An effective catalyst, $Cu–B_2O_3/SiO_2$, for hydrogenolysis of methyl formate and one-step synthesis of methanol in slurry-phase with potassium methoxide

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Some chromium-free copper-based catalysts are tested for the gas-phase hydrogenolysis of methyl formate, in which $Cu–B_2O_3/SiO_2$ catalyst is identified to be the most promising. The behaviors of $Cu–B_2O_3/SiO_2$ catalysts are also examined in the slurry-phase hydrogenolysis of methyl formate, along with a discussion of the promoting effect of B_2O_3. Also, $Cu–B_2O_3/SiO_2$ is used with potassium methoxide as a co-catalyst for the carbonylation of methanol to regenerate the potassium methoxide from potassium formate and potassium methyl carbonate. Moreover, the slurry-phase one-step synthesis of methanol is studied using $KOCH_3/Cu–B_2O_3/SiO_2$ mixed catalyst under relatively mild conditions.

Keywords: carbonylation; copper; boron oxide; hydrogenolysis; methanol; methyl formate; potassium methoxide; liquid-phase

1. Introduction

Commercial processes for manufacturing methanol involve gas-phase hydrogenation of CO over a copper/zinc oxide based catalyst at 250–300°C and 50–100 atm [1]. The synthesis of methanol from CO and H_2 is an exothermic reaction, which is thermodynamically unfavorable at higher temperatures. In 1919, Christiansen first proposed an alternative two-step synthesis of methanol from CO and H_2 at lower temperatures involving the carbonylation of methanol to methyl formate (reaction (1)) and the subsequent hydrogenolysis of methyl formate (reaction (2)):

$$CH_3OH + CO \rightleftharpoons HCOOCH_3 \qquad (1)$$

$$HCOOCH_3 + 2H_2 \rightarrow 2CH_3OH \qquad (2)$$

Recent studies [3–9] have reviewed and studied the two-step synthesis.

Previous investigators have studied the carbonylation of methanol homogeneously catalyzed by alkali alkoxides in a solution at 60–90°C and 30–65 atm [6,10,11]. The alkali alkoxides are subject to reaction with water and carbon dioxide, thereby not only producing alkali formate and alkali methyl carbonate, respectively, but also losing their activities [6,10]. Therefore, the commercial synthesis of methyl formate by carbonylation is performed at low levels of water (< 1 ppm) and carbon dioxide (< 10 ppm) to prevent catalyst deactivation [6,12]. Others studied the hydrogenolysis of methyl formate heterogeneously catalyzed by copper-based catalysts in the gas-phase [13–16] or slurry-phase [6,17] at 140–180°C and up to 75 atm. Those investigators revealed that the hydrogenolysis reaction is inhibited by carbon monoxide. Such an inhibitor effect is irreversible in gas-phase [16] and reversible in slurry-phase [6,17].

Liu et al. demonstrated that carbonylation and hydrogenolysis reactions can be performed in a single reactor using a mixed catalyst comprised of potassium methoxide and copper chromite [16,17] to improve the tolerance of water and carbon dioxide for potassium methoxide [8,9]. Palekar et al. proposed that the reaction pathway in a single reactor involves the potassium methoxide-catalyzed carbonylation followed by hydrogenolysis on copper chromite [8,9]. According to their results, the deactivated potassium methoxide can be regenerated on copper chromite catalyst in the presence of hydrogen [8,9]. The carbonylation reaction is subject to equilibrium, thereby confirming that the hydrogenolysis reaction is the rate-limiting step [7]. In this study, we develop a hydrogenolysis catalyst with a higher activity than copper chromite. Copper chromite catalysts are known as excellent catalysts for the hydrogenolysis of methyl formate. However, a problem arises with environmental pollution from chromium in the catalysts. This study also develops a chromium-free copper-based catalyst with comparable performance properties.

In this work, we test some copper-based catalysts and compare them with copper chromite in the gas-phase hydrogenolysis to find a catalyst for a one-step methanol synthesis. The $Cu–B_2O_3/SiO_2$ catalyst, i.e., the most active one for hydrogenolysis, is the target catalyst in this study. We also examine slurry-phase hydrogenolysis of methyl formate over $Cu–B_2O_3/SiO_2$ catalyst, carbonylation of methanol with potassium methoxide, and one-step synthesis of methanol with a mixed $KOCH_3 + Cu–B_2O_3/SiO_2$ catalyst. Moreover, the promoting role of boron oxide is also examined.

