Supplementary Information

Mechanistic Understanding of Ethane Dehydrogenation and Aromatization over Zn/ZSM-5: Effects of Zn Modification and CO_2 Co-reactant

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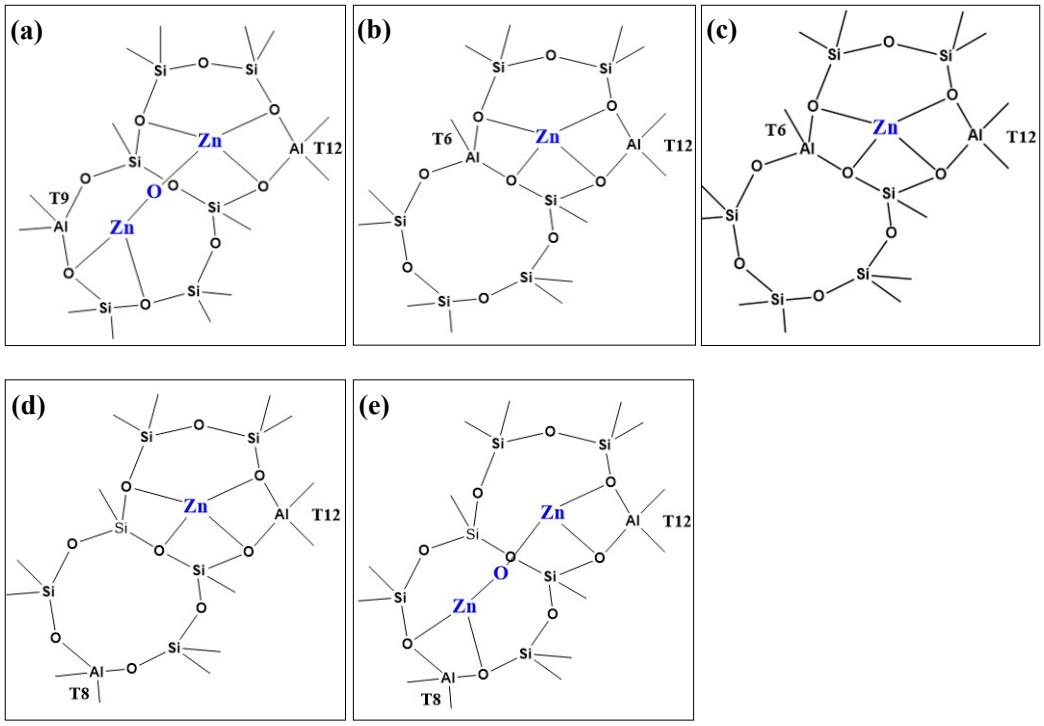


Figure S1. The catalyst models of (a) $(Zn\text{-}O\text{-}Zn)^{2+}$, (b) Z_sZn in the paper of Yakovlev and (c) ZnZ_s, (d) ZnZ_d, (e) $(Zn\text{-}O\text{-}Zn)^{2+}$ in the paper of Pidko.

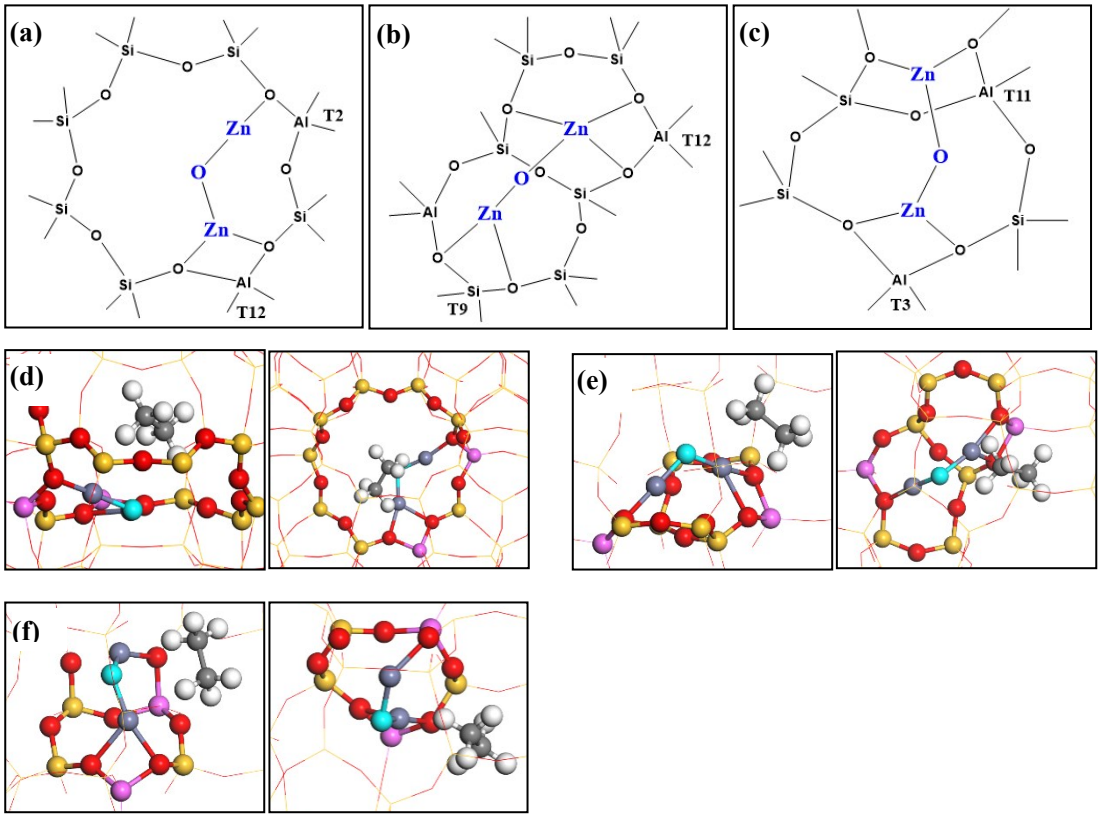


Figure S2. Zn/ZSM-5 models with different Al pair substitution as well as ethane adsorption configurations over these models. (a) T12-T2, (b) T12-T9, (3) T11-T3, (d) ethane adsorption with T12-T2, (e) ethane adsorption with T12-T9 and (f) ethane adsorption with T11-T3 (Pink: Al, Yellow:

Si, Red: O of ZSM-5 framework, Bright blue: O of $(Zn\text{-}O\text{-}Zn)^{2+}$ site, Light purple: Zn, Grey: C, White: H).

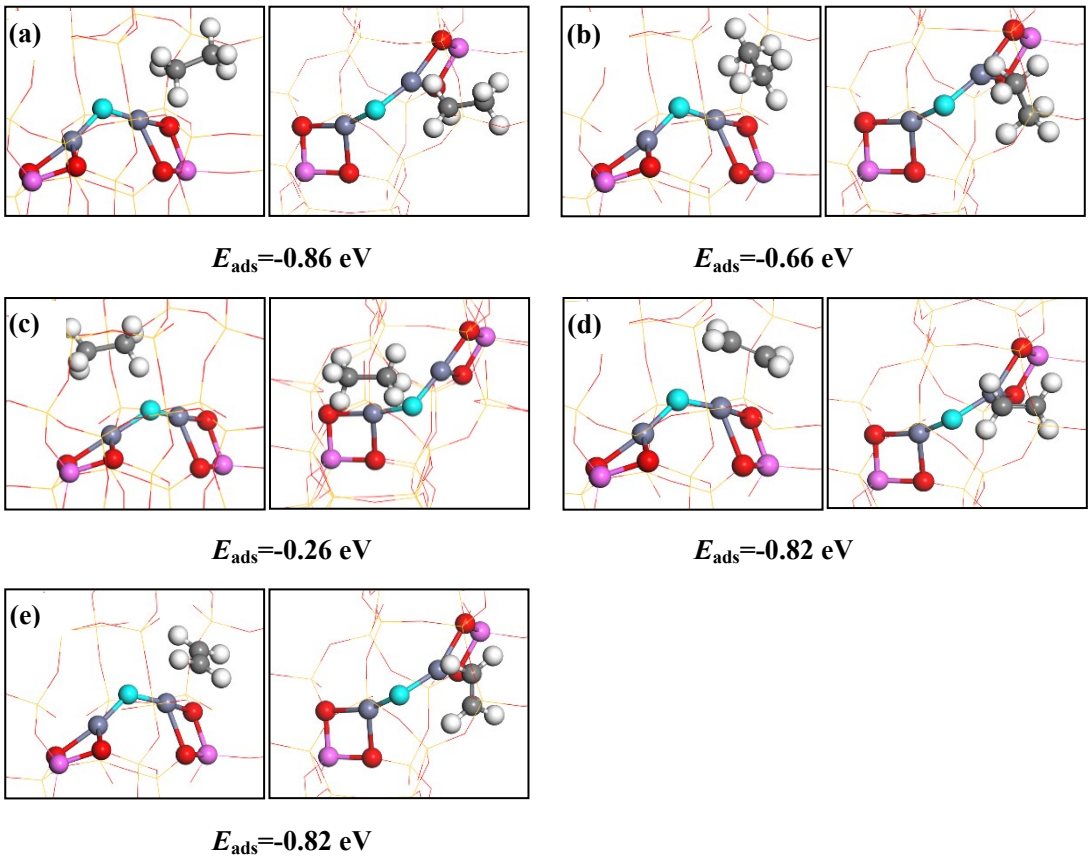


Figure S3. Stable adsorption configurations of (a), (b), (c) ethane and (d), (e) ethene over the $(Zn\text{-}O\text{-}Zn)^{2+}$ site of Zn-ZSM-5 (Pink: Al, Yellow: Si, Red: O of ZSM-5 framework, Bright blue: O of $(Zn\text{-}O\text{-}Zn)^{2+}$ site, Light purple: Zn, Grey: C, White: H).

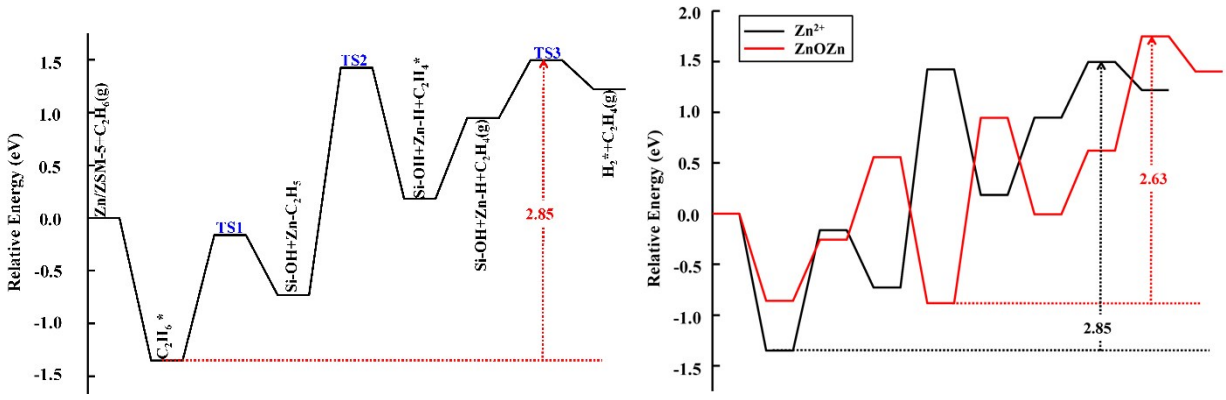


Figure S4. (a) Energy diagram of ethane dehydrogenating to ethene over the single Zn^{2+} site of Zn/ZSM-5 and (b) Comparison of the energy profiles for ethane dehydrogenating to ethene between the single Zn^{2+} site and the $(Zn\text{-}O\text{-}Zn)^{2+}$ site.

