Effects of zirconia promotion on the activity of Cu/SiO_2 for methanol synthesis from CO/H_2 and CO_2/H_2

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The effect of zirconia promotion on Cu/SiO_2 for the hydrogenation of CO and CO_2 at 0.65 MPa has been investigated at temperatures between 473 and 573 K. With increasing zirconia loading, the rate of methanol synthesis is greatly enhanced for both CO and CO_2 hydrogenation, but more significantly for CO hydrogenation. For example, at 533 K the methanol synthesis activity of 30.5 wt% zirconia-promoted Cu/SiO_2 is 84 and 25 times that of unpromoted Cu/SiO_2 for CO and CO_2 hydrogenation, respectively. For all catalysts, the rate of methanol synthesis from CO_2/H_2 is higher than that from CO/H_2. The apparent activation energy for methanol synthesis from CO decreases from 22.5 to 17.5 kcal/mol with zirconia addition, suggesting that zirconia alters the reaction pathway. For CO_2 hydrogenation, the apparent activation energies ($\sim$12 kcal/mol) for methanol synthesis and the reverse water–gas shift (RWGS) reaction are not significantly affected by zirconia addition. While zirconia addition greatly increases the methanol synthesis rate for CO_2 hydrogenation, the effect on the RWGS reaction activity is comparatively small. The observed effects of zirconia are interpreted in terms of a mechanism, in which zirconia serves to adsorb either CO or CO_2, whereas Cu serves to adsorb H_2. It is proposed that methanol is formed by the hydrogenation of the species adsorbed on zirconia.

Keywords: zirconia promotion for hydrogenation, Cu/SiO_2 activity in hydrogenation, methanol synthesis from CO/H_2, methanol synthesis from CO_2/H_2, CO and CO_2 hydrogenation

1. Introduction

The synthesis of methanol from either CO or CO_2 is an exothermic process, and consequently, the equilibrium yield of methanol declines with increasing temperature. For this reason, efforts have been undertaken to enhance the activity of supported Cu catalysts, so that they might be operated at lower temperature. These studies have shown that support composition can affect the methanol synthesis activity of copper, but that in most instances the effect is different depending on the composition of the feed (CO/H_2 vs. CO_2/H_2). Zirconia has emerged as a particularly interesting support material, since it enhances the activity of copper for methanol synthesis from both CO/H_2 and CO_2/H_2 [1–11]. While the effects of zirconia have been examined by various authors, there is no agreement regarding the means by which zirconia promotes methanol synthesis. For example, it has been proposed that the high methanol synthesis activity of zirconia-supported copper catalysts is due to electron density transfer from Cu to ZrO_2 [2], the formation of highly active sites resulting from microcrystalline Cu particle stabilization by ZrO_2 [8], Cu substitution into ZrO_2 sites [11], and the presence of amorphous zirconia stabilized by Cu ions [6]. In situ infrared studies of CO_2 hydrogenation over zirconia-supported Cu show the presence of formate groups; however, there appears to be no correlation between the disappearance of formate species and the rate of methanol formation [6]. Attempts to explain how zirconia influences the methanol synthesis activity of Cu are further clouded by the differences in catalyst preparation and reaction conditions used by different authors. Thus, it remains unclear whether zirconia acts as a textural promoter, a chemical promoter, or a bifunctional catalyst.

The present study was undertaken to investigate the effects of incremental levels of zirconia promotion on silica-supported Cu on the activity and selectivity of Cu for methanol from both CO/H_2 and CO_2/H_2, and to compare these results with those obtained for zirconia-supported copper and silica-supported copper. It was of interest to determine whether the presence of zirconia affects the activation energy for methanol synthesis from CO and CO_2. Since the hydrogenation of CO_2 can result in the formation of CO via the reverse water–gas shift (RWGS) reaction, the influence of zirconia on the progress of this reaction was also examined.

2. Experimental

The catalysts used in these investigations were prepared in two steps. The first step involved the preparation of Cu supported on SiO_2 by means of deposition–precipitation using the procedure described by van der Grift et al. [12]. Materials used were copper(II) nitrate

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($Cu(NO_3)_2{\cdot}6H_2O$, Alfa Products, 99.999%), urea (NH_2CONH_2, Alfa Products, 99.5%), nitric acid (HNO_3, Mallinckrodt, 70.5%), fumed silica (SiO_2, Cab-O-Sil, M-5, SA $= 200$ m^2/g), and distilled water. Precipitation of copper ions results from the elevation of the solution pH by the hydrolysis of urea at 363 K. A final pH of 7 was observed. Following copper ion precipitation, the precursor was filtered, washed, and dried in a vacuum oven at 373 K for 26 h. Subsequently, the precursor was calcined in air at a flow rate of 60 cm^3/min at 473 K for 1 h, at 573 K for 1 h, and finally at 723 K for 17 h. The deposition–precipitation procedure has been shown to produce Cu/SiO_2 catalysts with higher methanol synthesis activities than catalysts prepared by other techniques [13].

