

Supporting information

Roles of structural promoters for direct CO₂ hydrogenation to dimethyl ether over ordered mesoporous bifunctional Cu/M-Al₂O₃ (M = Ga or Zn)

Hyungwon Ham^a, Sung Woo Baek^b, Chae-Ho Shin^{*,b}, Jong Wook Bae^{,a}**

^aSchool of Chemical Engineering, Sungkyunkwan University (SKKU), 2066 Seobu-ro, Suwon, Gyeonggi-do, 16419, Republic of Korea

^bDepartment of Chemical Engineering, Chungbuk National University, Chungdae-ro 1, Cheongju, Chungbuk, 28644, Republic of Korea

*Corresponding author (C.H. Shin): Tel: +82-43-261-2376; Fax: +82-43-269-2370; E-mail: chshin@chungbuk.ac.kr

**Corresponding author (J.W. Bae): Tel.: +82-31-290-7347; Fax: +82-31-290-7272; E-mail address: finejw@skku.edu

Table S1. Catalytic activity for the direct CO₂ hydrogenation to DME on the bifunctional Cu/m-MAl catalysts at a maximum and steady-state

Table S2. Catalytic activity for the direct conversion of syngas containing CO₂ to DME on the bifunctional Cu/m-MAl at the temperature ranges of 220 - 300 °C

Table S3. Summarized results of XANES fitting through Linear combination fitting (LCF, %) for the fresh, reduced, hydrated and reacted bifunctional Cu/m-GaAl and Cu/m-ZnAl

Figure S1. TEM images of the (1) reduced and (2) used Cu/m-MAl catalysts; (A) Cu/m-GaAl and (B) Cu/m-ZnAl with a bright and dark field images (high angular annular dark field (HAADF)) and inset images for the elemental mapping images of copper and gallium (A) measured by TEM-EDS analysis

Figure S2. NH₃-TPD patterns of the fresh bifunctional Cu/m-MAl catalysts

Figure S3. TPR patterns of the fresh bifunctional Cu/m-Al and Cu/m-GaAl up to the temperature of 600 °C (Supporting TPR patterns of **Figure 1(D)**)

Figure S4. Conversion and product distribution of CO₂ hydrogenation to DME with time on stream (h) for 40 h on the (A) Cu/Al, (B) Cu/m-Al, (C) Cu/m-GaAl, and (D) Cu/m-ZnAl, which was tested at the reaction conditions of P = 5.0 MPa, T = 250 °C, H₂/CO₂ molar ratio = 3/1, and space velocity (SV) = 2000 L/(kg_{cat}·h) with 0.4 g catalyst

Figure S5. Product formation rate (mol/(g_{cat}·h)) such as (a) DME and (b) CO with time on stream (h) on the bifunctional Cu/m-MAl catalysts

Figure S6. Original and deconvoluted spectra of the Ga K-edge (red) of the reduced Cu/m-GaAl with the main phases of the Ga-O(tetrahedral) with green color, Ga-O(octahedral) with purple color and Ga-OH(octahedral) with pink color

Figure S7. Ex-situ XPS spectra of (A) Cu 2p_{3/2} and (B) Ga 2p of the fresh, reduced, hydrated and reacted Cu/m-GaAl catalyst obtained at different reaction times from 1 to 40 h

Figure S8. Ex-situ XPS spectra of (A) Cu 2p_{3/2} and (B) Zn 2p_{3/2} of the fresh, reduced and reacted Cu/m-ZnAl catalyst obtained at different reaction times from 1 to 40 h

Table S1. Catalytic activity for the direct CO₂ hydrogenation to DME on the bifunctional Cu/m-MAl catalysts at a maximum and steady-state

