Density functional theory study on the mechanism of toluene from dimethylcyclopentane catalyzed by $[GaH]^{2+}$ active site of Ga-ZSM-5

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Table S1 Geometric parameters of reactants, transition states and products in 1th HT, 1th DH and 2th HT from dimethylcyclopentane to methylcyclohexene

(The corresponding structures of A(A')，TS1(TS1'), B(B'), TS2(TS2'), G(G'), TS5(TS5') are shown in Figure 3)

/Å	A(A')	TS1(TS1')	B(B')	TS2(TS2')	G(G')	TS5(TS5')	I(I')
Ga-O1	1.956 (2.150)	2.005 (1.997)	2.047 (2.018)	1.964 (1.951)	-	-	
Ga-O2	1.877 (1.919)	1.960 (1.956)	2.025 (2.032)	1.918 (1.937)	-	-	
Ga-O3	2.773 (2.049)	2.864 (2.851)	3.140 (3.099)	2.817 (2.791)	3.053 (3.039)	3.193 (3.225)	3.307 (3.454)
C1-H1	1.146 (1.144)	1.410 (1.408)	-	-	-	-	
Ga- C1	2.709 (2.879)	2.110 (2.117)	-	-	1.961 (1.959)	3.351 (3.562)	3.838 (3.937)
O3-H1	2.263 (2.449)	1.283 (1.268)	0.974 (0.970)	1.320 (1.342)	-	-	
H-H1	-	-	4.273 (3.342)	0.944 (0.929)	-	-	
Ga- H	-	-	1.552 (1.558)	1.777 (1.760)	-	-	
C1-C6	-	-	-	-	1.539 (1.536)	1.382 (1.384)	1.338 (1.339)
C6-H7	-	-	-	-	1.091 (1.091)	1.289 (1.269)	2.275 (2.354)
O4-H7	-	-	-	-	2.438 (2.472)	1.400 (1.457)	0.986 (0.984)

Table S2 Mulliken charges of important atoms of reactants, transition states and products in 1th HT, 1th DH and 2th HT from dimethylcyclopentane to methylcyclohexene (The corresponding structures of A(A')，TS1(TS1'), B(B'), TS2(TS2'), G(G'), TS5(TS5') are shown in Figure 3)

/e	A(A')	TS1(TS1')	B(B')	TS2(TS2')	G(G')	TS5(TS5')	I(I')
Ga	0.463 (0.472)	0.201 (0.219)	0.092 (0.084)	0.350 (0.368)	0.604 (0.585)	0.414 (0.396)	0.446 (0.433)
O1	-0.611 (-0.660)	-0.598 (-0.594)	-0.583 (-0.562)	-0.585 (-0.583)	-	-	
O2	-0.515 (-0.537)	-0.546 (-0.546)	-0.545 (-0.563)	-0.556 (-0.570)	-	-	
O3	-0.641 (-0.610)	-0.638 (-0.632)	-0.503 (-0.497)	-0.646 (-0.646)	-	-	
C1	0.113 (0.184)	-0.126 (-0.102)	-	-	0.061 (0.045)	0.275 (0.269)	-0.191 (-0.226)
H1	0.102 (0.061)	0.440 (0.434)	0.387 (0.370)	0.360 (0.358)	-	-	
H	-	-	0.145 (0.123)	-0.015 (0.002)	-	-	
C6	-	-	-	-	-0.340 (-0.276)	-0.512 (-0.455)	-0.191 (-0.127)
H7	-	-	-	-	0.196 (0.191)	0.418 (0.411)	0.394 (0.390)
O4	-	-	-	-	-0.650 (-0.649)	-0.666 (-0.675)	-0.518 (-0.519)

Table S3 Geometric parameters from reactants to transition states in the ring expansion process from dimethylcyclopentane to methylcyclohexene

(The corresponding structures of E(E')，TS3(TS3'), F(F'), TS4(TS4') are shown in Figure 3)