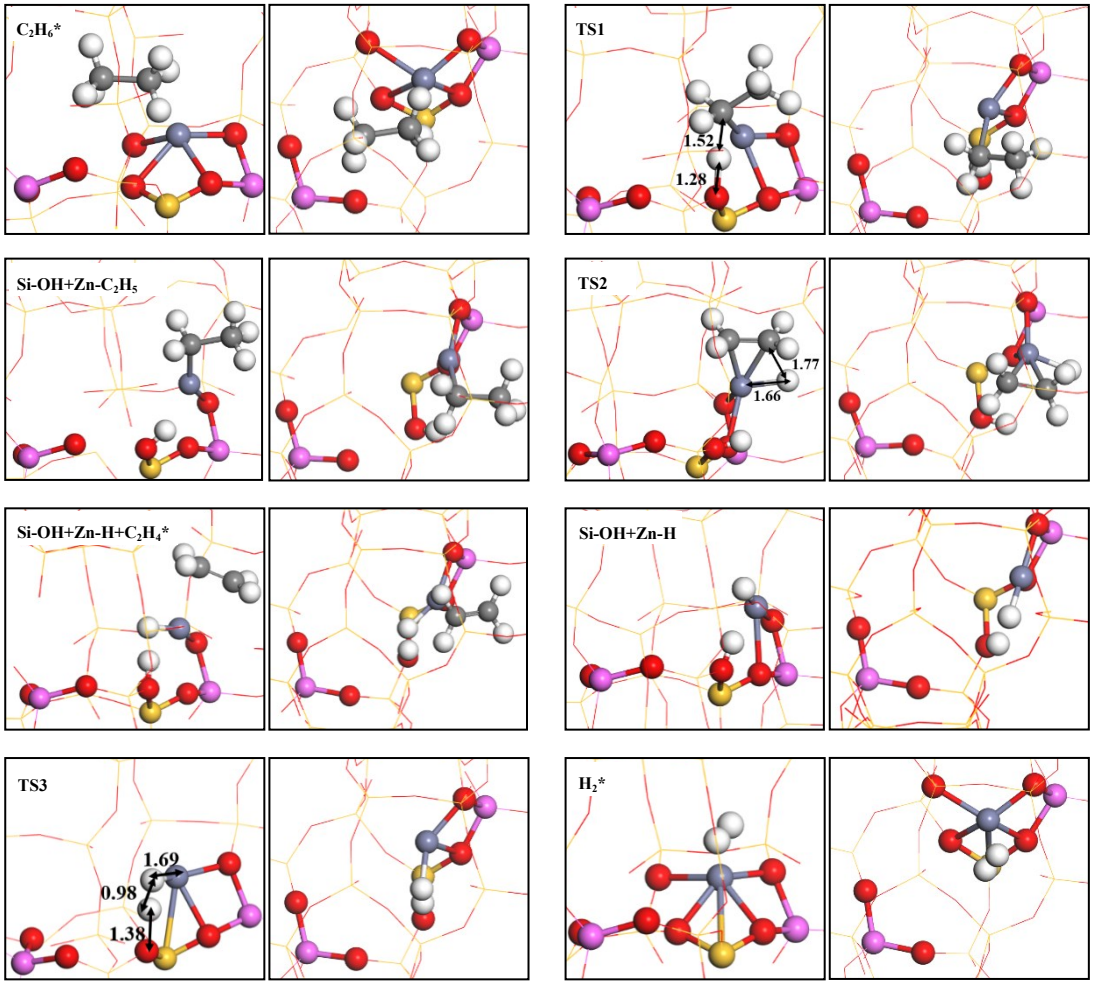


Figure S5. Optimized structures of all states involved in ethane dehydrogenating to ethene over the single Zn^{2+} site of Zn/ZSM-5 (Pink: Al, Yellow: Si, Red: O of ZSM-5 framework, Light purple: Zn, Grey: C, White: H).

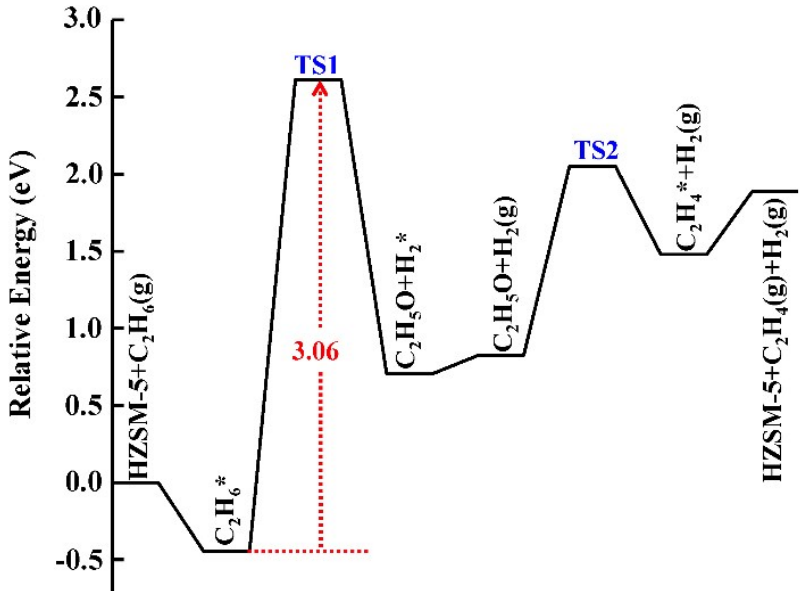


Figure S6. Energy diagram of ethane dehydrogenation to ethene over HZSM-5.

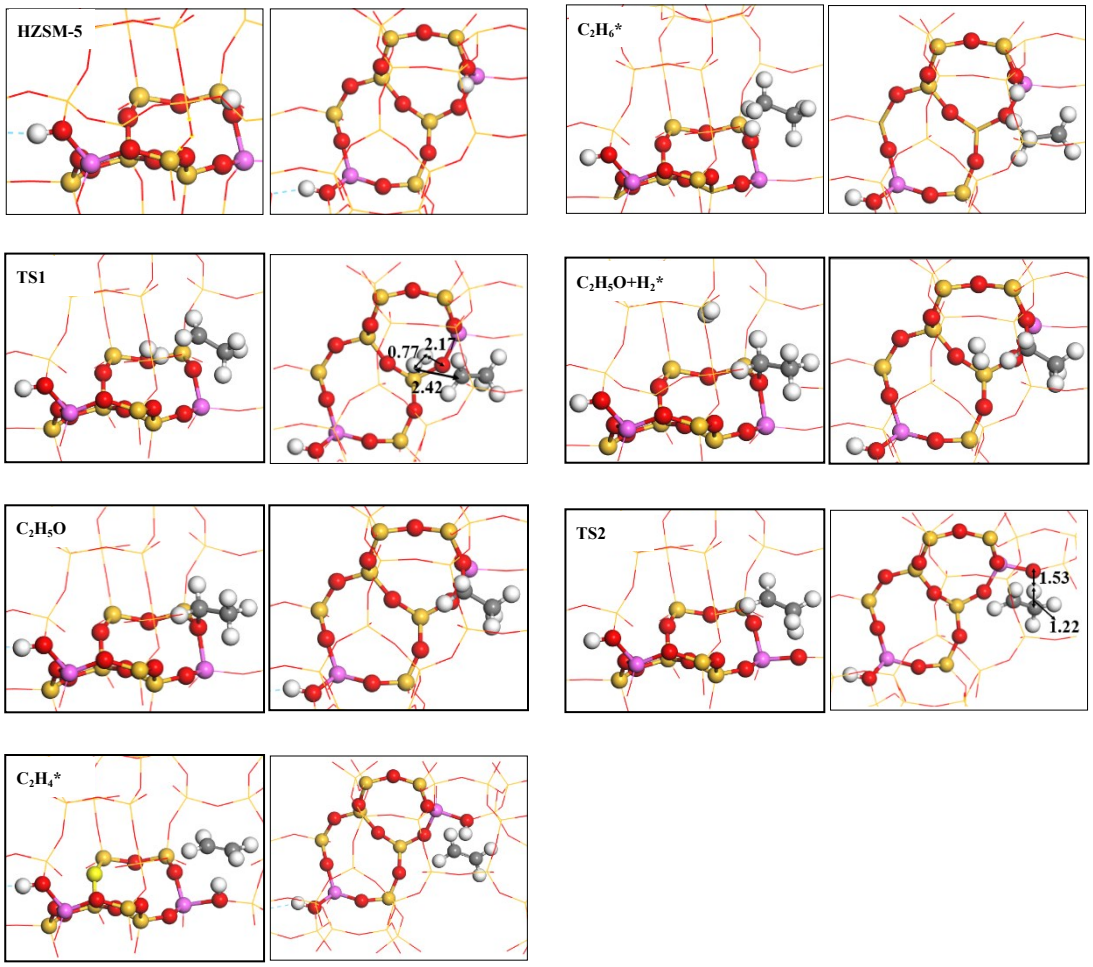
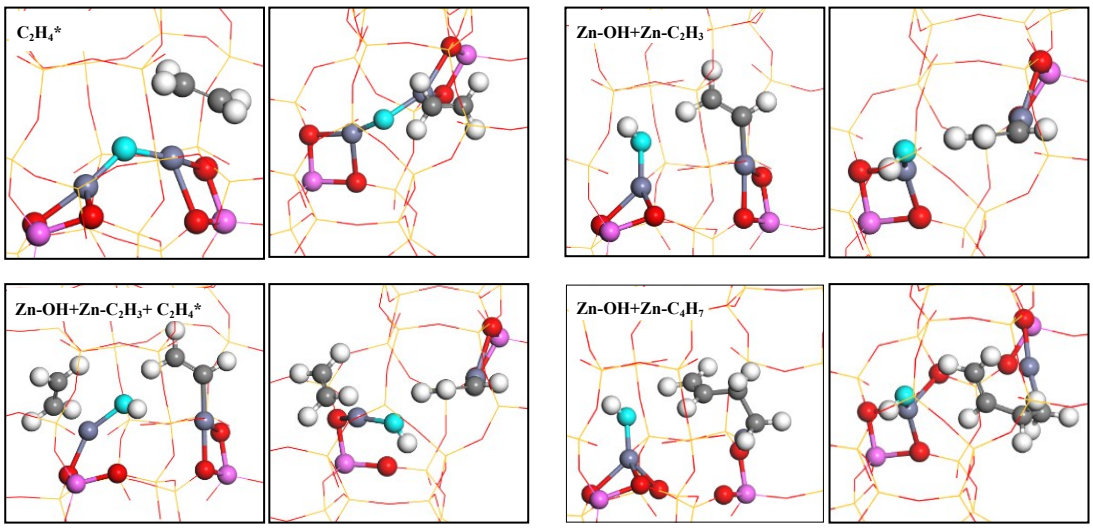
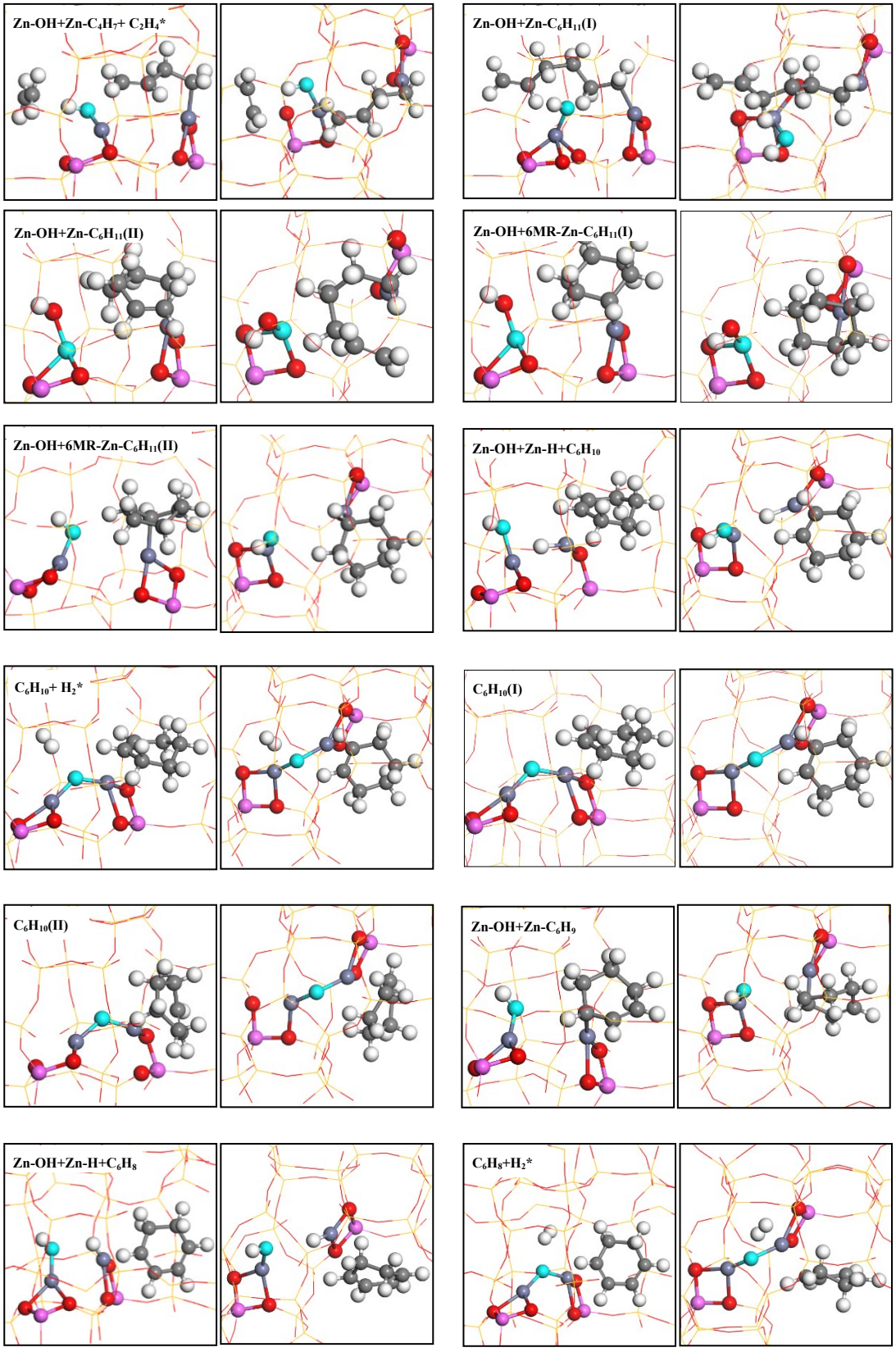