Notation	CO ₂ conversion (mol%) ^a	Product distribution (mol %) ^a				r _{M+D} ^b	r _D ^b	r _{CO} ^b
		CO	methanol	DME	BP			
Cu/Al	23.0 (max)	48.5	28.8	22.5	0.2	2.97	1.81	1.95
	21.7 (ss)	53.4	27.1	19.3	0.2	2.56	1.51	2.08
Cu/m-Al	22.0 (ss)	48.0	38.9	12.6	0.5	2.70	1.06	2.02
Cu/m-GaAl	24.3 (max)	46.0	35.1	18.5	0.4	3.10	1.59	1.98
	23.4 (ss)	46.7	41.2	11.9	0.2	2.88	1.06	2.07
Cu/m-ZnAl	24.5 (ss)	40.8	45.2	13.2	0.8	3.32	1.21	1.89

^aThe direct CO₂ hydrogenation to DME with product distributions was obtained at the reaction conditions of P = 5.0 MPa, T = 250 °C, and space velocity (SV) = 2000 L/(kg_{cat}·h) with H₂/CO₂ molar ratio = 3/1 with 0.4 g catalyst, and BP stands for the byproducts with the main C₁-C₂ paraffinic hydrocarbons. CO₂ conversion on the Cu/m-MAl was represented with the values of maximum (max) and steady-state (ss), respectively.

^bThe individual formation rates of products such as methanol (M), DME (D) and CO with the unit of mmol/(g_{cat}·h) was calculated by using the averaged values for 3 h reaction at a maximum and steady state.

Table S2. Catalytic activity for the direct conversion of syngas containing CO₂ to DME on the bifunctional Cu/m-MAI at the temperature ranges of 220 - 300 °C^a

Notation	Temp (°C)	CO conversion (mol%)	CO ₂ conversion (mol%)	CO conversion to CO ₂ (mol%)	Product distribution (mol %)		
					Methanol	DME	BP
Cu/m-Al	220	2.7	3.4	0.0	89.5	10.1	0.4
	250	14.1	1.8	0.0	56.8	42.4	0.8
	280	39.3	-5.6	2.4	25.7	72.9	1.4
	300	51.8	-10.9	4.7	18.5	79.8	1.7
Cu/m-GaAl	220	2.9	4.2	0.0	88.5	11.3	0.2
	250	14.2	2.8	0.0	55.5	43.9	0.6
	280	40.4	-5.0	2.1	25.7	73.2	1.1
	300	52.8	-10.1	4.3	17.6	80.9	1.5
Cu/m-ZnAl	220	4.5	0.7	0.0	74.2	23.9	1.9
	250	18.2	-1.1	0.5	38.4	60.4	1.2
	280	42.2	-8.9	3.8	17.3	81.2	1.5
	300	54.2	-13.4	5.7	12.0	85.8	2.2

^aThe direct hydrogenation of syngas containing CO₂ to DME with product distributions was obtained at the reaction conditions of P = 5.0 MPa, T = 220 – 300 °C, and space velocity (SV) = 2000 L/(kg_{cat}·h) with H₂/CO/CO₂/N₂ molar ratio = 66/21/9/4 (CO/CO₂/H₂ = 1/0.429/3.14) with 0.4 g catalyst, and BP stands for the byproducts with main C₁-C₂ paraffinic hydrocarbons.

Table S3. Summarized results of XANES fitting through linear combination fitting (LCF, %) for the fresh, reduced, hydrated and reacted bifunctional Cu/m-GaAl and Cu/m-ZnAl

Notation	treatment	Linear combination fitting (LCF, %)			
		Cu	Cu ₂ O	CuO	CuAl ₂ O ₄
Cu/m-GaAl	fresh	-	-	12.9	87.1
	reduced	13.1	-	32.6	54.3
	reaction (1 h)	-	14.6	28.5	56.9
	reaction (3 h)	24.3	25.3	-	50.4
	reaction (5 h)	12.5	6.5	22.0	59.0
	reaction (10 h)	5.4	13.4	24.1	57.1
	reaction (20 h)	-	31.9	25.8	42.3
	reaction (40 h)	-	42.2	25.7	32.1
	hydration	0.6	11.7	31.8	55.9
Cu/m-ZnAl	fresh	-	-	21.9	78.1
	reduced	15.6	-	29.5	54.9
	reaction (1 h)	5.8	19.7	56.3	18.2
	reaction (3 h)	3.6	52.6	28.0	15.8
	reaction (5 h)	12.1	-	18.7	69.2
	reaction (10 h)	-	34.4	42.2	23.4
	reaction (20 h)	-	33.0	30.3	36.7
	reaction (40 h)	-	26.3	22.4	51.3