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2. Experimental

2.1. Catalyst preparation

The $Cu–B_2O_3/SiO_2$ catalysts were prepared by incipient co-impregnation of copper nitrate and boron oxide dissolved in water, dried at 100°C for 6 h and calcined in air at 300°C for 3 h. The $Cu–B/SiO_2$ catalyst was also prepared by incipient impregnation of copper nitrate dissolved in water, dried and reduced with aqueous boronhydride solution (1 M) [18]. The copper chromite is a commercial catalyst (Engelhard Cu-1234 ; 23% Cu, 22% Cr, 120 m^2/g). The laboratory of Professor Chang [19] supplied the electroless plated Cu/Al_2O_3. The potassium methoxide was purchased from Merck Chemical Company, Inc.

2.2. Catalyst characterization

2.2.1. Temperature-programmed reduction and nitrous oxide chemisorption

TPR experiments were performed in a conventional apparatus consisting of a U-shaped quartz tube attached to a thermal-conductivity detector. The catalyst (40–60 mg) was first pretreated at 160°C for 1 h under a stream of argon, followed by cooling to room temperature. Next, the catalyst was progammedly reduced up to 350°C in a stream of 10% H_2/Ar (20 ml/min) at a rate of 5°C/min. The water produced was then trapped with 3A zeolites; hydrogen consumption was monitored via a thermal-conductivity detector.

Nitrous oxide chemisorption was used to determine the copper surface area [20,21]. It is assumed that the nitrous oxide molecule reacts selectively with reduced surface copper atom to form a monolayer of oxygen atoms with an O/Cu_s stoichiometry of 0.5, without oxidation of the bulk copper. The amount of chemisorbed oxygen was determined by temperature programmed reduction.

2.2.2. X-ray photoelectron spectroscopy (XPS)

The reduced catalysts were analyzed by a VG ESCA-210 spectrometer using a Mg Kα X-ray radiation source ($h\nu = 1253.6$ eV). Accurate binding energies were determined with the C_{1s} line at 284.6 eV.

2.2.3. X-ray diffraction (XRD)

The XRD patterns of the catalysts were obtained with a Siemens-D500 diffractometer using nickel-filtered copper Kα radiation ($\lambda = 0.1538$ nm).

2.3. Reaction studies

The gas-phase hydrogenolysis of methyl formate was carried out in a 4 mm i.d. U-shaped reactor at atmospheric pressure. The methyl formate was fed into the reactor by bubbling a flow of nitrogen through a saturator maintained at 0°C. The effluents of the reactor were analyzed by an on-line gas chromatograph with 1/8″ × 6′ Porpack Q column and thermal conductivity detector.

The slurry-phase hydrogenolysis of methyl formate was carried out in a magnetically stirred 160 ml batch reactor (Par-4546). The copper-based catalyst was prereduced under H_2 atmosphere in a U-tube from room temperature up to 200°C at a rate of 5°C/min and was kept at that temperature for 3 h. The amount of catalyst was sufficiently small and the speed of stirring was high enough to minimize mass transfer resistance. The reactor was maintained at constant temperature and pressure.

The slurry-phase carbonylation of methanol and one-step synthesis of methanol were carried out, respectively, in the same batch reactor system described above. The mixed catalyst composed of potassium methoxide and prereduced copper-based catalyst was used.

3. Results and discussion

3.1. Gas-phase hydrogenolysis

Copper chromite is a well known catalyst for the hydrogenolysis of methyl formate; however, a problem arises with environmental pollution from chromium. As aforementioned, this study aims to develop a chromium-free copper-based catalyst with performance properties comparable to copper chromite. The activities of Cu/SiO_2, Cu/Al_2O_3, electroless-Cu/Al_2O_3, Cu–B (copper boride) and $Cu–B_2O_3/SiO_2$ Cu-based catalysts were investigated at 170°C and 1 atm with a feed ratio of H_2/methyl formate (3/1). Table 1 summarizes the rates of methanol formation and selectivities over these catalysts, and also compares them with copper chromite. Of the catalysts tested, the $Cu–B_2O_3/SiO_2$ catalyst exhibited the highest activity, i.e., it was roughly ten times as active as the unpromoted one and two times as active as copper chromite. The electroless-Cu/Al_2O_3 catalyst with widespread copper on the support was inadequate

Table 1
Avtivities and selectivities of Cu-based catalysts for gas-phase hydrogenolysis of methyl formate

Catalyst [a]	Activity [b] (mmol MeOH/h g-Cu)	Selectivity MeOH (mol%)
Cu/SiO_2	75	93
$Cu–B_2O_3(3.2\%)/SiO_2$	709	88
$Cu–B_2O_3(3.2\%)/Al_2O_3$	187	91
Cu/Al_2O_3(electroless)	22	17
$Cu–B/SiO_2$	6	66
copper chromite [c]	355	88

[a] The loading of copper is 15 wt%.
[b] $T = 170$°C; $H_2/MF = 3/1$.
[c] Engelhard Cu-1234; 23 wt% Cu, 22 wt% Cr; 120 m^2/g.

