Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

Active sties and mechanism of the direct conversion of methane and carbon dioxide to acetic acid over the zinc-modified H-ZSM-5 zeolite

Peng Zhang[1,2,3], Xuejing Yang[3], Xiuli Hou*[,3], Jianli Mi[3], Zhizhong Yuan[3], Jun Huang*[,2], Catherine Stampfl*[,1]

[1] *School of Physics, The University of Sydney, Sydney, New South Wales 2006, Australia*

[2]*Laboratory for Catalysis Engineering, School of Chemical and Biomolecular Engineering, The University of Sydney, New South Wales 2006, Australia*

[3]*Institute for Advanced Materials, School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China*

**E-mail: houxiuli@ujs.edu.cn, jun.huang@sydney.edu.au, catherine.stampfl@sydney.edu.au*

Table S1. Adsorption energies (E_{ad}) of CH_4 on H-ZSM-5 with different size cluster models. The corresponding cluster models are shown in Fig. S1. All results are in unit of eV.

	Straight channel			Intersection cavity	
Site	M5	M6	Site	T10	ZnOZn-TA
22T	–0.86	–0.61	16T	–0.74	–0.31
46T	–0.87	–0.70	56T	–0.68	–0.37
58T	–0.88	–0.70			

In order to check if the cluster models used in this work (22T for sinusoidal and straight channels and 16T for intersection cavity) are suitable to describe the structure of H-ZSM-5, we performed some calculations on larger cluster models, including 46T and 58T cluster models for the straight channel and 56 T for the intersection cavity. As shown in Table S1, the variation of the adsorption energies of CH_4 is smaller than 0.09 eV, indicating that 22T and 16T are sufficient to describe the pore structure of H-ZSM-5.

Table S2. Adsorption energies (E_{ad}) of CH_3COOH on Zn/H-ZSM-5 with different size cluster models. All results are in unit of eV.

	Straight channel	
Site	M5	M6
22T	–2.07	–1.81
58T	–2.02	–1.85

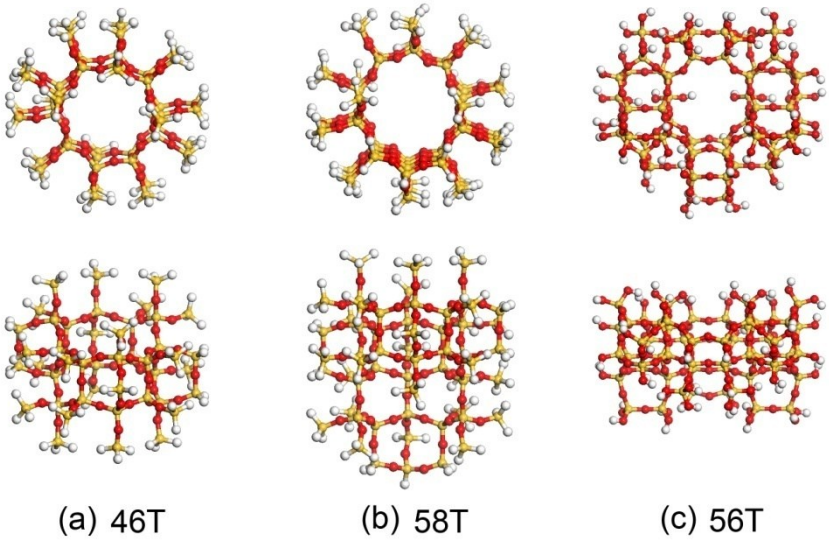

Fig. S1. The atomic structures of different cluster models used in Table S1.