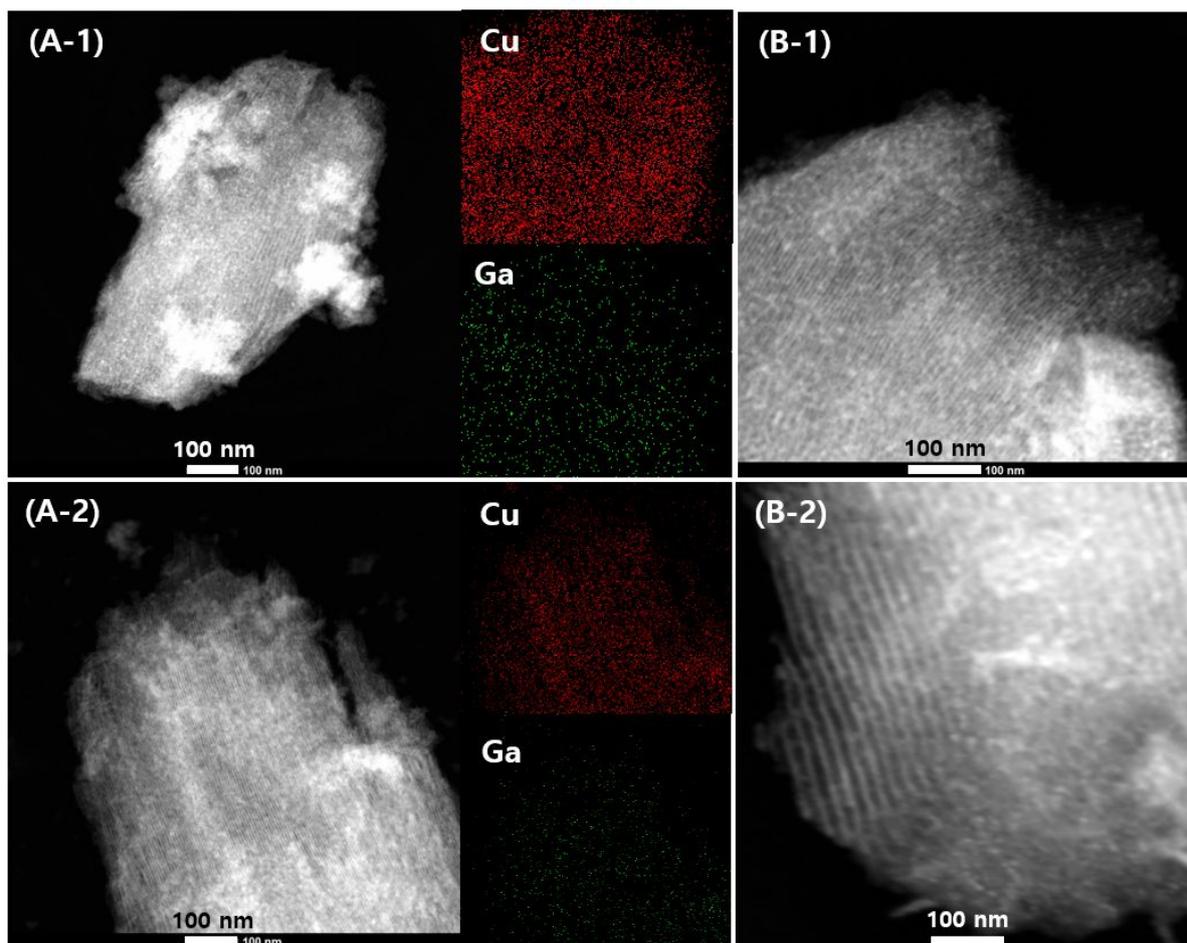


Figure S1. TEM images of the (1) reduced and (2) used Cu/m-MAI catalysts; (A) Cu/m-GaAl and (B) Cu/m-ZnAl with a bright and dark field images (high angular annular dark field (HAADF)) and inset images for the elemental mapping images of copper and gallium (A) measured by TEM-EDS analysis