Figure S7. Optimized structures of reactant, intermediates, transition states and product associated with ethane dehydrogenation to ethene over HZSM-5 (Pink: Al, Yellow: Si, Red: O, Grey: C, White: H).




Zn-OH+Zn-C4H7+ C2H4*
Zn-OH+Zn-C6H11(I)
Zn-OH+Zn-C6H11(II)
Zn-OH+6MR-Zn-C6H11(I)
Zn-OH+6MR-Zn-C6H11(II)
Zn-OH+Zn-H+C6H10
C6H10+ H2*
C6H10(I)
C6H10(II)
Zn-OH+Zn-C6H9
Zn-OH+Zn-H+C6H8
C6H8+H2*

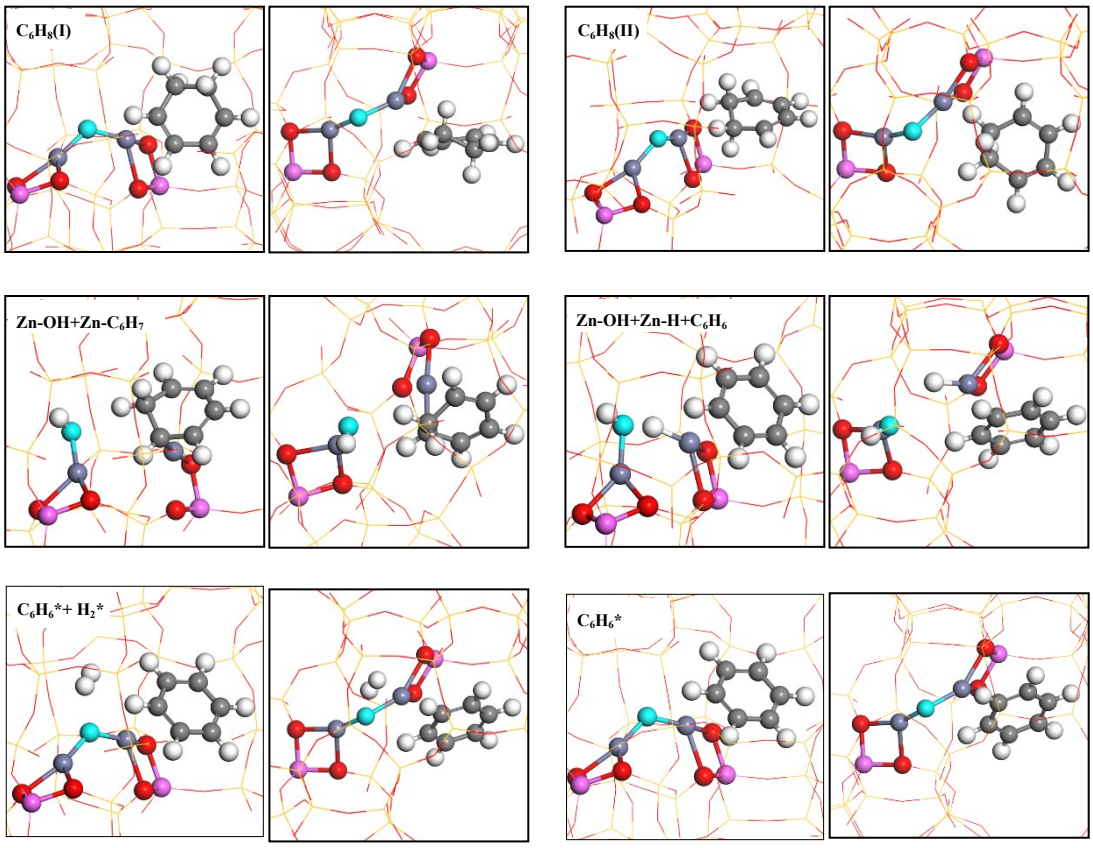


Figure S8. Optimized structures of reactant, intermediates and product associated with ethene aromatization to benzene over the $(Zn\text{-}O\text{-}Zn)^{2+}$ site of Zn/ZSM-5 (Pink: Al, Yellow: Si, Red: O of ZSM-5 framework, Bright blue: O of $(Zn\text{-}O\text{-}Zn)^{2+}$ site, Light purple: Zn, Grey: C, White: H).

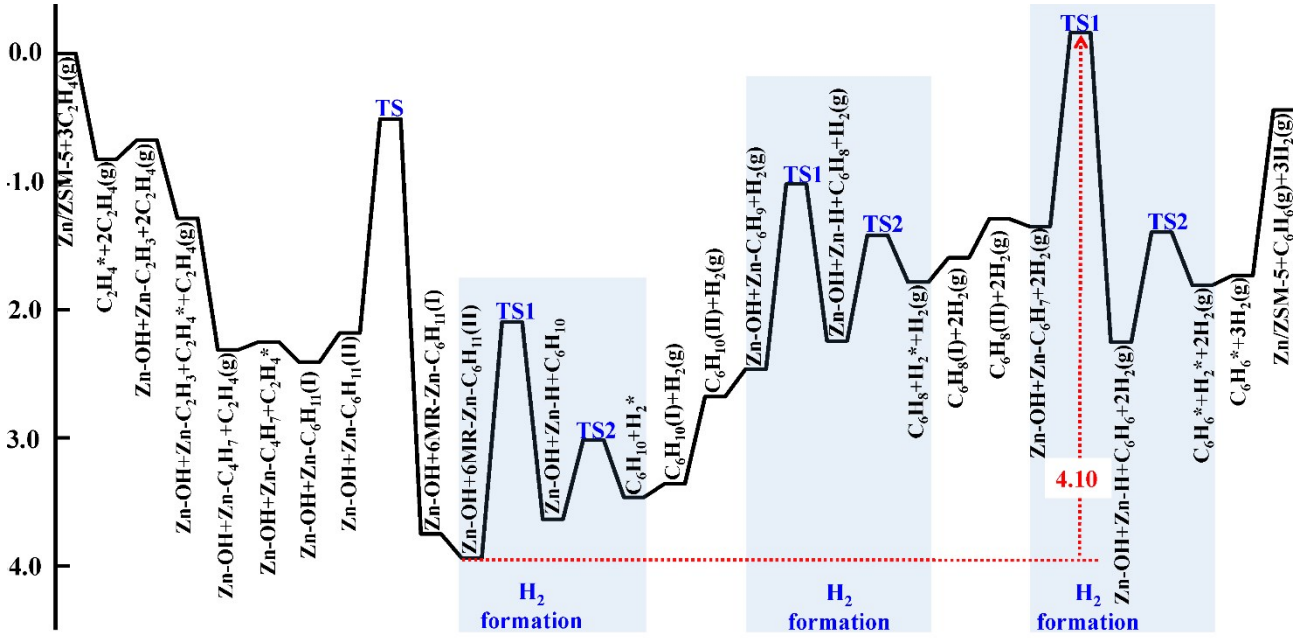
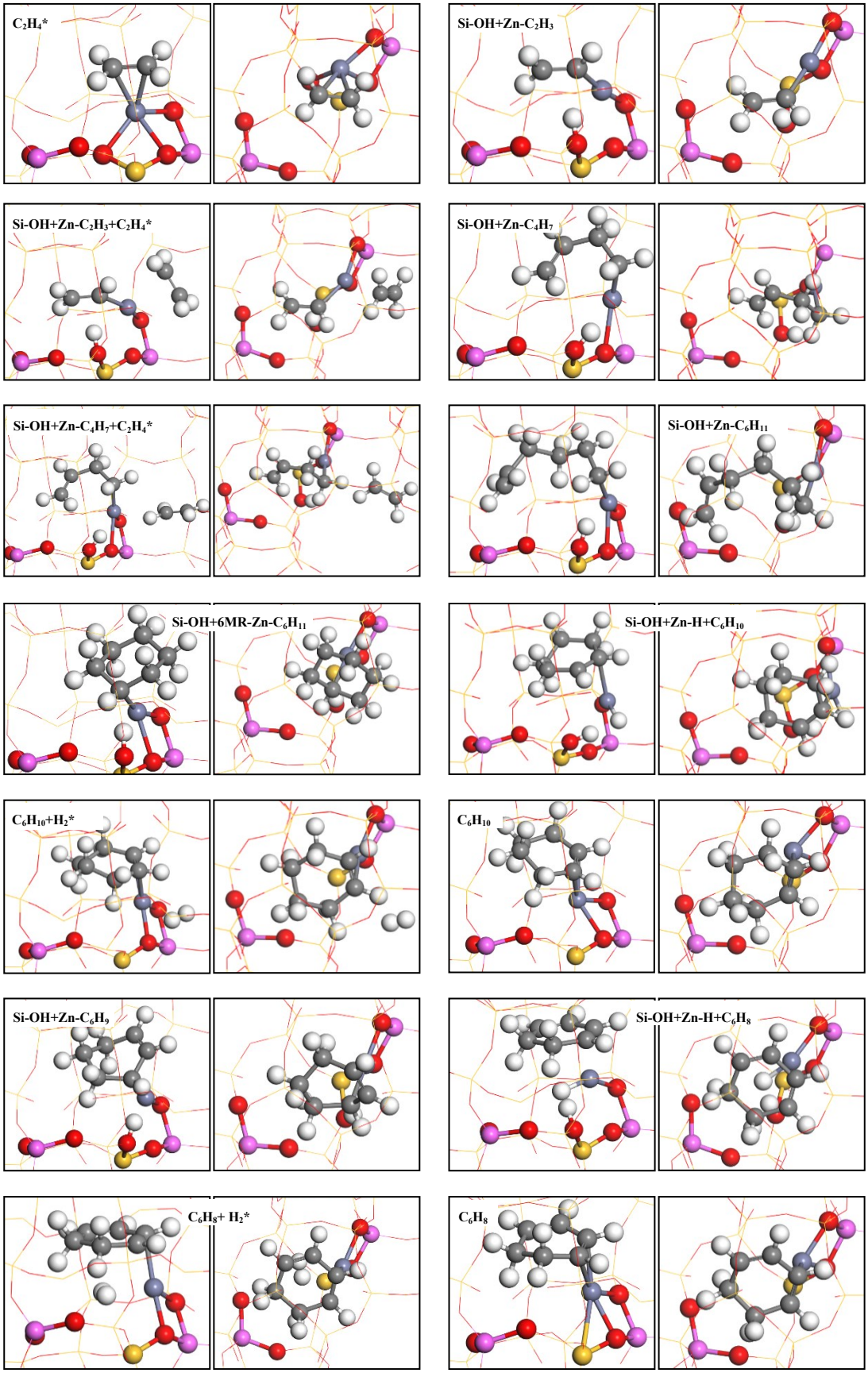


Figure S9. Energy diagram of ethene aromatization to benzene over the $(Zn\text{-}O\text{-}Zn)^{2+}$ site of Zn/ZSM-5 (The activation barriers associated with the three H_2 generation steps are included).


