JOURNAL OF CATALYSIS **178,** 511–519 (1998)
ARTICLE NO. CA982167

Basic Metal Oxides as Cocatalysts for Cu/SiO$_2$ Catalysts in the Conversion of Synthesis Gas to Methanol

A. Gotti and R. Prins[1]

Laboratory of Technical Chemistry, Swiss Federal Institute of Technology (ETH), 8092 Zürich, Switzerland

Received March 10, 1998; revised May 19, 1998; accepted May 20, 1998

The catalytic behavior of Cu catalysts supported on ultrapure silica and promoted with Ca, Zn, and La oxides was investigated in the hydrogenation of CO and CO$_2$ to methanol at high pressure. Cu on very pure silica produces hardly any methanol, while the addition of basic oxides and the use of γ-alumina as support improve the catalyst performance. The strong promoting effect of Ca and La oxide on the silica-supported Cu and the weak promoting effect for alumina-supported Cu suggest that the basic oxide additives must be close to or in contact with the Cu particles to be effective in methanol synthesis. The methanol activity of Zn/Cu/SiO$_2$ increased with increasing CO$_2$ content in a CO-CO$_2$-H$_2$ mixture, suggesting that CO$_2$ is the main carbon source for methanol.

Key Words: **methanol synthesis; Cu catalysts; ultrapure SiO$_2$; metal oxide additives; cocatalyst; promoter; hydrogenation of CO; hydrogenation of CO$_2$.**

INTRODUCTION

In industry, methanol is mainly produced from synthesis gas over Cu/ZnO-based catalysts. Methanol synthesis has been studied extensively but the reaction pathways and the nature of the active site still remain open to discussion. Originally, it was accepted that in copper-based catalysts metallic Cu particles were catalytically active (1, 2), because several authors reported linear relationships between metallic Cu surface area and catalyst activity (3–5). On the other hand, unsupported copper powder and copper supported on an inert material such as high purity silica were found to be inactive in methanol synthesis (6–8). Therefore, it was proposed that the active site in methanol synthesis is a Cu$^+$ species which is stabilized against reduction by the presence of promoters, such as ZnO, or by the support (9–11). The ionic copper content, and thus the methanol activity, would then be related to the size of the metal–promoter (metal–support) interface. Hydrogenation of intermediate species (formyl or formate) formed on the cationic site would occur by migrating hydrogen atoms supplied by the Cu surface. According to this model, the formation of methanol requires a pair of active centres (Cu-Cu$^+$) with different functions (bifunctional mechanism).

Several research groups were, however, unable to identify significant amounts of Cu$^+$ or even adsorbed oxygen on the working catalyst surface by means of spectroscopic or transient techniques (12–14). Others accepted that the formation of methanol needs a bifunctional catalyst, but claimed that the intermediate species (formate and carbonate) are formed at the copper–additive (copper–support) interface by the reaction of CO and CO$_2$ with surface hydroxyl groups (15–19). Distinct reaction pathways were proposed for the conversion of CO and of CO$_2$. Methanol synthesis from CO$_2$ would occur via hydrogenation of formate species formed on copper and migrated to the additive surface, while methanol synthesis from CO would proceed via hydrogenation of formate species formed on the additive with hydrogen atoms migrating from the copper surface (20).

Not only the nature of the active sites and the role of the catalyst components are still under discussion, but also the influence of the feed composition on the nature of the catalyst surface and on the catalyst activity. Chinchen *et al.* have proposed that metallic copper clusters are the active phase and that the surface of these crystallites is partially covered by oxygen resulting from the dissociation of CO$_2$. By means of isotope labelling studies it was found that over a precipitated Cu/ZnO/Al$_2$O$_3$ catalyst methanol is made directly from CO$_2$ and that the main function of CO is to scavenge the adsorbed oxygen to produce surface CO$_2$ (21). These results are in complete agreement with earlier results of Kagan *et al.* (22). Despite this convincing evidence, however, conflicting effects of the feed composition on the rate of methanol formation have been reported. High methanol synthesis rates were observed in the conversion of feeds containing small amounts of CO$_2$ and it was concluded that CO$_2$ helps to maintain the active copper sites in the 1+ oxidation state (23, 24) or prevents the overreduction of the ZnO component (25).

In order to better understand the role of the metallic component, we have investigated the catalytic behavior of Cu supported on silica and compared it with the performance

---

[1] Corresponding author. E-mail: prins@tech.chem.ethz.ch.

0021-9517/98 $25.00

of Pd/SiO_2 (26). In contrast with previous studies (7, 18, 27), the silica and the impregnated catalysts were synthesized under very clean conditions to avoid contaminations which could affect the catalytic properties, and the experiments were carried out under realistic industrial reaction conditions. Although it is generally accepted that the main role of alumina in industrial $Cu\text{-}ZnO\text{-}Al_2O_3$ catalyst is to act as structural stabilizer, Cu/Al_2O_3 catalysts have been tested as well to find out what role this support plays in the catalytic conversion of synthesis gas. Since the origin of the synergistic effects between copper and ZnO is not clear yet, Cu/SiO_2 and Cu/Al_2O_3 catalysts have been doped with different basic metal oxides in order to find correlations between properties of the basic additives and the methanol formation rate. To better understand the role of CO and CO_2 in the formation of methanol and the influence of the feed composition on the nature of the catalyst surface, the properties of the catalysts in the hydrogenation of CO, CO_2 as well as $CO\text{–}CO_2$ mixtures have been studied.

EXPERIMENTAL

Catalyst Preparation

Ultrapure silica prepared by hydrolysis of tetraethoxysilane (26) was ground, sieved to a 250–300 μm size fraction and stored in a dessicator until use. Similar to the synthesis of silica, ultra pure γ-alumina was prepared by hydrolysis of aluminium isopropoxide. To prevent the uptake of alkali and alkaline earth metal cations from glass, the preparation of the supports was carried out in polyethylene equipment which was previously washed with 5% boric acid and rinsed with doubly distilled water. Thereupon, 250 ml doubly distilled water were added to 40 g aluminium isopropoxide (Fluka, pract. >98%) and stirred vigorously at 353 K until gellation occurred (16 h). Excess water and isopropyl alcohol formed during hydrolysis were removed by drying the gel for 10 h at 393 K (reached at a heating rate of 120 $K \cdot h^{-1}$), and calcining the resulting material in flowing air for 16 h at 723 K (reached at 90 $K \cdot h^{-1}$). After grinding and sieving to a 250–300 μm size fraction, the material was stored in a dessicator until use. The XRD patterns confirmed that $\gamma\text{-}Al_2O_3$ had been obtained.

