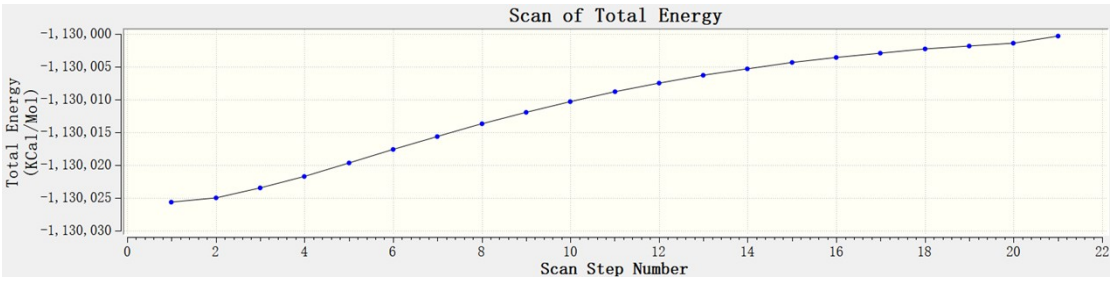
S1. Comparison of $Cr(CO)_6$ bond lengths with different basis groups, in Å.

Basis groups	r(C–Cr)/Å	r(C–O)/Å
Experimental	**1.914**	**1.141**
B3LYP/6-311G++(2d,p)	1.928	1.140
MPW1PW91/6-311G++(2d,p)	1.903	1.136
PBEPBE/6-311G++(2d,p)	1.906	1.153
HSHE1PBE/6-311G++(2d,p)	1.905	1.145
B3LYP/6-311G++(2d,p)-pfd	1.916	1.139
B3LYP/6-311G++(2d,p)-gd2	1.929	1.139
B3LYP/6-311G++(2d,p)-gd3bj	1.922	1.139
B3LYP/6-311G++(2d,p)-gd3	1.928	1.140
PBEPBE/6-311G++(2d,p)-gd2	1.907	1.153
PBEPBE/6-311G++(2d,p)-gd3	1.906	1.153
PBEPBE/6-311G++(2d,p)-gd3bj	1.903	1.153
PBEPBE/6-311G++(2d,p)-pfd	1.895	1.152
HSHE1PBE/6-311G++(2d,p)-pfd	1.893	1.136

S2. Specific details of CO, H_2O, H_2, CO_2 heat capacities and entropy calculations, in cal/(mol·K).

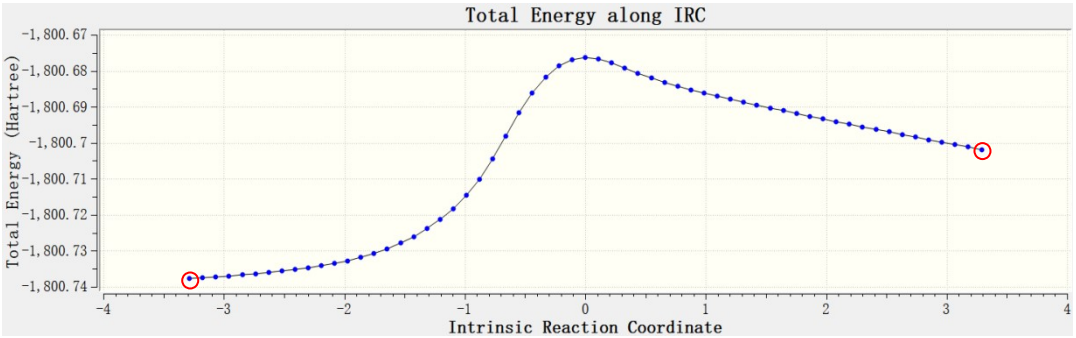
	CO		H_2O		H_2		CO_2	
	Cv	S	Cv	S	Cv	S	Cv	S
Total	4.973	47.193	6.011	45.091	4.968	31.140	6.836	51.035
Electronic	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Translational	2.981	35.923	2.981	34.608	2.981	28.080	2.981	37.270
Rotational	1.987	11.269	2.981	10.476	1.987	3.059	1.987	13.075
Vibrational	0.005	0.001	0.049	0.007	0.000	0.000	1.868	0.690

S3. Plot of scan of total energy variation for relaxed scanning step I, in kcal/mol.

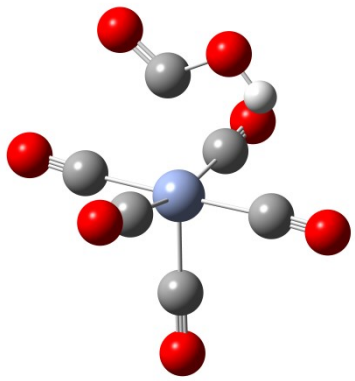


S4. IRC analysis was used to verify that the reactants and products of TS2b-3 point to intermediate 2b and intermediate 3, respectively, (a) Total Energy along IRC, (b) Structural diagram of the reactants of structure TS2b-3, and (c) Structural diagram of the products of structure TS2b-3.

