Supplementary Information

for

The promotional effect of gallium loading on the bifunctional Cu-Ga/γ-Al_2O_3 catalyst for CO_2 hydrogenation to methanol and dimethyl ether at atmospheric pressure

Osmanaga, S.;[a] Kaya, Y.;[a,b] Onal, I.;[a] Ipek, B*[a]

a Department of Chemical Engineering, Middle East Technical University, Dumlupinar Bulvari, 06800 Ankara, Turkey

b Rare Earth Elements Research Institute, Turkish Energy, Nuclear and Mineral Research Agency, 06980, Ankara, Turkey

*corresponding author: bipek@metu.edu.tr

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S1. Crystal Size Estimation Using Scherrer Equation.

The peak at $2\theta = 43.3°$ corresponding to Cu(111) and at $2\theta = 45.8°$ corresponding to γ-Al_2O_3 (400) are deconvoluted and fitted with a Voigt distribution as shown in Figure S2, and the full width at half maximum (FWHM) is found (Table S5) and used in Scherrer equation (Eq. 5).

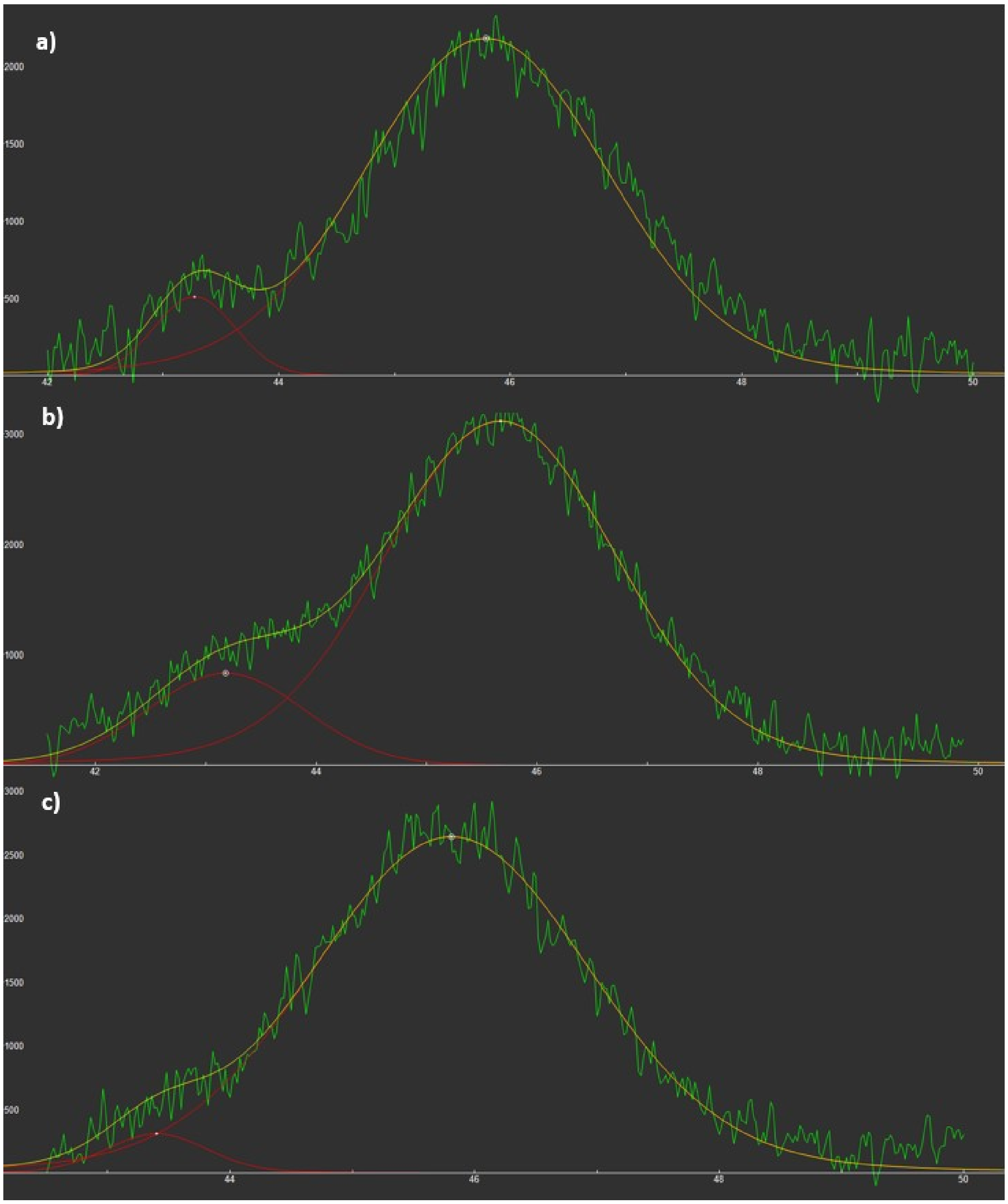

Figure S1. Deconvoluted peaks of Cu(111) and γ-Al_2O_3(400) fitted with a Voigt distribution, for a) Cu-5Ga/γ-Al_2O_3, b) Cu-10Ga/γ-Al_2O_3, and c) Cu-15Ga/γ-Al_2O_3.

Table S1. FWHM values for 10Cu-5Ga/γ-Al_2O_3, 10Cu-10Ga/γ-Al_2O_3, and 10Cu-15Ga/γ-Al_2O_3.

Catalyst	FWHM /°	FWHM /rad
10Cu-5Ga/γ-Al_2O_3	1	0.017444
10Cu-10Ga/γ-Al_2O_3	1.83	0.031923
10Cu-15Ga/γ-Al_2O_3	1.05	0.018317

For 10Cu-5Ga/γ-Al_2O_3, for example, given that:

$K = 0.9$

$\lambda = 1.5418$ Å

$\theta = 21.65°$ $\beta = 0.01744$ rad

b = 0.000292 rad

The crystal size can be found after substituting in Eqn. (5):

$$d_c = \frac{0.9 \times (1.5418 \times 10^{-1})}{(0.01744 - 0.000292) \times \cos(21.65)}$$

