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Irreversible catalytic methylcyclohexane dehydrogenation by surface protonics at low temperature

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First-principles calculation

Theoretical analysis for vibrational spectral analysis was conducted using DFT calculations. All calculations were conducted using the Vienna *ab initio* simulation package (VASP) ver. 5.4.1 [a, b]. Core–valence correlation effects were included with the projector-augmented wave (PAW)

method [b, c]. Using plane–wave basis sets with kinetic energy lower than 400 eV, the valence part wave functions were expanded. All calculations were conducted using re-parameterized Perdew–Burke–Ernzerhof (RPBE) as the exchange–correlation functional [d, e]. In terms of k-space, 0.04 Å^{-1} in Monkhorst–Pack reciprocal space was used. The first-order Methfessel–Paxton method with σ = 0.2 was adopted as the smearing method. These calculations were done in a spin-polarized manner. The Pt fcc (111) surface was modeled as having Pt 16 atoms 4 layers. During geometry optimization, the top two layers were relaxed. The model was constructed as repeated slabs separated by a 15 Å^{-1} vacuum layer. Equatorial MCH (C_7H_{14}) and dehydrogenated species (C_7H_{13}) were adsorbed over the Pt slab. The adsorbate geometries were fully relaxed. Furthermore, the DFT-D3 method of Grimme was adopted for correcting the van der Waals force. The adsorption energy was calculated using the following equation (eqns. S1 and S2).

E(MCH adsorption) = E(MCH/slab) – E(slab) – E(MCH) eqn. S1

E(C_7H_{13} adsorption) = E(C_7H_{13}/slab) – E(slab) – E(MCH) + E(H_2)/2 eqn. S2

The energy and geometry of MCH and H_2 molecules were optimized by placing the molecules in a 10 Å cubic box. Vibrational frequencies of adsorbates were calculated by diagonalizing the Hessian matrix computed using a finite-difference method.

(a) Kresse, G.; Hafner, J. *Ab initio* molecular dynamics for liquid metals. *Phys. Rev. B* **1993**, *47*, 558–561.

(b) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mat. Sci.* **1996**, *6*, 15–50.

(c) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758–1775.