C_2H_4*
Si-OH+Zn-C_2H_3
Si-OH+Zn-C_2H_3+C_2H_4*
Si-OH+Zn-C_4H_7
Si-OH+Zn-C_4H_7+C_2H_4*
Si-OH+Zn-C_6H_{11}
Si-OH+6MR-Zn-C_6H_{11}
Si-OH+Zn-H+C_6H_{10}
C_6H_{10}+H_2*
C_6H_{10}
Si-OH+Zn-C_6H_9
Si-OH+Zn-H+C_6H_8
C_6H_9+ H_2*
C_6H_8

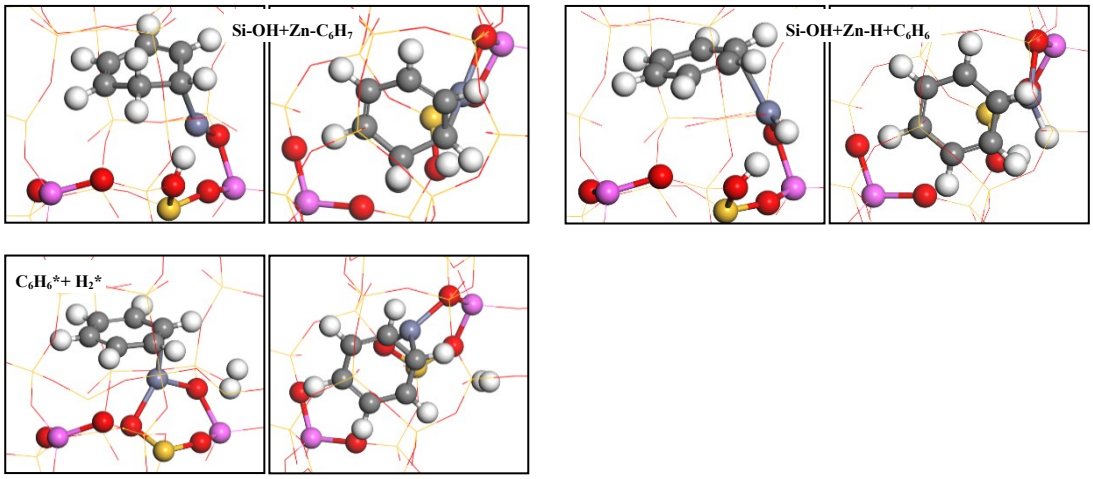


Figure S10. Optimized structures of reactant, intermediates and product associated with ethene aromatization to benzene over the single Zn^{2+} site of Zn/ZSM-5 (Pink: Al, Yellow: Si, Red: O of ZSM-5 framework, Light purple: Zn, Grey: C, White: H).

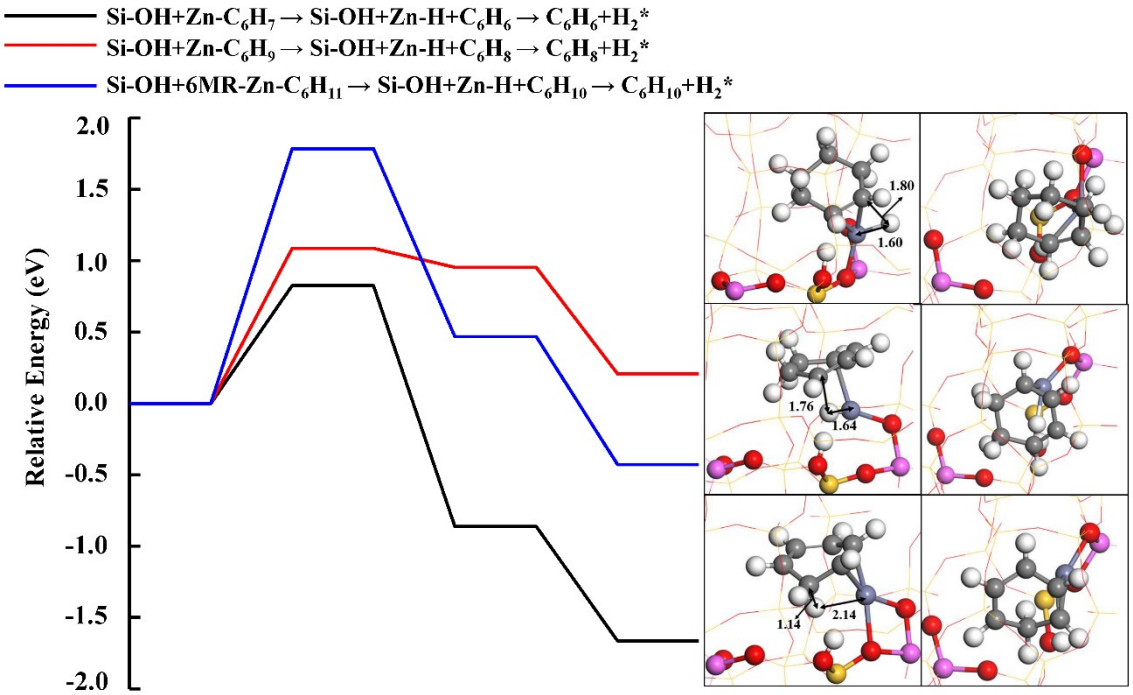


Figure S11. Energy diagram of the three H_2 generation steps involved in ethene aromatization to benzene over the single Zn^{2+} site of Zn/ZSM-5. The optimized structures of transition states associated with these reactions are shown in the figure (Pink: Al, Yellow: Si, Red: O of ZSM-5 framework, Light purple: Zn, Grey: C, White: H).

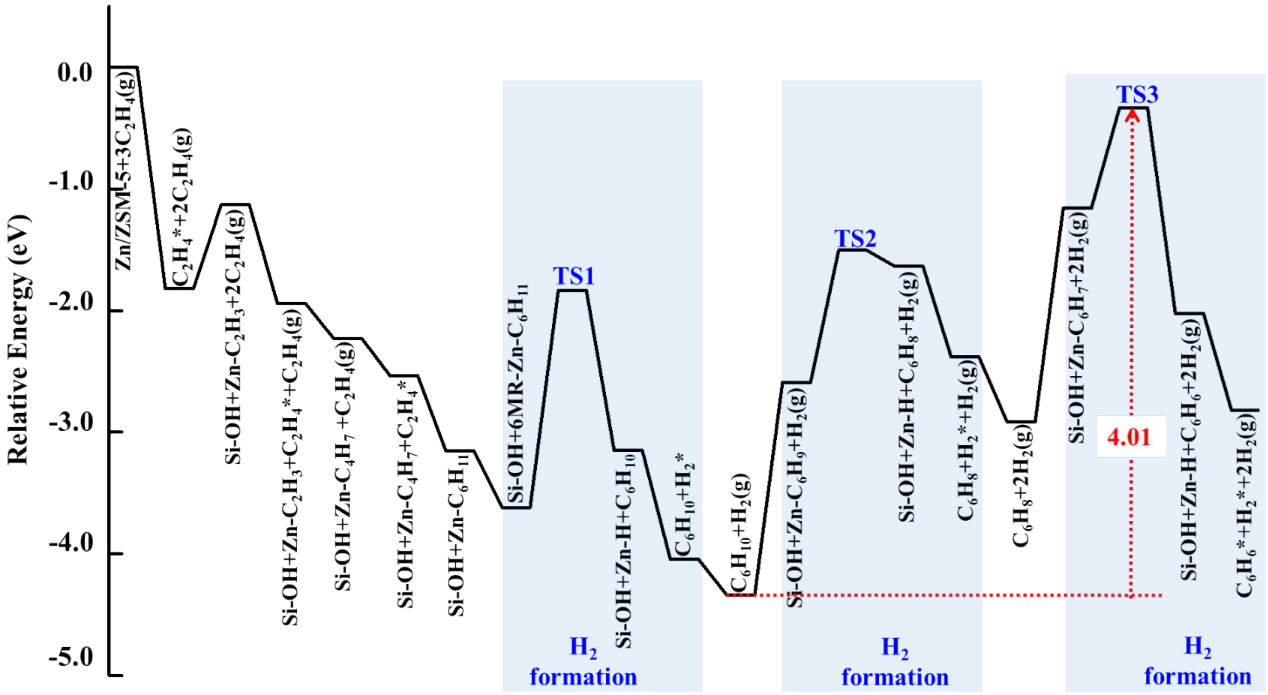
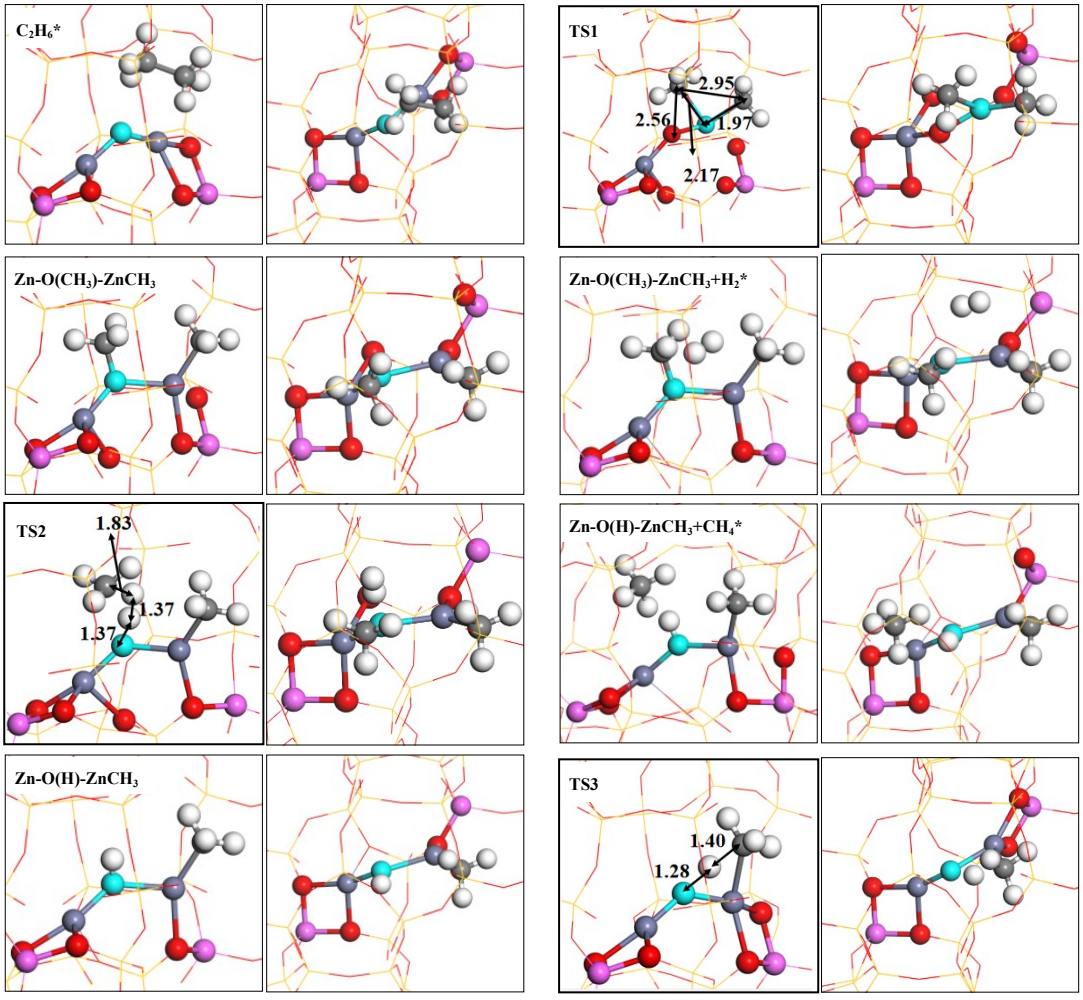


Figure S12. Energy diagram of ethene aromatization to benzene over the single Zn^{2+} site of Zn/ZSM-5 (The activation barriers associated with the three H_2 generation steps are included).



