Formic acid assisted synthesis of highly efficient Cu/ZnO catalysts: effect of HCOOH/Cu molar ratios

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Supporting Information

Results and Discussion

1. The total carbon TOFs of the as-prepared catalysts.

The total carbon TOFs of the as-prepared catalysts before and after reduction, which were calculated by N_2O pulse method, were shown in Table S1. Except for C_6, C_7, C_8 and C_9, all the other catalysts with and without reduction suggested a similar TOF, indicating that the promotion effect of Cu by ZnO was not influenced by $HCOOH/Cu^{2+}$ ratios during dissolution and calcination processes. For C_6, C_7, C_8 and C_9 before reduction, Cu_2O species, which were proved by XRD and TPR analysis, were left in the as-burnt catalysts. Cu_2O species could be reduced to metallic Cu by syngas during the reaction and contributed to the conversion of syngas to methanol, but were not included in calculation of metallic Cu surface, leading to higher TOF value of C_6, C_7, C_8 and C_9.

2. The stability of the as-synthesized catalysts.

In order to give insight into the stability of the as-synthesized catalysts, the continuous reaction results for low-temperature methanol synthesis at 443 K and 5.0 MPa for 40 h using C_{24} of 3 g were reported in our former manuscript[1]. For contrast, $C_{24\text{-reduction}}$, which was further reduced by a flow of 5% hydrogen in nitrogen at 523 K for 6 h, was also conducted at the same reaction conditions and the reaction results were compared in Fig. S1. At the initial stage of the reaction, 40 mL dead volume of the reactor and 5 mL cold trap must be filled by the pressurized feed gas. Thus, the apparent conversions were initially low but increased gradually. After 10 h, the conversions were stable. CO conversion was about 27.5%, whereas CO_2 conversion was about -1.9%. The total carbon conversion was about 23.5%. At the initial 10 h, the CO_2 conversion dropped to the minimum -10.5%, then returned to about -1.9%. The negative CO_2 conversion proved that CO was first converted to CO_2 through the water-shift reaction, and then CO_2 was hydrogenated to methanol. The balance between CO_2 formation and formate formation was reached after 10 h. After 40 h reaction, the methanol selectivity calculated was as high as 97.5%. Compared with former reported results of C_{24}, the reaction results and the stabilities of C_{24} and $C_{24\text{-reduction}}$ were nearly the same.

3. The characterization results of the catalysts before and after reaction.

The characterization results of C_{24}, $C_{24\text{-used}}$ (after 40 h reaction), $C_{24\text{-reduction}}$, and $C_{24\text{-reduction-used}}$ (after 40 h reaction) were compared in Table S2. The crystallite sizes of Cu and ZnO, and the metallic Cu^0 surface area of C_{24} and $C_{24\text{-used}}$ after 40 h reaction were of no much difference. The similar phenomenon was also observed in $C_{24\text{-reduction}}$ and $C_{24\text{-reduction-used}}$. The results indicated that the aggregation of the as-burnt catalysts prepared by formic acid assisted solid-state method after 40 h reaction was not obviously observed.

4. The influence of calcination environment.

The metal-formic acid precursor with $HCOOH/Cu^{2+} = 30/1$ was separately calcined in Ar, N_2, and H_2 at 673 K for 3 h and then passivated by 1% oxygen diluted by nitrogen for 4 h to get as-burnt catalysts, noted as $C_{30\text{-Ar}}$, $C_{30\text{-N2}}$, and $C_{30\text{-H2}}$, respectively. As displayed in Table S3, Cu crystallite sizes, metallic Cu^0 surface areas, total carbon conversions, methanol selectivities, and methanol yields of $C_{30\text{-Ar}}$ and $C_{30\text{-N2}}$ were nearly the same. But, it was very interesting that $C_{30\text{-H2}}$, which was burnt in H_2 atmosphere, exhibited much smaller Cu crystallite size and much higher metallic Cu^0 surface area, higher total carbon conversion, as well as higher methanol selectivity. In agreement with phenomena reported in this manuscript, larger metallic Cu^0 surface area led to higher total carbon conversion and smaller Cu crystallite size resulted in higher methanol selectivity. However, compared with $C_{\text{co-precipitation}}$ prepared by conventional co-precipitation method in Table S3, $C_{30\text{-H2}}$ demonstrated higher methanol selectivity, whereas with much larger Cu crystallite size. According to above mentioned results and discussion, we considered that the calcination environment was very important and significantly influenced the reduction process, which resulted in the formation of Cu/ZnO catalysts with remarkable activity and selectivity differences. The reduction processes and mechanisms in different atmosphere will be further studied in detail.