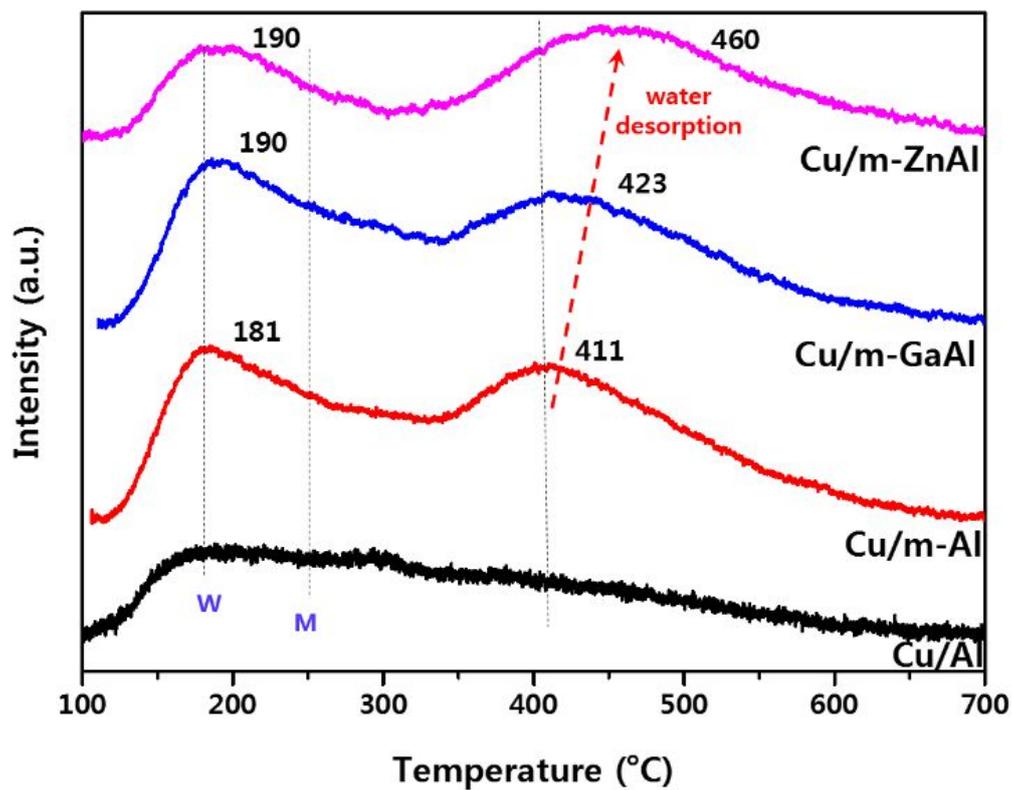


Figure S2. NH₃-TPD patterns of the fresh bifunctional Cu/m-MAI catalysts

