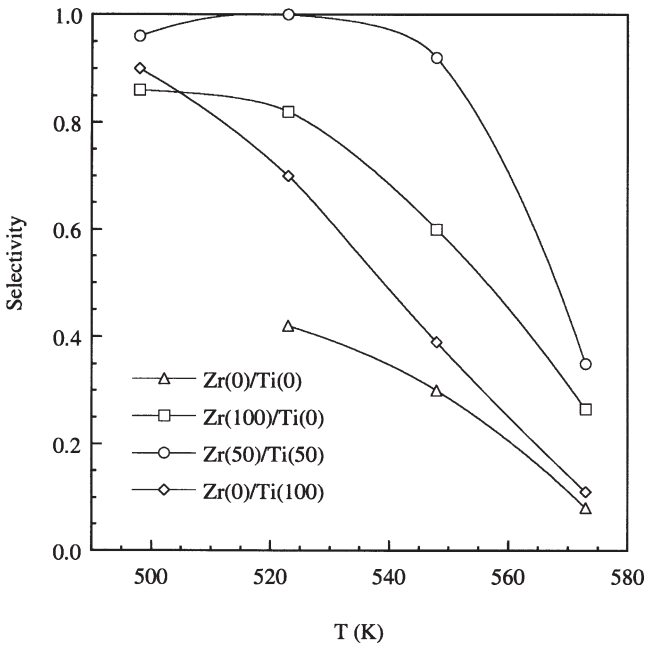

Figure 8. Effect of temperature on the methanol selectivity for CO_2 hydrogenation from $T = 498$ to 573 K: Catalyst mass = 0.25 g; $P = 0.65$ MPa; $H_2/CO_2 = 3$; total flow rate = 60 cm^3 (STP)/min. Selectivity = conversion of CO_2 to CH_3OH/(conversion of CO_2 to CH_3OH + conversion of CO_2 to CO).

<0.03. The highest selectivity to methanol is achieved for the catalyst containing equivalent amounts of zirconia and titania, independent of the reaction temperature. As temperature increases, the selectivity to methanol decreases as a consequence of the approach of the methanol synthesis

reaction to equilibrium at the same time that the RWGS remains far from equilibrium.

4. Discussion

The addition of ZrO_2/TiO_2 mixtures to Cu/SiO_2 has distinctly different effects on the hydrogenation of CO and CO_2. In the case of CO hydrogenation, the highest methanol synthesis activity is found for the catalyst in which only ZrO_2 is added to Cu/SiO_2. Decreasing the proportion of ZrO_2 and raising the proportion of TiO_2 reduces the methanol synthesis activity monotonically. The addition of ZrO_2 to Cu/SiO_2 also enhances the methane synthesis activity. Reducing the proportion of ZrO_2 relative to that of TiO_2 has little effect on the methane synthesis activity until the weight fraction of ZrO_2 falls below 25%, at which point the activity decreases back towards that characteristic of Cu/SiO_2.

The increase in catalyst activity for methanol synthesis from CO/H_2 when ZrO_2 is added to Cu/SiO_2 has been ascribed to the preferential adsorption of CO on ZrO_2 [12]. CO, being a weakly basic molecule, is thought to interact with the Brønsted acidic sites on the surface of ZrO_2, leading to the formation of formate groups. Since both ZrO_2 and TiO_2 are amphoteric [14], the bridging OH groups present on the surface of these oxides can act as either acids or bases depending on the character of the adsorbate. Consistent with this interpretation, the infrared absorbance of bridging OH groups present on the surface of ZrO_2 decreases upon adsorption of CO and concurrently the infrared absorbance of bands associated with formate groups increases [22]. The decrease in methanol synthesis activity upon displacement of ZrO_2 by TiO_2 suggests that the strength of the acid sites present on the mixed metal oxide is lower than that for ZrO_2 alone, even though it has been shown that the concentration of acidic sites of a fixed strength passes through a maximum for a 50/50 mixture of ZrO_2/TiO_2 [17]. Further interpretation of the effects of the ZrO_2/TiO_2 ratio on the methanol synthesis activity of Cu/SiO_2 will require characterization of the strength and concentration of the acidity present on the surface of the mixed metal oxide.