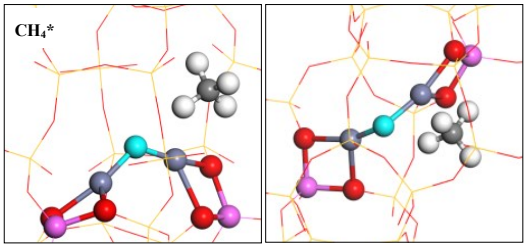


Figure S13. Optimized structures of reactant, intermediates, transition states and product associated with ethane hydrogenolysis to methane over the $(Zn\text{-}O\text{-}Zn)^{2+}$ site of Zn/ZSM-5 (Pink: Al, Yellow: Si, Red: O of ZSM-5 framework, Bright blue: O of $(Zn\text{-}O\text{-}Zn)^{2+}$ site, Light purple: Zn, Grey: C, White: H).

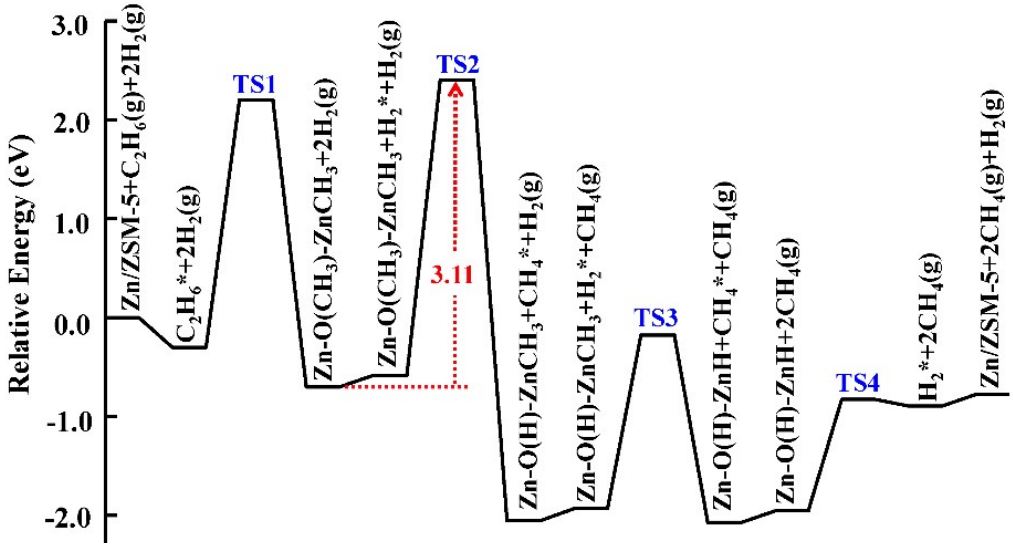
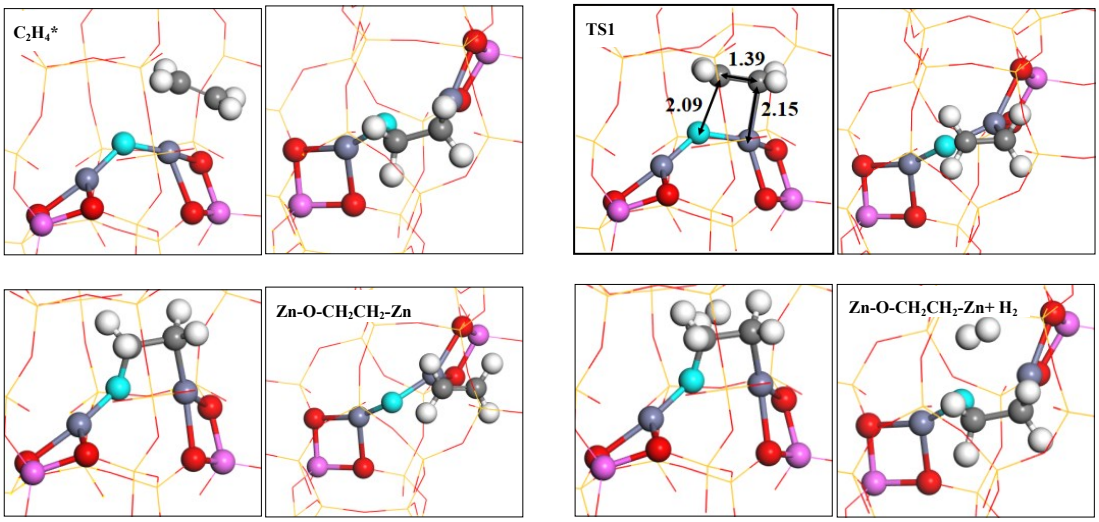


Figure S14. Energy diagram of methane formation from ethane hydrogenolysis with two H_2 molecules over the $(Zn\text{-}O\text{-}Zn)^{2+}$ site of Zn/ZSM-5.



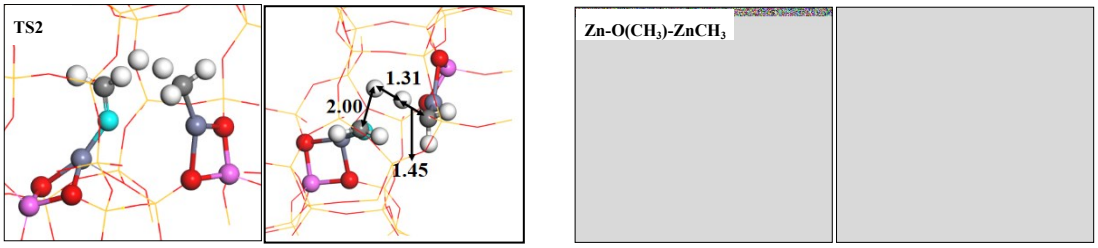


Figure S15. Optimized structures of reactant, intermediates and transition states associated with ethene hydrogenolysis to Zn-O(CH_3)-$ZnCH_3$ over the $(Zn\text{-}O\text{-}Zn)^{2+}$ site of Zn/ZSM-5 (Pink: Al, Yellow: Si, Red: O of ZSM-5 framework, Bright blue: O of $(Zn\text{-}O\text{-}Zn)^{2+}$ site, Light Grey: Zn, Grey: C, White: H).

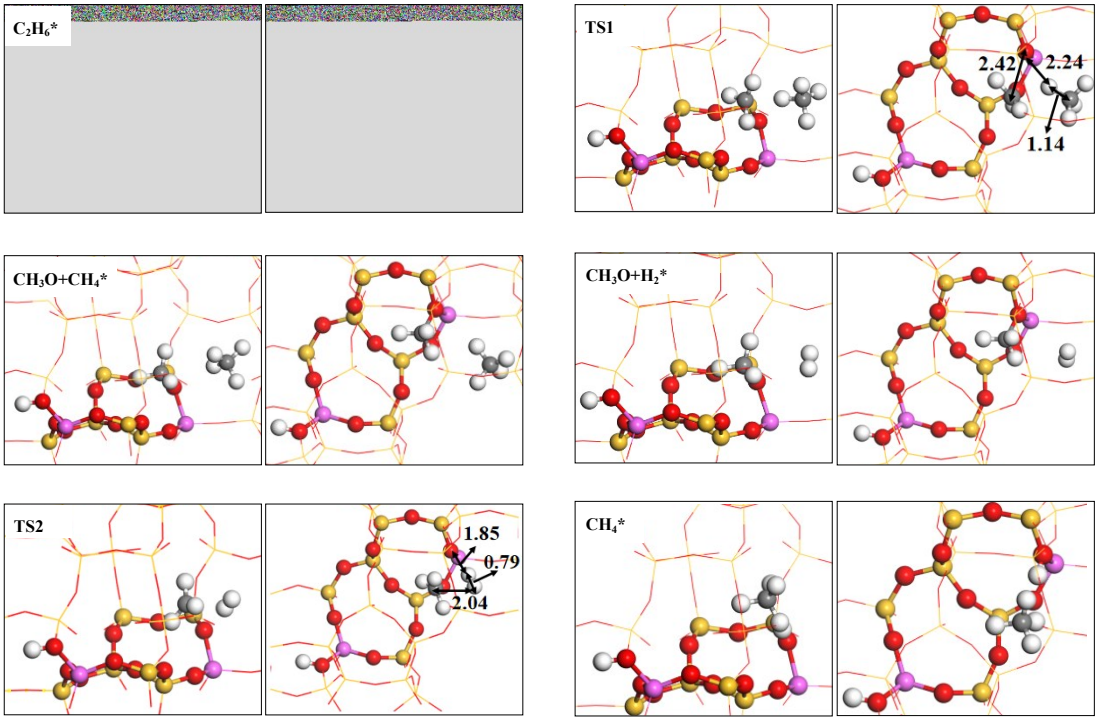


Figure S16. Optimized structures of reactant, intermediates, transition states and product associated with ethane hydrogenolysis to methane over HZSM-5 (Pink: Al, Yellow: Si, Red: O, Grey: C, White: H).

