Electronic Supplementary Information (ESI)

New and revisited insights into the promotion of methanol synthesis catalysts by CO_2

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H_2O co-feeding cycles

Two co-feeding cycles of H_2O at $R = 6$ (maximum of CO_2 promotion) and $R = 100$ have been conducted (Fig. SI1) complementary to the one at $R = 0$ (Fig. 2). Initially, H_2O can be utilized to convert CO into CO_2 by WGS when carbon monoxide is present in large amounts ($R = 6$) and thus the activity is less affected until $H_2O{:}CO_x = 0.3$. Upon further increasing the feed H_2O concentration, the activity is abruptly decreased to the same level irrespective of the syngas composition.

It was discussed that H_2O most likely causes similar surface alterations as CO_2 does, which will be one reason for the deactivation of the catalyst. Additionally, steam will also enhance the concentration of surface hydroxyls. These surface species were attributed to be inhibiting at higher amounts. Consequently, the coverage by hydroxyls should be a reversible process. Indeed, the activity at the end of the H_2O co-feeding cycles at $R = 0$ and 6 is the same as for the dry CO cycle. Excess of carbon monoxide appears to be efficient by removing the hydroxyls through WGS.

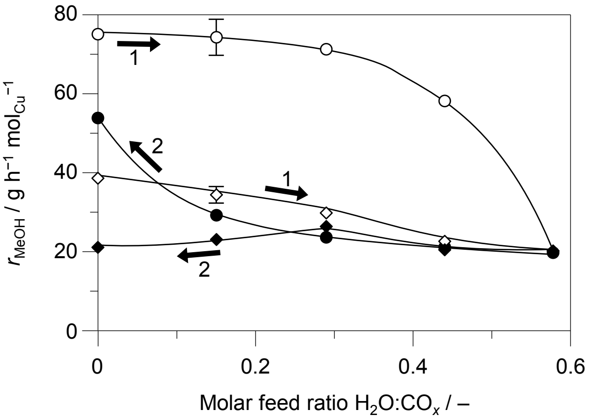

Fig. SI1 H_2O cycles over CuZnAl at 513 K, 5.0 MPa, $H_2{:}CO_x = 7$, $R = 6$ (circles) and 100 (diamonds).

Monitoring surface alterations upon CO_2-promoted methanol synthesis

The Auger electron spectra revealed a slight shift of the Zn LMM signal to higher kinetic energies (Fig. SI2). Zn^0 species are usually expected at such high energies; however, a clear distinction between Zn^{2+} and Zn^0 is not possible on the basis of our results because of the broadness of the peaks. In any case, the main fraction of zinc will remain in oxidized form according to the position of the peak. CO_2 promotion has been nevertheless already observed over pure CuZn alloy catalysts even though this study does not provide an established structure-performance relationship (A. Coteron and A. N. Hayhurst, *Chem. Eng. Sci.*, 1994, **49**, 209).

Our results demonstrated that the interaction of Cu, ZnO, and Al_2O_3 (Fig. 6 and 7) is the key of understanding CO_2-promoted methanol synthesis rather than the particular oxidation states of Cu and Zn. The dependence on this interplay is different for both CO and CO_2 hydrogenation. The surface composition of CuZnAl has been monitored over the different experiments (Table SI1). The particular trends have been discussed detailed in the paper.