/Å	E(E')	TS3(TS3')	F(F')	TS4(TS4')
C6-H6(Å)	1.097 (1.099)	1.443 (1.418)	-	-
C1-H6(Å)	2.148 (2.152)	1.249 (1.284)	-	-
C1-C6(Å)	1.522 (1.520)	1.399 (1.396)	1.544 (1.541)	1.395 (1.402)
C6-C2(Å)	-	-	2.556 (2.587)	2.010 (1.949)
C1-C2(Å)	-	-	1.551 (1.551)	1.756 (1.693)

Table S4 Mulliken charges of important atoms from reactants to transition states in the ring expansion process from dimethylcyclopentane to methylcyclohexene

(The corresponding structures of E(E')，TS3(TS3'), F(F'), TS4(TS4') are shown in Figure 3)

/e	E(E')	TS3(TS3')	F(F')	TS4(TS4')
C1	0.286 (0.283)	0.041 (0.141)	-0.116 (-0.070)	-0.072 (-0.034)
C6	-0.542 (-0.548)	-0.068 (-0.112)	-0.199 (-0.202)	0.001 (0.035)
H6	0.199 (0.189)	0.235 (0.225)	-	-
C2	-	-	0.091 (-0.312)	-0.017 (-0.341)

Table S5 Geometric parameters of reactants, transition states and products from methylcyclohexene to methylcyclohexadiene
(The corresponding structures of J(J')，TS6(TS6'), K(K'), TS7(TS7'), M(M'), TS8(TS8'), N(N')are shown in Figure 4)

/Å	J(J')	TS6(TS6')	K(K')	TS7(TS7')	M(M')	TS8(TS8')	N(N')
Ga-O1	2.125	1.978	2.006	1.938		-	
	(2.121)	(1.980)	(1.986)	(1.934)			
Ga-O2	1.931	1.954	2.026	1.919	-	-	
	(1.926)	(1.955)	(2.022)	(1.929)			
Ga-O3	2.038	2.717	3.140	3.060	3.204	3.080	3.161
	(2.038)	(2.717)	(3.183)	(2.939)	(3.009)	(3.112)	(3.321)
O3-H8	2.531	1.307	0.970	1.425	-	-	
(O3-H5)	(2.453)	(1.298)	(1.002)	(1.395)			
Ga-C2	2.901	2.121	-	-	1.984	3.251	3.220
(Ga-C5)	(2.851)	(2.086)			(1.949)	(3.242)	(3.332)
C2-H8	1.160	1.442	-	-	-	-	
(C5-H5)	(1.142)	(1.408)					
H7-H8	-	-	2.284	0.871	-	-	
(H7-H5)			(3.656)	(0.901)			
Ga- H7	-	-	1.561	1.793	-	-	
			(1.554)	(1.790)			
C2-C3	-	-	-	-	1.544	1.390	1.347
(C5-C4)					(1.543)	(1.388)	(1.344)
C3-H3	-	-	-	-	1.092	1.393	2.176
(C4-H4)					(1.092)	(1.356)	(2.295)
O4-H3	-	-	-	-	2.475	1.255	0.988
(O4-H4)					(2.548)	(1.316)	(0.985)

Table S6 Mulliken charges of important atoms of reactants, transition states and products from methylcyclohexene to methylcyclohexadiene

(The corresponding structures of J(J')，TS6(TS6'), K(K'), TS7(TS7'), M(M'), TS8(TS8'), N(N')are shown in Figure 4)

/e	J(J')	TS6(TS6')	K(K')	TS7(TS7')	M(M')	TS8(TS8')	N(N')
Ga	0.444 (0.468)	0.220 (0.274)	0.105 (0.106)	0.352 (0.414)	0.541 (0.572)	0.446 (0.431)	0.458 (0.454)
O1	-0.657 (-0.661)	-0.589 (-0.601)	-0.561 (-0.561)	-0.587 (-0.572)	-	-	
O2	-0.540 (-0.540)	-0.543 (-0.551)	-0.538 (-0.550)	-0.546 (-0.566)	-	-	
O3	-0.601 (-0.605)	-0.640 (-0.644)	-0.489 (-0.513)	-0.645 (-0.644)	-	-	
C2(C5)	0.226 (-0.035)	-0.070 (-0.354)	-	-	0.355 (0.125)	0.469 (0.264)	0.152 (-0.125)
H8(H5)	0.058 (0.084)	0.450 (0.448)	0.388 (0.388)	0.329 (0.341)	-	-	
H7	-	-	0.116 (0.155)	0.009 (-0.000)	-	-	
C3(C4)	-	-	-	-	-0.351 (-0.352）	-0.562 (-0.533）	-0.334 (-0.246)
H3(H4)	-	-	-	-	0.208 (0.210)	0.427 (0.425)	0.398 (0.396)
O4	-	-	-	-	-0.651 (-0.648)	-0.630 (-0.648)	-0.517 (-0.520)