(d) Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(e) Hammer, B.; Hansen, L.B.; Nøskov, J.K. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Phys. Rev. B* **1999**, *59*, 7413–7421.
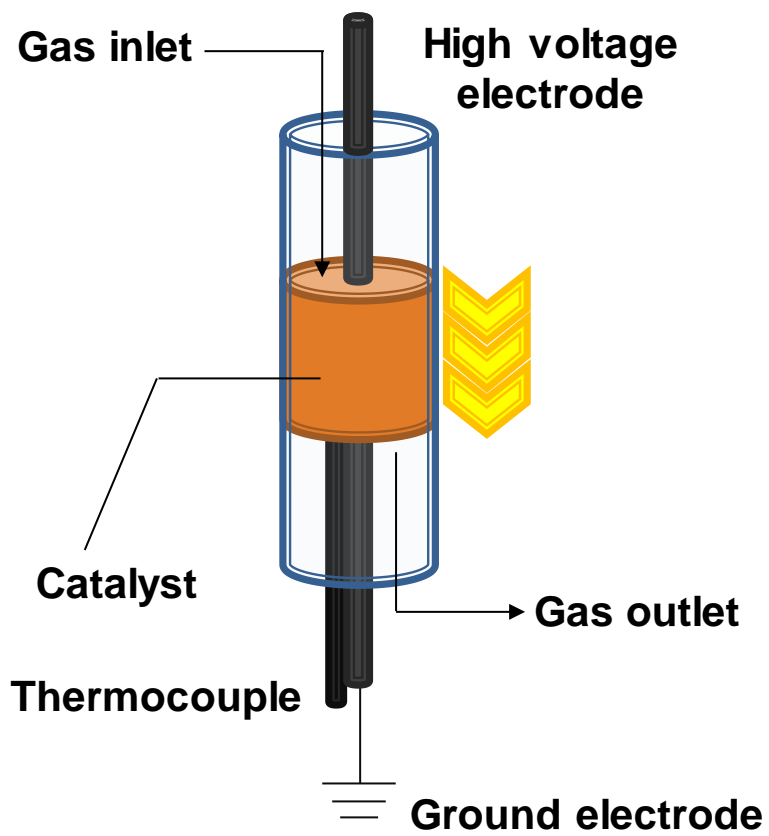
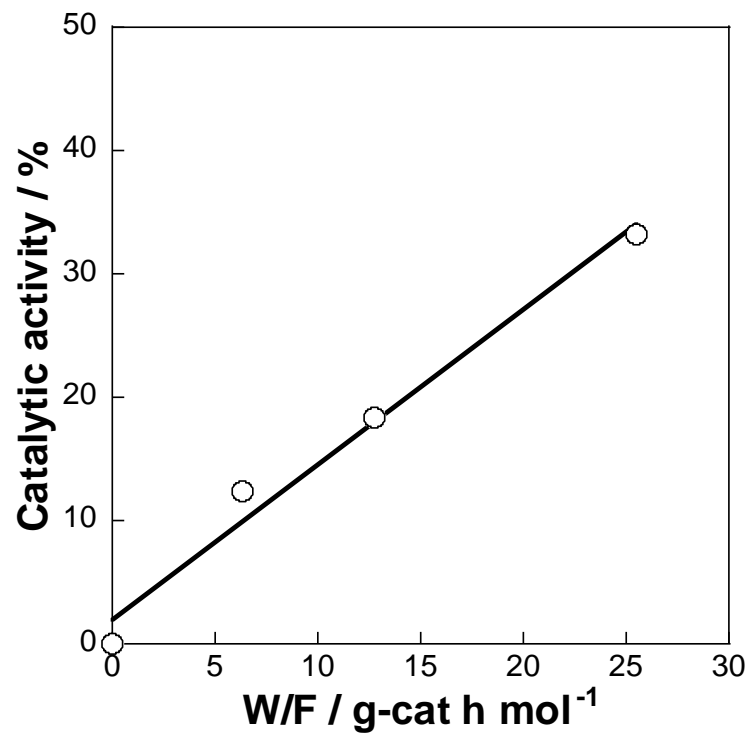Figure S1 Catalyst bed set-up for MCH dehydrogenation in the electric field.