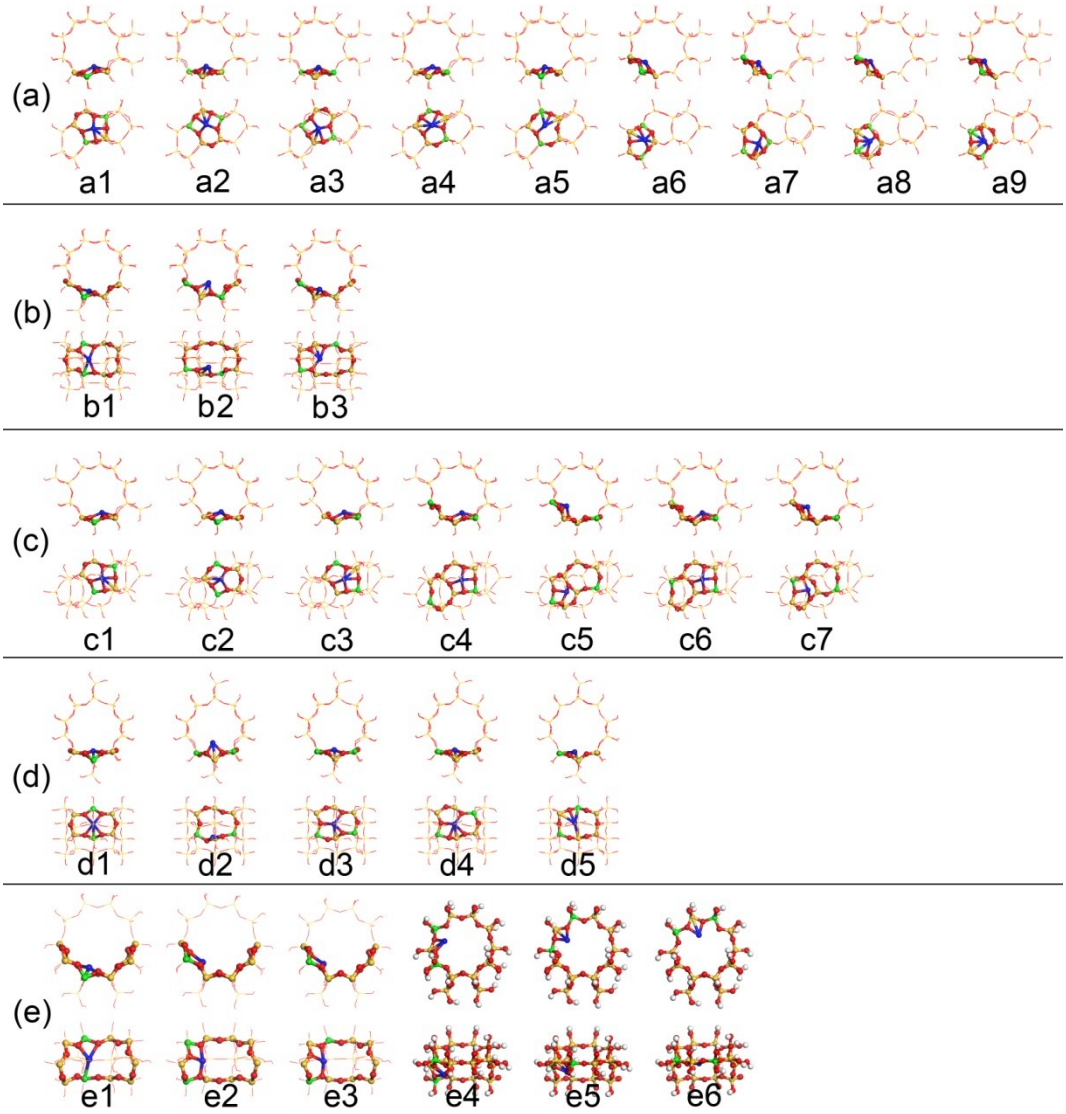

Fig. S2. Atomic structures of Zn^{2+} modified H-ZMS-5 with different doped Al sites: (a) five-membered zeolite rings in the sinusoidal channel, (b) eight-membered zeolite rings in the sinusoidal channel,(c) five-membered zeolite rings in the straight channel, (d) six-membered zeolite rings in the sinusoidal channel, and (e) ten-membered zeolite rings in the intersection cavity.

Table S3. The relative energy of Zn^{2+} modified H-ZMS-5 with different doped Al atom sites. All results are in unit of eV. All atomic structures are shown in Fig. S2.