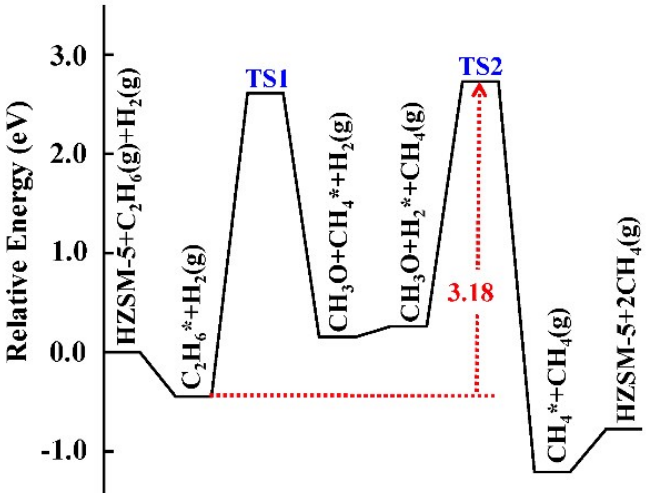
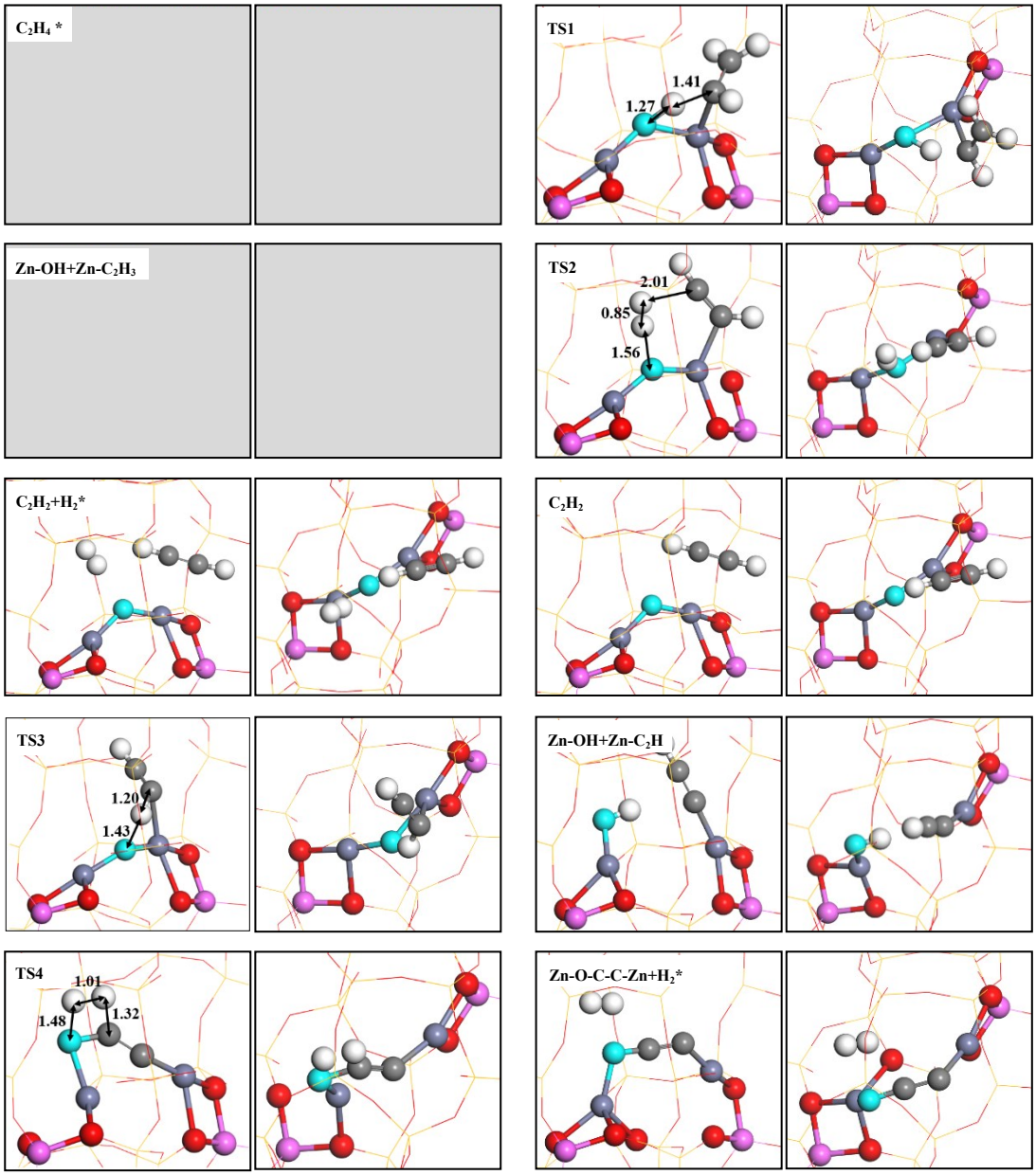
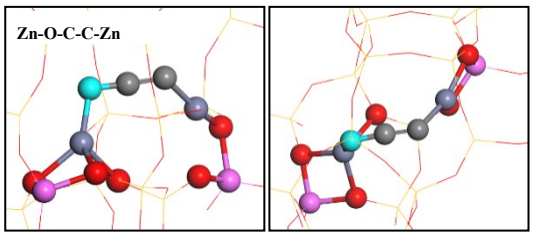
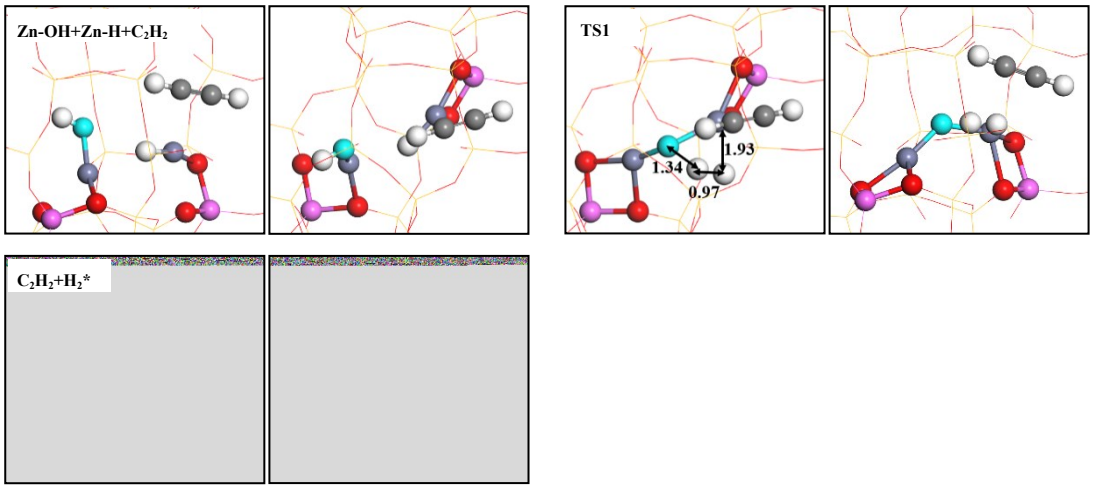


Figure S17. Energy diagram of methane formation from ethane hydrogenolysis over HZSM-5.

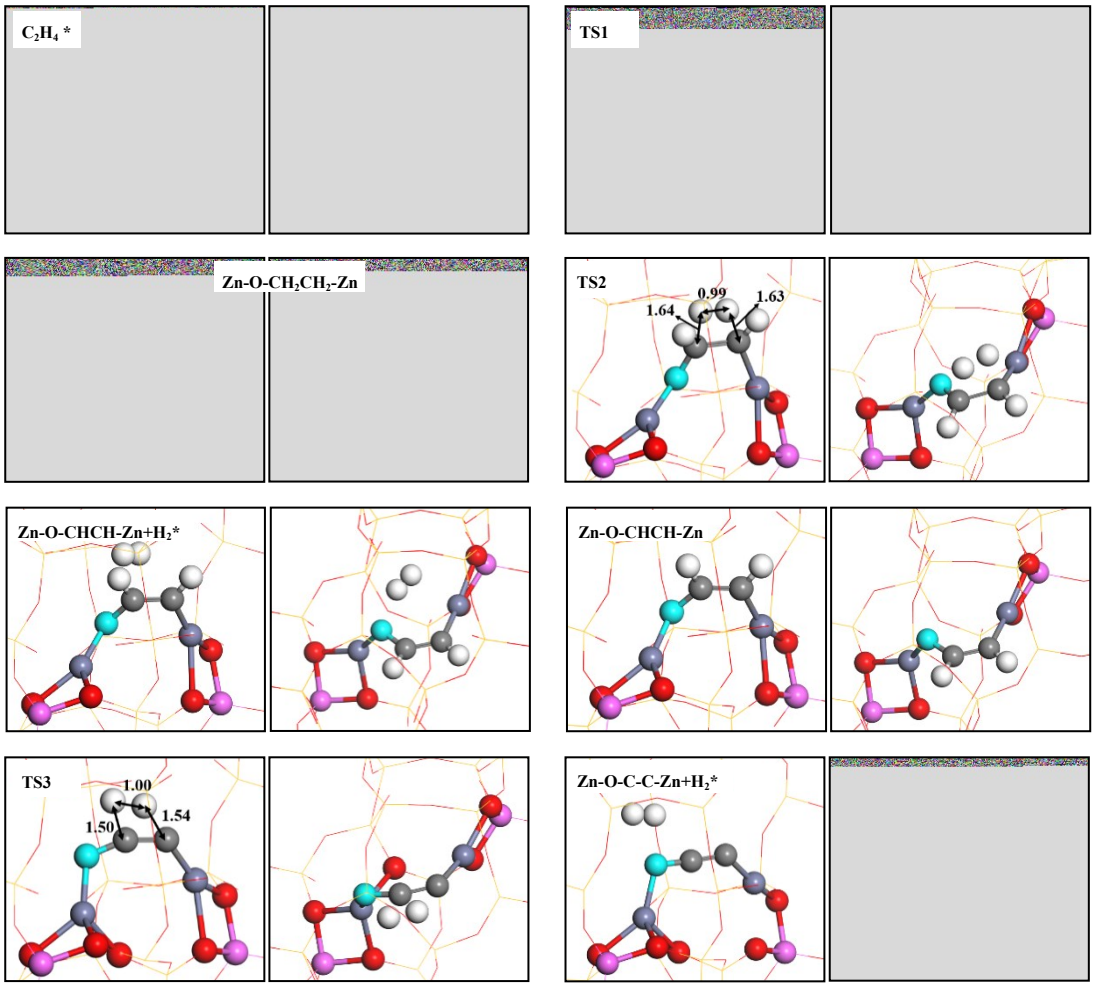




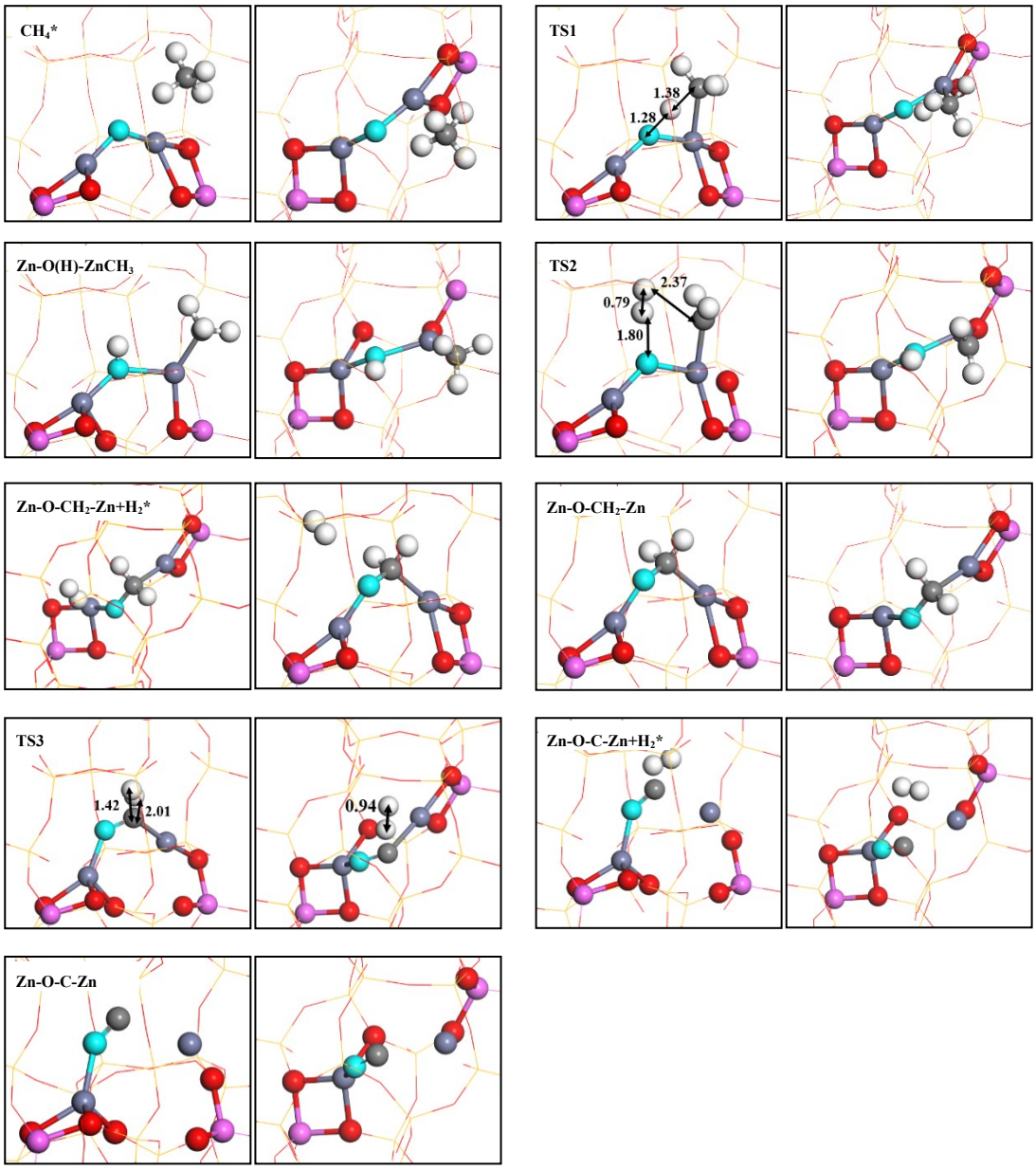
(a) Coke species formation from ethene (pathway I)



(b) Coke species formation from ethene (pathway II)



(c) Coke species formation from ethene (pathway III)



(d) Coke species formation from methane

Figure S18. Optimized structures of all states associated with coke species formation from (a), (b), (c) ethene and (d) methane over the $(Zn\text{-}O\text{-}Zn)^{2+}$ site of Zn/ZSM-5 (Pink: Al, Yellow: Si, Red: O of ZSM-5 framework, Bright blue: O of $(Zn\text{-}O\text{-}Zn)^{2+}$ site, Light Grey: Zn, Grey: C, White: H).

