Electronic Supplementary Material (ESI) for Catalysis Science & Technology. This journal is © The Royal Society of Chemistry 2018

Electronic supplementary information for

Role of mesopores in Co/ZSM-5 for the direct synthesis of

liquid fuel by Fischer–Tropsch synthesis

Ji-Eun Min,^{a,1} Sungtak Kim,^{b,1} Geunjae Kwak,^{a,c} Yong Tae Kim,^{a,c} Seung Ju Han,^a Yunjo Lee,^a Ki-Won Jun,^{a,c}

Seok Ki Kim^{a,c,*}

^aCarbon Resource Institute, Korea Research Institute of Chemical Technology, Daejeon 34114, Republic of Korea

^bPlant Engineering Division, Energy & Environment Research Team, Institute for Advanced Engineering, Yongin 17180, Republic of Korea

^cAdvanced Materials and Chemical Engineering, University of Science & Technology, Daejeon 34113, Republic of Korea

*Corresponding author: skkim726@krict.re.kr

¹These authors contributed equally.

Contents

Table S1. Textural properties of the catalyst samples.	3
Figure S1. (a) Ar adsorption-desorption isotherm and (b) pore size distribution of Co/Al2O3 and Co/Al-MCM	[-
41	4
Figure S2. SEM images of (a) Co/HZ-con-micro, (b) Co/HZ-TD-meso, (c) Co/HZ-BU-micro, and (d) Co/HZ	<u>'</u> -
3U-meso	5
Table S2. Acid properties of the catalyst samples.	6
Figure S3. (a) XRD patterns and relative crystallinities and (b) TPR profiles of ZSM-5-based catalyst samples.	7
Figure S4. TPR profiles of Co/Al ₂ O ₃ and Co/Al-MCM-41	8
Figure S5. (a) CO conversion and (b) product selectivity as a function of time on stream for FTS catalysts prepare	d
n the present study. Reaction conditions: $H_2/CO = 2$, $T = 240$ °C, $P = 2$ MPa, space velocity = 4,000 mL/g _{cat} /h.	9
Figure S6. Hydrocarbon distribution in the liquid products obtained using catalysts prepared in the present stud	7. 0
Figure S7. Simulated distillation curved of the liquid products1	1

Catalyst	Specific surface area (m ² /g)			Pore volume (cm^3/g)		Pore size (Å)	
	Total ^a	Micro ^b	Meso ^c	Micro ^d	Meso ^e	Micro ^f	Meso ^g
Co/HZ-con-micro	289.6	254.1	35.5	0.10	0.08	5.5	55.9
Co/HZ-TD-meso	322.3	241.2	81.0	0.09	0.18	5.6	77.4
Co/HZ-BU-micro	324.9	304.3	20.6	0.12	0.05	5.5	48.6
Co/HZ-BU-meso	327.4	249.4	78.1	0.09	0.15	5.5	73.4
Co/NaZ-BU-micro	323.1	286.3	36.8	0.11	0.08	5.4	64.3
Co/NaZ-BU-meso	318.2	260.6	57.6	0.12	0.12	5.4	65.7
Co/Al ₂ O ₃	109.6	n/a	109.6	0.30	0.35	10.5	99.6
Co/Al-MCM-41	544.8	534.1	10.6	0.24	0.21	9.9	28.0

Table S1. Textural properties of the catalyst samples.

^a BET specific surface area

^b t-Plot micropore area

^c t-Plot External surface area

^d t-Plot micropore volume

 $^{\rm e}$ BJH desorption cumulative volume of pores between 20 Å and 500 Å diameter

^f Median pore width determined using the Horvath–Kawazoe method

 $^{\rm g}$ BJH Desorption average pore diameter between 20 Å and 500 Å



Figure S1. (a) Ar adsorption–desorption isotherm and (b) pore size distribution of Co/Al2O3 and Co/Al-MCM-41 $\,$



Figure S2. SEM images of (a) Co/HZ-con-micro, (b) Co/HZ-TD-meso, (c) Co/HZ-BU-micro, and (d) Co/HZ-BU-meso.

Catalyst	Acidity ^a	Acidity ^a (µmol NH ₃ /g)				Acidity ^b (µmol Py/g)			
	Weak	Middle	Strong	Total	CB	CL	B/L	Total	
Co/HZ-con-micro	134	212	369	716	153	249	0.61	402	
Co/HZ-TD-meso	98	220	313	631	91	115	0.79	206	
Co/HZ-BU-micro	131	222	451	804	66	194	0.34	260	
Co/HZ-BU-meso	109	170	414	693	52	138	0.38	190	
Co/NaZ-BU-micro	113	200	116	430	51	91	0.57	142	
Co/NaZ-BU-meso	132	214	117	463	71	94	0.75	165	
Co/Al ₂ O ₃	99	234	182	515	1	44	0.03	45	
Co/Al-MCM-41	98	160	736	994	47	223	0.21	271	

 Table S2. Acid properties of the catalyst samples.

^a Obtained using NH₃-TPD ^b Obtained using Py-IR



Figure S3. (a) XRD patterns and relative crystallinities, and (b) TPR profiles of ZSM-5-based catalyst samples.



Figure S4. TPR profiles of Co/Al₂O₃ and Co/Al-MCM-41



Figure S5. (a) CO conversion and (b) product selectivity as a function of time on stream for FTS catalysts prepared in the present study. Reaction conditions: $H_2/CO = 2$, T = 240 °C, P = 2 MPa, space velocity = 4,000 mL/g_{cat}/h



Figure S6. Hydrocarbon distribution in the liquid products obtained using catalysts prepared in the present study.



Figure S7. Simulated distillation curved of the liquid products