The second step in catalyst preparation involved the impregnation of zirconia from an aqueous solution of zirconium dinitrate oxide ($ZrO(NO_3)_2{\cdot}xH_2O$, Alfa Products, 99.9985%). Following impregnation the catalysts were dried in a vacuum oven at 373 K for 26 h, and calcined in air at a flow rate of 60 cm^3/min at 473 K for 1 h, at 573 K for 1 h, and finally at 723 K for 17 h. Cu/SiO_2 catalysts with zirconia loadings from 0 to 30.5 wt% were prepared using this procedure.

Zirconia and Cu/ZrO_2 catalysts were also prepared as reference catalysts. The ZrO_2 support (SA $= 20$ m^2/g) was prepared by decomposing zirconium dinitrate oxide at 573 K for 4 h in 1 atm of air flowing at 60 cm^3/min atmospheric pressure air. The addition of Cu was performed by the same deposition–precipitation method as for the Cu/SiO_2 catalysts.

The Cu and Zr contents of the catalysts were determined by X-ray fluorescence analysis. The Cu surface areas of the catalysts were determined by N_2O titration, following the procedure described by Evans et al. [14]. After catalyst reduction (conditions of which are described shortly), the samples were cooled in flowing He to 333 K. Pulses of 3% UHP N_2O in He were introduced into the reactor, and the N_2O consumption was quantified using a Varian model 3700 gas chromatograph equipped with a thermal conductivity detector and a 1.8 m long column packed with Porapak Q. Exposed copper surface areas were calculated assuming a reaction stoichiometry of two copper atoms per oxygen atom and a copper surface density of 1.46×10^{19} Cu $atoms/m^2$ [13]. ZrO_2 by itself did not consume measurable quantities of N_2O.

Matheson UHP H_2, CO, and He and Coleman instrument purity CO_2 were purified prior to use. Hydrogen was passed through a Deoxo unit (Engelhard) to remove O_2 impurities by forming water which is subsequently removed by a molecular sieve trap (3A Davidson grade 564). CO was passed through a bed of glass beads at 573 K to remove iron carbonyls followed by an ascarite trap for CO_2 removal and a molecular sieve trap for water removal. Ar was passed through an oxysorb (CrO_3) trap to remove O_2 and then a molecular sieve trap. CO_2 was passed through a hopcalite trap (80% MnO_2 + 20% CuO) to remove CO and a molecular sieve trap to remove water.

Reactions were carried out in a stainless steel microreactor (7.7 mm i.d.) heated by a small furnace. Catalyst samples weighing 0.15 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 analysis of the effluent gas composition was accomplished with a quadrupole mass spectrometer (EAI model 250B).

Prior to all experiments fresh catalysts were reduced in 10% H_2 in He at a total flow rate of 60 cm^3/min from ambient temperature to 523 K at 2 K/min, followed by pure hydrogen at 523 K and 40 cm^3/min for > 8 h. Catalyst samples were re-reduced in pure hydrogen at 523 K and 40 cm^3/min for > 8 h. Catalyst activities were determined at a total gas pressure of 0.65 MPa and temperatures between 473 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/min. Product composition measurements were made after 2 h on stream at 473 K after which the reactor temperature was increased by 20 K increments and measurements were taken after 1 h following the 20 K temperature increase.

Reaction activities are reported as turnover frequencies (TOF), molecules of product formed per copper surface atom per second. The copper surface areas obtained by N_2O titration were used in calculating the TOF's. Reported selectivities are defined as molecules of product formed per molecule of CO or CO_2 converted.

3. Results

The composition and Cu surface areas of the catalysts tested are listed in table 1. Pure ZrO_2 was also tested but found to have negligible acitivity for the reactions of interest under the conditions used in this study.

The temperature dependence of CO conversion to methanol for Cu/SiO_2, ZrO_2-promoted Cu/SiO_2, and

Table 1
Cu surface areas of Cu/SiO_2, ZrO_2-promoted Cu/SiO_2, and Cu/ZrO_2 catalysts

Cu content (wt%)	ZrO_2 content (wt%)	Cu surface area (m^2/g-cat)
5.7	0.0	1.36
5.4	1.7	1.07
5.7	3.8	1.01
5.4	6.5	0.99
5.7	16.4	1.24
5.7	30.5	0.76
5.7	94.3	1.68

Cu/ZrO$_2$ is presented in fig. 1. The equilibrium conversion of CO is also shown for comparison. For each catalyst the CO conversion to methanol increases with increasing temperature and approaches the equilibrium conversion at high temperature. The highest conversion is observed for Cu/ZrO$_2$. Promotion of Cu/SiO$_2$ with ZrO$_2$ increases the catalyst activity (TOF) for methanol formation monotonically, as shown in fig. 2. The data are normalized to the methanol synthesis activity for Cu/SiO$_2$, which is 1.87×10^{-3}, 4.23×10^{-3}, and 7.94×10^{-3} s^{-1} at 533, 553, and 573 K, respectively. The selectivity to methanol for all of the catalysts is approximately 96%, with the only other product observed being methane. Fig. 3 shows that the apparent activation energy for methanol synthesis decreases from 22.5 kcal/mol to 17.5 kcal/mol as the loading of ZrO$_2$ increases from zero to 6.5 wt%, and then remains essentially constant as the loading increases to 30.5 wt%. The apparent activation energy for methanol synthesis over Cu/ZrO$_2$ is 13.1 kcal/mol. Only those rate data for which the CO conversion was far from the equilibrium conversion were used to determine the apparent activation energy for methanol synthesis.