5. FT-IR analysis of the as-burnt catalysts.

As reference, the catalyst prepared by citric acid assisted solid-state method was noted as

$C_{citric\ acid}$. The FT-IR spectra of the precursors and as-burnt catalysts $C_{citric\ acid}$ as well as C_{argon} were compared in Fig. S2. Assignment of the bands for adsorption species was made by analogy with the spectra of known compounds and by comparison with published literatures. In Fig. S2a for the precursor of $C_{citric\ acid}$, the bands at 820 and 1380 cm^{-1} were assigned to the NO_3^-. Other complicated bands were attributed to carboxyl ions (COO^-) and free carboxylic group. However for the precursor of C_{argon} in Fig, S2b, no bands were found at 820 and 1380 cm^{-1}, suggesting that no NO_3^- was left in the precursor of C_{argon} which was prepared by this formic acid assisted solid state method. The bands at about 1351 and 1542 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of the bidentate formate species (OCO) on Cu, (H-COO-Cu). The band at about 1370 cm^{-1} came from the asymmetric stretching vibrations of the bidentate formate species on Zn, (H-COO-Zn), while two bands occurred near 1570 and 1595 cm^{-1}, representing the asymmetric stretching vibrations of formate on Zn. It was clear that the FT-IR spectra of the precursor for C_{argon} in Fig. S2b were all attributed to metal formate species, without any NO_3^-.

For the burnt catalysts (in argon), two broad bands at about 1400 and 1565cm^{-1} were presented in Fig. S2c of $C_{citric\ acid}$, which were assigned to the asymmetric and symmetric stretching vibrations for carboxyl ions (COO^-) from metal carboxylates. These results clarified that a part of carbonic residues (carboxyl ions) were left in $C_{citric\ acid}$ when citric acid was used as assisting chelating agent and reductant. A broad band at about 840 cm^{-1} was another proof for the formation of carbonates which were generated during the combustion process and left in $C_{citric\ acid}$. However for C_{argon} in Fig. S2d, almost no bands were found at about 840, 1351, 1400, and 1560 cm^{-1}, which indicated that when this formic acid assisted solid stated method was applied to directly prepare metallic catalysts, almost no carbonic residues were left in the as-burnt products, as no C-C bond in the simplest organic acid, HCOOH. Therefore, we considered that almost no organic residues were left in the as-burnt catalysts prepared by formic acid assisted solid stated method.

6. The proposed mechanism for low-temperature methanol synthesis.

According to our former reports[1,2], the formate species were formed from syngas adsorbed on Cu/ZnO catalysts. Then, gas-phase and physisorbed ethyl formate, the reactive intermediate, was obtained by the reaction of adsorbed formate with gas-phase ethanol, as shown in Fig. S3. Cu^+ and ZnO were both the active sites for the formation of ethyl formate. This reaction was a nucleophilic addition-elimination reaction. Ethanol with lone pair electrons in oxygen atom was the nucleophilic reagent. The nucleophilic reaction process was illustrated in Fig. S4. Finally, gas-phase and physisorbed ethyl formate were hydrogenated by hydrogen atoms on Cu to form gas-phase methanol. Gas-phase and liquid phase had the same reaction mechanism. In our proposed low-temperature methanol synthesis mechanism, Cu^+ and Cu were the active site for the formation of ethyl formate, but only Cu^0 was the active site for the hydrogenation of ethyl formate to produce methanol.