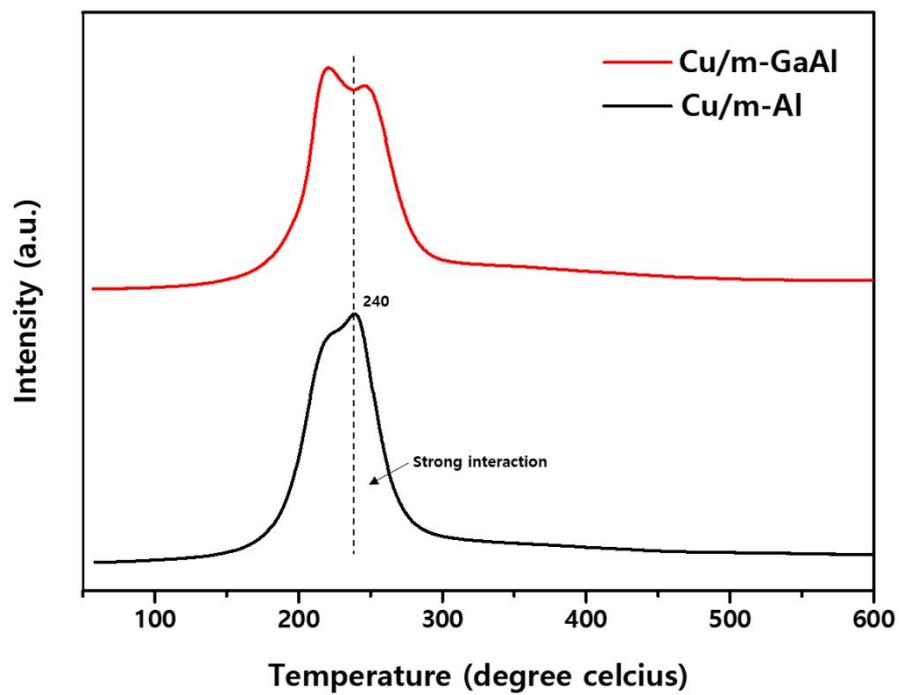


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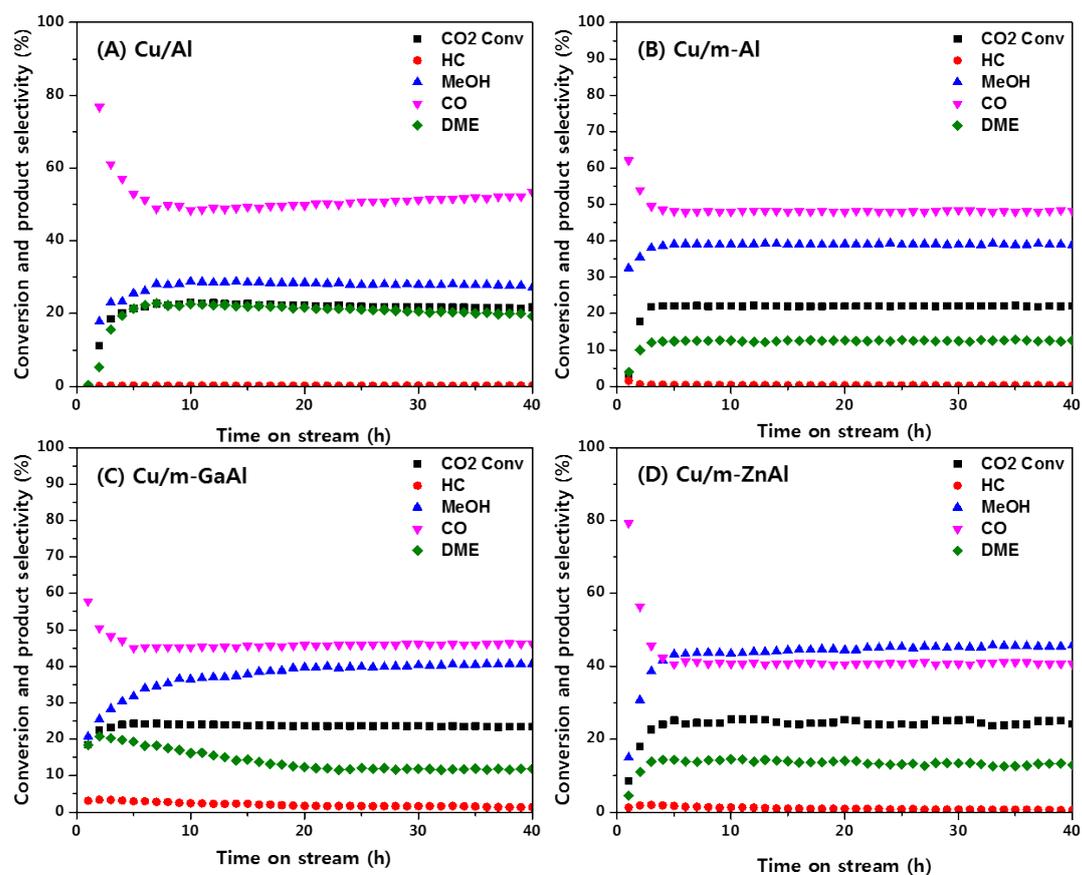