Table 2
Activities and selectivities of Cu–B_2O_3(x%) / SiO_2 catalysts for gas-phase hydrogenolysis of methyl formate

B_2O_3 x (wt%)	Cu surface area (m^2/g-cat.)	Dispersion (%)	Activity[a] (mmol MeOH/ h g-Cu)	Selectivity MeOH (mol%)
0	11.0	10.8	75	93
1.6	15.9	15.7	514	87
3.2	39.3	38.7	709	88
4.8	32.2	31.8	680	87
6.4	23.2	22.9	682	87

[a] $T = 170°C$; $H_2/MF = 3/1$; $W/F = 0.02\,g/0.523\,mmol\,min^{-1}$.

for this structure-sensitive reaction. The utrafine-alloy catalyst of copper boride supported on SiO_2 (Cu–B/ SiO_2), as prepared by chemical reduction with $NaBH_4$, was only one-tenth as active as Cu/ SiO_2. When comparing Cu–B/ SiO_2 with Cu–B_2O_3/ SiO_2, boron and boron oxide seemed to exhibit opposite effects on copper for the hydrogenolysis of methyl formate. Those opposite effects are discussed later. The B_2O_3-promoted Cu/ SiO_2 catalysts were selected as the target catalysts in this work.

Various amounts of boron oxide were introduced into Cu/ SiO_2 catalyst by the co-impregnation method. As indicated in table 2, the specific surface area and dispersion of copper increased with the doped amount of B_2O_3 up to 3.2 wt%. X-ray diffraction study of these catalysts (fig. 1) revealed that only diffraction patterns due to copper at 2θ of 43.4° and 35.6° were detected. The intensity of diffraction decreased with the doped amount of B_2O_3; in addition, no well defined diffraction peak appeared beyond the doped amount of 3.2 wt%. The crystallite size of copper apparently decreased with the doped amount of B_2O_3 and was beyond the detectable limit as the doped amount exceeded 3.2 wt%. The XRD results did not entirely correlate with the copper surface areas of those catalysts. As the doped amount exceeded 3.2 wt%, the containment of boron oxide on copper might have led to the decrease in copper surface area. The TPR profiles (fig. 2) reveal that those catalysts are reduced at about 210°C and the doped ones are more easily reduced. The larger amount of doped B_2O_3 caused the lower initial and final reduction temperatures. The aforementioned decrease of copper crystallite size implied the more easy reduction of Cu–B_2O_3 / SiO_2 catalysts.

Conditions of 1 atm, 170°C, $H_2/MF = 3/1$ were used for the hydrogenolysis reaction. As indicated in table 2,

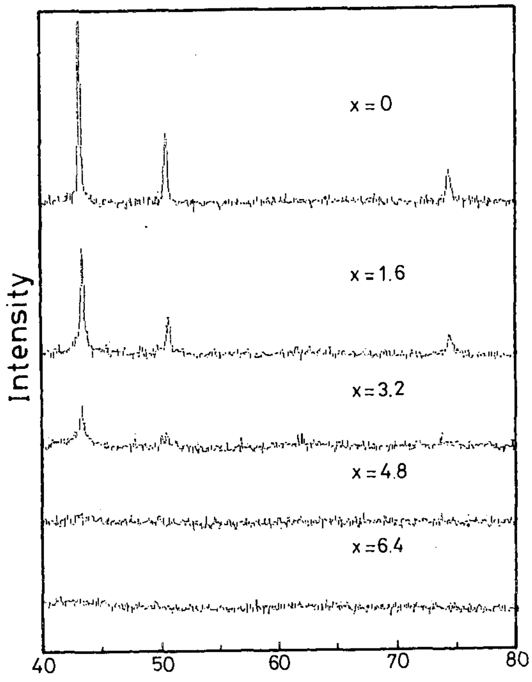

Fig. 1. X-ray diffraction of Cu–B_2O_3(x%) / SiO_2 catalysts.

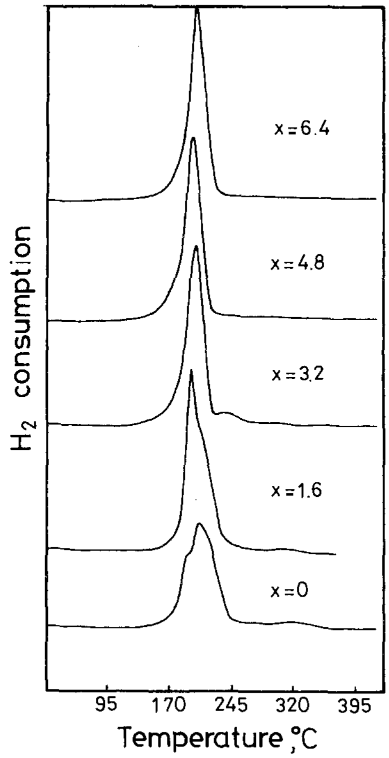

Fig. 2. TPR profiles of Cu–B_2O_3(x%) / SiO_2 catalysts.