Cu/SiO_2 and Cu/Al_2O_3 catalysts were prepared by pore volume impregnation of the ultra-pure SiO_2, and ultra-pure and commercial (Condea) γ-alumina supports, respectively, with an aqueous $Cu(NO_3)_2$ (Johnson Matthey) solution. The impregnations were carried out in carefully cleaned polyethylene beakers, as in the synthesis of ultra pure silica described above. The catalyst precursors were dried at 393 K (60 $K \cdot h^{-1}$) for 16 h and calcined in flowing air for 2 h at 623 K. The Cu loading was 7.0 wt% in all cases. $X/Cu/SiO_2$ and $X/Cu/Al_2O_3$ catalysts ($X = $ Ca, Zn, La) with X/Cu atomic ratios of 0.2 were obtained by impregnation of the Cu/SiO_2 and the Cu/Al_2O_3 precursors with nitrate solutions of the additives. The catalysts were dried and calcined as described above.

Characterization Techniques

Surface area and pore size distribution of ultra-pure SiO_2, ultra-pure γ-alumina and Condea γ-alumina were determined from the nitrogen adsorption and desorption isotherms measured at 77 K and equilibrium pressures between 0.5 and 100 kPa. CO chemisorption was performed on catalysts containing about 6 mg of Cu reduced in flowing H_2 at 623 K (300 $K \cdot h^{-1}$) for 2 h and evacuated at 10^{-2} Pa for another 2 h. Since the presence of weakly reversibly adsorbed CO molecules will affect the results, the backsorption method was applied. The CO_{irr}/Cu value was obtained by subtraction of the backsorption isotherm from the total adsorption isotherm (26). The fraction of the exposed metal atoms, i.e. the dispersion, was calculated assuming that the saturated coverage of CO_{irr} on copper amounts to 0.18 monolayer (28). TPR profiles were measured on catalysts containing between 25 and 55 μmol of reducible species as described in (26).

Catalyst Testing

Synthesis gas conversion was performed in a fixed bed reactor (26). About 150 mg of catalyst precursor was reduced in a flow of pure hydrogen at 623 K and 0.1 MPa for 2 h. Unless stated otherwise, the catalysts were tested at 553 K, 2.5 MPa, $H_2/CO = 2$ ($flow_{feed} = 0.11\ mol \cdot h^{-1}$), $H_2/CO_2 = 3$ ($flow_{feed} = 0.15\ mol \cdot h^{-1}$), and at a space velocity of 770 $mol_{feed} \cdot h^{-1}/mol_{Cu}$. The product activities and selectivities were summarized in four main classes: CH_4, C_{2+} (paraffins and olefins with $n \geq 2$), $C_{1\text{-}oxo}$ (methanol and dimethyl ether), and $C_{2\text{-}oxo}$ (acetaldehyde and ethanol).

RESULTS

Catalyst Characterization

The same ultrapure silica as used to support Pd (26) was employed to prepare the Cu/SiO_2 catalysts. Cu/Al_2O_3 catalysts were obtained by impregnation of ultra pure as well as commercial (Condea) γ-alumina supports. The BET surface area (264 m^2/g) and pore volume (0.54 ml/g) of the impurity-free γ-alumina were very similar to those of the commercial Condea support (226 m^2/g and 0.51 ml/g, respectively). The pore size distribution indicated that the major part of the pore volume of the ultra pure and the Condea alumina comes from pores with diameter in the 50–100 Å, respectively 50–80 Å range.

The TPR profiles of the Cu/SiO_2 and Cu/Al_2O_3 catalysts showed two peaks around 510 and 590, and 500 and 550 K, respectively. Since for Cu/SiO_2 some hydrogen consumption was observed above 623 K as well, the reduction behavior of the catalyst was further investigated by measuring

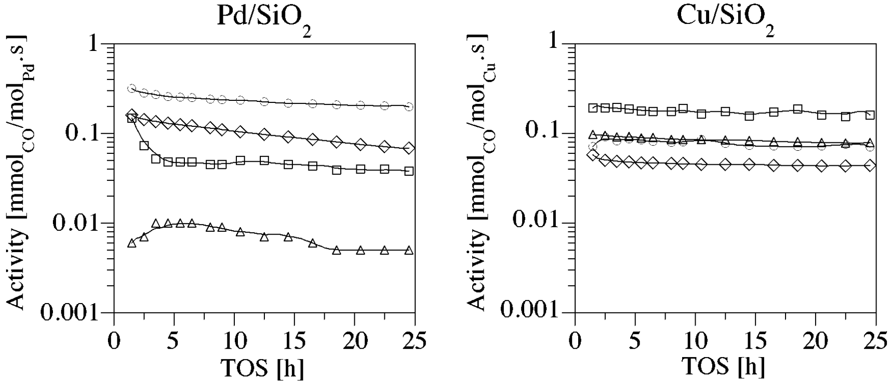

FIG. 1. Product activities in the CO hydrogenation over Pd/SiO_2 and Cu/SiO_2: (◇) CH_4; (△) C_{2+}; (○) C_1-oxo; (□) CO_2.

its hydrogen uptake during temperature ramping and subsequent holding for 2 h at 623 K. The resulting H_2/M values (0.99 for the silica and 1.01 for the alumina-supported catalyst) indicate that reduction of Cu^{2+} to Cu^0 is complete after reduction at 623 K for 2 h in a flow of pure hydrogen.

