Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2022

Electronic Supplementary Information: Methane Assisted Catalyst Synthesis and Catalytic Conversion of Oleic Acid

4 Jack S. Jarvis, Zhaofei Li, Shijun Meng, & Hua Song*

- 6 Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr
- 7 NW, Calgary, Alberta T2N 1N4, Canada

- 18 *Corresponding author
- 19 Fax: +1 (403) 284-4852; Tel: +1 (403) 220-3792;
- 20 E-mail: sonh@ucalgary.ca
- 22 Keywords: Methane Activation, ZSM-5, Oleic Acid, Dry Gel Conversion, imprinting

25 Contents:

26	Supplementary Figures 1-7
27	Supplementary Tables 1-3
28	
29	
30	
31	
32	
33	
34	
35	
36	
37	
38	
39	
40	
41	
42	
43	
44	



46 Figure S1. XRD patterns of Z-CH4 (grey), Z-Ar (red), and Ce-Ga-Pt/Z-CH₄ (blue)

















Figure S2. (a) High resolution TEM image of 5%Ce-0.5%Ga-0.5%Pt/Z-CH₄ catalyst, (b) TEM/EDX image of Ce species on 5%Ce-0.5%Ga-0.5%Pt/Z-CH₄ catalyst, (c) TEM/EDX image of Ga species on 5%Ce-0.5%Ga-0.5%Pt/Z-CH₄ catalyst, (d) TEM/EDX image of Pt species on 5%Ce-0.5%Ga-0.5%Pt/Z-CH₄ catalyst, (e) distribution of metal particles on 5%Ce-0.5%Ga-0.5%Pt/Z-CH₄ catalyst. (f) High resolution TEM image of 5%Ce-0.5%Ga-0.5%Pt/Z-Ar catalyst, (g) TEM/EDX image of Ce species on 5%Ce-0.5%Ga-0.5%Pt/Z-Ar catalyst, (h) TEM/EDX image of Ga species on 5%Ce-0.5%Ga-0.5%Pt/Z-Ar catalys, (i) TEM/EDX image of Pt species on 5%Ce-0.5%Ga-0.5%Pt/Z-Ar catalyst, (j) distribution of metal particles on 5%Ce-0.5%Ga-0.5%Pt/Z-Ar catalyst.









Figure S3. (a) XPS spectrum of the Pt4f region of the fresh 5%Ce-0.5%Ga-0.5%Pt/Z-CH₄ 130 catalyst, (b) the fresh 5%Ce-0.5%Ga-0.5%Pt/Z-Ar catalyst, (c) the spent 5%Ce-0.5%Ga-131 0.5%Pt/Z-CH₄ catalyst, (d) the spent5%Ce-0.5%Ga-0.5%Pt/Z-Ar catalyst.



Figure S4. XPS spectrum of the Ga2p region of the fresh 5%Ce-0.5%Ga-0.5%Pt/Z-CH₄ catalyst (magenta), the fresh 5%Ce-0.5%Ga-0.5%Pt/Z-Ar catalyst (blue), the spent 5%Ce-0.5%Ga-135 0.5%Pt/Z-CH₄ catalyst (orange), and the spent 5%Ce-0.5%Ga-0.5%Pt/Z-Ar catalyst (grey).





binding energy (eV)



146 **Figure S5.** (a) XPS spectrum of the Ce3d region of the fresh 5%Ce-0.5%Ga-0.5%Pt/Z-CH₄ 147 catalyst, (b) the fresh 5%Ce-0.5%Ga-0.5%Pt/Z-Ar catalyst, (c) the spent 5%Ce-0.5%Ga-148 0.5%Pt/Z-CH₄ catalyst, (d) the spent5%Ce-0.5%Ga-0.5%Pt/Z-Ar catalyst.



149

150 Figure S6. TGA-DSC methane probe of 5%Ce-0.5%Ga-0.5%Pt/Z-Ar and 5%Ce-0.5%Ga-

151 0.5%Pt/Z-CH₄ catalysts at 25°C.