in the hydrogenolysis reaction conversion increased with the amount of boron oxide doped up to 3.2 wt%; in addition, the selectivity to methanol decreased. Nevertheless, as shown in table 1 the selectivity of the $Cu–B_2O_3/SiO_2$ catalyst was still comparable with the commercial copper chromite catalyst. Undoubtedly, the chromium-free catalyst $Cu–B_2O_3/SiO_2$ was a potential one for the hydrogenolysis of methyl formate. The reactivity ratio of $Cu–B_2O_3(3.2\%)/SiO_2$ to Cu/SiO_2 was 9.5, significantly larger than the surface ratio of 3.6. Therefore we can infer that the boron oxide acts not only as a textural promoter but also as a structural promoter. With respect to the aforementioned promoting effect of boron oxide in $Cu–B_2O_3/SiO_2$ and the repressive effect of boron in the $Cu–B/SiO_2$ catalyst for the hydrogenolysis of methyl formate (table 1), the electronic interaction between Cu and B_2O_3 might be contradictory to that between Cu and B. Our previous studies involving CO hydrogenation over metal boride catalysts [22] also noted these contradictory effects of boron oxide and boron on nickel. XPS analysis of boride catalysts indicated boron to be an electron donor [23] that increases the electron density of metal. The XPS spectra of $Cu–B_2O_3/SiO_2$ and Cu/SiO_2 catalysts (fig. 3) reveal that the binding energy of the most intense peak of copper $2p_{3/2}$ is 932.3 eV with a 0.9 eV positive shift in respect to that of copper. Such a positive shift might be attributed to the electron drawing effect of boron oxide, which resulted in the enrichment of copper with a partially oxidized state on the catalyst. Kim et al. [24] reported that the activity of copper chromite in hydrogenolysis of methyl formate depends heavily on the existence of cuprous and copper metallic phases in a catalyst. In their work, they demonstrated that the catalyst activity is sensitively dependent on the cuprous state ($CuCrO_2$). The cuprous state or the partially oxidized state of copper might promote the dissociative adsorption of hydrogen and facilitate the hydrogenolysis reaction.

The major byproduct of hydrogenolysis is carbon monoxide decarbonylated from methyl formate. As shown in fig. 4, a selectivity greater than 90% could be obtained at a reaction temperature below 170°C; the selectivies later decreased with temperature. The conversion increased with W/F, but the selectivity was not a strong function of conversion beyond the conversion of 35% (fig. 5). This finding supports the assumption that decarbonylation takes place in parallel with hydrogenolysis. Table 3 summarizes the effects of H_2/MF feed ratios. The selectivity increased with the ratio; however, the rate of methanol formation is not a strong function of H_2/MF. This finding supports the assumption that the adsorption strength of methyl formate is much stronger than that of hydrogen.

3.2. *Slurry-phase hydrogenolysis and carbonylation*

One-step synthesis of methanol from H_2 and CO involves carbonylation of methanol to methyl formate and subsequent hydrogenolysis of methyl formate in the slurry-phase. Next, hydrogenolysis and carbonylation were examined, respectively, to more thoroughly understand the behavior of $Cu–B_2O_3/SiO_2$ in a slurry system. The hydrogenolysis was carried out at a pressure of hydrogen (P_{H_2}) greater than 400 psia and a temperature below 170°C. Similar to the behaviors of $Cu–B_2O_3/SiO_2$ in the gas-phase hydrogenolysis, the activity was enhanced with the doped amount of B_2O_3 and later

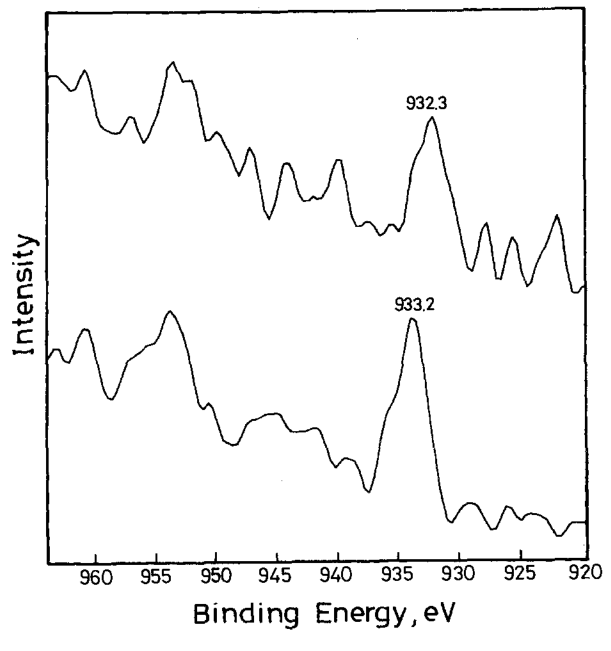

Fig. 3. XPS of $Cu–B_2O_3(3.2\%)/SiO_2$ catalyst.