CO and CO_2 Hydrogenation over Cu/SiO_2

The product activities in the CO hydrogenation over unpromoted Pd/SiO_2 and Cu/SiO_2 catalysts, as presented in Fig. 1 as a function of time on stream (TOS), are quite similar. Thus, since Pd/SiO_2 has a low activity (26), Cu/SiO_2 is not particularly efficient in the hydrogenation of CO either. The product distributions are different, however (Table 1). Pd/SiO_2 produces modest amounts of methane, traces of C_2-C_3 hydrocarbons and CO_2, while methanol and dimethyl ether are the only oxygenated products observed (26). In agreement with the results of Nonneman and Ponec (7), also Cu supported on a very pure silica has an extremely low methanol activity. As observed by Brown Bourzutschky *et al.* (29), the formation of hydrocarbons (mainly C_2-C_8 paraffins) is not insignificant in the hydrogenation of CO over a silica-supported Cu catalyst, and the chain-growth probability factor α, calculated from the hydrocarbon distribution, amounts to 0.50. Thus, although the activity for C_{2+}-hydrocarbons was low, it was almost an order of magnitude higher over Cu than over Pd. Therefore also the formation of carbon dioxide, formed by reaction of CO with water molecules produced in the synthesis of hydrocarbons and in the dehydration of methoxy species to dimethyl ether, was higher over Cu/SiO_2 than over Pd/SiO_2.

The catalytic properties of Pd/SiO_2 and Cu/SiO_2 in the hydrogenation of CO_2 are presented in Fig. 2 as a function of time on stream. The total activity of the Cu catalyst was seven times higher in the conversion of CO_2 than in that of CO, while over Pd/SiO_2 the total activity hardly depended on the carbon source used. Carbon monoxide, produced by the reverse water–gas shift reaction is the main product for Pd/SiO_2 as well as Cu/SiO_2 (Table 2). Over Cu/SiO_2, the formation of methanol occurred nearly three times faster from CO_2 than from CO, whereas in the hydrogenation of CO_2 over Pd/SiO_2 only very small amounts of methanol were formed. Thus, in the synthesis of methanol from CO_2, as well as in the reverse water-gas shift reaction, the Cu catalyst is almost one order of magnitude more active than the Pd catalyst.

TABLE 1

Catalytic Properties after 24 h in the Hydrogenation of CO and CO_2

	CO		CO_2	
	Pd/SiO_2	Cu/SiO_2	Pd/SiO_2	Cu/SiO_2
Dispersion	0.16	0.17	0.16	0.17
Activity ($mmol_{COx}/mol_{Cu} \bullet s$)	0.3	0.4	0.4	2.7
TOF ($10^{-3} \bullet s^{-1}$)	1.9	2.3	2.5	15.9
Selectivity CO_x (%)[a]	12.3	43.8	81.8	90.8
Selectivity CH_4 (%)	22.1	12.7	13.6	0.7
Selectivity C_{2+} (%)	1.5	23.1	0.0	0.1
Selectivity $C_{1\text{-oxo}}$ (%)	64.1	20.4	4.6	8.4

[a] CO_2 selectivity for CO hydrogenation; CO selectivity for CO_2 hydrogenation.

TABLE 2

Catalytic Properties after 24 h of *X*/Cu/SiO_2 Catalysts (*X*/Cu = 0.2) in the Hydrogenation of CO and CO_2

Feed	Additive	Activity ($mmolCO_x$/ $mol_{Cu} \bullet s$)	Selectivities (%)				
			CO	CO_2	CH_4	C_{2+}	$C_{1\text{-oxo}}$
CO	—	0.4		43.8	12.7	23.1	20.4
CO	Ca	0.7		34.7	7.6	13.2	44.5
CO	Zn	0.3		48.0	13.6	23.4	15.0
CO	La	0.7		35.5	6.7	10.6	47.2
CO_2	—	2.7	90.8		0.7	0.1	8.4
CO_2	Ca	2.3	88.7		0.7	0.2	10.4
CO_2	Zn	1.8	64.6		1.2	0.2	34.0
CO_2	La	2.6	85.4		0.7	0.1	13.8

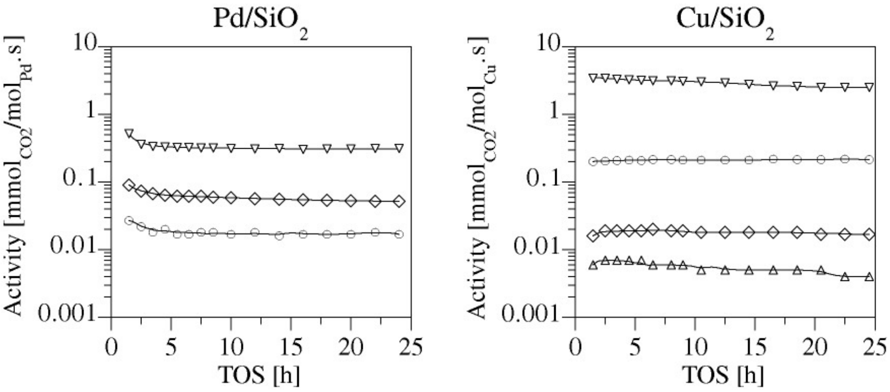

FIG. 2. Product activities in the CO_2 hydrogenation over Pd/SiO_2 and Cu/SiO_2: (◇) CH_4; (△) C_{2+}; (○) C_1-oxo; (▽) CO.

Effect of Basic Metal Oxides on Cu/SiO₂

Several authors reported that the addition of basic metal oxides or the use of basic supports in the preparation of Cu catalysts, significantly increased the conversion of synthesis gas to methanol (7, 9, 10, 18, 29). In order to better understand the role of these components the catalytic properties of Cu/SiO_2 catalysts doped with Ca, Zn, and La oxide in the hydrogenation of CO and CO_2 have been investigated. As with doped Pd/SiO_2 catalysts (26), it was observed that impregnation of Cu/SiO_2 precursors with solutions of $Ca(NO_3)_3$ and $La(NO_3)_3$, followed by calcination, positively affected the catalyst activity in the hydrogenation of CO to methanol (Fig. 3 and Table 2). Neither $Zn/Pd/SiO_2$ (26), nor $Zn/Cu/SiO_2$ proved active in the methanol synthesis from CO. In this respect, it should be mentioned that van Herwijnen and de Jong (30) and King and Nix (25) indicated that in the conversion of CO_2-free synthesis gas ZnO is susceptible to reduction, since under reaction conditions CO is a more effective reducing agent than H_2.