References

1 L. Shi, W.Z. Shen, G.H. Yang, X.J. Fan, Y.Z. Jin, C.Y. Zeng, K. Matsuda, N. Tsubaki,

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2 N. Tsubaki, M. Ito, K. Fujimoto, *J. Catal*., 2001, **197**,224-227.

Figure captions

1. Table S1 The total carbon TOFs of as-prepared catalysts.

2. Fig. S1. Variations of CO, CO_2, and total carbon conversions with reaction time for continuous synthesis of methanol (Reaction conditions: T = 443 K, P = 5.0 MPa, catalyst: 3 g $C_{24\text{-reduction}}$, solvent: ethanol 40 mL, stirring speed: 2000 rpm, reaction time: 40 h, syngas: $Ar/CO/CO_2/H_2$ = 3.13/33/5.23/58.64, 20 mL/min).

3. Table S2 Characterization results of C_{24}, $C_{24\text{-used}}$ $C_{24\text{-reduction}}$, and $C_{24\text{-reduction-used}}$.

4. Table S3 Characterization and reaction results of $C_{30\text{-Ar}}$, $C_{30\text{-N2}}$, and $C_{30\text{-H2}}$ catalysts.

5. Fig. S2. F1 FT-IR analysis of (a) the precursor of $C_{\text{citric acid}}$, (b) the precursor of C_{argon}, (c) $C_{\text{citric acid}}$, and (d) C_{argon}.

6. Fig. S3 Proposed mechanism for low-temperature methanol synthesis (M is Cu/ZnO).

7. Fig. S4 Nucleophilic reaction process.

Table S1 The total carbon TOFs of as-prepared catalysts.

Catalysts	$HCOOH/Cu^{2+}$ (mol ratios)	TOF[a] ($10^{-3}s^{-1}$)	Crystallite Sizes (nm)[b] Cu or CuO	ZnO	S_{Cu}[c] (m^2/g)
$C_{0\text{-reduction}}$	0/1	13.02	56.2 (Cu)	80.70	2.65
$C_{2\text{-reduction}}$	2/1	12.89	54.5 (Cu)	76.20	2.74
$C_{4\text{-reduction}}$	4/1	12.43	52.7 (Cu)	71.30	3.05
C_6	6/1	23.94	21.6 (CuO)	54.50	0.65
C_7	7/1	17.29	15.0 (CuO)	55.80	1.11
$C_{7\text{-reduction}}$	7/1	12.09	48.0 (Cu)	50.90	3.31
C_8	8/1	15.85	10.0 (CuO)	35.30	1.83
$C_{8\text{-reduction}}$	8/1	11.86	46.0 (Cu)	38.40	3.61
C_9	9/1	12.99	10.0 (CuO)	36.00	2.63
$C_{9\text{-reduction}}$	9/1	11.70	45.0 (Cu)	32.90	3.71
C_{12}	12/1	11.64	43.0 (Cu)	33.30	3.77
$C_{12\text{-reduction}}$	12/1	11.58	43.0 (Cu)	34.20	3.92
C_{16}	16/1	11.50	41.0 (Cu)	21.50	4.06
$C_{16\text{-reduction}}$	16/1	11.55	42.0 (Cu)	22.60	4.03
C_{20}	20/1	11.50	39.0 (Cu)	18.30	4.11
$C_{20\text{-reduction}}$	20/1	11.50	40.0 (Cu)	20.30	4.05
C_{24}	24/1	11.17	36.0 (Cu)	17.90	4.42
$C_{24\text{-reduction}}$	24/1	11.40	40.0 (Cu)	20.20	4.27
C_{30}	30/1	11.11	35.0 (Cu)	18.40	4.56
$C_{30\text{-reduction}}$	30/1	11.22	38.2 (Cu)	19.30	4.36

[a] TOF was the total carbon turnover frequency.

[b] Calculated by Scherrer formula.

[c] Determined from N_2O pulse chemisorption.