Table S7 Geometric parameters of reactants, transition states and products from methylcyclohexadiene to toluene
(The corresponding structures of P(P')，TS9(TS9'), Q(Q'), TS10(TS10'), S(S'), TS11(TS11'), T(T')are shown in Figure 4)

/Å	P(P')	TS9(TS9')	Q(Q')	TS10(TS10')	S(S')	TS11(TS11')	T(T')
Ga-O1	2.127	1.955	1.997	1.952	-	-	
	(2.160)	(1.961)	(1.990)	(1.918)			
Ga-O2	1.931	1.936	2.026	1.919	-	-	
	(1.910)	(1.947)	(2.024)	(1.920)			
Ga-O3	2.050	2.827	3.041	2.682	3.206	3.415	3.444
	(2.059)	(2.811)	(3.041)	(2.904)	(2.805)	(3.076)	(3.785)
O3-H5	2.814	1.267	0.976	1.308	-	-	
(O3-H9)	(2.278)	(1.268)	(0.969)	(1.382)			
Ga-C5	2.868	2.055	-	-	2.052	4.529	3.801
(Ga-C2)	(2.556)	(2.066)			(2.093)	(4.819)	(4.945)
C5-H5	1.092	1.383	-	-	-	-	
(C2-H9)	(1.115)	(1.390)					
H3-H5	-	-	3.377	0.959	-	-	
(H4-H9)			(2.338)	(0.894)			
Ga-H3	-	-	1.560	1.769	-	-	
(Ga-H4)			(1.563)	(1.774)			
C4-C5	-	-	-	-	1.533	1.438	1.393
(C2-C3)					(1.545)	(1.434)	(1.396)
C4-H4	-	-	-	-	1.085	1.225	2.567
(C3-H3)					(1.088)	(1.250)	(2.468)
O4-H4	-	-	-	-	2.699	1.580	0.975
(O4-H3)					(2.629)	(1.500)	(0.979)

Table S8 Mulliken charges of important atoms of reactants, transition states and products from methylcyclohexadiene to toluene

(The corresponding structures of P(P')，TS9(TS9'), Q(Q'), TS10(TS10'), S(S'), TS11(TS11'), T(T')are shown in Figure 4)

/e	P(P')	TS9(TS9')	Q(Q')	TS10(TS10')	S(S')	TS11(TS11')	T(T')
Ga	0.472 (0.498)	0.249 (0.261)	0.123 (0.139)	0.423 (0.381)	0.481 (0.488)	0.435 (0.436)	0.463 (0.475)
O1	-0.654 (-0.675)	-0.590 (-0.591)	-0.562 (-0.558)	-0.583 (-0.581)	-	-	
O2	-0.540 (-0.542)	-0.540 (-0.549)	-0.564 (-0.532)	-0.567 (-0.541)	-	-	
O3	-0.611 (-0.621)	-0.654 (-0.641)	-0.500 (-0.495)	-0.663 (-0.654)	-	-	
C5(C2)	-0.049 (-0.200）	-0.382 (-0.407)	-	-	-0.051 (-0.026)	0.118 (0.094)	-0.214 (-0.319)
H5(H9)	0.155 (0.143)	0.433 (0.439)	0.377 (0.386)	0.364 (0.347)	-	-	
H3(H4)	-	-	0.144 (0.126)	-0.001 (0.017)	-	-	
C4(C3)	-	-	-	-	-0.259 (-0.078)	-0.471 (-0.275)	-0.133 (0.143)
H4(H3)	-	-	-	-	0.220 (0.218)	0.402 (0.406)	0.386 (0.397)
O4	-	-	-	-	-0.651 (-0.629)	-0.683 (-0.667)	-0.519 (-0.502)