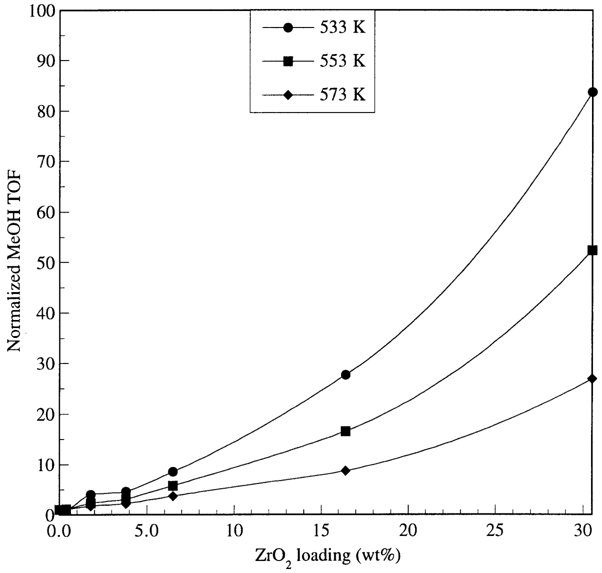


Fig. 2. Effect of ZrO$_2$ loading on the TOF for methanol synthesis of ZrO$_2$-promoted Cu/SiO$_2$ relative to that of Cu/SiO$_2$: catalyst mass = 0.15 g; $P = 0.65$ MPa; H$_2$/CO = 3; total flow rate = 60 cm^3/min.

Fig. 4 shows a plot of CO$_2$ conversion to methanol versus temperature for Cu/SiO$_2$, ZrO$_2$-promoted Cu/SiO$_2$, and Cu/ZrO$_2$. Also shown is the equilibrium conversion versus temperature. For each catalyst, conversion rises and then approaches the equilibrium conversion curve asymptotically. The effect of temperature on the conversion of CO$_2$ to CO via the reverse water–gas shift (RWGS) reaction is illustrated in fig. 5. While the conversion of CO$_2$ to CO rises with temperature for each catalyst, the conversion remains about two orders of magnitude below that corresponding to equilibrium for the RWGS reaction.

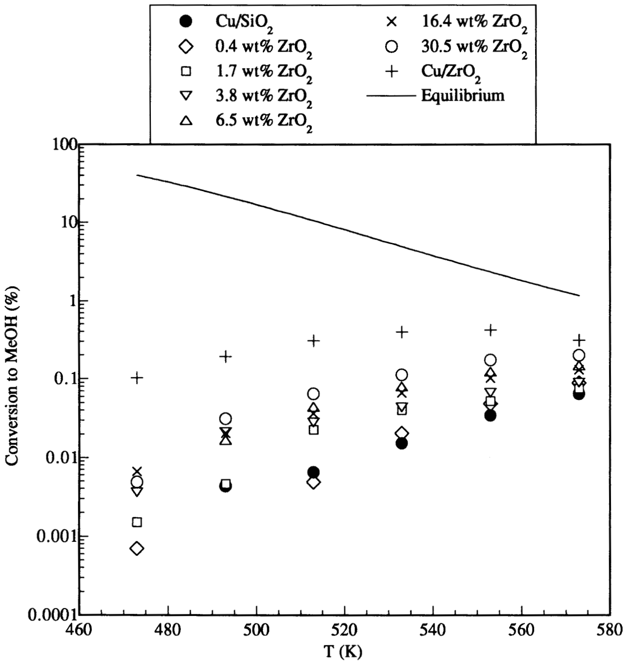


Fig. 1. Effect of temperature on the conversion of CO to methanol during CO hydrogenation over Cu/SiO$_2$, ZrO$_2$-promoted Cu/SiO$_2$, and Cu/ZrO$_2$: catalyst mass = 0.15 g; $P = 0.65$ MPa; H$_2$/CO = 3; total flow rate = 60 cm^3/min.

The effects of ZrO$_2$ promotion on the rates of methanol synthesis and the RWGS reaction are shown in fig. 6. The data are again normalized to the activity for Cu/SiO$_2$, which is 2.75×10^{-3}, 8.24×10^{-3}, 1.38×10^{-2}, 2.14×10^{-2} and 2.15×10^{-2} s^{-1} for methanol synthesis, and 7.65×10^{-3}, 1.51×10^{-2}, 2.77×10^{-2}, 4.87×10^{-2}

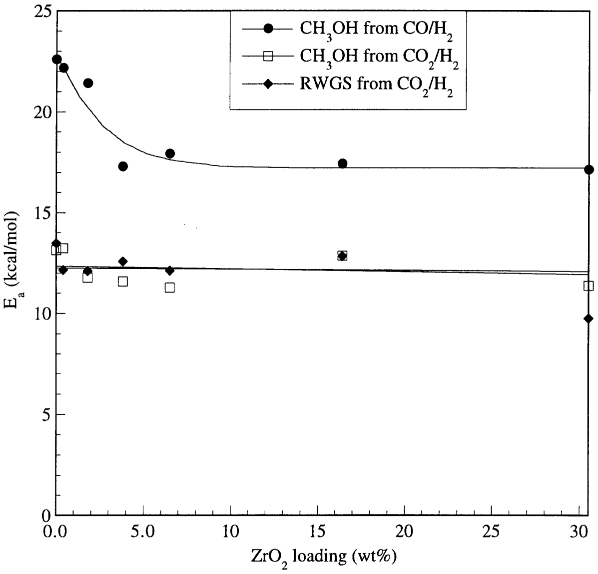


Fig. 3. Effect of ZrO$_2$ promotion on the apparent activation energies for methanol synthesis and RWGS reaction.