The undoped Cu/SiO_2 catalyst is quite active in the hydrogenation of CO_2. However, since the reverse water–gas shift reaction occurs much faster than the formation of methanol (31), methanol is produced with a selectivity of less than 10%. The addition of Ca and La oxides hardly changes the catalyst activity and methanol selectivity (Fig. 3 and Table 2). Zinc oxide, however, promoted the methanol formation and decreased the reverse water–gas shift reaction. This is in accordance with results of Nakamura *et al.* who found that Zn deposited on a Cu (111) single crystal surface promoted the methanol synthesis from CO_2 and H_2 (32). These authors ascribed the promotion to Cu-Zn alloy formation, because they observed such a surface in an STM investigation under UHV conditions. However, we do not believe that a surface alloy will be stable under their reaction conditions. In the hydrogenation of CO_2, ZnO should be formed (or stabilized) by the slightly oxidizing reaction conditions (30). The presence of CO_2 or H_2O prevents the formation of a Cu-Zn alloy, and therefore ZnO can show its full promotional properties, like CaO and La_2O_3. In the presence of CO and H_2, however, alloy formation may suppress the promotional effects of ZnO.

The influence of the reaction temperature on the activity and the product distibution in the hydrogenation of CO_2

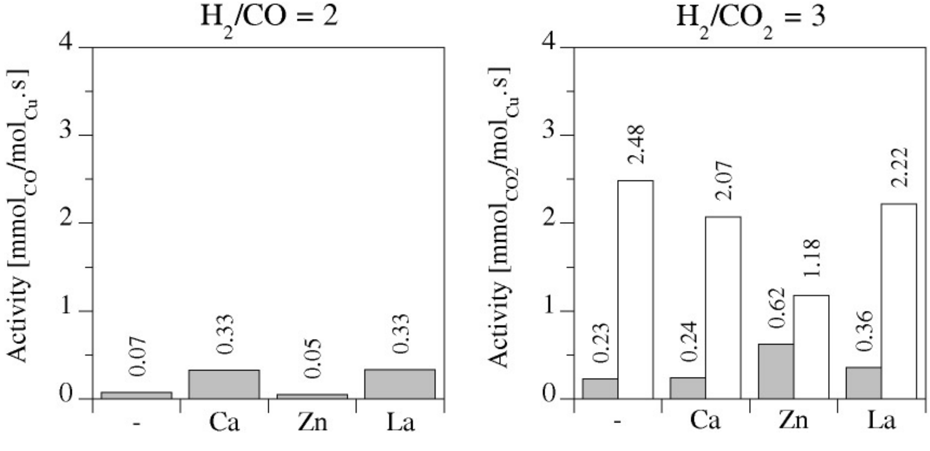

FIG. 3. Product activities after 24 h of $X/Cu/SiO_2$ catalysts in the hydrogenation of CO and CO_2: (■) C_1-oxo; (□) CO.

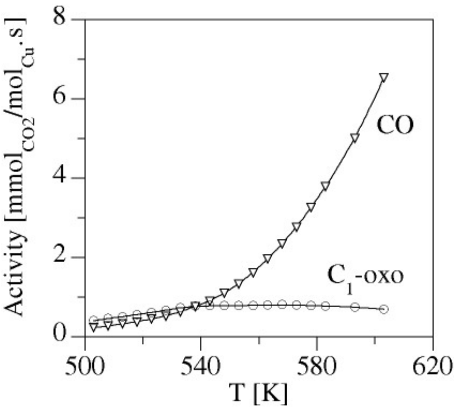

FIG. 4. Effect of the reaction temperature in the CO_2 hydrogenation over $Zn/Cu/SiO_2$: (○) C_1-oxo; (▽) CO.

over $Zn/Cu/SiO_2$ is shown in Fig. 4. The reaction temperature has a strong influence on the catalyst activity as well as on the selectivity. Below 540 K, methanol selectivity is higher than 50%. At higher temperatures, the production of CO rapidly increases, while the rate of methanol formation remains stable, even though the methanol yield is much lower than the maximal thermodynamic yield. Thus, above 540 K the increasing CO partial pressure may overreduce the ZnO surface.

Hydrogenation of CO-CO_2 Mixtures over $Zn/Cu/SiO_2$

The rate of methanol formation decreased with increasing CO partial pressure when a mixture of 25% $CO + CO_2$ and 75% H_2 was fed over the $Zn/Cu/SiO_2$ catalyst (Fig. 5), opposite to the behavior for a $Ca/Pd/SiO_2$ catalyst (26). This decrease is in agreement with the fact that CO_2 is the primary carbon source of methanol for a Cu catalyst (21). The decrease in the rate of methanol formation was especially strong at very low CO_2 content which suggests that at low CO_2 partial pressures the catalyst not only loses activity because of the low CO_2 partial pressure, but in addition becomes deactivated by overreduction of the ZnO patches (25, 30).

CO and CO_2 Hydrogenation over Cu/Al_2O_3

In order to verify the role of the support properties, Cu/Al_2O_3 catalysts were tested and the results were compared with the performance of Cu/SiO_2. Moreover, eventual contamination effects due to the presence of metal cations in commercial supports have been investigated by comparing the catalytic behavior of ultrapure and Condea alumina-supported Cu catalysts.

The product activities in the hydrogenation of CO over Cu/SiO_2 and Cu/Al_2O_3 catalysts are presented in Fig. 6. The two alumina-supported catalysts had very similar properties and therefore only the results for the ultrapure Al_2O_3 are presented. The presence of impurities in the commercial support (metal oxides in concentrations between 10 and 100 ppm) apparently did not affect the Cu particle size, catalytic activity, or product distribution significantly. Thus, whereas impurities in the silica support easily end up in the vicinity of the active metal particles, metal oxides present in γ-alumina are less easily leached out of the lattice during wet catalyst preparation and affect the catalyst properties hardly.

Much more evident are the differences in the catalytic behavior of Cu/SiO_2 and Cu/Al_2O_3. The use of an amphoteric oxide such as γ-alumina as supporting material improves the catalyst activity by almost one order of magnitude and influences the product distribution. These effects cannot be ascribed exclusively to an increased metal dispersion (0.17 for Cu/SiO_2, 0.32 for Cu/Al_2O_3 Condea, and 0.28 for Cu/Al_2O_3 ultrapure) but must also originate from the chemical characteristics of the support. The use of materials with basic properties, as additive or support, positively affects the formation of C_1-oxo products (methanol and dimethyl ether).

