Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Removal of H_2S to produce hydrogen in the presence of CO on a transition metal-doped ZSM-12 catalyst: a DFT mechanistic study

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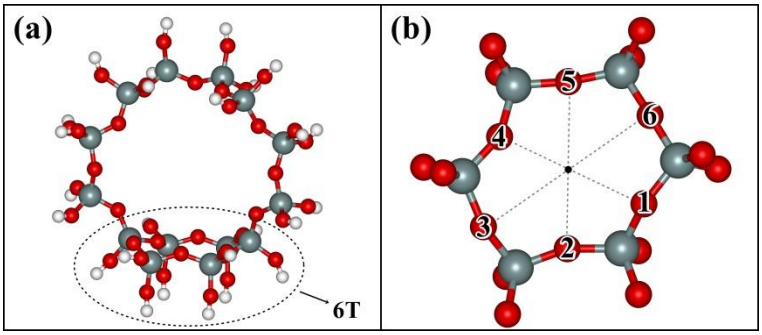

Fig. S1 (a) Side view of the MTW zeolite cluster (the main pore or 14T channel), (b) a snapshot top view of the 6T ring channel in the MTW zeolite cluster (the black dotted lines indicate the center point of the 6T ring). The white, red, and grey balls represent H, O, and Si atoms, respectively.

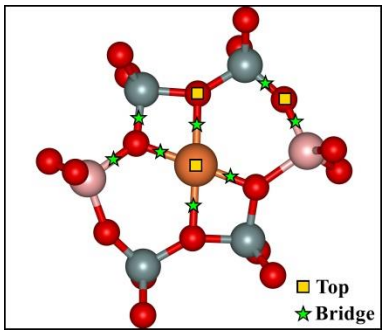

Fig. S2 All possible adsorption sites on the TM-ZSM-12.

Table S1 Comparison between replaced Al system and non-replaced Al system on the TM-ZSM-12 cluster by various transition metals

TM-ZSM-12	**Replaced system**		**Non-replaced system**	
	E_B **(eV)**	Δq_{TM} **(*e*)**	E_B **(eV)**	Δq_{TM} **(*e*)**
Cu–ZSM-12	-7.57	+0.493	-1.14	-0.386
Pd–ZSM-12	-6.95	+0.304	-0.84	-0.307
Ag–ZSM-12	-5.70	+0.262	-0.81	-0.265
Ir–ZSM-12	-9.36	+0.362	-1.02	-0.315
Pt–ZSM-12	-8.61	+0.289	-1.74	-0.189
Au–ZSM-12	-5.48	+0.221	-0.85	-0.278

Table S2 The calculated imaginary frequency for all TS structures of TS1, TS2, TS3, and TS4 by various TM-ZSM-12 clusters.

TM-ZSM-12	Imaginary frequency (cm^{-1})					
	TS1	**TS2**	**TS3a**	**TS3b**	**TS4a**	**TS4b**
Cu–ZSM-12	-622.95	-934.99	-926.50	-1089.46	-910.97	-1059.77
Ir–ZSM-12	-896.98	-1495.82	-846.51	-1428.24	-962.30	-1217.65
Pd–ZSM-12	-672.06	-1468.74	-811.50	-1459.70	-826.22	-1072.28