$$d_c \approx 9\ nm$$

S2. N_2 Adsorption Isotherm

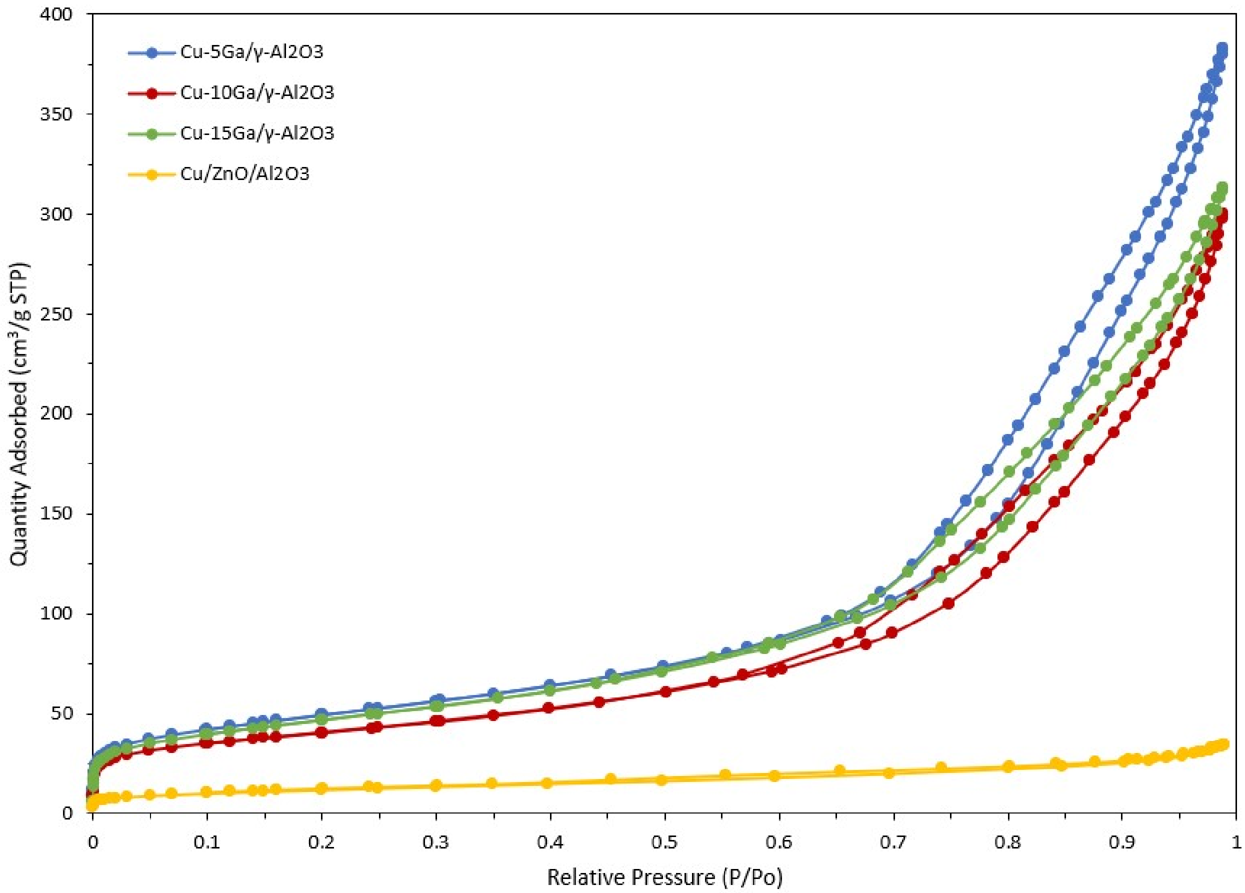

Figure S2. N_2 adsorption isotherms for 10Cu-xGa/γ-Al_2O_3 and Cu/ZnO/Al_2O_3.

S3.Kinetic Data

The equilibrium conversion of methanol dehydration reaction to DME between 200 ℃ and 260 ℃ varies from approximately 90% to 87%.[1] The methanol conversion in this study is found assuming that methanol dehydration reaction is the main route for DME formation (Eq. S1).

$$X_{CH_3OH} = \frac{2 * r_{DME}}{2 * r_{DME} + r_{MeOH}} \cdot 100\%$$

Table S2. Activity test results for 10Cu-10Ga/γ-Al_2O_3 at different GHSV at 220 ℃ and H_2:CO_2 ratio of 9:1

GHSV /mL $g_{cat}^{-1}h^{-1}$	GHSV /h^{-1}	r_{MeOH} /μmol g_{cat}^{-1} h^{-1}	r_{DME} /μmol g_{cat}^{-1} h^{-1}	r_{CO} /μmol g_{cat}^{-1} h^{-1}	S_{MeOH} /%	S_{DME} /%	S_{CO} /%	X_{CO2} /%	X_{MeOH} /%	$Y_{MeOH+DME}$/ %
8571	7000	27	21	761	3.3	5.0	91.7	2.6	61	0.18
12000	10000	34	33	970	3.2	6.1	90.7	2.4	66	0.19
20000	17000	26	29	745	3.1	7.0	89.9	1.1	69	0.09
30000	25000	42	42	927	4.0	8.0	88	0.7	67	0.09

Table S3. Activity test results for 10Cu-10Ga/γ-Al_2O_3 at different feed ratios and GHSV at 220 ℃