Furthermore, it was observed that the alumina support substantially affects the hydrocarbon distribution. Whereas the methanation reaction occurred almost 10 times faster over Cu/Al_2O_3 than over Cu/SiO_2, neither the higher metal dispersion nor the presence of acid sites had any effect on the formation of higher hydrocarbons. The total amounts (cf. Tables 2 and 3) and the distributions (with Schulz–Flory factors $\alpha = 0.50$ for Cu/SiO_2 and $\alpha = 0.49$ for Cu/Al_2O_3 for the C_2-C_8 fraction) were very similar. It is possible that part of the methoxy species adsorbed on the alumina surface (33–35) are completely hydrogenated to methane and water by hydrogen atoms spilled over from the Cu surface. Thus, the increased methane formation could be a consequence of the higher concentration of methoxy groups and the higher

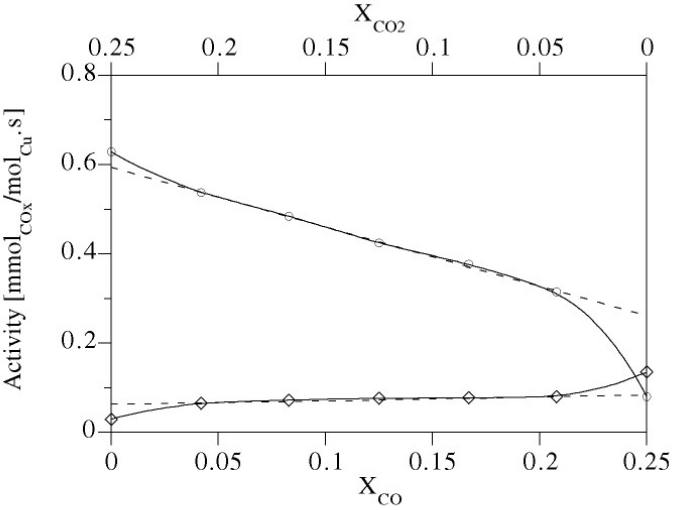

FIG. 5. Product activities of $Zn/Cu/SiO_2$ in the conversion of $CO/CO_2/H_2$ $(x/(0.25 - x)/0.75)$ mixtures: (◇) C_{1+}; (○) C_1-oxo.

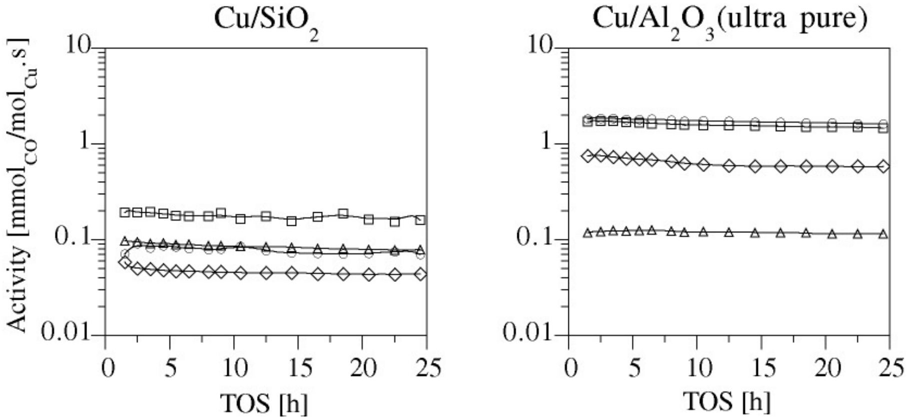

FIG. 6. Product activities in the CO hydrogenation over Cu/SiO_2 and Cu/Al_2O_3: (◇) CH_4; (△) C_{2+}; (○) C_1-oxo; (□) CO_2.

reactivity of these species due to the interaction with the alumina acid sites.

As for the hydrogenation of CO, also in the hydrogenation of CO_2 the two alumina-supported catalysts had similar properties, while there were substantial differences in the catalytic behavior of Cu/SiO_2 and Cu/Al_2O_3 (Fig. 7). The use of γ-alumina as support not only affected the formation of methanol but also the conversion of CO_2 to CO. The Cu/Al_2O_3 catalysts are almost three times more active than the Cu/SiO_2. However, since the increased catalytic performance is mainly the result of the promotion of the reverse water–gas shift reaction, the methanol selectivity improved only slightly.

Effect of Basic Metal Oxides on Cu/Al_2O_3

As observed for Cu/SiO_2, the impregnation of Cu/Al_2O_3 with Ca and La nitrate solutions and subsequent calcination improved the methanol activity of the catalyst in the hydrogenation of CO (Table 3). Although the rate enhancements were much more modest than those reported for Ca- and La-doped Pd/SiO_2 catalysts (26), it is evident that, due to the addition of these metal oxides, the number of basic sites and, consequently, the surface concentration of formate species increases. As suggested for Ca/Pd/Al_2O_3 (26), the modest promotional effect of basic additives for the alumina-supported catalysts may be ascribed to their strong interaction with the alumina acid sites. As a consequence, the mobility of the oxidic clusters over the support and, therefore, the formation of a Cu-additive interface will be constrained.

Further information about the acid–base properties of the additives comes from the determination of the methanol to dimethyl ether ratio of the different X/Cu/Al_2O_3 catalysts (Table 3). The strongly basic calcium oxide significantly inhibited the dehydration of surface methoxy groups to dimethyl ether which is catalyzed by acid sites, while less basic oxides (e.g. La_2O_3) only had a moderate effect.

Similar to the results obtained with Zn/Cu/SiO_2, the catalytic properties of Cu/Al_2O_3 are not substantially influenced by the presence of Zn on the catalyst surface. It can be supposed that also in the case of alumina-supported Cu catalysts, the promoting effect of ZnO is partially suppressed by the formation of a Cu-Zn alloy.