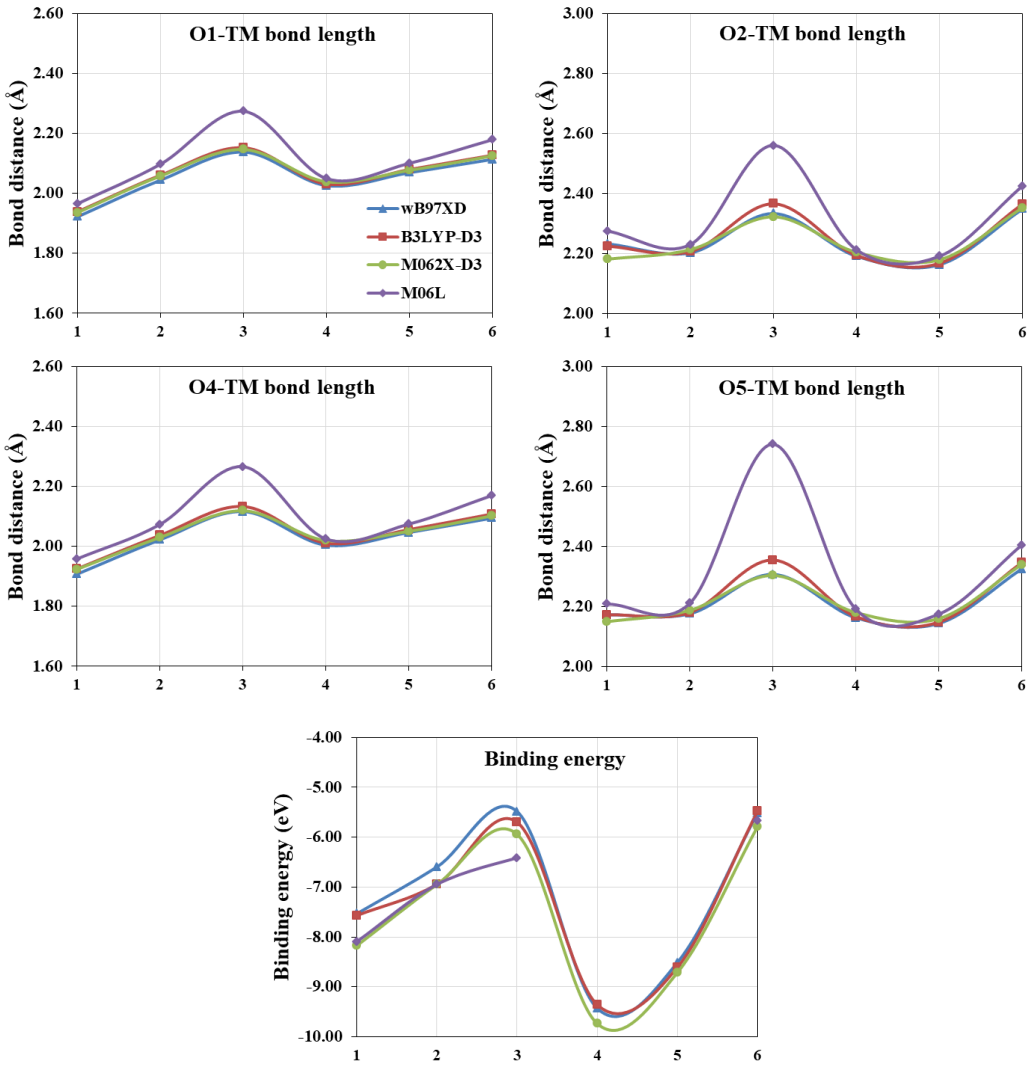

Fig. S3 The comparison of DFT-D functional such as ωB97XD, B3LYP-D3, M062X-D3, and M06L on the bond distance and binding energy. X axis is transition metal; where 1=Cu, 2=Pd, 3=Ag, 4=Ir, 5=Pt, and 6=Au. Note that Ir and Pt atoms cannot perform by M06L functional.