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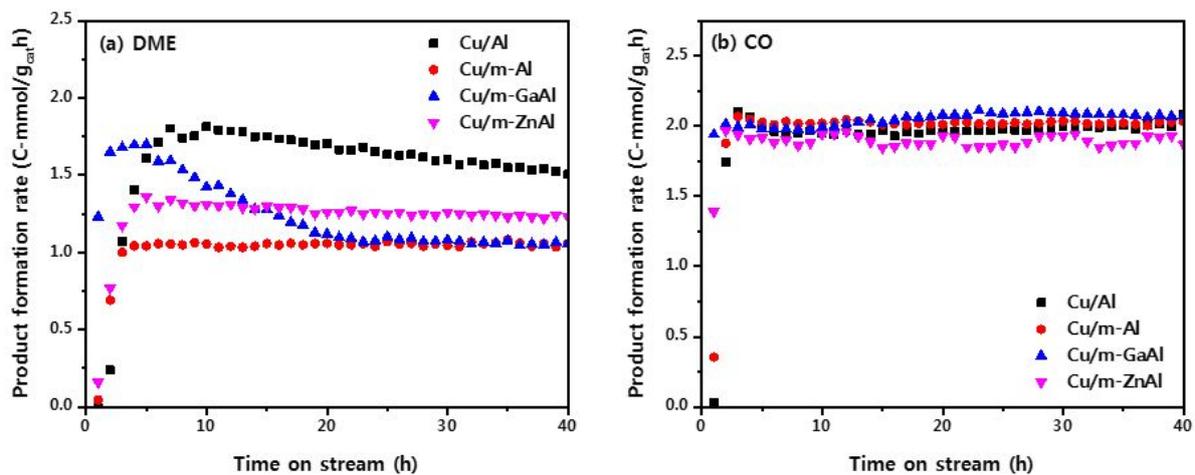


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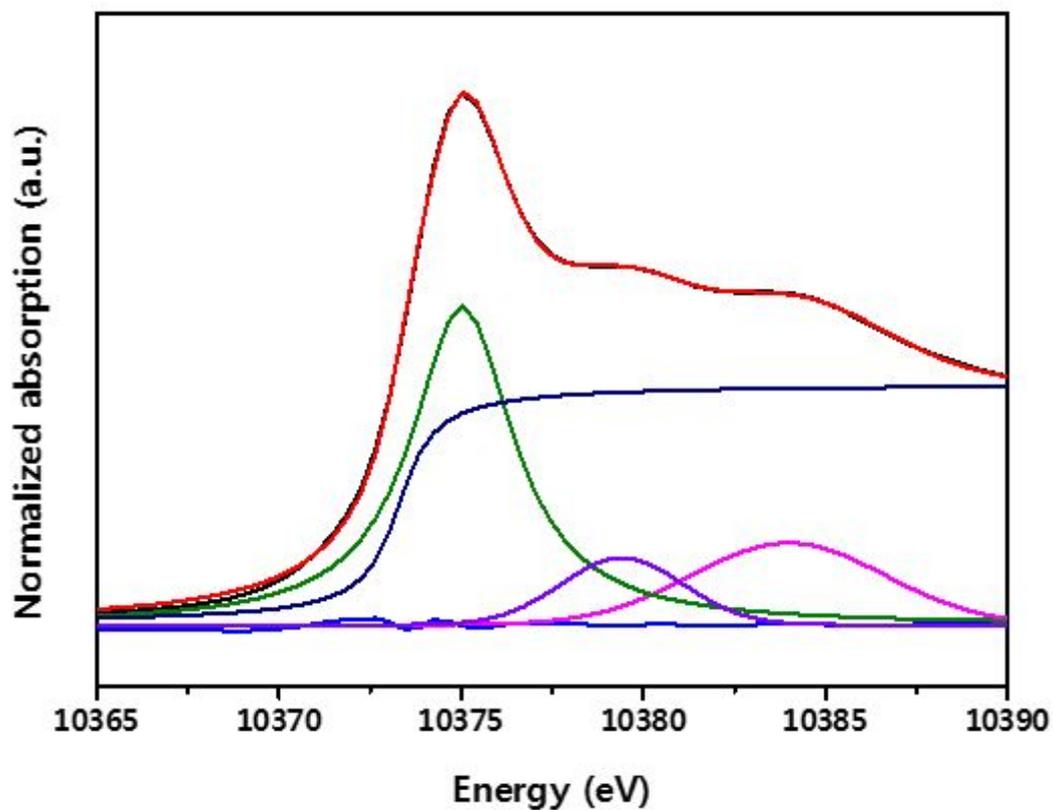