As reported for Rh (36) and Pd catalysts (26), the addition of basic additives to Cu/Al_2O_3 is accompanied by

TABLE 3

Catalytic Properties after 24 h of X/Cu/Al_2O_3 Catalysts (X/Cu = 0.2) in the Hydrogenation of CO and CO_2

Feed	Additive	Activity (mmol$_{COx}$/mol$_{Cu}$ • s)	Selectivities (%) CO	CO_2	CH_4	C_{2+}	$C_{1\text{-oxo}}$	MeOH/DME	α
CO	—	2.8		41.2	16.6	2.5	39.7	0.08	0.49
CO	Ca	3.5		25.3	2.9	2.3	69.5	1.20	0.52
CO	Zn	3.1		38.9	9.9	1.8	49.4	0.09	0.49
CO	La	5.5		35.0	2.0	1.2	61.8	0.11	0.52
CO_2	—	8.2	85.3		0.1	0.0	14.6	2.7	
CO_2	Ca	8.5	84.9		0.1	0.0	15.0	116	
CO_2	Zn	9.0	84.9		0.1	0.0	15.0	4.8	
CO_2	La	8.7	85.1		0.1	0.0	14.8	24.2	

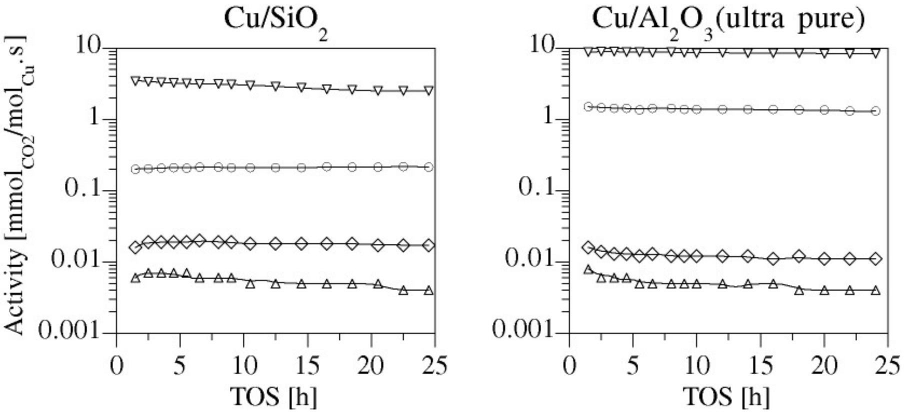

FIG. 7. Product activities in the CO_2 hydrogenation over Cu/SiO_2 and Cu/Al_2O_3: (◇) CH_4; (△) C_{2+}; (○) C_1-oxo; (▽) CO.

a decrease of the hydrocarbon formation (Table 3). However, in contrast with the previous results, this decrease is mainly the result of the inhibition of the methanation reaction, while the synthesis of higher hydrocarbons seems to be unaffected by the presence of metal oxides on the catalyst surface, as confirmed by the C_{2+} yields (selectivity times activity) and chain-growth probabilities (α factors) calculated from Schulz–Flory distribution plots (Table 3). If methanation over Cu/Al_2O_3 indeed occurs via dissociation and hydrogenation of methoxy intermediates, then the increased stabilization of these species due to their interaction with strong basic sites induces a decrease in the rate of methane formation.

The change in $C_{1\text{-oxo}}$ production with increasing reaction temperature in the CO hydrogenation over $La/Cu/Al_2O_3$ is shown in Fig. 8. The formation of $C_{1\text{-oxo}}$ products (mainly dimethyl ether) increases steadily until 600 K. High conversion of synthesis gas at high temperature may be achieved by removal of methanol by chemical conversion. Coproduction of methanol and dimethyl ether offers this opportunity (37). In a catalyst with acidic and basic properties, methanol synthesis and dehydration to dimethyl ether can be combined and the water–gas shift reaction can also occur simultaneously when the following reactions proceed:

$$\text{Methanol synthesis} \quad 2\,CO + 4\,H_2 \rightarrow 2\,CH_3OH \qquad [1]$$

$$\text{DME synthesis} \quad 2\,CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad [2]$$

$$\text{Water-gas shift} \quad H_2O + CO \rightarrow H_2 + CO_2 \qquad [3]$$

$$\text{Net} \quad 3\,H_2 + 3\,CO \rightarrow CH_3OCH_3 + CO_2 \qquad [4]$$

By combining these reactions, the thermodynamic limitation for methanol synthesis can be avoided and much higher syngas conversions become possible (Fig. 8).

In contrast with the results obtained with silica-supported catalysts, the addition of basic oxides to Cu/Al_2O_3 does not significantly affect conversion and product distibution in the hydrogenation of CO_2 (Table 3). Thus, neither the formation of C_1-oxo products nor the reverse water–gas shift reaction are influenced by the increased number of basic sites. In the case of Ca-doped Cu/Al_2O_3, the methanol activity was much higher, but this was actually the result of the suppression of the dimethyl ether formation due to the decreased number of acid sites on the alumina surface, and not the result of an improved $C_{1\text{-oxo}}$ formation (Table 3). On the other hand, the addition of less basic oxides such as ZnO and La_2O_3 had only a moderate effect on the methanol to dimethyl ether ratio.

DISCUSSION

In accordance with previous results (7), we found that Cu supported on an impurity-free silica is not a good catalyst for the hydrogenation of CO to methanol. The addition of

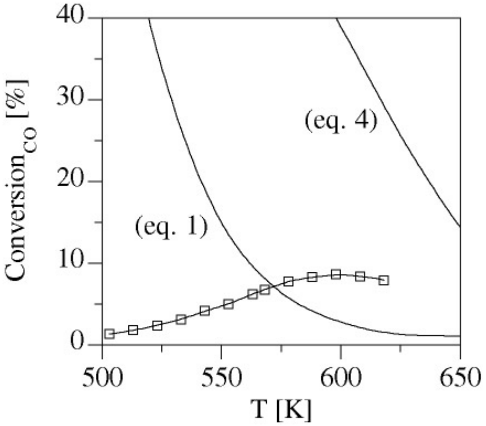

FIG. 8. Effect of the reaction temperature in the CO hydrogenation over $La/Cu/Al_2O_3$: (□) CO conversion to DME; (-) thermodynamic yields.

basic oxides to Cu/SiO_2 improves the methanol formation from CO. Although the observed rate enhancements are much more modest than in the case of doped Rh and Pd catalysts, these results support the idea that also over Cu catalysts the synthesis of methanol from CO proceeds via hydrogenation of formate species formed on the basic surface sites. Moreover, it does not seem very probable in such a reductive gas phase as a H_2/CO mixture that the presence of oxidic promoters can prevent the reduction of surface Cu^+ cations which would be active sites for the formation of formyl or formate species (38).