Structure	a1	a2	a3	a4	a5	a6	a7	a8	a9
Energy/eV	0	0.14	0.42	1.70	1.45	1.27	0.27	0.53	0.76
Structure	b1	b2	b3	b4					
Energy/eV	0	0.03	1.69	1.11					
Structure	c1	c2	c3	c4	c5	c6	c7		
Energy/eV	0	0.40	0.76	1.65	1.45	1.42	1.64		
Structure	d1	d2	d3	d4	d5				
Energy/eV	0	2.12	1.50	1.23	7.34				
Structure	e1	e2	e3	e4	e5	e6			
Energy/eV	0	0.78	0.96	2.73	2.29	2.46			

The energies of a1, b1, c1, d1 and e1, which are used as the models of Zn/H-ZSM-5, are set as 0 eV. The larger the relative energy, the less stable the structure is. The positive energiesof other structures indicate a1, b1, c1, d1 and e1 are most stable in the corresponding zeolite rings.

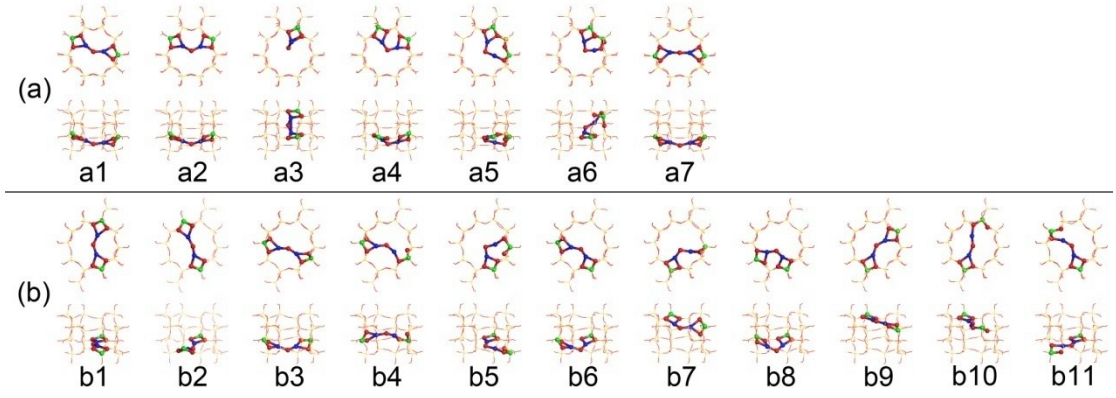

Fig. S3. Atomic structures of ZnOZn modified H-ZMS-5 with different doped Al atom sites: (a) in the sinusoidal channel and (b) in the straight channel.

Table S4. The relative energy of ZnOZn modified H-ZMS-5 with different doped Al atom sites. All results are in unit of eV. All atomic structures are shown in Fig. S3. The energies of a1 and b1are set as 0 eV. a1 and a2 in the sinusoidal channel and b1 and b2 in the straight channel are used in this work as the models of ZnOZn modified H-ZMS-5.

Structure	a1	a2	a3	a4	a5	a6	a7				
Energy/eV	0	0.18	0.58	0.23	0.27	0.33	0.10				
Structure	b1	b2	b3	b4	b5	b6	b7	b8	b9	b10	b11
Energy/eV	0	0.24	0.17	0.52	1.03	0.01	0.48	0.43	0.82	0.66	0.65