GHSV /mL $g_{cat}^{-1}h^{-1}$	H_2/CO_2	r_{MeOH} /μmol $g_{cat}^{-1}h^{-1}$	r_{DME} /μmol $g_{cat}^{-1}h^{-1}$	r_{CO} /μmol $g_{cat}^{-1}h^{-1}$	S_{MeOH} /%	S_{DME} /%	S_{CO} /%	X_{CO2} /%	X_{MeOH} /%	$Y_{MeOH+DME}$ / %
30000	3/1	43	33	1324	3.0	4.6	92.4	1.1	61	0.07
	6/1	37	36	1019	3.3	6.4	90.3	0.8	66	0.07
	9/1	42	42	927	4.0	8.0	88	0.7	67	0.07
12000	3/1	51	22	1273	3.7	3.2	93.1	1.0	46	0.08
	6/1	43	24	961	4.1	4.6	91.3	0.8	53	0.08
	9/1	37	25	836	4.0	5.4	90.6	0.7	57	0.08

Table S4. Activity test results for 10Cu-10Ga/γ-Al_2O_3 at different reaction temperatures and GHSV at a H_2:CO_2 ratio of 9:1

GHSV /mL $g_{cat}^{-1}h^{-1}$	T /℃	r_{MeOH} /μmol g_{cat}^{-1} h^{-1}	r_{DME} /μmol g_{cat}^{-1} h^{-1}	r_{CO} /μmol g_{cat}^{-1} h^{-1}	S_{MeOH} /%	S_{DME} /%	S_{CO} /%	X_{CO2} /%	X_{MeOH} /%	$Y_{MeOH+DME}$ / %
30000	200	27	28	317	6.7	13.9	79.4	0.3	67	0.06
	220	42	42	927	4.0	8.0	88	0.8	67	0.09
	240	62	44	2133	2.7	3.8	93.4	1.7	59	0.11
12000	220	40	25	929	3.9	4.9	91.2	1.9	56	0.17
	240	50	19	1995	2.4	1.8	95.8	3.9	43	0.16
	260	27	7	3070	0.9	0.5	98.7	5.8	41	0.08