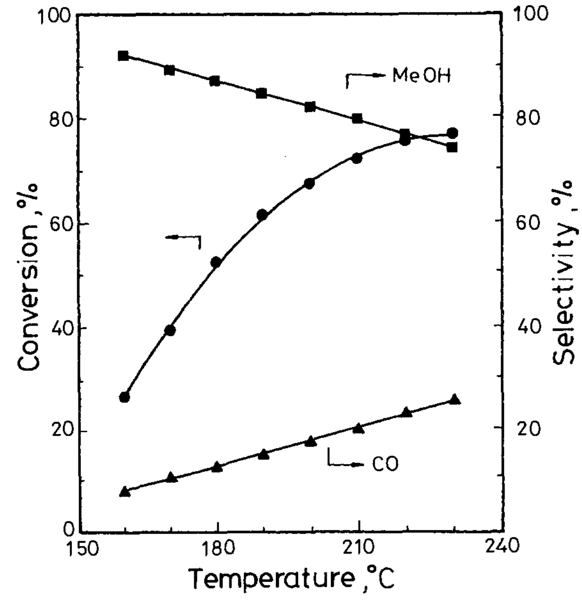

Fig. 4. Effect of temperature on gas-phase hydrogenolysis of methyl formate over $Cu–B_2O_3(3.2\%)/SiO_2$ catalyst (W/F_{MF} = 0.02 g/0.523 mmol min^{-1}; $H_2/MF = 3/1$).

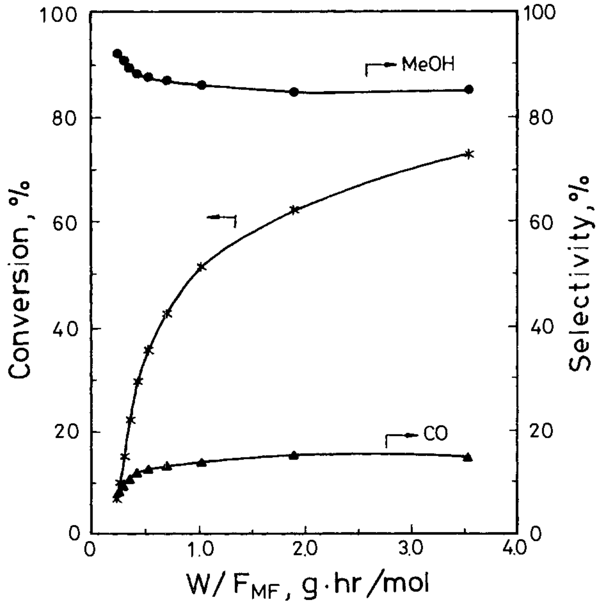

Fig. 5. Effect of W/F_{MF} on gas-phase hydrogenolysis of methyl formate over Cu–B_2O_3(3.2%)/SiO_2 catalyst (170°C; H_2/MF = 3/1; W = 0.02 g-cat.).

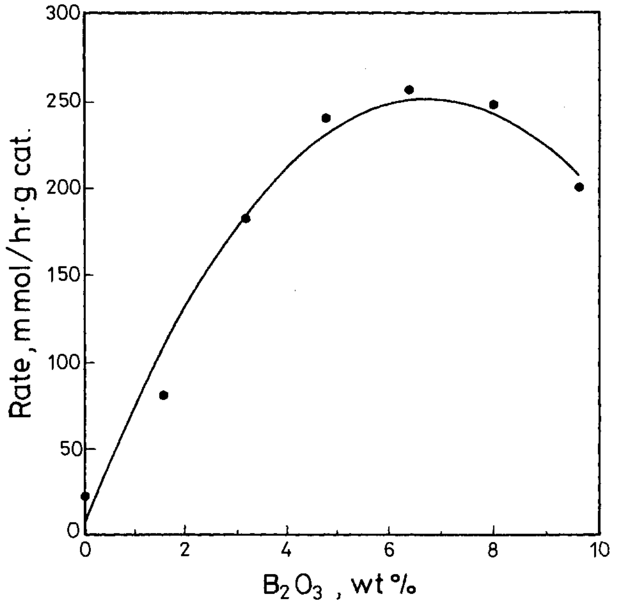

Fig. 6. Effect of amount of doped B_2O_3 on Cu–B_2O_3(x%)/SiO_2 catalysts for slurry-phase hydrogenolysis of methyl formate (rate: initial rate; 150°C, P_{H_2} = 400 psia; MF/Cu–B_2O_3(x%)/SiO_2 = 80 ml/0.8 g).