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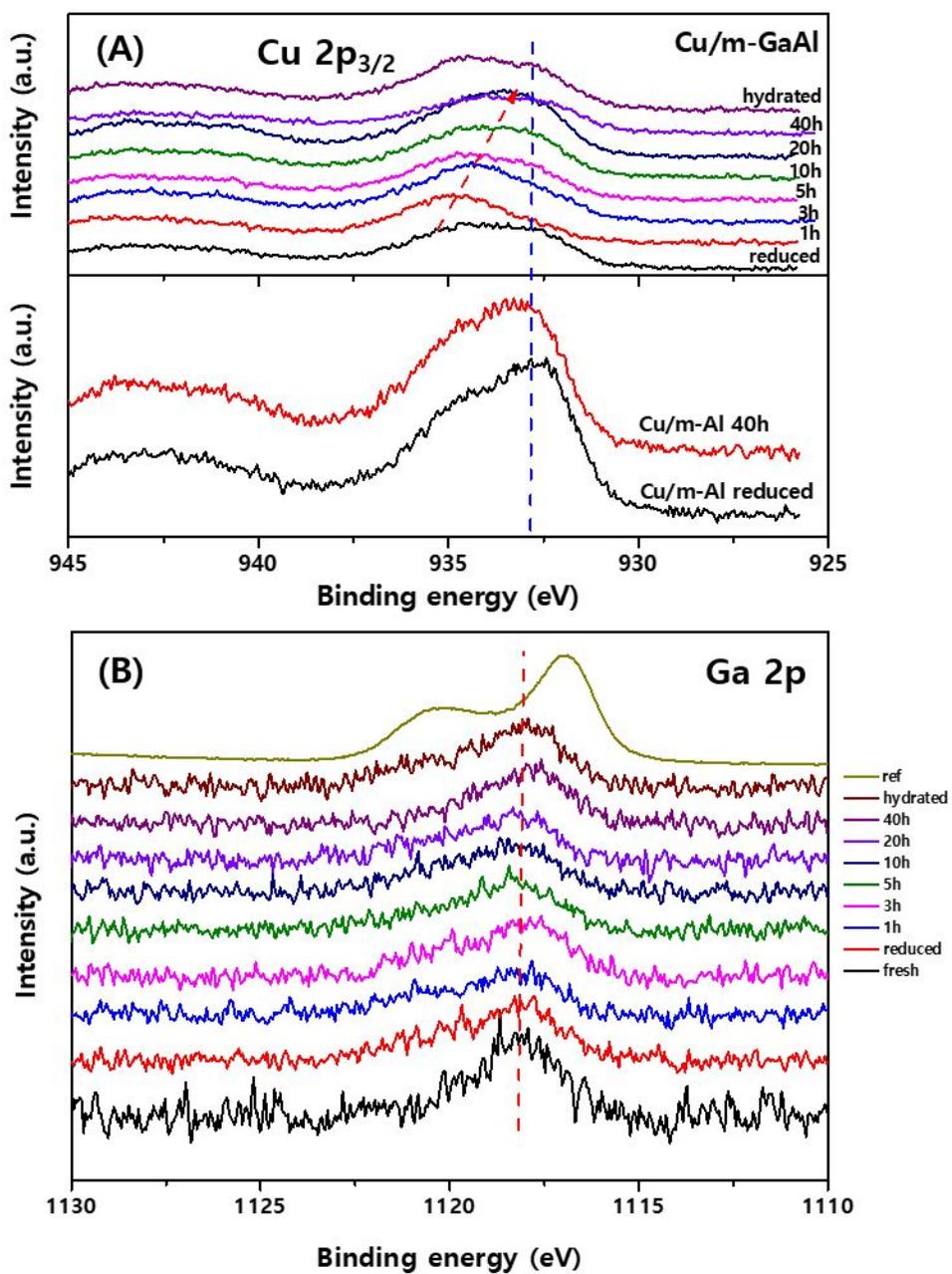