153 Figure S7. TGA-DSC methane probe of empty (no catalyst) pan at 200°C (black) and 400°C154 (red).



Catalyst	BET surface area External surf		Micropore area	Micropore	Total pore	Average pore
	(m²/g)	area (m²/g)	(<i>m²/g</i>)	volume (cm³/g)	volume (cm³/g)	diameter (nm)
Z-CH₄	403.52	136.94	266.58	0.14	0.45	4.48
Z-Ar	369.55	115.59	253.95	0.13	0.27	2.88
Ce-Ga-Pt/Z-CH₄	312.78	156.80	155.98	0.08	0.45	5.73

Ce-Ga-Pt/Z-Ar	371.15	129.09	242.06	0.13	0.31	3.35
Ce-Ga-Pt/Z-CH₄ (CH₄)	204.50	107.14	97.35	0.06	0.32	6.31
Ce-Ga-Pt/Z-Ar (CH₄)	263.26	94.60	168.66	0.10	0.24	3.58
159						

160 Table S2. ICP-OES data for metal loading of the two supports

	Catalyst	Ce loading	Pt loading	Ga loading
		(wt%)	(wt%)	(wt%)
	Ce-Ga-Pt/Z-CH₄	4.98	0.54	0.56
	Ce-Ga-Pt/Z-Ar	4.91	0.53	0.56
161	I			
162				
163				
164				
165				
166				
167				

168 Table S3. Product distribution data for all reactions

	Ce-Ga-	Ce-Ga-	Ce-Pt/Z-	Ce-Ga/Z-	Ga-Pt/Z-	Ce-Ga-Pt/Z-	Ce-Ga-Pt/Z-
	Pt/Z-CH₄	Pt/Z-Ar	CH₄	CH_4	CH₄	CH4 (N2)	Ar (N ₂)
gas yield	40.9	40.5	40	41.6	39.3	36.5	37.1
(wt%							

liquid yield (wt%)	57.03	57.03	57.87	57	58.73	56.6	57.5
solid yield (wt%)	2.8	3.2	2.6	2.3	3.2	6.1	4.7
CH₄ conversion (wt%)	3.2	2.1	1.6	3	2.8		
mass balance	100.7	100.7	100.5	100.9	101.3	99.2	99.3
H ₂	0.3	0.2	0.2	0.1	0.2	0.1	0.1
=(C ₂ .C ₅)=	6.6	10.9	9.1	5.4	10.5	12.6	12.5
-(C ₂ -C ₅)-	19.1	17.4	16.5	20.1	16.4	8	10
со	2.2	2.9	2	4.2	1.9	6.5	6
CO ₂	12.6	9.2	12.2	11.9	10.4	8.0	7.3
CH₄						1.2	1.2
paraffins	2.4	3.6	5.1	6.1	6.4	2.9	2.1
PAH	1.1	2.6	1.6	1.5	2	5	5.6
aromatics	50.8	44.6	46.9	43.5	45.2	40	39.6
olefins	0.9	2.4	1.2	0.6	0.9	4.9	5
naphthenes	0.9	0.6	1.8	3.7	2.9	1.7	1.9
water	0.7	2.7	1.2	1.2	1.1	1.5	2.3
oxygenates	0.3	0.5	0.2	0.4	0.2	0.7	0.9
benzene	3.4	4.4	5.5	4.1	4.6	4	2.7
toluene	40.1	26.8	36.8	40.7	41.2	38.9	28.7
EB	7.8	5.8	5.5	5.6	7.9	6.7	9

xylenes	16.8	22.6	18.3	17.1	20.2	19.1	24
C ₉ aromatics	21.2	24.8	22.4	15.9	16.9	19	28
C ₁₀ aromatics	10.7	15.6	11.5	16.5	9.2	12.4	7.5
CO ₂ (mmol)	5.2	4.2	5.2	4.8	4.3	3.3	3
CO (mmol)	0.7	0.9	0.5	1.3	0.6	2.1	1.9
other (mmol)	0.5	1.3	0.7	0.2	1.5	1	1.5



170 *All values are given as total selectivity in wt% unless mmol, yield, mass balance, and CH_4

171 conversion are specified.