The lack of activity for the Zn-doped catalysts in CO hydrogenation can be attributed to the formation of a Cu-Zn alloy or a Zn-hydride phase due to the strong reductive conditions of the H_2-CO mixture. On the other hand, only $Zn/Cu/SiO_2$ was found to significantly improve the hydrogenation of CO_2 to methanol. In contrast with the results obtained in the hydrogenation of CO-CO_2 mixtures over $Ca/Pd/SiO_2$, the methanol activity of a Zn-doped Cu catalyst increased with the CO_2 partial pressure of the feed. Although it is generally accepted that CO_2 is the main carbon source of methanol, the lower methanol formation rate at high CO partial pressure may also be explained by the fact that the promoting effect of the additive is suppressed by reduction of the ZnO surface.

Recent studies are in agreement with a bifunctional mechanism for the formation of methanol. IR and TPD investigations of Fujita *et al.* (20) indicate that CO_2 hydrogenation on Cu/ZnO occurs via Cu-formate formation, hydrogenation of this species to Cu-methoxide, migration of the methoxide to the ZnO surface, and hydrolysis of the Zn-methoxide. For the CO hydrogenation, on the other hand, they suggested that CO reacts on the ZnO surface to Zn-formate, which is hydrogenated by hydrogen atoms spilled over from the Cu. The resulting Zn-methoxide is hydrolysed. The absence of water, and the slower hydrogenation of Zn-formate than of Cu-formate explain the slower methanol formation from CO and H_2 than from CO_2 and H_2 over Cu/ZnO (20). The IR study of Fisher and Bell (39) on the formation of methanol from CO_2 and H_2 over ZrO_2-promoted Cu/SiO_2 shows that Cu enhances the formation of Zr-formate and the rate at which this species is hydrogenated to Zr-methoxide. They ascribe the main role of Cu to adsorbing H_2 dissociatively and spilling the resulting H atoms over to ZrO_2. A bifunctional mechanism with spillover from Cu to ZnO might also explain why Burch *et al.* observed that even physical mixtures of Cu/SiO_2 and ZnO/SiO_2 showed a synergistic effect in the reaction of a CO-CO_2-H_2 mixture, while combinations of consecutive catalyst beds, separated by plugs of glass wool, did not show any promotional effect (27, 40).

Alumina improves the activity of Cu catalysts significantly. This cannot be ascribed exclusively to an increased metal dispersion but must also be related to the chemical properties of the support. An amphoteric metal oxide, as additive or support, may promote the formation as well as the conversion of the intermediate species. Such a metal oxide can adsorb CO in the form of formate species on the basic sites (41) and can activate the hydrogenation of this intermediate to methanol by the interaction of the carbonyl oxygen with the acid sites (42). The addition of metal oxides, such as CaO and La_2O_3, to Cu/Al_2O_3 improved the catalytic activity in the hydrogenation of CO to methanol significantly. Most likely, a correlation between the number of basic sites, surface concentration of formate species, and methanol activity exists. In the hydrogenation of CO_2, however, the presence of basic metal oxides did not affect the formation of $C_{1\text{-oxo}}$ products nor the reverse water–gas shift reaction (Table 3). Only the formation of dimethyl ether was inhibited by the decrease in the number of acid sites on the alumina surface. To our surprise and in contrast to the belief that the formation of methanol occurs faster from CO_2 than from CO, over doped Cu/Al_2O_3 catalysts, the highest methanol activities were observed in the hydrogenation of CO. Thus, the higher conversions achieved in the hydrogenation of CO_2 rather than in the hydrogenation of CO are actually the result of a very fast reverse water–gas shift reaction. This suggests that formate intermediates on the alumina surface can quickly dehydrate to CO. The presence of additional Ca (or La) basic sites will not further improve the methanol activity. On the contrary, due to the strong acid–base interaction, the hydrogenation of Ca-formate species may be more difficult than the hydrogenation of Al-formate, and as a result Ca-formate will hardly play more than a spectator role in the methanol formation over Cu/Al_2O_3.

All this is in accordance with the assumption that metal oxides (used as additive or as support) are directly involved in the synthesis of methanol as *co-catalysts* and that the catalytic reaction occurs through *formate intermediates* adsorbed on the support or the additive surface, independently of the carbon source used. Thus, in the hydrogenation of CO, formate is formed on the support (or additive) surface by reaction with the hydroxyl groups and is hydrogenated to methoxy species by hydrogen dissociatively adsorbed on the reduced metal and spilled over to the support; hydrolysis eventually gives methanol. On the other hand, CO_2 may react with a hydrogen atom on the metal surface to formate, just like the insertion of CO_2 into the M-H bond in organometal hydride complexes (44, 45). A basic metal oxide on the surface of the metal may promote this insertion by increasing the CO_2 coverage of the metal surface and by stabilizing the formate formed (46). The formate may be hydrogenated on the metal surface to methoxy, which then spills over to the support or additive surface and become hydrolyzed to methanol. Alternatively, the formate species on the metal may spill over to the support or additive surface and be hydrogenated by spilled over H atoms.

This model can also explain why the hydrogenation of CO_2 to methanol is faster than that of CO over Cu catalysts, while the reverse is true for Pd catalysts. Copper is more electron rich than palladium and can therefore more easily insert CO_2 into the M-H bond (44–46). At the same time, H_2 adsorption on Cu is an activated process and the Cu-H bond is weaker than the Pd-H bond. As a consequence, the coverage of H atoms at the Pd surface will be higher than at the Cu surface, resulting in better spillover from Pd than from Cu and thus faster hydrogenation of the formate species on the support or additive. CO_2 hydrogenation is therefore favored over Cu and CO hydrogenation over Pd.

A completely different type of catalyst which can produce methanol from synthesis gas is molybdenum sulfide promoted by an alkali metal. K-MoS_2 as well as K-Co-MoS_2 proved to be H_2S tolerant methanol catalysts (47–49). The explanation for their excellent behavior may be that K-Co-MoS_2 functions just as Cu or Pd promoted by a basic oxide. CO reacts on the basic component to formate which then reacts to methanol with hydrogen atoms supplied by Cu or Pd, or by Co-MoS_2 in the case of the sulfidic catalyst.

