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The Effects of Active Site and Support on Hydrogen Elimination over Transition-Metal-Functionalized Yttria-Decorated Metal–Organic Frameworks

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Energies of transition-metal-functionalized Y_2O_2@NU-1000 complexes

Kohn-Sham density functional calculations were performed using the M06-L exchange-correlation functional. The 6-31G* basis set was used for C, O, and H atoms, and the def2-TZVP basis set was used for metal atoms. All frequencies were scaled[1] with a factor of 0.976. Frequencies below 100 cm^{-1} were raised to 100 cm^{-1}.[2,3]

Table S1. Computed energies (kcal/mol) for V, Nb, Ta, Cr, Mo, and W-based complexes. For the propyl complexes, the V, Nb, Ta, and Cr are in +3 formal oxidation state; for the bis(propyl) complexes, the Mo and W are in +4 formal oxidation state.

"TS (I)" and "TS (II)" denote the transition structures for α- and β-hydrogen elimination reactions, respectively.

"ads" denotes a weakly adsorbed molecule.

"+ propene" denotes that the propene molecule is optimized as a separate entity.

"*" denotes that the corresponding geometry is not stable under the specific spin configuration, and as such, the corresponding electronic energy (***E***) is calculated by a single point calculation using the optimized geometry of other spin multiplicities.

			E	H_0	H_{298}	G
V	propyl	singlet	0.0	0.0	0.0	0.0
		triplet	-8.9	-9.3	-9.2	-10.3
	TS (I)	singlet	15.4	12.2	11.9	12.2
		triplet*	46.9	—	—	—

			E	H_0	H_{298}	G
	hydride propylidene	singlet	1.8	-0.8	-0.8	-1.0
		triplet	24.2	19.5	19.9	18.5
	TS (II)	singlet	8.9	5.4	5.1	5.7
		triplet	13.6	9.8	9.7	9.0
	hydride propene (ads)	singlet	-7.8	-10.6	-10.9	-10.3
		triplet	7.9	3.3	3.7	2.4
	hydride + propene	singlet	36.4	32.7	33.2	20.0
		triplet	20.4	15.5	16.3	1.8
Nb	propyl	singlet	0.0	0.0	0.0	0.0
		triplet*	107.0	—	—	—
	TS (I)	singlet	7.5	5.5	5.2	5.8
		triplet	11.2	6.7	6.4	6.8
	hydride propylidene	singlet	-13.4	-14.9	-15.1	-14.6
		triplet	8.2	3.9	4.0	3.8
	TS (II)	singlet	5.3	2.5	2.2	3.2
		triplet*	7.0	—	—	—
	Hydride propene (ads)	singlet	-19.8	-22.1	-22.4	-21.4
		triplet*	10.7	—	—	—
	hydride + propene	singlet	33.5	29.7	30.3	17.1
		triplet	29.4	25.0	25.6	11.7
Ta	propyl	singlet	0.0	0.0	0.0	0.0
		triplet	-9.1	-10.3	-10.4	-10.4
	TS (I)	singlet	8.9	6.7	6.2	7.2
		triplet	10.8	6.0	5.6	6.4
	hydride propylidene	singlet	-15.9	-17.5	-18.0	-16.6
		triplet	3.6	-1.0	-1.1	-0.8
	TS (II)	singlet	6.8	4.1	3.5	4.9
		triplet	9.0	5.0	4.4	5.3
	hydride propene (ads)	singlet	-20.9	-23.1	-23.6	-22.1
		triplet	-6.8	-11.0	-11.2	-10.6
	hydride + propene	singlet	33.5	29.7	30.1	17.3
		triplet	34.9	30.0	30.7	16.8
Cr	propyl	doublet	0.0	0.0	0.0	0.0
		quartet	-22.5	-22.4	-22.4	-22.8
	TS (I)	doublet	23.1	20.3	20.0	20.4
		quartet	30.7	26.8	26.7	26.5
	hydride propylidene	doublet	9.4	6.7	6.7	6.9
		quartet	25.2	21.5	21.8	21.0

			E	H_0	H_{298}	G
	TS (II)	doublet	15.7	12.5	12.2	13.0
		quartet*	16.5	—	—	—
	hydride propene (ads)	doublet	-1.4	-3.8	-4.1	-3.3
		quartet	2.9	-0.4	0.0	-1.1
	hydride + propene	doublet	33.1	28.9	29.5	16.2
		quartet	10.6	6.1	6.8	-7.0
Mo	bis(propyl)	singlet	0.0	0.0	0.0	0.0
		triplet	0.5	-1.9	-1.6	-2.7
	TS (I)	singlet	35.8	32.5	32.2	32.8
		triplet	46.4	40.1	40.4	39.2
	hydride propyl propylidene	singlet	22.7	20.2	20.2	20.3
		triplet	45.5	41.1	41.4	40.2
	TS (II)	singlet	31.9	29.1	28.7	29.6
		triplet*	44.3	—	—	—
	hydride propyl propene (ads)	singlet	15.0	13.0	12.7	13.5
		triplet	32.7	29.1	29.4	28.1
	hydride propyl + propene	singlet	31.3	27.2	27.7	14.6
		triplet	35.6	29.1	30.2	15.1
W	bis(propyl)	singlet	0.0	0.0	0.0	0.0
		triplet	-0.3	-3.3	-2.9	-4.1
	TS (I)	singlet	36.6	32.4	32.1	32.7
		triplet	44.7	38.8	38.7	38.7
	hydride propyl propylidene	singlet	13.7	10.8	10.8	10.7
		triplet	35.9	30.7	31.0	29.8
	TS (II)	singlet	27.3	24.3	23.9	24.9
		triplet	31.8	29.0	28.6	29.5
	hydride propyl propene	singlet	10.1	7.7	7.3	8.3
		triplet*	72.3	—	—	—
	hydride propyl + propene	singlet	30.0	26.1	26.6	13.5
		triplet	30.0	22.9	23.8	9.5

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