Figure S2 Relation between catalytic activity and W/F ratio in the electric field at 423 K: gas supply MCH : Ar = (3.2, 6.4, 12.8) : (15, 30, 60) (total flow 18.2, 36.4, 72.8 mL min^{-1}); input current 3 mA.
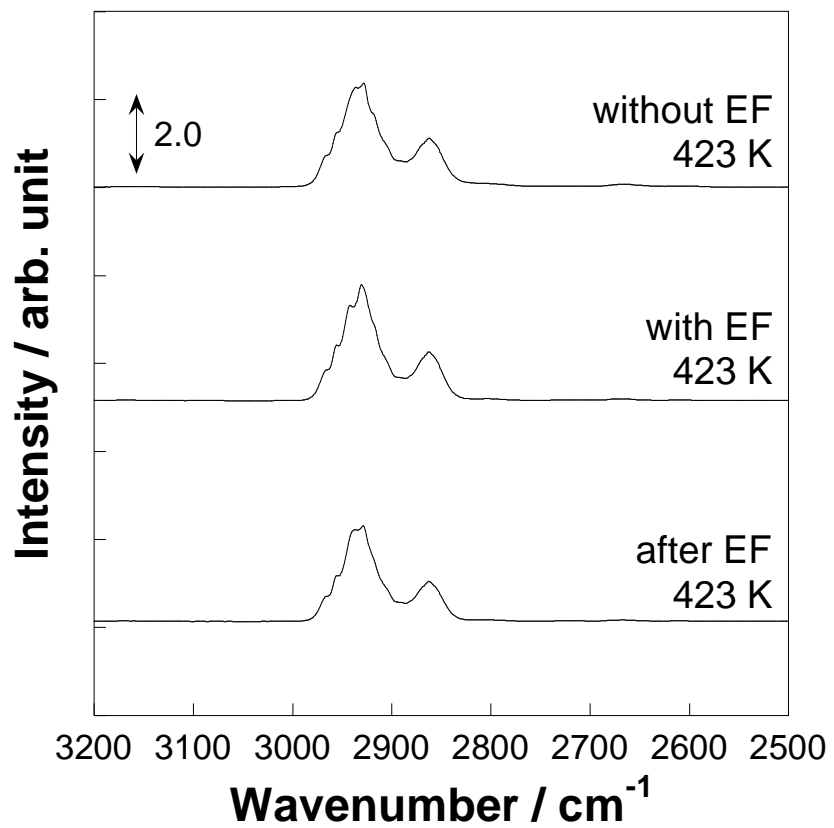
Figure S3 Spectra of *operando* DRIFTS measurements of bare CeO_2 in the electric field at 423 K.
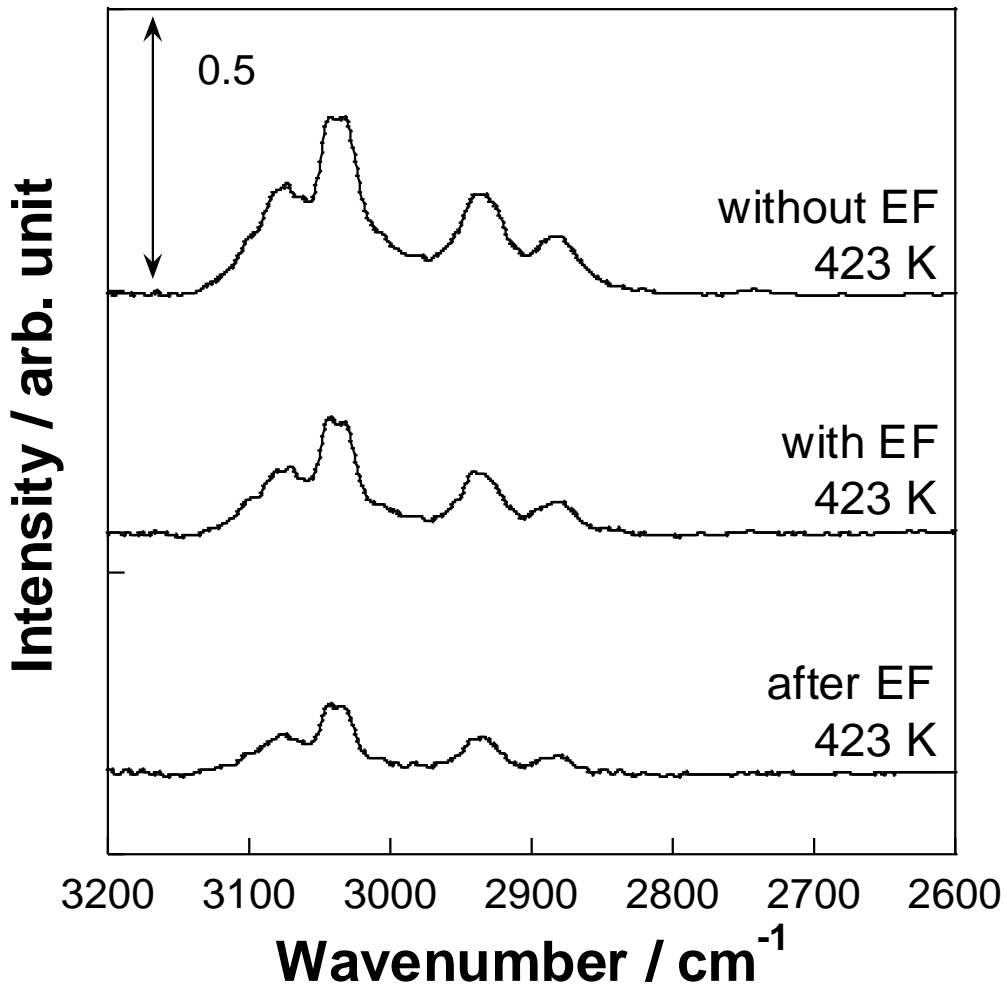
Figure S4 Spectra of *operando* DRIFTS measurements of 3wt%Pt/CeO$_2$ during toluene feed in the electric field at 423 K.