reached a maximum at the doped amount of 6.4 wt% (fig. 6), i.e., eleven times as active as an undoped one and 1.4 times as active as the commercial copper chromite catalyst. The conversion obviously increased with temperature, but the selectivity decreased only slightly – 100% to 99.3% (table 4) which is much larger than that in the gas-phase hydrogenolysis. The high selectivity seems to be an advantage of hydrogenolysis in the slurry-phase. Moreover, the initial rate of hydrogenolysis increased with the partial pressure of hydrogen in the apparent order of 0.8. To examine the effects of carbon monoxide that are essential for methyl formate formation, a series of experiments with added carbon monoxide (50, 100, 200 psia) were conducted at 150°C as (fig. 7). In general, carbon monoxide adsorbs more strongly than hydrogen on metal catalysts. Carbon monoxide might displace adsorbed hydrogen from the catalyst surface, thereby inhibiting the hydrogenolysis of methyl formate with an apparent order of −0.38.

The carbonylation of methanol with potassium methoxide catalyst was undertaken at 60–150°C and 200–600 psia. The potassium methoxide catalyst was directly transferred to the reactor for carbonylation under air. It reacted with H_2O and CO_2 to form potassium formate and potassium methyl carbonate [6,10] and lose its activity. As some hydrogen (100 psia) and an appropriate amount of prereduced Cu–B_2O_3 (6.4%)/SiO_2 or copper chromite were added as a co-catalyst, the carbonylation readily approached equilibrium (fig. 8). The Cu–B_2O_3/SiO_2 catalyst could catalyze the regeneration of the potassium methoxide catalyst from potassium formate and potassium methyl carbonate as follows [8,9],

$$KOOCH + 2H_2 \rightleftharpoons KOCH_3 + H_2O ;$$

$$KOCOOCH_3 + H_2 \rightleftharpoons CH_3OH + KOOCH$$

Table 3

Effect of H_2/MF ratio for gas-phase hydrogenolysis of methyl formate over Cu–B_2O_3(3.2%)/SiO_2 catalyst

H_2/MF	Activity[a]		Selectivity MeOH (mol%)
	(mmol MF/ h g-cat.)	(mmol MeOH/ h g-cat.)	
1.5	371	632	85
2.0	353	633	90
3.0	401	709	88
4.0	373	674	90
5.0	386	702	91
5.5	351	648	92
6.3	327	608	93
7.0	312	587	94

[a] T = 170°C; W/F = 0.02 g/0.52 mmol min^{-1}.

Table 4

Selectivities of Cu–B_2O_3 (6.4%) for slurry-phase hydrogenolysis of methyl formate at different temperatures

Temperature (°C)	Conversion[a] (mol%)	Selectivity[b] MeOH (mol%)
130	26	99.9
140	39	99.8
150	58	99.7
170	84	99.3

[a] P_{H_2} = 400 psia; MF/catalyst = 80 ml/0.8 g; conversion in 6 h.

[b] The selectivity is obtained from the analysis of products in liquid and vapor phases.

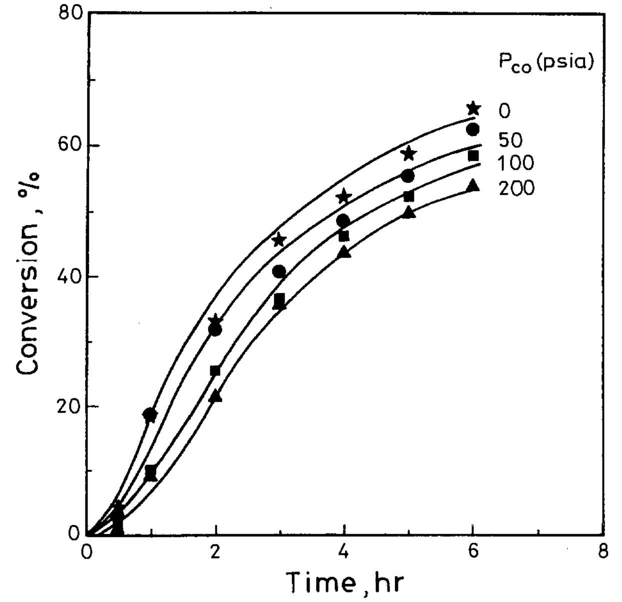

Fig. 7. Effect of carbon monoxide on slurry-phase hydrogenolysis of methyl formate over $Cu\text{–}B_2O_3(6.4\%)/SiO_2$ catalyst (150°C, $P_{H_2} = 400$ psia; $MF/Cu\text{–}B_2O_3(6.4\%)/SiO_2 = 80\,ml/0.8\,g$).

$$KOOCH + 2H_2 \rightleftharpoons KOCH_3 + H_2O$$

Here, the $Cu\text{–}B_2O_3(6.4\%)/SiO_2$ accompanying the potassium methoxide was used as a co-catalyst for carbonylation. Those results indicated that the carbonylation of methanol was reversible, readily approached equilibrium in 10–30 min and was selective to methyl formate. As indicated in table 5 and fig. 9 , the carbonylation of methanol was thermodynamically favored at a lower temperature and higher partial pressure of carbon monoxide.