Table S5. Activity test results for 10Cu-xGa/γ-Al_2O_3 at 220 °C and GHSV of 30000 mL $g_{cat}^{-1}h^{-1}$ and a H_2:CO_2 ratio of 9:1

Ga percentage /x	r_{MeOH} /µmol g_{cat}^{-1} h^{-1}	r_{DME} /µmol g_{cat}^{-1} h^{-1}	r_{CO} /µmol g_{cat}^{-1} h^{-1}	S_{MeOH} /%	S_{DME} /%	S_{CO} /%	X_{CO2} /%	X_{MeOH} /%
0	49	44	478	8.0	14.3	77.7	0.5	64
5	53	96	957	4.4	16.0	79.5	0.9	78
10	42	42	927	4.0	8.0	88	0.8	67
12	51	34	693	6.2	8.4	85.4	0.6	57
15	50	42	788	5.4	9.1	85.4	0.7	59
Cu/ZnO/Al_2O_3	60	0	779	7.2	0	92.8	0.6	0

S4. Methanol Dehydration Reaction

We tested the dimethyl ether formation activity of the optimized catalyst by comparing the Cu-5Ga/γ-Al_2O_3 catalyst to 5Ga/γ-Al_2O_3 and γ-Al_2O_3(Alfa Aesar, 44757). For that, we prepared 5 wt.% Ga/γ-Al_2O_3 using wet impregnation method following the procedure given for Cu-xGa/γ-Al_2O_3 catalysts without the Cu source. 200 mg of pelleted and sieved (between 200 and 450 μm) catalysts were stabilized in Quartz reactors having an inside diameter of 7 mm using glass wool. Prior to the reaction, reduction of the catalyst was performed using equimolar flow of hydrogen gas (Hatgaz, 99.999%) and helium gas (Hatgaz, 99.999%) at a total volumetric flow rate of 100 sccm for 2 h at 250 °C (using a heating rate of 5 °C min^{-1}). After 2 h, the catalyst was flushed under 100 sccm He flow for 20 minutes to ensure the removal of the chemisorbed hydrogen on the catalyst surface. After reaching 220 °C, the gas flow was switched to 100 sccm He flow that is directed through a methanol saturator kept at 21 °C and the reaction was carried out at 220 °C. The products were analyzed every 20 minutes using a gas chromatography (GC, Agilent 7820A) equipped with a Pora-Plot Q column (CP7554, 25 m, 0.53 mm, 20 μm), a flame ionization detector (FID), a thermal conductivity detector (TCD). The methanol conversion and carbon-based dimethyl ether selectivity was calculated based molar flow rates as given in following equations:

$$X_{CH_3OH} = \frac{F_{CH_3OH,fed} - F_{CH_3OH,effluent}}{F_{CH_3OH,fed/gcat}} \cdot 100\% \qquad S2$$

$$S_{DME}(\%) = \frac{2\,F_{DME}}{\sum n\,F_{C_n}} \cdot 100\% \qquad S3$$

Table S6. The methanol conversion and dimethyl ether selectivity on Cu-5Ga/γ-Al_2O_3, 5Ga/γ-Al_2O_3 and γ-Al_2O_3. WHSV of 5 g_{CH3OH} g_{cat}^{-1} h^{-1}, 220 °C (200 mg catalyst)

Catalyst	**X_{CH3OH} / %**	**S_{DME} %**
γ-Al_2O_3	33.9 ± 0.3	100
5Ga/γ-Al_2O_3	42.6 ± 0.9	100
Cu-5Ga/γ-Al_2O_3	68.9 ± 0.9	99 ± 1

S5. DFT Results

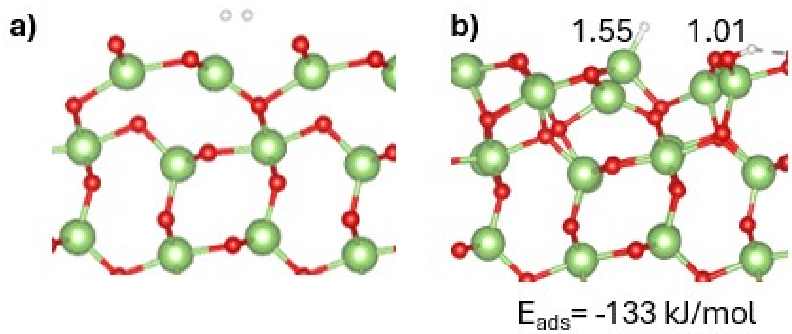

Figure S3. H_2 dissociative adsorption on β-Ga_2O3(001) surface a) starting geometry b) optimized geometry (sideview) (Ga: green, O: red, H: white, distances are in Å)