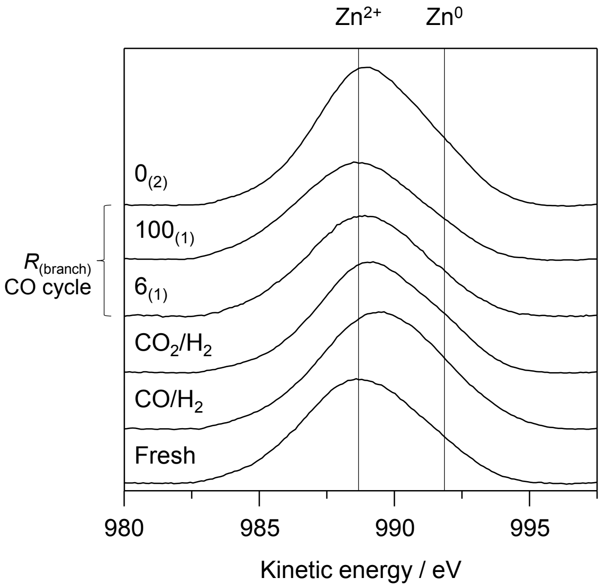

Fig. SI2 AES Zn LMM of CuZnAl fresh, along the CO cycle, and exposed to CO/H_2 or CO_2/H_2 syngas compositions, respectively (complementary to Fig. 5b). Reference data retrieved from W. L. Dai, Q. Sun, J. F. Deng, D. Wu and Y. H. Sun, *Appl. Surf. Sci.*, 2001, **177**, 172.

Table SI1 Surface composition of CuZnAl according to the different experiments conducted.

Entry	Status	Molar Cu:Zn:Al on surface[f]	$Cu^{red}:(Cu^{2+}+Cu^{red})^{g}$ / –
1	fresh[a]	22.9:25.6:51.5	0.9
2	after CO cycle[b]	18.5:24.6:56.9	1.0
3	$R = 6_{(1)}$[b, c]	22.1:22.2:55.7	0.8
4	$R = 100_{(1)}$[b, c]	22.4:26.4:51.1	0.7
5	re-activated[d]	17.8:26.2:56.0	1.0
6	CO cycle[b] after re-activation[d]	21.6:46.3:32.1	0.3
7	after CO/H_2[b, e]	17.9:26.5:55.6	1.0
8	after CO_2/H_2[b, e]	23.4:23.5:53.1	0.7

[a] dried (433 K, 2 K min^{-1}, 30 min, N_2) and reduced (503 K, 2 K min^{-1}, 2 h, 0.5 MPa, 5 mol-% H_2 in N_2). [b] 513 K, 5.0 MPa, $H_2:CO_x = 7$, WHSV = 7.5 h^{-1}. [c] along CO cycle. [d] after one CO cycle: re-calcination (573 K, 2 K min^{-1}, 2 h, 0.5 MPa, 2 mol-% O_2 in N_2) and re-reduction (*vide supra*). [e] same time-on-stream as CO or CO_2 cycle, respectively. [f] identified by X-ray photoelectron spectroscopy (XPS). [g] $Cu^{red} = Cu^{+}+Cu^{0}$.

Reducibility of spray-dried catalysts

Reducibility of copper in the methanol synthesis catalysts has been discussed to influence CO hydrogenation. The easier reducibility of the impregnated catalysts (Fig. SI3) corroborates this result found for the co-precipitated CuZn samples of different metal ratios (Fig. 7): the shift to lower temperatures in the H_2-TPR profile leads to enhanced CO hydrogenation activity (Table SI2).

Table SI2 Carbon-based rate of product formation at $R = 0_{(1)}$ for co-precipitated CuZnAl and the two impregnated catalysts.

Catalyst	$r_C{}^{a}$ / mol h^{-1} $mol_{Cu}{}^{-1}$
CP	1.06
SD	4.35
Cu@Zn	7.45

[a] rate summarizes production of methanol and dimethyl ether which itself is formed *via* methanol.

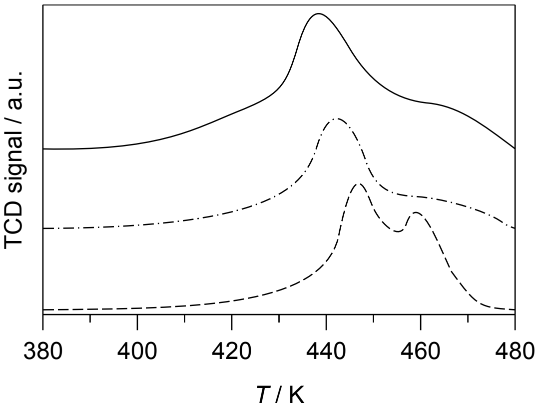

Fig. SI3 H_2-TPR profiles of co-precipitated CuZnAl (CP, – –), simultaneously (SD, –·–) and sequentially (Cu@Zn, —) impregnated $Cu/ZnO/Al_2O_3$. Signals are normalize d to copper content.