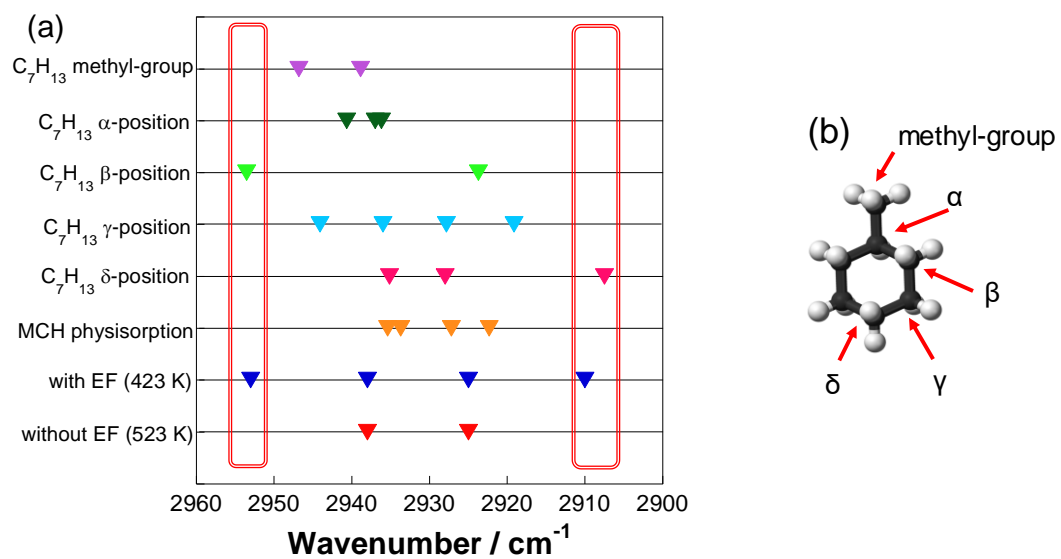
Figure S5 Theoretical wavenumbers of C–H stretching for IR peaks in various positions based on DFT calculation and experimental wavenumber of them for both conditions: with the electric field at 423 K and without the electric field at 523 K.
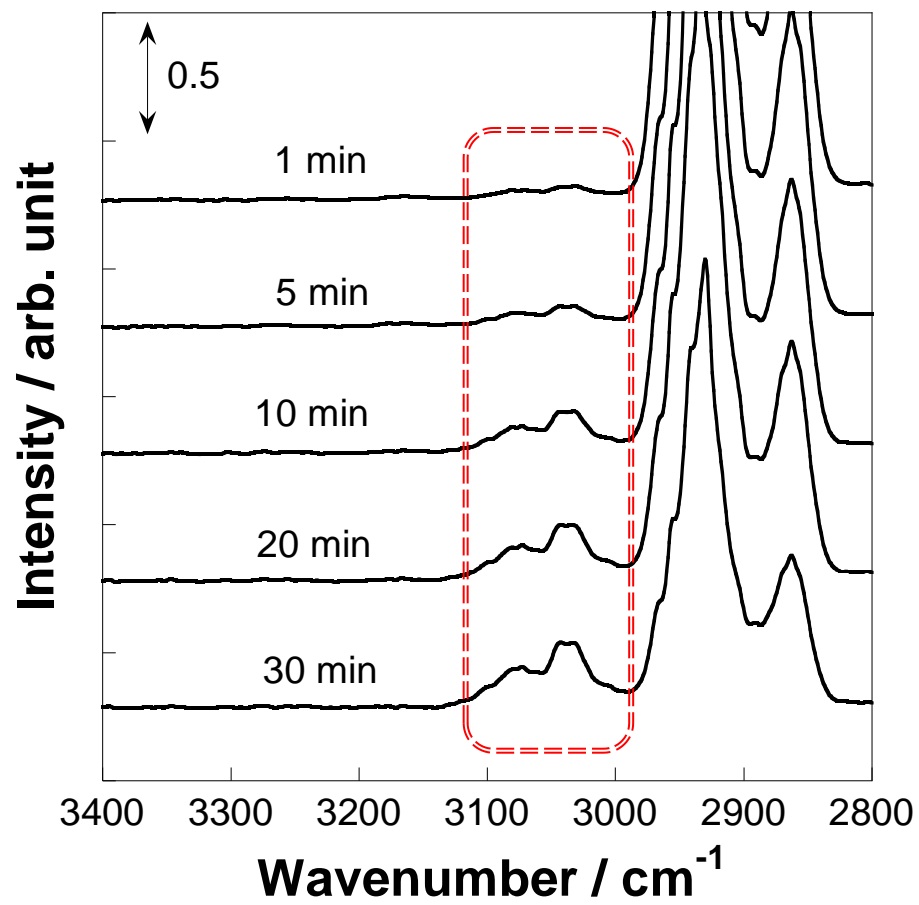
Figure S6 Spectra of *operando* DRIFTS measurements of 3wt%Pt/CeO$_2$ without the electric field at 523 K in the time course; wavenumbers 2800–3400 cm^{-1}.