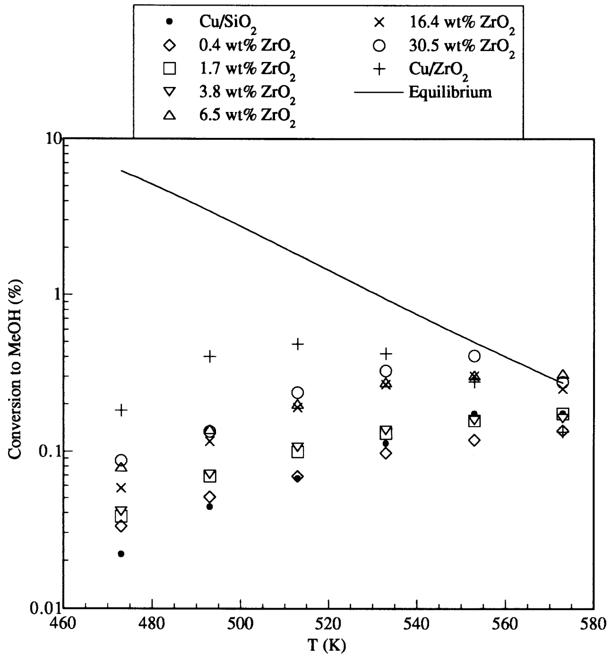


Fig. 4. Effect of temperature on the conversion of CO_2 to methanol during CO_2 hydrogenation over Cu/SiO_2, ZrO_2-promoted Cu/SiO_2, and Cu/ZrO_2: catalyst mass = 0.15 g; $P = 0.65$ MPa; $H_2/CO_2 = 3$; total flow rate = 60 cm^3/min.

and 9.22×10^{-2} s^{-1} for the RWGS reaction at 473, 513, 533, 553, and 573 K, respectively. With increasing ZrO_2 loading, the turnover frequency for methanol synthesis rises monotonically. By contrast, the turnover frequency for the RWGS reaction at first decreases slightly until it reaches a minimum for a ZrO_2 loading of 3.8 wt%, whereafter it rises very slowly. The effects of ZrO_2 on methanol selectivity at 493 and 573 K are presented in fig. 7. As for CO hydrogenation the selectivity to methane was small and < 3% in all cases. At 493 K the methanol selectivity is 34% for unpromoted Cu/SiO_2, rises to a maximum of about 87% for a ZrO_2 loading of 3.8 wt%, and then decreases to about 33% for ZrO_2 loading higher than 16.4 wt%. At 573 K the maximum selec-

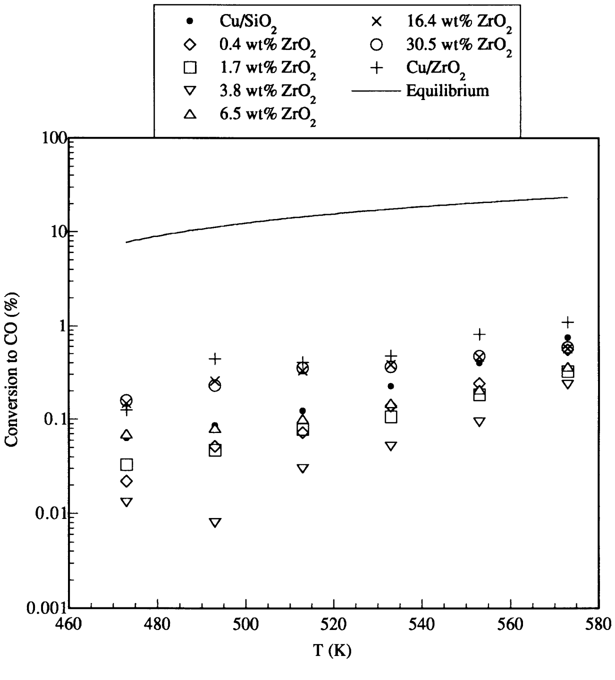


Fig. 5. Effect of temperature on the conversion of CO_2 to CO during CO_2 hydrogenation over Cu/SiO_2, ZrO_2-promoted Cu/SiO_2, and Cu/ZrO_2: catalyst mass = 0.15 g; $P = 0.65$ MPa; $H_2/CO_2 = 3$; total flow rate = 60 cm^3/min.