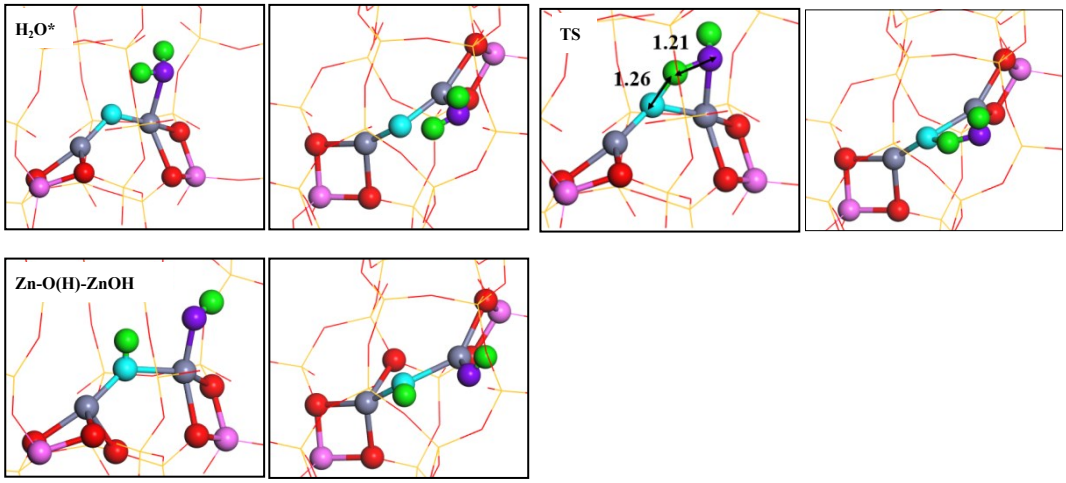


Figure S19. Optimized structures of states involved in the hydrolysis of $(Zn\text{-}O\text{-}Zn)^{2+}$ site to form the new Zn-O(H)-ZnOH site over Zn/ZSM-5 (Pink: Al, Yellow: Si, Red: O of ZSM-5 framework, Bright blue: O of $(Zn\text{-}O\text{-}Zn)^{2+}$ site, Purple: O of H_2O, Light purple: Zn, Green: H of H_2O).

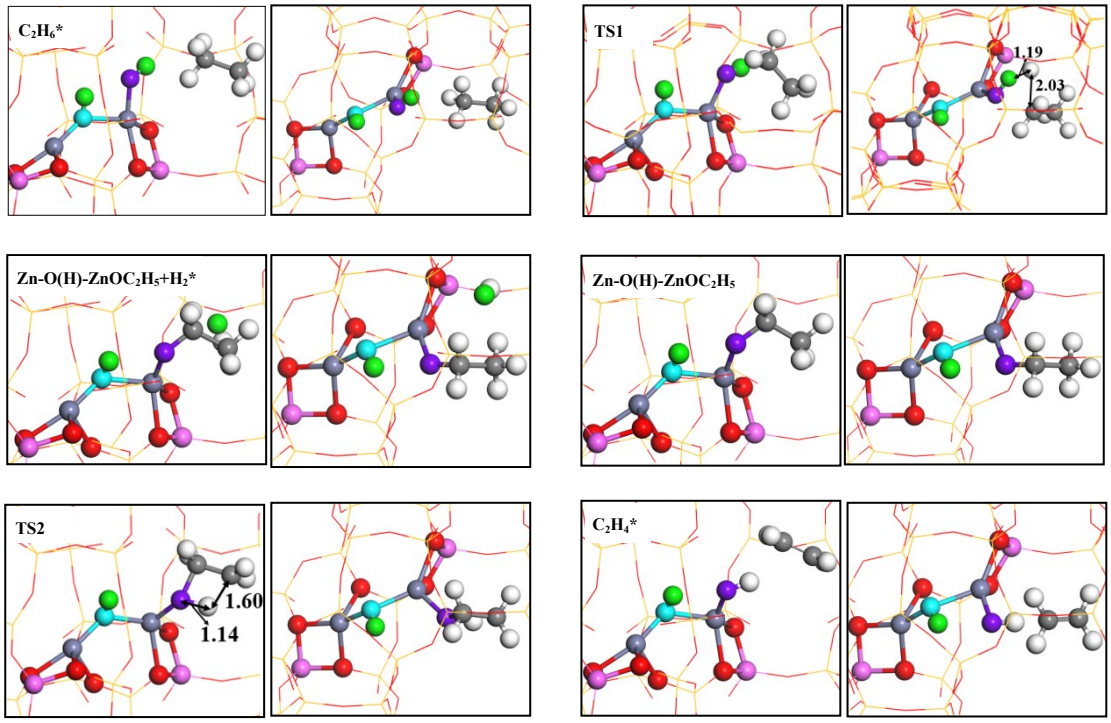


Figure S20. Optimized structures of reactant, intermediates, transition states and product associated with ethane dehydrogenation to ethene over the newly generated Zn-O(H)-ZnOH site of Zn/ZSM-5 (Pink: Al, Yellow: Si, Red: O of ZSM-5 framework, Bright blue: O of $(Zn\text{-}O\text{-}Zn)^{2+}$ site, Purple: O of H_2O, Light purple: Zn, Grey: C, White: H, Green: H of H_2O).

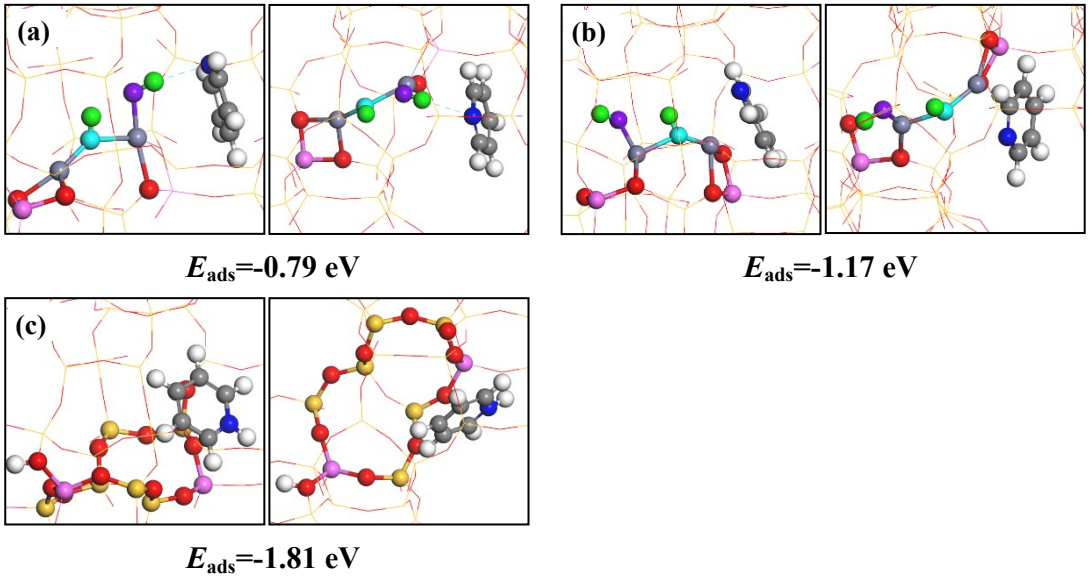
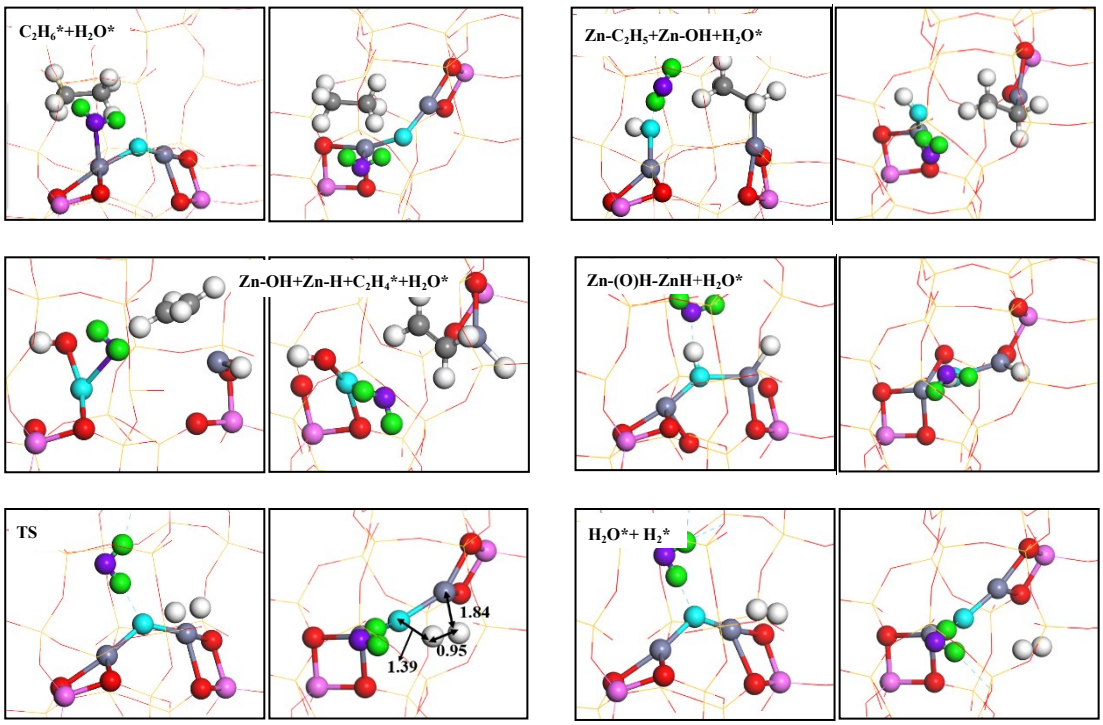
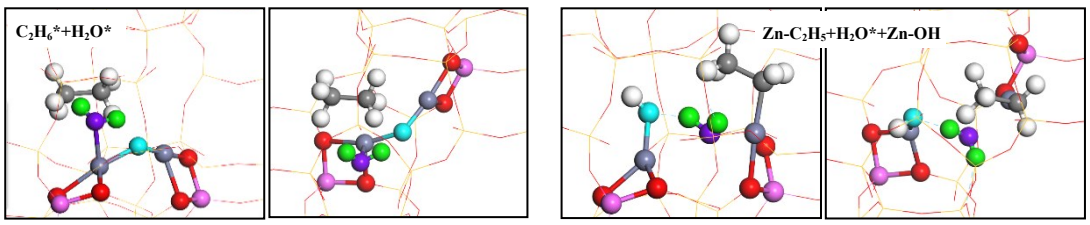
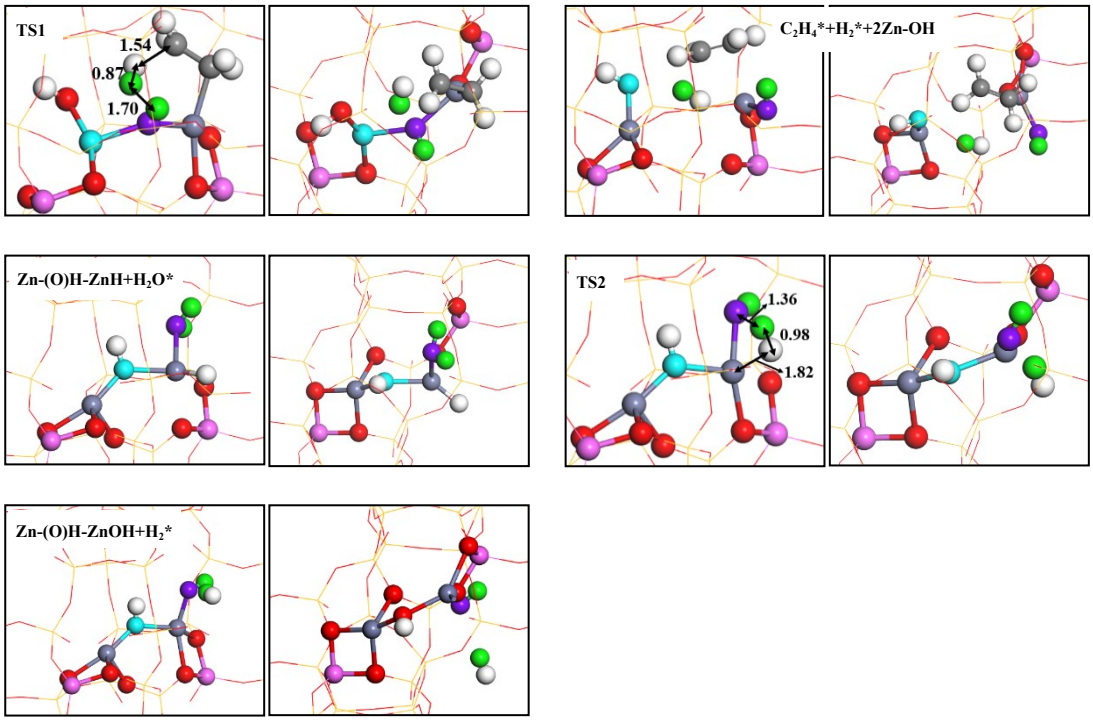