Table S2 Characterization results of C_{24}, $C_{24\text{-used}}$ $C_{24\text{-reduction}}$, and $C_{24\text{-reduction-used}}$.

	HCOOH/Cu^{2+}	Crystallite Sizes (nm)[b]		S_{Cu}[c]
Catalysts	(mol ratios)	Cu or CuO	ZnO	(m^2/g)
C_{24}	24/1	36.0 (Cu)	17.90	4.42
$C_{24\text{-used}}$	24/1	37.0 (Cu)	18.00	4.39
$C_{24\text{-reduction}}$	24/1	40.0 (Cu)	20.20	4.27
$C_{24\text{-reduction-used}}$	24/1	40.5 (Cu)	20.30	4.21

[a] TOF was the total carbon turnover frequency.

[b] Calculated by Scherrer formula.

[c] Determined from N_2O pulse chemisorption.

Table S3 Characterization and reaction results of $C_{30\text{-}Ar}$, $C_{30\text{-}N2}$, and $C_{30\text{-}H2}$ catalysts.

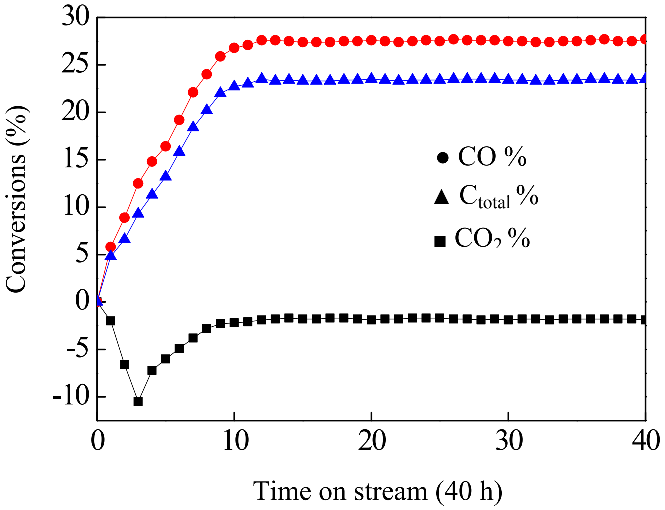
Catalysts	Crystallite Sizes [a]	S_{Cu} [b]	Conversion（%）			Selectivity（%）		Yield（%）	
	Cu (nm)	(m^2/g)	CO	CO_2	C_{Total} [b]	CH_3OH	$HCOOC_2H_5$	CH_3OH	$HCOOC_2H_5$
$C_{30\text{-}Ar}$	35.0	4.56	38.7	72.3	43.3	80.2	19.8	34.72	8.57
$C_{30\text{-}N2}$	35.3	4.42	37.2	71.8	42.0	76.6	23.4	32.17	9.83
$C_{30\text{-}H2}$	18.0	9.61	56.2	71.4	58.3	93.8	6.2	54.69	3.61

Reaction conditions: T = 443 K, P = 5.0 MPa, catalyst weight: 1 g, ethanol solvent: 40 mL, stirring speed: 2000 rpm, reaction time: 4 h, syngas: $Ar/CO/CO_2/H_2$ = 3.13/33/5.23/58.64.

[a] Calculated by Scherrer formula.

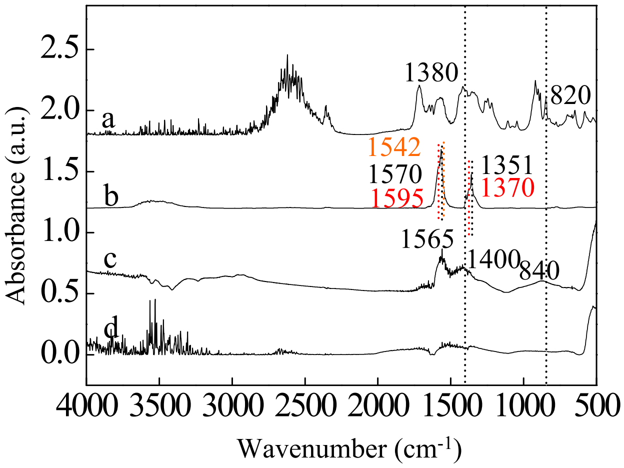
[b] Determined from N_2O pulse chemisorption.