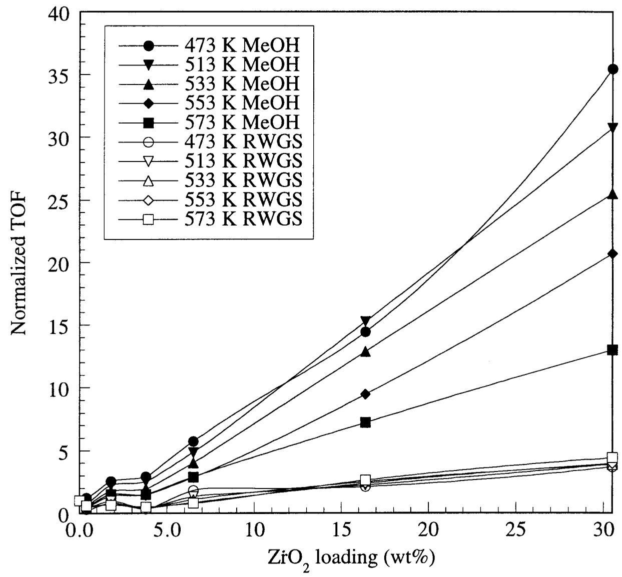


Fig. 6. Effect of ZrO_2 loading on the TOF's for methanol synthesis and RWGS of ZrO_2-promoted Cu/SiO_2 relative to those of Cu/SiO_2: catalyst mass = 0.15 g; $P = 0.65$ MPa; $H_2/CO_2 = 3$; total flow rate = 60 cm^3/min.

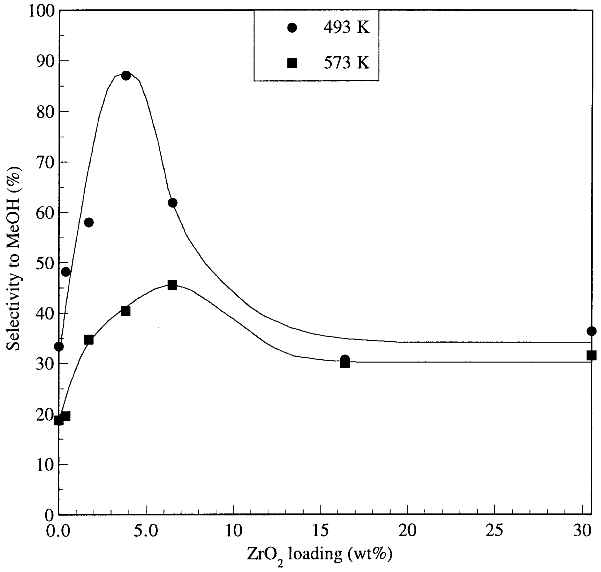


Fig. 7. Effect of ZrO_2 loading on the methanol selectivity of ZrO_2-promoted Cu/SiO_2: catalyst mass = 0.15 g; $P = 0.65$ MPa; $H_2/CO_2 = 3$; total flow rate = 60 cm^3/min.

tivity to methanol observed is 45% and is obtained on the 6.5 wt% ZrO_2 Cu/SiO_2 catalyst. The influence of temperature on methanol selectivity is given in fig. 8. In all cases the selectivity to methanol is nearly constant at low temperatures and then decreases at higher temperatures as the conversion of CO_2 to methanol approaches equilibrium. The selectivity to methanol is generally well above that projected by thermodynamic equilibrium since the RWGS reaction is far from equilibrium.

The dependence of the apparent activation energies for methanol synthesis and RWGS from CO_2 are shown in fig. 3. The activation energies for both reactions are essentially the same, and only small decreases in the activation energies of each reaction are observed as the loading of ZrO_2 increases. The apparent activation energies for methanol synthesis and the RWGS reaction on Cu/ZrO_2 were determined to be 11.9 and 11.6 kcal/mol, respectively, which is very close to that determined for ZrO_2-promoted Cu/SiO_2.

4. Discussion

Consistent with previous studies [15,16], we find that the activity of Cu/SiO_2 for methanol synthesis from CO/H_2 is quite small in comparison to that for methanol synthesis from CO_2/H_2. The difference in the reactivities of CO and CO_2 can be attributed to differences in the reaction pathways for CO and CO_2 hydrogenation to methanol. In the case of CO, adsorbed CO is thought to undergo hydrogenation to form a formyl species before subsequent hydrogenation can take place to produce formaldehyde, methoxy species, and ultimately methanol [15 and references therein]. The formation of formyl species is energetically unfavorable [17], and hence the surface concentration of this species is exceedingly small. By contrast, the hydrogenation of CO_2 is believed to produce formate species [15 and references therein, 18]. Subsequent hydrogenation of formate species to form methylenebisoxy species, formaldehyde, methoxy species, and ultimately methanol is more rapid.