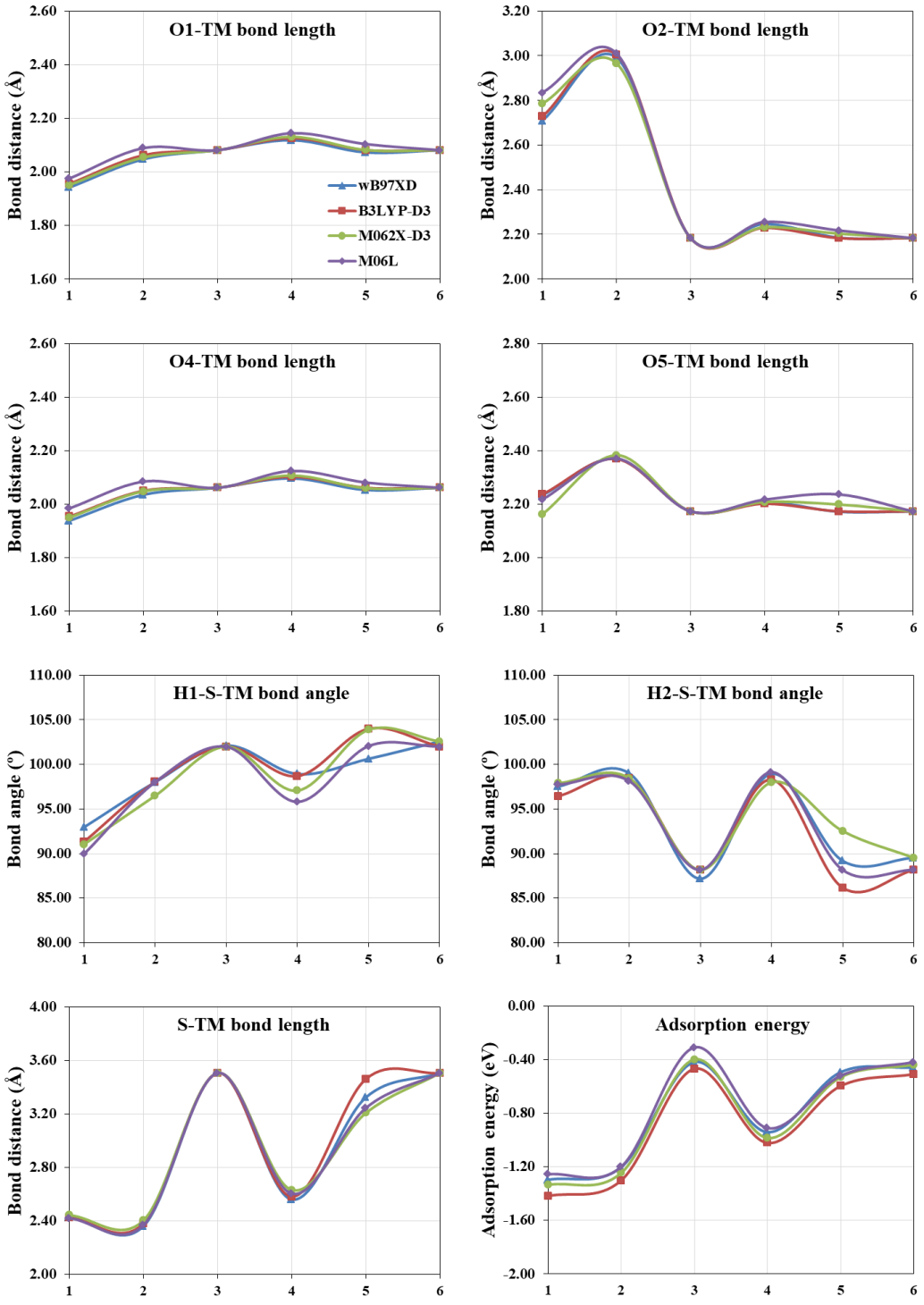

Fig. S4 The comparison of DFT-D functional such as ωB97XD, B3LYP-D3, M062X-D3, and M06L on the bond distance, bond angle, and adsorption energy. X axis is transition metal; where 1=Cu, 2=Pd, 3=Ag, 4=Ir, 5=Pt, and 6=Au.