[c] C_{Total} = CO conv. × a/(a + b) + CO_2conv. × b/(a + b) (a, b were the contents of CO, CO_2 in the feed gas)



Conversions (%)
30
25
20
15
10
5
0
-5
-10
0
10
20
30
40
Time on stream (40 h)
● CO %
▲ C_{total} %
■ CO_2 %

Fig. S1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Wavenumber (cm-1)
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1.5
1.0
0.5
0.0
4000
3500
3000
2500
2000
1500
1000
500
a
b
c
d
1380
820
1542
1570
1595
1351
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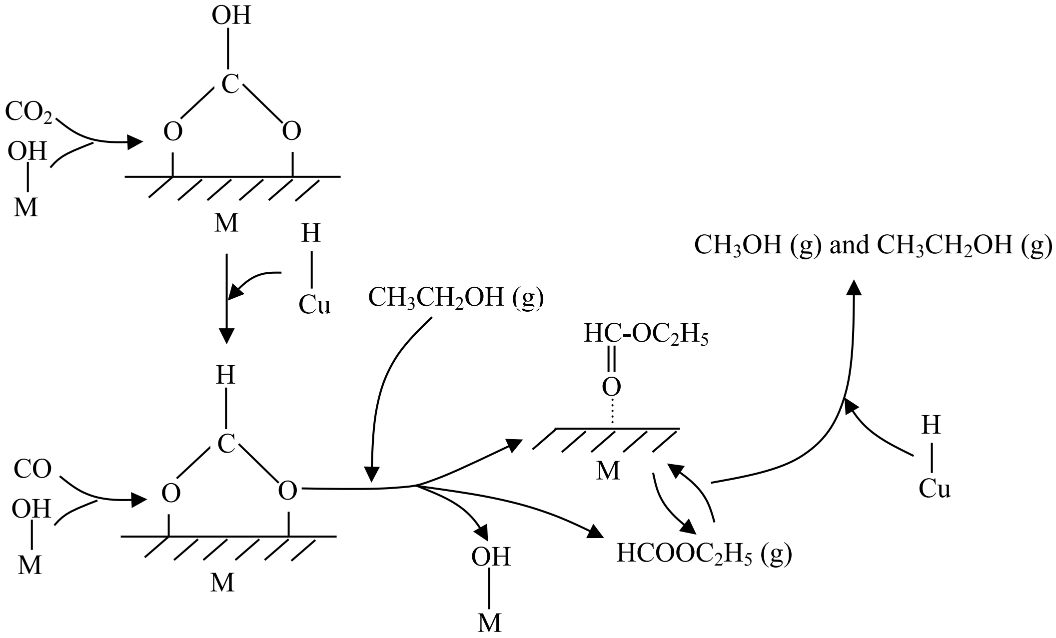
1565
1400
840

Fig. S2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C
O
O
CO2
OH
M
M
H
Cu
CH3CH2OH (g)
CH3OH (g) and CH3CH2OH (g)
HC-OC2H5
O
H
C
O
O
CO
OH
M
M
M
OH
M
HCOOC2H5 (g)
H
Cu

Fig. S3

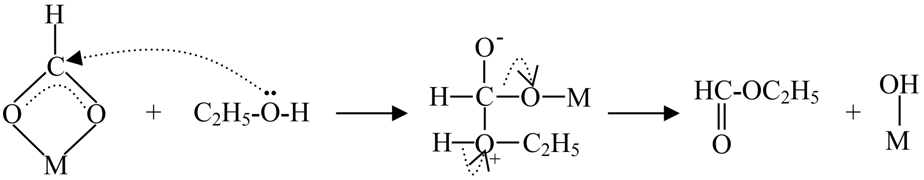

Fig. S4