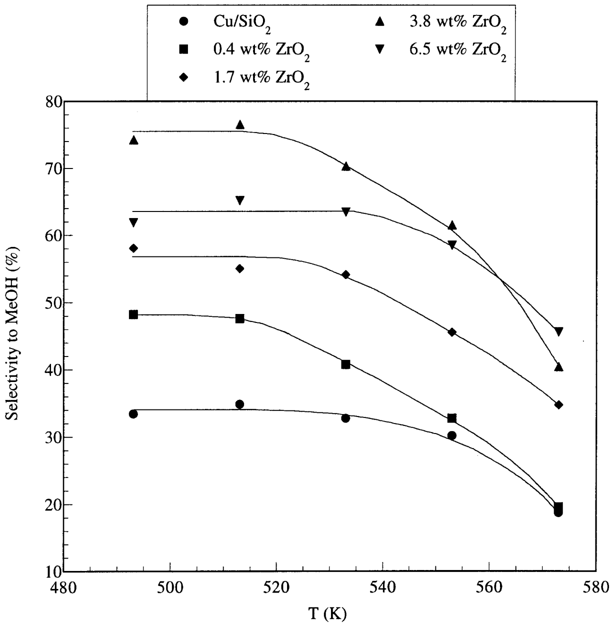
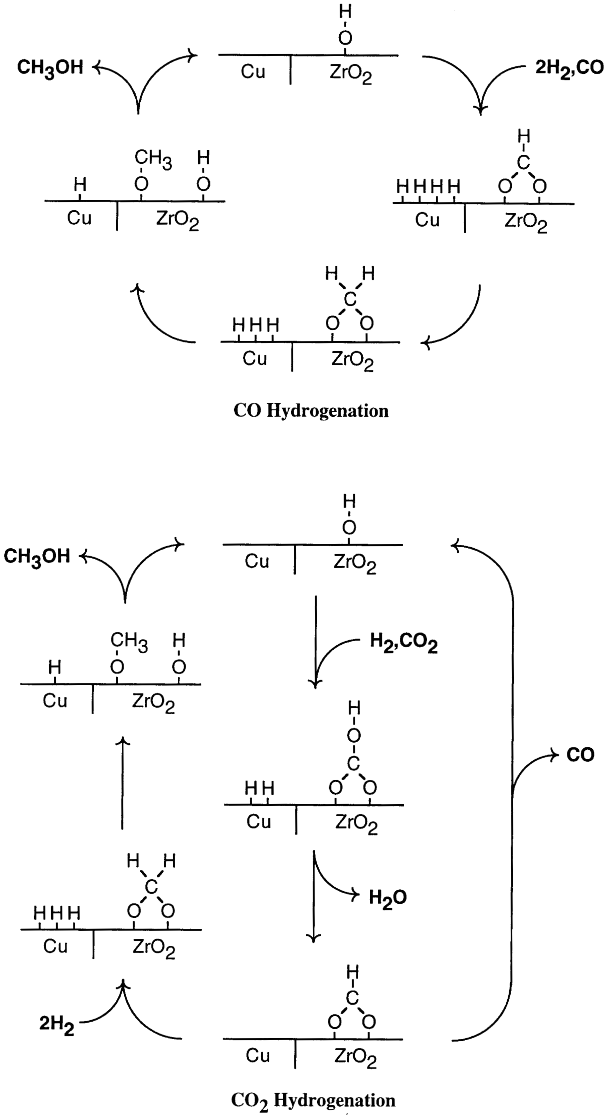


Fig. 8. Effect of temperature on the methanol selectivity of ZrO_2-promoted Cu/SiO_2: catalyst mass $= 0.15$ g; $P = 0.65$ MPa; H_2/$CO_2 = 3$; total flow rate $= 60\,cm^3$/min.

ZrO_2 promotion of Cu/SiO_2 enhances the rate of methanol synthesis from CO/H_2 by as much as a factor of 85 at 533 K and up to a factor of 25 at 573 K. ZrO_2 promotion of Cu also reduces the activation energy for methanol synthesis by about 5 kcal/mol. Since the variation in the methanol synthesis turnover frequency with zirconia promotion at a given temperature is much larger than the variation in Cu surface area, the effects of the promoter are attributed to intimate contact between the promoter and the particles of supported Cu, rather than to differences in Cu dispersion between catalyst samples. While the exact mode of contact between ZrO_2 and Cu has not been established, it is reasonable to suggest that at least a portion of the ZrO_2 decorates the surface of the Cu particles in manner similar to that established for a number of metal-oxide-promoted metals [19]. Under such circumstances, one can envision that CO molecules adsorbed on Cu in the vicinity of the ZrO_2 might interact with either exposed Zr^{4+} cations or with OH groups present on the surface of ZrO_2. The first of these interactions is identical to that proposed to explain the role of ZrO_2 and other oxides such as TiO_2 in enhancing the activity of Rh and other transition metals for CO hydrogenation to methane [19,20]. In that case the interaction is thought to facilitate the cleavage of the C–O bond in either CO or partially hydrogenated species such as HCO or H_2CO. Thus, it is conceivable that in the case of Cu, the interaction of the oxygen end of CO with a Zr^{4+} cation produces a Lewis acid–base adduct which undergoes hydrogenation more readily than CO adsorbed on Cu alone, but that the net effect of the interaction is insufficient to cleave the C–O bond, and hence, methanol formation results. An alternative interpretation is that CO interacts with an OH group on the ZrO_2 to form a formate group, as shown in fig. 9. Since formate groups can be hydrogenated to produce methanol, a new pathway not requiring the formation of formyl species is created. The creation of a lower energy pathway to methanol by ZrO_2 promotion is suggested by the decrease in the apparent activation energy observed with the addition of ZrO_2. The role of formate groups in zirconia-containing Cu catalysts is suggested by in situ infrared observations of CO hydrogenation over zirconia-promoted Cu/SiO_2 [21], which show that Cu accelerates the rate at which formate species adsorbed on zirconia are converted to methanol. Formate species have also been observed to form during CO adsorption on zirconia [22] and to participate in methanol synthesis