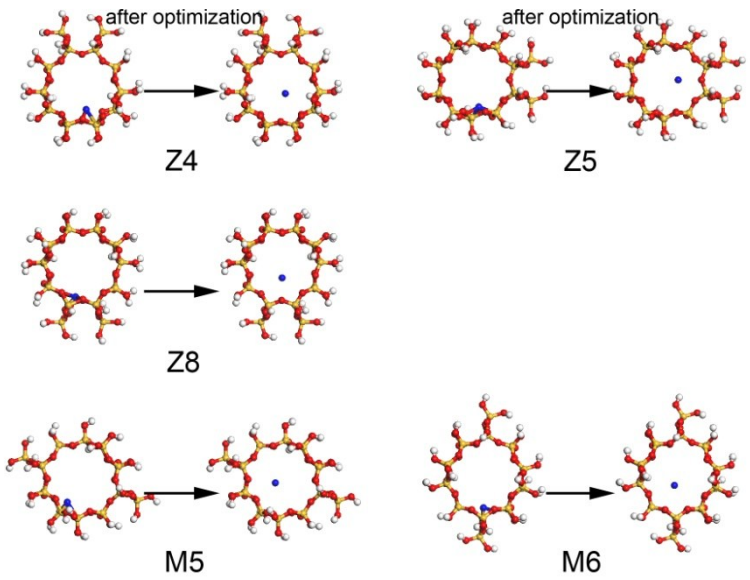

Fig. S4. The atomic structures of Zn modified ZSM-5 without substitutional Al atoms before and after structural optimization. It is clear that the Zn atoms do not form bonds with the zeolite.

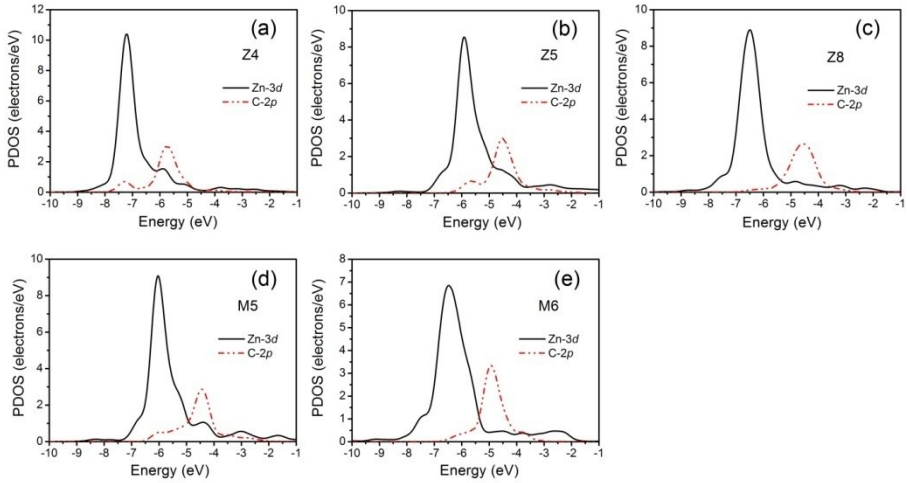

Fig. S5. Partial density of states (PDOS) for CH_4 adsorbed on Zn/H-ZSM-5. The energy zero corresponds to the Fermi energy.