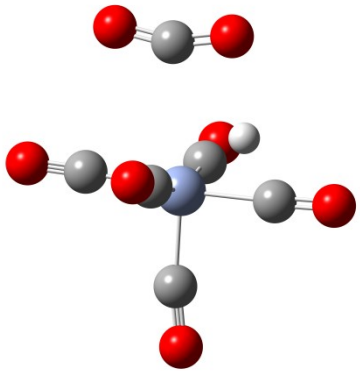
(a)



(b)



(c)



S5. All possible TDI, TDTS, and their Gibbs free energy values and δE in the catalytic process, in kcal/mol.

Type	TDTS	G_{TDTS}	TDI	G_{TDI}	δE
gaseous	TS 2a-2b	-40.90	2a	-49.87	8.97
			3	-58.82	5.79
	TS 2b-3	-13.41	2a	-49.87	36.46
			3	-58.82	33.28
	TS 3-4	-24.41	3	-58.82	34.41
			5	-42.91	6.37
	TS 5-2a	-37.40	3	-58.82	21.42
			2a	-49.87	12.47
aqueous	TS 2a-2b	-89.95	2a	-98.17	8.22
			3	-107.27	8.74
	TS 2b-3	-61.59	2a	-98.17	36.58
			3	-107.27	37.10
	TS 3-4	-69.86	3	-107.27	28.83
			5	-89.86	11.42
	TS 5-2a	-82.22	3	-107.27	25.05
			2a	-98.17	15.95

S6. The Gibbs free energy of the transition states and intermediates in the reaction pathway at temperatures ranging from 300K to 900K, in kcal/mol.

Temperature	Type	$1+OH^-$ $+CO+H_2O$	$2a+CO+$ H_2O	$TS(2a+2b)$ $+CO+H_2O$	$2b+CO$ $+H_2O$	$TS(2b-3)$ $+CO+H_2O$	$3+H_2O+$ $CO+CO_2$	$TS\ (3-4)$ $+CO+CO_2$	$4+CO+$ CO_2	$5+CO+CO_2$ $+H_2$	$TS(5-2a)$ $+H_2+CO_2$	$2a+H_2+$ CO_2
300K	gaseous	0.00	-53.03	-44.08	-52.80	-16.57	-57.98	-27.56	-41.68	-42.91	-40.57	-65.13
	aqueous	0.00	-14.60	-6.34	-13.22	22.03	-20.12	13.71	-2.44	-3.09	1.37	-23.16
400K	gaseous	-23.71	-72.59	-64.19	-72.96	-36.55	-80.26	-47.40	-61.66	-64.41	-60.20	-83.70
	aqueous	-22.21	-34.21	-26.45	-32.67	2.12	-42.57	-6.26	-22.70	-24.74	-18.11	-41.78
500K	gaseous	-49.34	-93.98	-86.16	-95.01	-58.40	-104.37	-69.07	-83.51	-87.78	-81.74	-104.14
	aqueous	-46.35	-55.66	-48.42	-53.96	-19.65	-66.86	-28.10	-44.81	-48.26	-39.49	-62.28
600K	gaseous	-76.58	-116.94	-109.70	-118.66	-81.84	-130.03	-92.32	-106.95	-112.75	-104.89	-126.18
	aqueous	-72.08	-78.67	-71.98	-76.81	-43.03	-92.70	-51.53	-68.54	-73.39	-62.50	-84.38

700K	gaseous	-105.20	-141.26	-134.62	-143.71	-106.67	-157.04	-116.96	-131.81	-139.11	-129.46	-149.62
	aqueous	-99.20	-103.05	-96.91	-101.03	-67.79	-119.91	-76.36	-93.68	-99.92	-86.93	-107.89
800K	gaseous	-135.03	-166.78	-160.75	-169.99	-132.73	-185.26	-142.83	-157.92	-166.71	-155.27	-174.31
	aqueous	-127.54	-128.65	-123.06	-126.46	-93.79	-148.32	-102.43	-120.07	-127.68	-112.60	-132.65
900K	gaseous	-165.97	-193.40	-187.98	-197.40	-159.91	-214.57	-169.83	-185.16	-195.42	-182.22	-200.12
	aqueous	-156.98	-155.34	-150.32	-152.98	-120.90	-177.82	-129.63	-147.60	-156.56	-139.41	-158.54