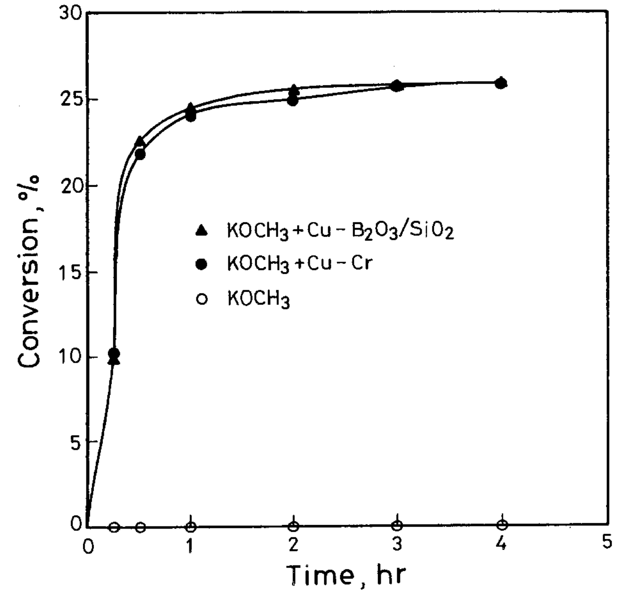

Fig. 8. Carbonylation of methanol with a Cu-based co-catalyst.

Table 5
Equilibrium conversion of carbonylation of methanol at different temperatures

Temperature (°C)	Equilibrium conversion (mol %)	
	experiment [a]	theory [b]
60	48.6	49.7
80	35.1	34.2
100	25.7	22.6
120	16.7	14.9
140	9.3	10.0
150	8.2	8.1

[a] $P_{CO} = 500$ psia, $P_{H_2} = 100$ psia; $Cu\text{–}B_2O_3(6.4\%)/SiO_2/KOCH_3 = 0.6\,g/2.2\,g$.

[b] $K_e = 3.37 \times 10^{-7} \exp(3870/T)$ [6].

3.3. One-step synthesis of methanol

Table 5 reveals that equilibrium limits the conversion of methanol to methyl formate for carbonylation. A lower reaction temperature is used in industrial processes to attain a high conversion. For instance, at 80°C, the equilibrium conversion is 34% at a carbon monoxide partial pressure of 500 psi. Otherwise, the hydrogenolysis of methyl formate, which rarely occurs below 100°C, is normally carried out at higher temperature (140–80°C) to obtain an acceptable reaction rate. If the carbonylation is to be carried out with the hydrogenolysis in one reactor for a one-step synthesis of methanol, a compromise must be made. Table 6 lists the average rates of methanol formation for different reaction temperatures (130–160°C) at P_{H_2+CO} of 500 psia ($H_2/CO = 2/1$). At temperatures below 150°C some methyl formate was obviously detected during reaction; this implies that the

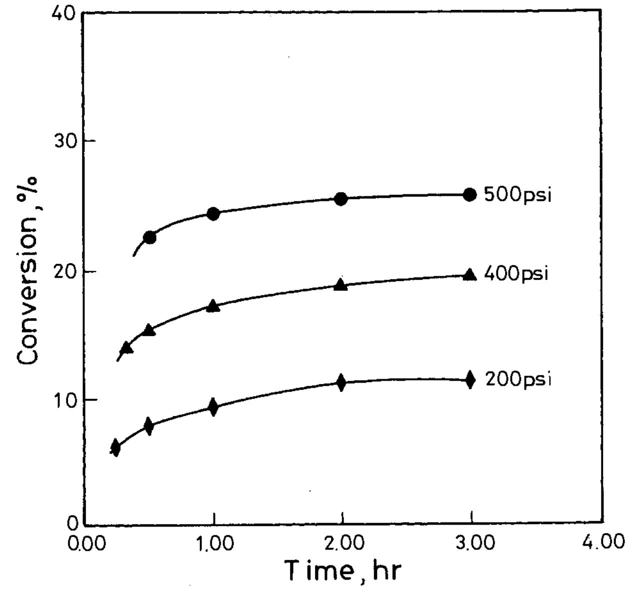

Fig. 9. Effect of carbon monoxide on carbonylation (100°C, $P_{H_2} = 100$ psia; $MeOH/KOCH_3/Cu\text{–}B_2O_3(6.4\%)/SiO_2 = 80\,ml/3\,g/0.8\,g$).