CO Hydrogenation

CO$_2$ Hydrogenation

Fig. 9. Proposed reaction pathways for methanol synthesis from CO/H$_2$ and CO$_2$/H$_2$ over ZrO$_2$-containing Cu catalysts.

from CO over pure zirconia [23]. A scheme similar to that shown in fig. 9 has been proposed previously to explain the effects of ZnO on the rate of methanol synthesis from CO over Cu [24,25].

The effects of ZrO$_2$ on the hydrogenation of CO$_2$ are more complex than on the hydrogenation of CO, because the former reaction produces CO via the RWGS reaction in addition to methanol. At low CO$_2$ conversions, where both reactions can be taken to be irreversible, previous studies carried out with ZrO$_2$-supported Cu have shown that methanol and CO are produced via parallel processes [8,26]. The nearly identical apparent activation energies for both processes (see fig. 3) suggest that the rate-limiting steps for both reactions involve a common intermediate. Evidence from in situ infrared studies of CO$_2$ hydrogenation over Cu/SiO$_2$ and the effects of H$_2$ versus D$_2$ on the rates of methanol synthesis and the RWGS reaction suggest that O=CO–H, an isomer of formate, is a common intermediate leading to both methanol and CO [15]. Similarly, bond-order-conservation Morse-potential (BOC-MP) calculations suggest that formate species are intermediates for both CO and methanol formation from CO$_2$ and H$_2$, and indicate that the magnitude of the energy barrier for CO formation from formate species is only 1 kcal/mol greater than that for methanol formation from formate species [17]. The independence of the activation energies on ZrO$_2$ loading is surprising and not readily explained. At least two possibilities exist. The first is that the barriers for methanol synthesis and the RWGS reaction are fortuitously the same on Cu and ZrO$_2$. A second possibility is that a critical part of the reaction sequence always occurs on Cu.

It is notable that ZrO$_2$ affects the activities of Cu for methanol synthesis and the RWGS reaction in significantly different ways (see fig. 6). The data show that, while the addition of ZrO$_2$ enhances the methanol synthesis, the effects of ZrO$_2$ on the RWGS reaction are more complex. Small additions of ZrO$_2$ suppress the rate of the RWGS reaction relative to that observed on unpromoted Cu, whereas larger loadings enhance the rate of this reaction. This suggests that different zirconia species may be involved in the suppression and enhancement of the RWGS reaction. It has been reported that isolated formate species on oxide surfaces are fairly inert with respect to hydrogenation [13,27], whereas formate species located near Cu particles or with access to adsorbed hydrogen may undergo hydrogenation [13]. Therefore, it is conceivable that at low ZrO$_2$ loadings, small ZrO$_2$ particles are formed and hence formate species formed have access to adsorbed hydrogen and hydrogenate further to methanol rather than decompose to CO, causing the initial suppression in RWGS activity at low ZrO$_2$ loadings. As the ZrO$_2$ loading increases, the ZrO$_2$ particle size increases and a larger portion of the formate species are "isolated" from a supply of hydrogen and hence are more likely to decompose to CO, causing the rise in RWGS activity above about 5 wt% ZrO$_2$.

Along similar lines, it may be argued that the rates of methanol synthesis for both CO/H$_2$ and CO$_2$/H$_2$ increase monotonically with increasing ZrO$_2$ promotion because the concentration of formate species available for hydrogenation increases as the ZrO$_2$ particles grow with increasing ZrO$_2$ loadings. This reasoning would also explain the observed maximum in methanol selectivity at low ZrO$_2$ loadings (fig. 7). An implicit assumption here is that the hydrogenation and decomposition of formate species are the rate determining steps for methanol synthesis and RWGS reactions, respectively.

The decrease in methanol selectivity at high temperatures (> 520 K) is a consequence of the increasing rate of methanol decomposition as the equilibrium constraint is approached. Since the RWGS reaction never reaches equilibrium under the conditions studied, the conversion of CO$_2$ to CO continues to increase with increasing temperature. Together, these effects account for the decrease in methanol selectivity above 520 K. A possible mechanism for methanol synthesis and the RWGS reaction is shown in fig. 9.

We propose that the interaction of CO_2 with ZrO_2-promoted Cu/SiO_2 or Cu/ZrO_2 results in the formation of bicarbonate species as a consequence of reaction with OH groups present on the surface of ZrO_2. This view is supported by preliminary infrared studies conducted with 30.5 wt% ZrO_2-promoted Cu/SiO_2 [19]. In the presence of hydrogen, the bicarbonate species can produce formate species. Hydrogenation of formate species leads to the formation of methanol, whereas decomposition of these species results in the formation of CO. The near equivalence of the apparent activation energies for methanol synthesis and the RWGS reaction implies that the activation barriers for formate hydrogenation and decomposition are similar.