Figure S21. The adsorption configuration and strength of pyridine molecule over different Zn sites of Zn/ZSM-5. (a) Zn-O(H)-ZnOH, (b) ZnOH+ZnOH and (c) HZSM-5 (Pink: Al, Yellow: Si, Red: O of ZSM-5 framework, Bright blue: O of $(Zn\text{-}O\text{-}Zn)^{2+}$ site, Purple: O of H_2O, Light purple: Zn, Grey: C, White: H, Green: H of H_2O, Dark blue: N).



(a) H bonding interaction





(b) H-transfer participating

Figure S22. The intrinsic effect of H_2O on ethane dehydrogenation to ethene over the $(Zn\text{-}O\text{-}Zn)^{2+}$ site of Zn/ZSM-5 via (a) H-bonding interaction and (b) H-transfer participation (Pink: Al, Yellow: Si, Red: O of ZSM-5 framework, Bright blue: O of $(Zn\text{-}O\text{-}Zn)^{2+}$ site, Purple: O of H_2O, Light purple: Zn, Grey: C, White: H, Green: H of H_2O).

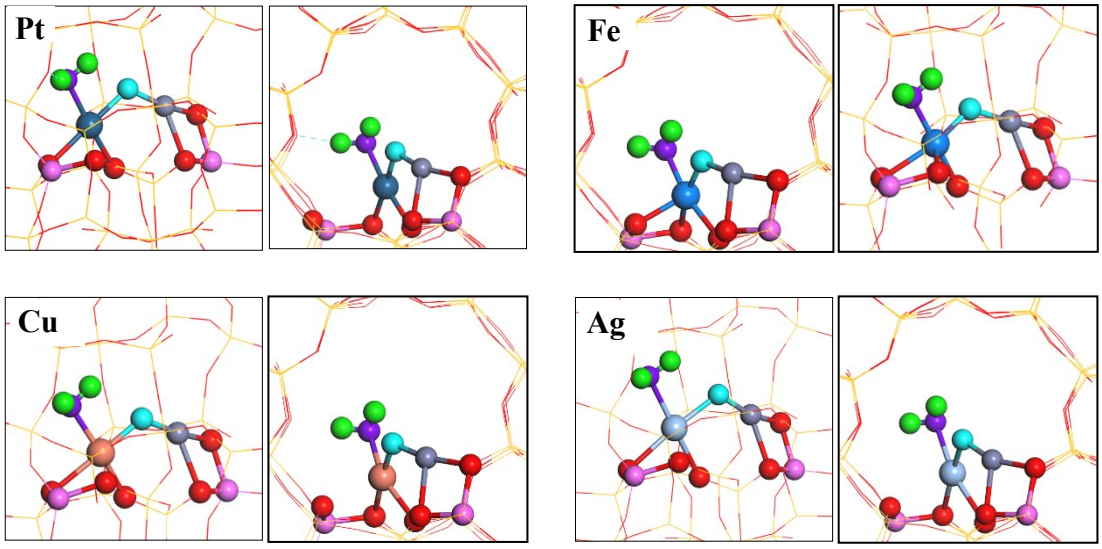


Figure S23. Optimized structures of H_2O adsorption on different metal sites as second modifiers of Zn/ZSM-5 (Pink: Al, Yellow: Si, Red: O of ZSM-5 framework, Bright blue: O of $(Zn\text{-}O\text{-}Zn)^{2+}$ site, Light purple: Zn, Purple: O of H_2O, Green: H of H_2O, Dark blue: Pt, Light blue: Ag, Blue: Fe, Orange: Cu).

Table S1. The adsorption energy of ethane over the Zn-O-Zn site of models with different Al pair substitution.

	T12-T8 (used)	**T12-T2**	**T12-T9**	**T11-T3**
E_{ads} **(eV)**	-0.86	-0.49	-0.54	-0.55

Table S2. The imaginary vibrational frequency of each transition state obtained in this work.

Process	**Elementary step**	**Imaginary vibrational frequency/cm^{-1}**
Section (I)		
C_2H_6→H_2+ C_2H_4 over the (Zn-O-Zn)$^{2+}$ site of Zn/ZSM-5	C_2H_6(II)*→Zn-OH+Zn-C_2H_5	-1204.7
	Zn-OH+Zn-C_2H_5→Zn-O(H)-ZnH+C_2H_4*	-737.6
	Zn-O(H)-ZnH+C_2H_4(g)→H_2*+C_2H_4(g)	-883.5
C_2H_6→H_2+ C_2H_4 Over HZSM-5	C_2H_6*→C_2H_5O+H_2*	-334.5
	C_2H_5O+H_2(g)→C_2H_4*+H_2(g)	-106.7
Aromatization of C_2H_4 over the (Zn-O-Zn)$^{2+}$ site of Zn/ZSM-5	Zn-OH+6MR-Zn-C_6H_{11}(II)→Zn-OH+Zn-H+C_6H_{10}	-1041.0
	Zn-OH+Zn-H+C_6H_{10}→C_6H_{10}+H_2*	-817.1
	Zn-OH+Zn-C_6H_9+H_2(g)→Zn-OH+Zn-H+C_6H_8+H_2(g)	-958.8
	Zn-OH+Zn-H+C_6H_8+H_2(g)→C_6H_8+H_2*+H_2(g)	-845.7
	Zn-OH+Zn-C_6H_7+2H_2(g)→Zn-OH+Zn-H+C_6H_6+2H_2(g)	-1040.7
	Zn-OH+Zn-H+C_6H_6+2H_2(g)→C_6H_6+H_2*+2H_2(g)	-852.5
	Zn-OH+Zn-C_6H_{11}(II)→Zn-OH+6MR-Zn-C_6H_{11}(I)	-568.3
Section (II)		
C_2H_6→CH_4 over the (Zn-O-Zn)$^{2+}$ site of Zn/ZSM-5	C_2H_6*+H_2(g)→Zn-O(CH_3)-ZnCH_3+H_2(g)	-293.3
	Zn-O(CH_3)-ZnCH_3+H_2*→Zn-O(H)-ZnCH_3+CH_4*	-1354.7
	Zn-O(H)-ZnCH_3+CH_4(g)→CH_4*+CH_4(g)	-1305.9

C_2H_4→CH_4 over the $(Zn\text{-}O\text{-}Zn)^{2+}$ site of Zn/ZSM-5	C_2H_4*+2H_2(g)→Zn-O-CH_2CH_2-Zn+2H_2(g)	-144.9
	Zn-O-CH_2CH_2-Zn+H_2*+H_2(g)→Zn-O(CH_3)-$ZnCH_3$+H_2(g)	-1410.6
	Zn-O(CH_3)-$ZnCH_3$+H_2*→Zn-O(H)-$ZnCH_3$+CH_4*	-1354.7
	Zn-O(H)-$ZnCH_3$+CH_4(g)→CH_4*+CH_4(g)	-1336.6
C_2H_6→CH_4 over HZSM-5	C_2H_6*+H_2(g)→CH_3O+CH_4*+H_2(g)	-457.6
	CH_3O+H_2*+CH_4(g)→CH_4*+CH_4(g)	-822.5
C_2H_6→CH_4 with 2 CH_4 over the $(Zn\text{-}O\text{-}Zn)^{2+}$ site of Zn/ZSM-5	Zn-O(H)-$ZnCH_3$+H_2*+CH_4(g)→Zn-O(H)-ZnH+CH_4*+CH_4(g)	-1539.6
	Zn-O(H)-ZnH+2CH_4(g)→H_2*+2CH_4(g)	-883.5
Section (III)		
The hydrolysis of $(Zn\text{-}O\text{-}Zn)^{2+}$ site to form the new Zn-O(H)-ZnOH site over Zn/ZSM-5	H_2O*→Zn-O(H)-Zn-OH	-820.7
C_2H_6→H_2+C_2H_4 over the newly generated Zn-O(H)-ZnOH site of Zn/ZSM-5	C_2H_6*→Zn-O(H)-$ZnOC_2H_5$+ H_2*	-873.5
	Zn-O(H)-$ZnOC_2H_5$+H_2(g)→C_2H_4*+H_2(g)	-1247.9
Section (IV)		
Coke species formation from ethene (pathway I)	C_2H_4*→Zn-OH+Zn-C_2H_3	-1304.1
	Zn-OH+Zn-C_2H_3→Zn-OH+Zn-H+C_2H_2	- 574.8
	Zn-OH+Zn-H+C_2H_2→H_2*+C_2H_2	- 896.8
	C_2H_2+H_2(g)→Zn-OH+Zn-C_2H+H_2(g)	-709.3
	Zn-OH+Zn-C_2H+H_2(g)→Zn-O-C-C-Zn+H_2*+H_2(g)	- 1452.3
Coke species formation from ethene (pathway II)	Zn-OH+Zn-C_2H_3→H_2*+C_2H_2	-766.4
Coke species formation from ethene (pathway III)	C_2H_4*→Zn-O-CH_2CH_2-Zn	-144.9

	Zn-O-CH_2CH_2-Zn→Zn-O-CHCH-Zn+H_2*	-6850.4
	Zn-O-CHCH-Zn+H_2(g)→Zn-O-C-C-Zn+H_2*+H_2(g)	-1487.9
Coke species formation from methane	CH_4*→Zn-O(H)-$ZnCH_3$	-1248.4
	Zn-O(H)-$ZnCH_3$→Zn-O-CH_2-Zn+H_2*	-538.6
	Zn-O-CH_2-Zn+H_2(g)→Zn-O-C-Zn+H_2*+H_2(g)	-732.3
Section (V)		
C_2H_6→H_2+ C_2H_4 over the single Zn^{2+} site	C_2H_6*→Si-OH+Zn-C_2H_5	-1128.8
	Si-OH+Zn-C_2H_5→Si-OH+Zn-H+C_2H_4*	-693.2
	Si-OH+Zn-H+C_2H_4(g)→H_2*+C_2H_4(g)	-265.1
Aromatization of C_2H_4 over the single Zn^{2+} site	Si-OH+6MR-Zn-C_6H_{11}→Si-OH+Zn-H+C_6H_{10}	-902.0
	Si-OH+Zn-C_6H_9+H_2(g)→Si-OH+Zn-H+C_6H_8+H_2(g)	-347.2
	Si-OH+Zn-C_6H_7+2H_2(g)→Si-OH+Zn-H+C_6H_6+2H_2(g)	-138.7
Section (VI)		
H_2O effect via H-bonding interaction	Zn-(O)H-ZnH+H_2O*→H_2O*+H_2*	-908.0
H_2O effect via H-transfer participation	Zn-C_2H_5+H_2O*+Zn-OH→C_2H_4*+H_2*+2Zn-OH	-596.9
	Zn-(O)H-ZnH+H_2O*→Zn-(O)H-ZnOH+H_2*	-1090.2