REFERENCES

1. Liu, G., Wilcox, D., Garland, M., and Kung, H. H., *J. Catal.* **90**, 139 (1984).
2. Chinchen, G. C., Denny, P. J., Parker, D. G., Spencer, M. S., and Whan, D. A., *Appl. Catal.* **30**, 333 (1987).
3. Chinchen, G. C., Denny, P. J., Jennings, J. R., Spencer, M. S., and Waugh, K. C., *Appl. Catal.* **36**, 1 (1988).
4. Burch, R., Golunski, S. E., and Spencer, M. S., *Catal. Lett.* **5**, 55 (1990).
5. Robinson, W. R. A. M., and Mol, J. C., *Appl. Catal.* **60**, 73 (1990).
6. Chu, P. J., Gerstein, B. C., and King, T. S., *J. Catal.* **115**, 194 (1989).
7. Nonneman, L. E. Y., and Ponec, V., *Catal. Lett.* **7**, 213 (1990).
8. Fujita, S., Usui, M., Hanada, T., and Takezawa, N., *React. Kinet. Catal. Lett.* **56**, 15 (1995).
9. Klier, K., *Adv. Catal.* **31**, 243 (1982).
10. Sheffer, G. R., and King, T. S., *J. Catal.* **115**, 376, 488 (1989).
11. Nakamura, J., Nakamura, I., Uchijima, T., Kanai, Y., Watanabe, T., Saito, M., and Fujitani, T., *Catal. Lett.* **31**, 325 (1995).
12. Muhler, M., Törnqvist, E., Nielsen, L. P., Clausen, B. S., and Topsøe, H., *Catal. Lett.* **25**, 1 (1994).
13. Yoshiara, J., Parker, S. C., Schafer, A., and Campbell, C. T., *Catal. Lett.* **31**, 313 (1995).
14. Liu, Y., Zhong, B., Peng, S., Wang, Q., Hu, T., Xie, Y.-N., and Ju, X., *Catal. Today* **30**, 177 (1996).
15. Fakley, M. E., Jennings, J. R., and Spencer, M. S., *J. Catal.* **118**, 483 (1989).
16. van den Bussche, K. M., and Froment, G. F., *Appl. Catal. A* **112**, 37 (1994).
17. Bailie, J. E., Rochester, C. H., and Millar, G. J., *Catal. Lett.* **31**, 333 (1995).
18. Millar, G. J., Rochester, C. H., and Waugh, K. C., *J. Catal.* **155**, 52 (1995).
19. Fisher, I. A., Woo, H. C., and Bell, A. T., *Catal. Lett.* **44**, 11 (1997).
20. Fujita, S., Usui, M., Ito, H., and Takezawa, N., *J. Catal.* **157**, 403 (1995).
21. Chinchen, G. C., Waugh, K. C., and Whan, D. A., *Appl. Catal.* **25**, 101 (1986).
22. Kagan, Y. B., Liberov, L. G., Slivinskii, E. V., Loktev, S. M., Lin, G. T., Rozovsskii, A. Y., and Bashkirov, A. N., *Dokl. Akad. Nauk. SSSR* **221**, 1093 (1975).
23. Klier, K., Chatikavanij, V., Herman, R. G., and Simmons, G. W., *J. Catal.* **74**, 343 (1982).
24. Lee, J. S., Lee, K. H., Lee, S. Y., and Kim, Y. G., *J. Catal.* **144**, 414 (1993).
25. King, D. S., and Nix, R. M., *J. Catal.* **160**, 76 (1996).
26. Gotti, A., and Prins, R., *J. Catal.* **175**, 302 (1998).
27. Burch, R., and Chappel, R. J., *Appl. Catal.* **45**, 131 (1988).
28. Parris, G. E., and Klier, K., *J. Catal.* **97**, 374 (1986).
29. Brown Bourzutschky, J. A., Homs, N., and Bell, A. T., *J. Catal.* **124**, 52, 73 (1990).
30. van Herwijnen, T., and de Jong, W. A., *J. Catal.* **34**, 209 (1974).
31. Clarke, D. B., and Bell, A. T., *J. Catal.* **154**, 314 (1995).
32. Nakamura, J., Nakamura, I., Uchijima, T., Watanabe, T., and Fujitani, T., *Stud. Surf. Sci. Catal.* **101B**, 1389 (1996).
33. Robbins, J. L., and Marucchi-Soos, E., *J. Phys. Chem.* **93**, 2885 (1989).
34. Hsiao, E. C., and Falconer, J. L., *J. Catal.* **132**, 145 (1991).
35. Flesner, R. L., and Falconer, J. L., *J. Catal.* **150**, 301 (1994).
36. Gotti, A., and Prins, R., *Catal. Lett.* **37**, 143 (1996).
37. Handen, J. B., and Joensen, F., *Stud. Surf. Sci. Catal.* **61**, 265 (1991).
38. Driessen, J. M., Poels, E. K., Hindermann, J. P., and Ponec, V., *J. Catal.* **82**, 26 (1983).
39. Fisher, I. A., and Bell, A. T., *J. Catal.* **172**, 222 (1997).
40. Burch, R., Golunski, S. E., and Spencer, M. S., *J. Chem. Soc. Faraday Trans.* **86**, 2683 (1990).
41. Gopal, P. G., Schneider, R. L., and Watters, K. L., *J. Catal.* **105**, 366 (1987).
42. Tagawa, T., Nomura, N., Shimakage, M., and Goto, S., *Res. Chem. Intermed.* **21**, 193 (1995).
43. Chaumette, P., Courty, P., Barbier, J., Fortin, T., Lavalley, J. C., Chauvin, C., Kiennemann, A., Idriss, H., Sneeden, R. P. A., and Denise, B., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988," Vol. 2, p. 585. The Chemical Society of Canada, Ottawa, 1988.
44. Sakaki, S., and Ohkubo, K., *Inorg. Chem.* **28**, 2583 (1989).
45. Leitner, W., *Angew. Chem. Int. Ed.* **34**, 2207 (1995).
46. Darensbourg, D. J., and Ovalles, C., *Chem. Tech.* 636 (1985).
47. Xie Youchang, Naasz, B. M., and Somorjai, G. A., *Appl. Catal.* **27**, 233 (1986).
48. Dianis, W. P., *Appl. Catal.* **30**, 99 (1987).
49. Santiesteban, J. G., Bogdan, C. E., Herman, R. G., and Klier, K., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988," Vol. 2, p. 561. The Chemical Society of Canada, Ottawa, 1988.