Table S1 Activity of toluene hydrogenation on 3wt%Pt/CeO$_2$; gas supply toluene : H$_2$: Ar = 6.4 : 19.2 : 10.8 (total flow 36.4 mL min^{-1}); input current 3 mA.

Condition	Furnace Temp. / K	T_{tc} / K	Voltage / V	Toluene conv. / %
with EF	423	420	265	7.3
	473	465	250	31.6
	523	503	239	10.5
	573	543	225	1.9
	623	591	183	0.2
	673	636	147	0.0
without EF	423	423	-	21.5
	473	473	-	49.4
	523	523	-	15.8
	573	573	-	1.6
	623	623	-	0.1
	673	673	-	0.0

T_{tc}: Catalyst bed temperature measued using a thermocouple

Table S2 Catalytic activity and response voltage on 3wt% Pt/CeO$_2$; gas supply MCH : Ar = 6.4 : 30 (total flow 36.4 mL min-1); input current 3 mA.

Time	with EF (423 K)		without EF (523 K)
/ min	H$_2$ yield / %	Voltage /V	H$_2$ yield / %
2	14.7	219	21.6
10	21.5	206	21.5
25	21.4	200	21.4
40	20.8	195	21.2
55	20.1	192	20.7
70	19.3	185	20.6
85	18.5	183	20.2
100	18.2	181	19.8
115	18.0	178	18.5
145	17.7	179	18.2
175	17.8	179	18.0
205	17.9	180	17.2
235	17.9	178	16.9
265	17.7	178	16.9
295	18.0	179	16.5
325	18.0	178	16.3
355	18.3	181	15.5
385	18.0	180	14.1
415	18.1	178	13.5
445	18.1	177	12.7
475	18.0	177	12.1

Table S3 Dispersion and metal surface area 3wt%Pt/CeO$_2$ after each treatment.

Treatment	Dispersion / %	Metal surface area / m^2 g^{-1}
Pt/CeO$_2$ asmade	15.1	1.12
Pt/CeO$_2$ after reaction with EF (423 K)	14.5	1.07
Pt/CeO$_2$ after reaction without EF (523 K)	14.8	1.09