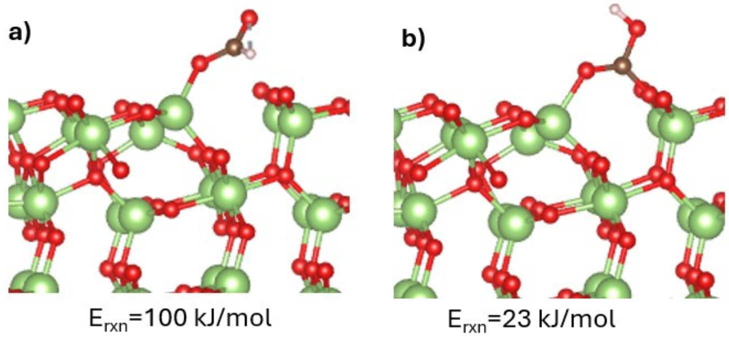

Figure S4. a) Formate and b) carboxyl formation on β-Ga_2O3(001) surface (Ga: green, O: red, H: white, C: brown)

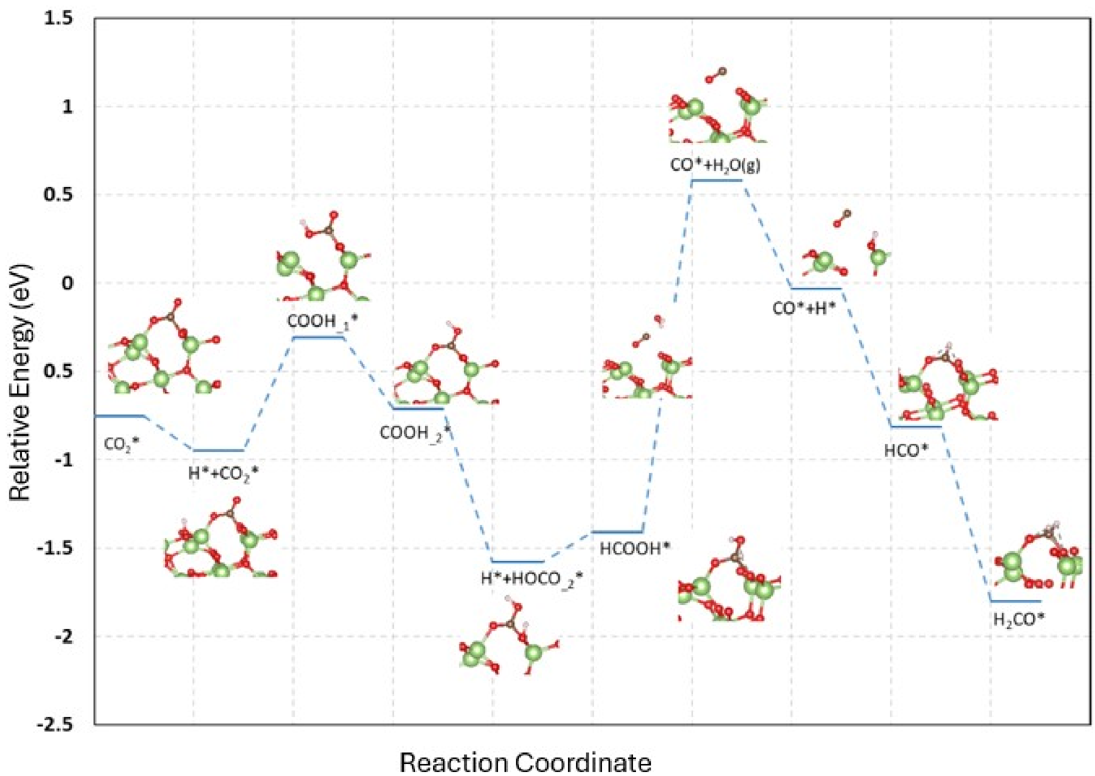

Figure S5. Possible CO_2 hydrogenation mechanism on β-Ga2O3(001) surface (Ga: green, O: red, H: white, C: brown)

References

1 W. Alharbi, E. F. Kozhevnikova and I. V. Kozhevnikov, *ACS Catal*, 2015, 5, 7186–7193.