The enhancement in the methane synthesis activity of Cu/SiO_2 upon addition of ZrO_2 is similar to that reported previously for Rh [23]. This effect can be interpreted in the following manner. CO molecules adsorbed on Cu sites that lie in close proximity to ZrO_2 can interact through their O end with Lewis acid sites (e.g., Zr^{4+} cations) exposed at the surface of the oxide. Such Lewis acid–base interactions have been shown to weaken the C–O bond thereby contributing to its dissociation, or to its cleavage after partial hydrogenation of the CO molecule [23]. While TiO_2 is known to affect CO in a manner similar to ZrO_2, and for TiO_2 to be somewhat more effective than ZrO_2 in promoting the hydrogenation of CO to CH_4 [23], this appears not to be the case in the studies reported here. This may have something to do with the manner in which TiO_2 interacts with ZrO_2, and the manner in which the mixed metal oxide contacts the Cu particles dispersed on SiO_2.

The effects of ZrO_2/TiO_2 additions on the activity of Cu/SiO_2 for the synthesis of methanol from CO_2/H_2 are easier to interpret than for the case of methanol synthesis from CO/H_2. CO_2, a Lewis acid, has been shown to interact with the bridging OH groups present on the ZrO_2 surface to form bicarbonate species [13]. Bicarbonate species are a crucial intermediate for methanol synthesis from CO_2 on $Cu/ZrO_2/SiO_2$ catalysts [13]. Work done by others has shown a maximum in concentration of basic sites measured at intermediate compositions of ZrO_2 and TiO_2 [17]. The presence of a maximum in the methanol synthesis activity as the ratio of ZrO_2/TiO_2 is varied parallels the maximum in basic sites present, indicating the possibility of greater surface concentrations of methanol synthesis intermediates. *In situ* infrared studies of methanol synthesis from CO_2/H_2 are currently in progress and are aimed at identifying in detail the role of acid/base characteristics of ZrO_2/TiO_2 mixtures added to Cu/SiO_2.

5. Conclusions

Addition of ZrO_2 to Cu/SiO_2 increases the rate of methanol synthesis from CO and H_2 over that observed over Cu/SiO_2. Substitution of a portion of the ZrO_2 by TiO_2 decreases the methanol synthesis relative to that observed with ZrO_2 alone. The higher activity of $ZrO_2/Cu/SiO_2$ compared to Cu/SiO_2 is attributed to the presence of acidic bridging OH groups on the surface of ZrO_2 that can adsorb Lewis basic CO to form formate groups, a key intermediate along the pathway from CO to methanol. Substitution of ZrO_2 by TiO_2 appears to lower the strength of the acid sites and hence the catalyst activity for methanol synthesis. The presence of ZrO_2 also enhances the activity of Cu for methane synthesis from CO and H_2. This effect is attributed to the occurrence of Lewis acid–base interactions between the O atom of CO adsorbed on Cu and exposed Zr^{4+} cations present on the surface of the dispersed ZrO_2.

The methanol synthesis activity of Cu/SiO_2 for CO_2 hydrogenation goes through a maximum as the ratio of ZrO_2 to TiO_2 added to the catalyst is varied. The highest activity is achieved for a 50/50 wt% mixture of ZrO_2 and TiO_2. This pattern is attributed to the variation in the concentration of basic adsorption sites on the surface of the mixed metal oxide. Such sites are desirable for the adsorption of CO_2 to form bicarbonate groups, which can then undergo hydrogenation to form methanol. The rate of the reverse water–gas-shift (RWGS) reaction is unaffected by the composition of the dispersed oxide and occurs at the same rate as on Cu/SiO_2, leading to the conclusion that the RWGS reaction takes place solely on the surface of Cu.

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