5. Conclusions

The addition of increasing amounts of zirconia to Cu/SiO_2 catalysts results in a monotonic increase in the rate of methanol synthesis for both CO and CO_2 hydrogenation. The methanol synthesis rate is more significantly affected by zirconia addition for CO than CO_2 hydrogenation. At the same reaction conditions the rate of methanol synthesis is higher for CO_2 hydrogenation than for CO hydrogenation on all catalysts studied. The apparent activation energy for CO hydrogenation to methanol decreases by about 5 kcal/mol upon the addition of zirconia to Cu/SiO_2, suggesting that a lower-energy pathway to methanol is available. For CO_2 hydrogenation the apparent activation energies for methanol synthesis and RWGS reactions are not significantly affected by zirconia addition to Cu/SiO_2, suggesting that the pathways for these reactions are similar on Cu/SiO_2 and zirconia-promoted Cu/SiO_2. The activity of the RWGS reaction is suppressed at low zirconia loadings but enhanced at higher zirconia loadings as compared to Cu/SiO_2, resulting in a maximum selectivity to methanol at intermediate zirconia loadings (3.8–6.5 wt%) for CO_2 hydrogenation. The effect of zirconia addition on the rate of the RWGS reaction is small compared to the influence of zirconia on the rate of methanol synthesis from CO_2. It is proposed that the observed effects of zirconia can be interpreted in terms of the scheme shown in fig. 9, which envisions that zirconia provides the sites for the adsorption of CO or CO_2, whereas Cu provides the sites for the dissociative adsorption of H_2. Hydrogenation of the species adsorbed on zirconia (i.e., formate or bicarbonate) leads to the formation of methanol via a pathway paralleling that occurring on the surface of Cu.

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References

[1] B. Denise and R.P.A. Sneeden, Appl. Catal. 28 (1986) 235.
[2] H.W. Chen, J.M. White and J.G. Ekerdt, J. Catal. 99 (1986) 293.
[3] Y. Amenomiya, Appl. Catal. 30 (1987) 57.
[4] B. Denise, R.P.A. Sneeden, B. Beguin and O. Cherifi, Appl. Catal. 30 (1987) 353.
[5] G.J.J. Bartley and R. Burch, Appl. Catal. 43 (1988) 141.
[6] R.A. Koeppel, A. Baiker, Ch. Schild and A. Wokaun, in: *Preparation of Catalysts V*, Stud. Surf. Sci. Catal., Vol. 63, eds. G. Poncelet, P.A. Jacobs, P. Grange and B. Delmon (Elsevier, Amsterdam, 1991) p. 59.
[7] N. Kanoun, M.P. Astier and G.M. Pajonk, Catal. Lett. 15 (1992) 231.
[8] R.A. Koeppel, A. Baiker and A. Wokaun, Appl. Catal. A 84 (1992) 77.
[9] Y. Sun and P.A. Sermon, J. Chem. Soc. Chem. Commun. (1993) 1242.
[10] Y. Nitta, O. Suwata, Y. Ikeda, Y. Okamoto and T. Imanaka, Catal. Lett. 26 (1994) 345.
[11] Y. Sun and P.A. Sermon, Catal. Lett. 29 (1994) 361.
[12] C.J.G. van der Grift, P.A. Elberse, A. Mulder and J.W. Geus, Appl. Catal. 59 (1990) 275.
[13] J.L. Robbins, E. Iglesia, C.P. Kelkar and B. DeRites, Catal. Lett. 10 (1991) 1.
[14] J.W. Evans, M.S. Wainwright, A.J. Bridgewater and D.J. Young, Appl. Catal. 7 (1983) 75.
[15] D.B. Clarke and A.T. Bell, J. Catal. 154 (1995) 314.
[16] J.A. Brown Bourzutschky, N. Homs and A.T. Bell, J. Catal. 124 (1990) 73.
[17] E. Shustorovich and A.T. Bell, Surf. Sci. 253 (1991) 386.
[18] P.A. Taylor, P.B. Ramussen, C.V. Ovesen, P. Stoltze and I. Chorkendorff, Surf. Sci. 261 (1992) 191.
[19] A.T. Bell, J. Mol. Catal. A 100 (1996) 1.
[20] A. Boffa, C. Lin, A.T. Bell and G.A. Somorjai, J. Catal. 149 (1994) 149.
[21] I.A. Fisher, H.C. Woo and A.T. Bell, unpublished.
[22] W. Hertl, Langmuir 5 (1989) 96.
[23] M.-Y. He and J.G. Ekerdt, J. Catal. 87 (1984) 381.
[24] Y. Kikuzono, S. Kagami, S. Naito, To. Onishi and K. Tamaru, Faraday Discussions Chem. Soc. 72 (1981) 135.
[25] M.E. Fakley, J.R. Jennings and M.S. Spencer, J. Catal. 118 (1989) 483.
[26] D. Gasser and A. Baiker, Appl. Catal. 48 (1989) 279.
[27] C. Chauvin, J. Saussey, J.C. Lavalley, H. Idriss, J.P. Hindermann, A. Kiennemann, P. Chaumette and P. Courty, J. Catal. 121 (1990) 56.