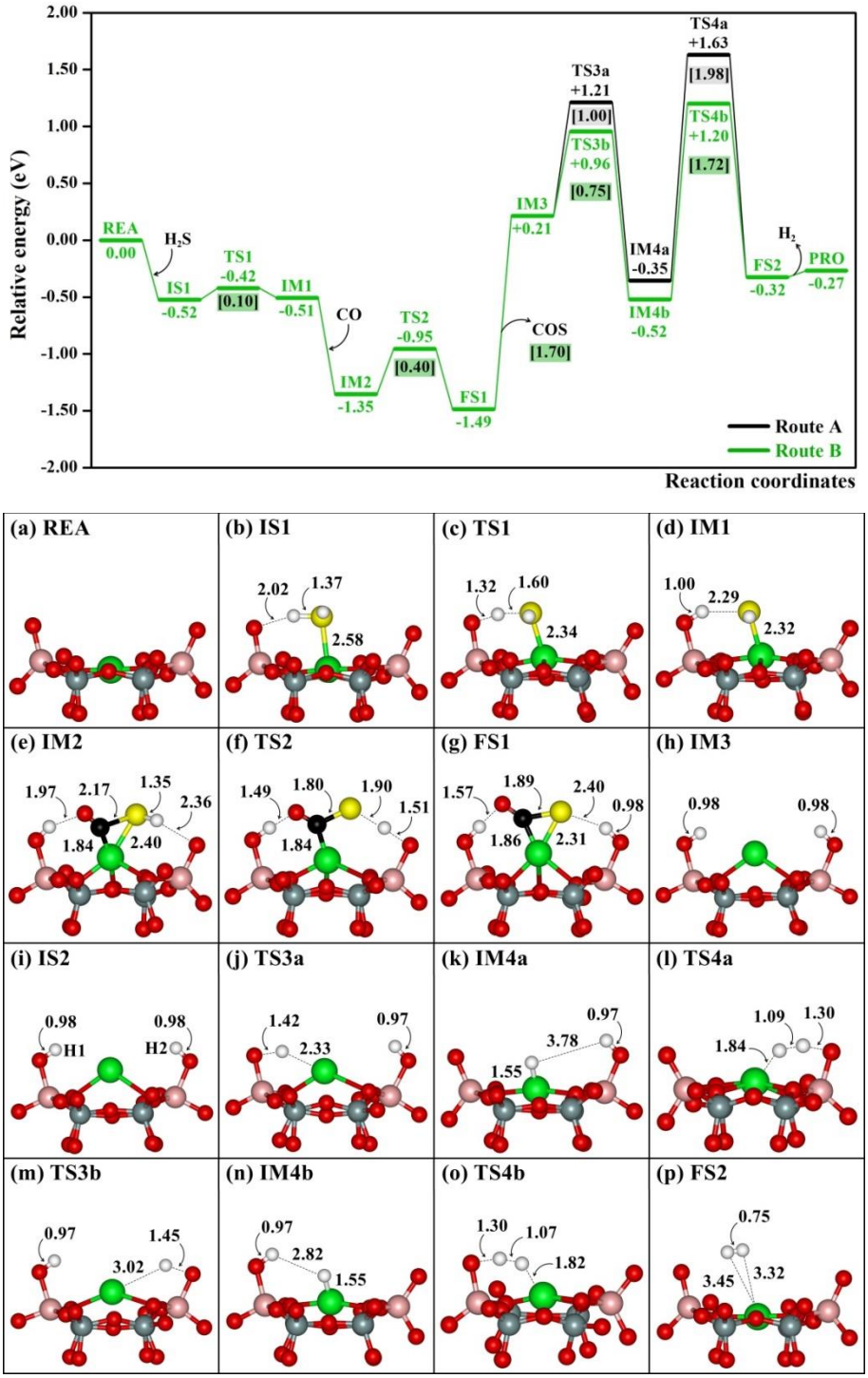

Fig. S5 The calculated potential energy profiles obtained from the summation of electronic and thermal correction Gibbs free energy ($E_0 + G_{corr}$) at 298.15 K, and the optimized structures of all intermediates and transition states for the reaction mechanism of H_2S removal by CO over the Ir–ZSM-12 cluster. The white, red, black, grey, light-pink, and yellow balls represent H, O, C, Si, Al, and S atoms, respectively.