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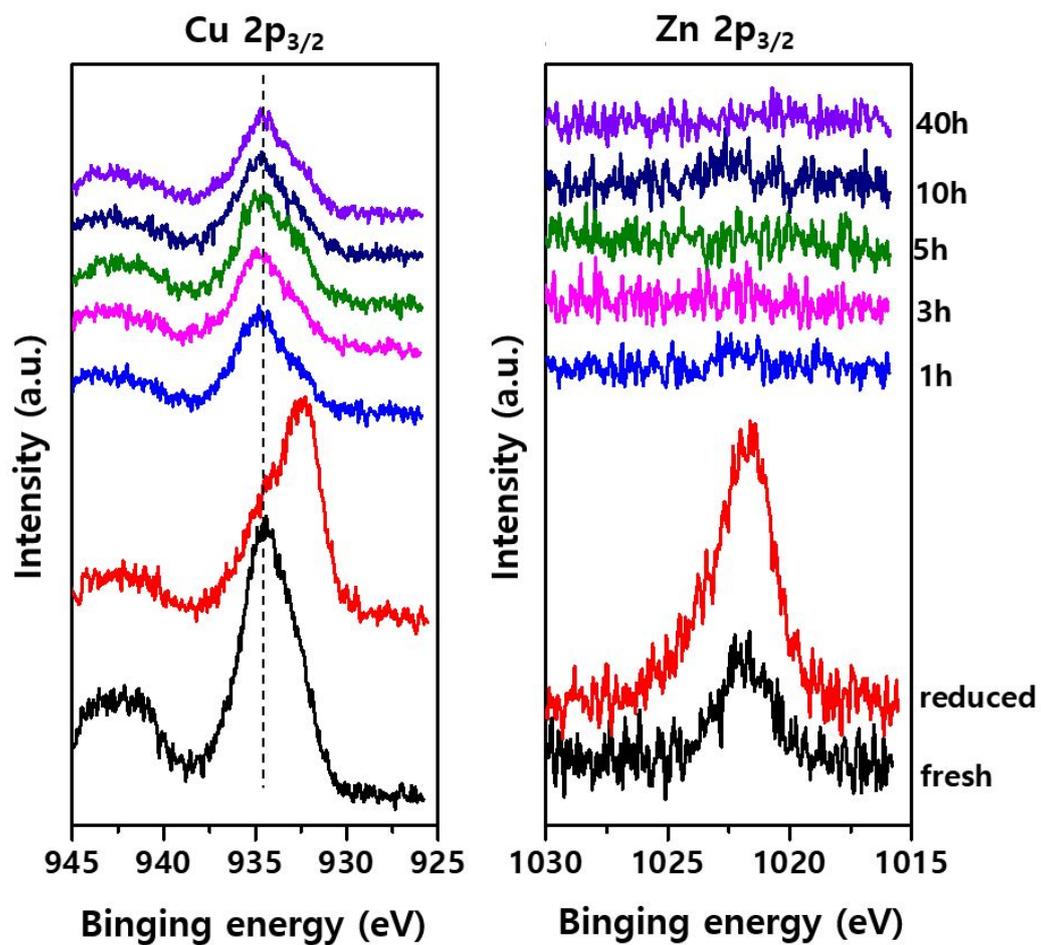


Figure S8. Ex-situ XPS spectra of (A) Cu 2p_{3/2} and (B) Zn 2p_{3/2} of the fresh, reduced and reacted Cu/m-ZnAl catalyst obtained at different reaction times from 1 to 40 h