Table 6
Average rates of methanol formation for one-step methanol synthesis at different temperatures

Temperature (°C)	Rate of MeOH formation [a] (mmol/h)	MF [b] (mol%)
130	43.9	6.1
140	46.0	< 5
150	48.0	–
160	43.7	–

[a] $P_{H_2+CO} = 500$ psia, $H_2/CO = 2/1$; Cu–B_2O_3(6.4%)/SiO_2/$KOCH_3$ = 0.6 g/2.2 g; average formation rate in 10 h.

[b] The molar composition of methyl formate in the reaction system.

rate of methanol formation was limited by the hydrogenolysis of methyl formate. On the other hand, the rate was limited by the carbonylation equilibrium above 150°C. Under such a compromise, the temperature of 150°C was used in the following discussion.

The partial pressure of carbon monoxide is another factor for which a compromise must be made between carbonylation and hydrogenolysis. A higher partial pressure of CO thermodynamically favored the carbonylation; but carbon monoxide inhibited the copper-based catalyst for the hydrogenolysis mentioned above. To avoid the limitation of the carbonylation equilibrium, the partial pressure of carbon monoxide was increased from 100 to 400 psia. Moreover, to weaken the inhibitory effect of CO on hydrogenolysis, the partial pressure of hydrogen was also increased from 200 to 1200 psia. As shown in fig. 10, the average rate of methanol formation increased with the partial pressures of CO and H_2. Potentially a one-step synthesis of methanol could be conducted to attain a good rate at a higher partial pressure of CO to overcome the equilibrium of carbonylation and at a much higher partial pressure of hydrogen. Consequently the rate of hydrogenolysis would be improved.

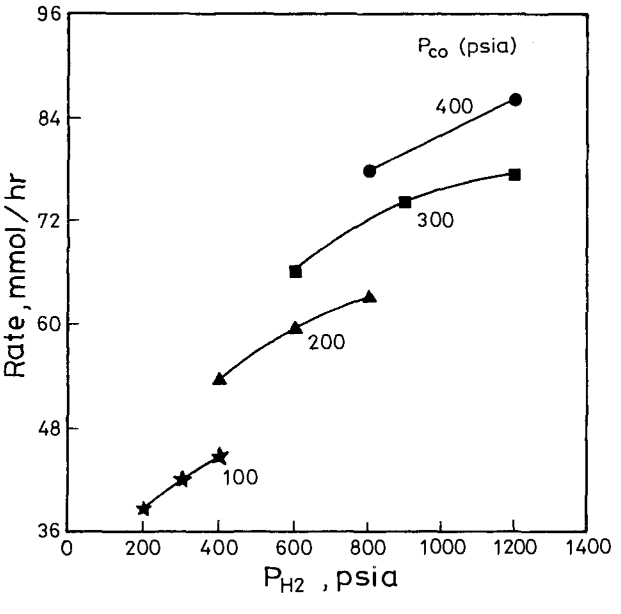

Fig. 10. Effects of H_2 and CO partial pressures on one-step synthesis of methanol (rate: average rate of methanol formation in 10 h; 100°C; MeOH/$KOCH_3$/Cu–B_2O_3(6.4%)/SiO_2 = 80 ml/3 g/0.8 g).

4. Conclusion

The Cu–B_2O_3/SiO_2 catalyst can potentially replace copper chromite as a catalyst for the hydrogenolysis of methyl formate in the gas-phase or slurry-phase, and for one-step methanol synthesis. Boron oxide not only functioned as a textural promoter to increase the dispersion of copper, but also acted as a structural promoter to decrease the electron density of the copper. The optimum loading of B_2O_3 is about 6 wt%. The Cu–B_2O_3/SiO_2 catalyst could also catalyze the regeneration of the potassium methoxide catalyst for carbonylation. In addition, the carbonylation of methanol was thermodynamically favored at low temperature and high pressure of carbon monoxide.

A compromise must be made between temperature and partial pressure of CO for the one-step synthesis of methanol. To prevent the formation of methanol from the limitation of equilibrium conversion of carbonylation or the hydrogenolysis rate, a mediate temperature (150°C) and a high pressure of carbon monoxide (400 psia) must be used. Furthermore to weaken the inhibitory effect of carbon monoxide on the copper catalyst for hydrogenolysis in a one-step synthesis of methanol, the reaction could be performed at a higher partial pressure of hydrogen (> 1000 psia).

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