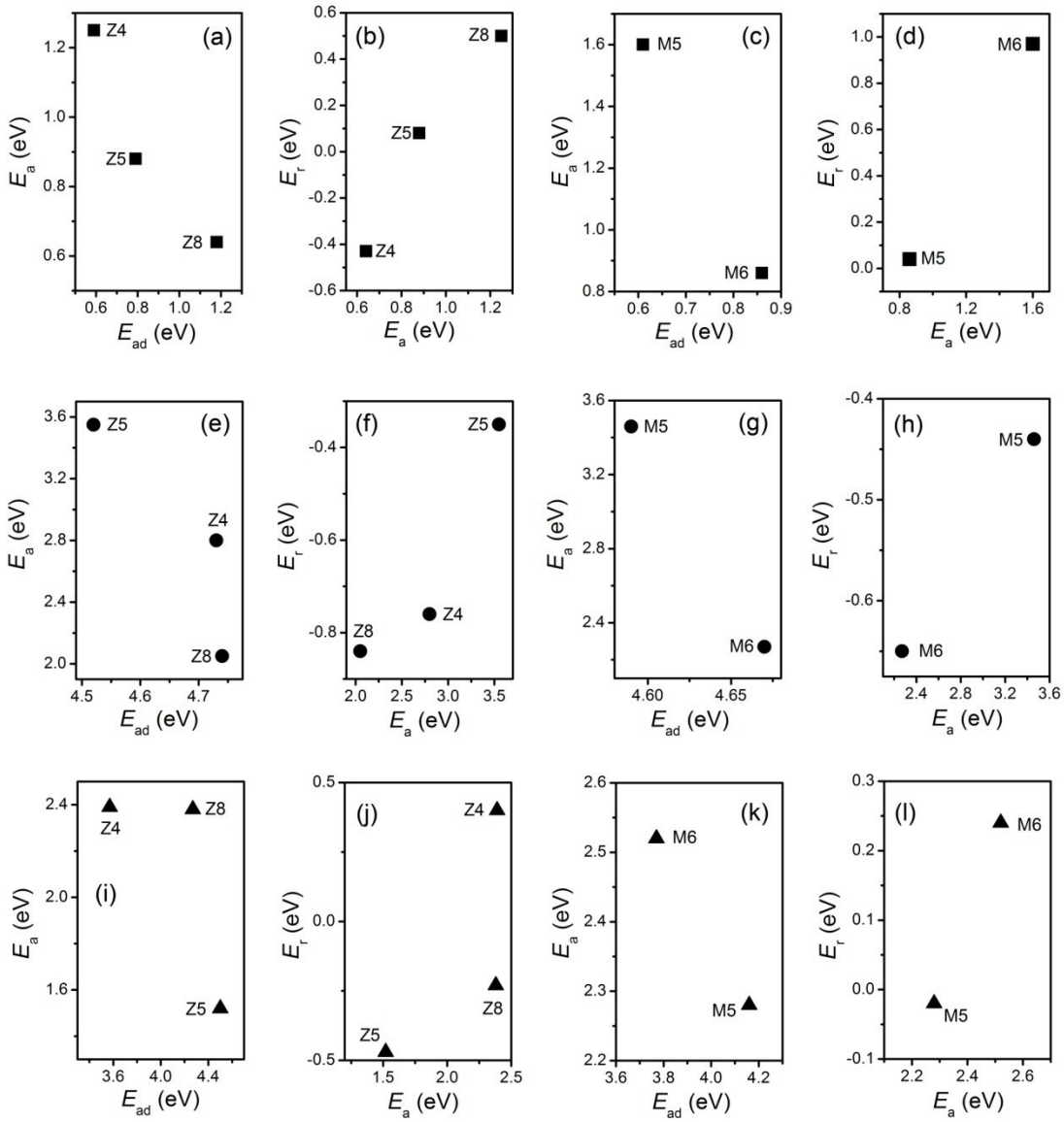

Fig. S6. Plots of activation energy (E_a) against the adsorption energy ($E_{ad\text{-}CH4}$ or $E_{ad\text{-}CH3COO}$) for the dissociation of CH_4 in sinusoidal (a) and straight (c) channels, for CO_2 insertion in sinusoidal (e) and straight (g) channels via the direct pathway, and for CO_2 insertion in sinusoidal (i) and straight (k) channels via the indirect pathway. Plots of the reaction energy (E_r) against the activation energy (E_a) for the dissociation of CH_4 in sinusoidal (b) and straight (d) channels, for CO_2 insertion in sinusoidal (f) and straight (h) channels via the direct pathway, and for CO_2 insertion in sinusoidal (j) and straight (l) channels via the indirect pathway.

Table S5. The C-Zn bond length of CH_4 on Zn/H-ZSM-5 and on ZnOZn/H-ZSM-5 and the charge transfer from CH_4 to Zn/H-ZSM-5 and ZnOZn/H-ZSM-5.

sites	C-Zn bond length/Å	charge transfer/*e*
Z4	2.213	0.301
Z5	2.345	0.199
Z8	2.611	0.121
M5	2.337	0.218
M6	2.587	0.112
T10	2.358	0.218
ZnOZn-ZA	3.220	0.036
ZnOZn-ZB	3.243	0.052
ZnOZn-MA	3.050	0.053
ZnOZn-MB	2.934	0.040
ZnOZn-TA	3.151	0.034