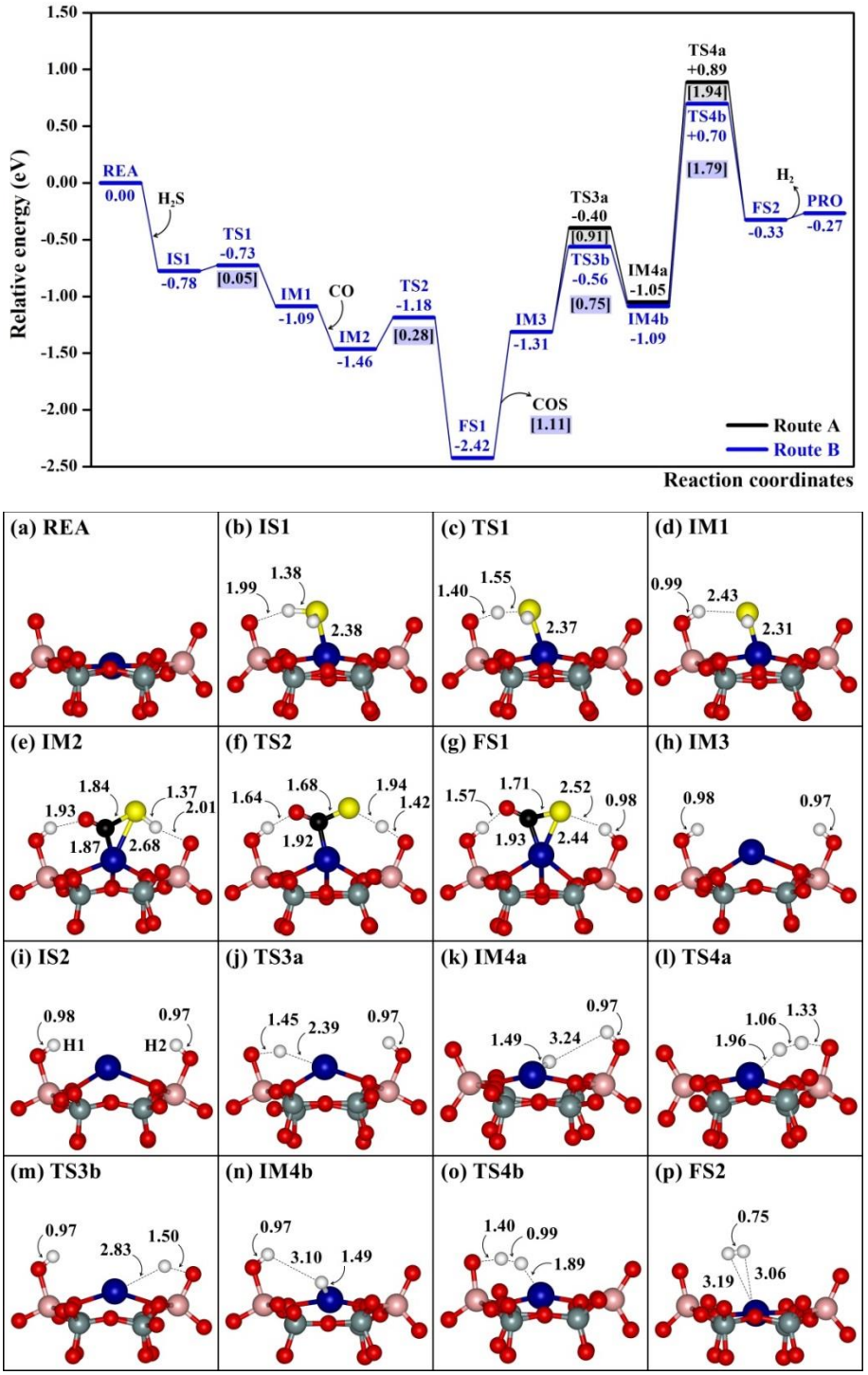

Fig. S6 The calculated potential energy profiles obtained from the summation of electronic and thermal correction Gibbs free energy (E_0 + G_{corr}) at 298.15 K, and the optimized structures of all intermediates and transition states for the reaction mechanism of H_2S removal by CO over the Pd–ZSM-12 cluster. The white, red, black, grey, light-pink, and yellow balls represent H, O, C, Si, Al, and S atoms, respectively.