

Electronic Supplementary Information

Pt modified MoO₃ catalyst for electrochemically selective C=O hydrogenation of cinnamaldehyde

Jialu Wang^{a, b}, Meng Jin^{a, b}, Yiyang Sun^c, Haimin Zhang^{a, b*}

^a *Key Laboratory of Materials Physics, Centre for Environmental and Energy Nanomaterials, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei 230031, China*

^b *University of Science and Technology of China, Hefei 230026, China*

^c *Department of Materials Science and Engineering, College of Engineering, Yonsei University, Seoul 03722, Republic of Korea*

*Corresponding author.

E-mail address: zhanghm@issp.ac.cn (H. Zhang)

1. Experimental section

1.1 Chemicals and materials

Hydrochloric acid (HCl, 36.0-38.0%), potassium hydroxide (KOH), potassium phosphate dibasic (K_2HPO_4), potassium phosphate monobasic (KH_2PO_4), platinum bis(acetylacetonate) ($Pt(acac)_2$), molybdenum(V)chloride ($MoCl_5$), ascorbic acid (VC), oleylamine, cinnamyl aldehyde, cinnamyl alcohol, benzenepropanal, phenolpropanol, acetonitrile (CH_3CN), cyclohexane (C_6H_{12}), diethyl ether ($C_4H_{10}O$), acetone (C_3H_6O) and ethanol (C_2H_5OH) were purchased from Aladdin Reagent Company. Nafion solution (5.0 wt.%) was purchased from Sigma-Aldrich. Carbon black (Vulcan XC-72) was purchased from CABOT. All chemicals were directly used as received without further purification. All aqueous solutions were prepared using ultrapure water obtained from a Millipore Milli-Q system (18.2 M Ω).

1.2 Synthesis of catalysts

The Pt-MoO₃/C catalyst was fabricated using wet chemical method. In detail, 5.0 mg $Pt(acac)_2$, 10.0 mg $MoCl_5$, 30 mg ascorbic acid (VC) and 5.0 mL oleylamine were mixed with 30 mg carbon black (CB), and then ultrasonic stirred in a 20 mL round bottom glass bottle for 1 hour. In the synthesis process, ascorbic acid is a reductive reagent and oleylamine is a stabilizer, preventing the formed catalyst particles from aggregation. Subsequently, the bottle was sealed and heated to 80 °C for 12 hours with oil bath. When the sample cooled to room temperature, it was washed by ethanol and cyclohexane to remove extra oleylamine and dried in the oven at 60°C overnight. The obtained sample was marked as Pt-MoO₃/C.

For comparison, single composition catalysts Pt/C and MoO₃/C were also synthesized using the method similar to that of Pt-MoO₃/C expect for the addition of Mo or Pt precursors.

1.3 Characterization

The metal compositions of catalysts before and after reaction were determined by inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher Scientific ICP 6300). The morphological and structural characterizations were characterized by HR-TEM and HAADF-STEM (FEI Tecnai G2 F20) with acceleration of 200 kV. The X-ray diffraction (XRD) patterns were analyzed by a Philips X-Pert Pro diffractometer with a Ni-filtered monochromatic Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 keV and 40 mA. The Brunauer-Emmett-Teller (BET) surface area and pore structure properties were obtained using a surface area and porosity analyzer (AutosorbIQ Station 2). To analyze the chemical compositions was investigated by an X-ray photoelectron spectroscopy (XPS, ESCALAB250). Raman spectra were recorded on LabRAMHR800 Confocal Microscope Raman system (Horiba Jobin Yvon) at excitation laser wavelength of 532 nm at room temperature. Fourier transform infrared (FT-IR) spectroscopy was recorded by a Thermo Nicolet NEXUS FI-IR spectrophotometer using the KBr pellet method.

1.4 Electrochemical measurement

All electrochemical tests were conducted in a single-apartment cell with CHI660E workstation. The catalyst material (10mg) was well dispersed in a mixture of 1.0 mL DI water, 0.5 mL ethanol and 10 μ L Nafion solution (5 wt.% Nafion: iso-

propanol=1:10, v/v) with ultrasonic treatment for more than 2 hours. Prior to each test, 150 μL ink was dropped onto the surface of $1 \times 1 \text{ cm}^2$ carbon cloth and dried at ambient temperature for 30 min as a working electrode. The catalyst loading was about 1.0 mg/cm^2 . Platinum grid electrode ($1 \times 1 \text{ cm}^2$) was used as counter electrode. Hg/HgO or Ag/AgCl electrode specialized for organic experiment were used as reference electrode in alkaline or neutral and acid environment, respectively. A mixed solution of diluted hydrochloric acid and acetonitrile (volume ratio 3:1) was employed as electrolyte, of which acetonitrile favored dissolving of CAL. All electrochemical experiments were carried out at room temperature ($20 \text{ }^\circ\text{C}$). Prior to reaction, a certain amount of cinnamyl aldehyde was added into the electrolyte as substrate and stirred to form a uniform solution. Linear sweep voltammetry (LSV) measurements were conducted at a scan rate of 10 mV/s . The electrochemical surface area (ECSA) was measured by cyclic voltammetry (CV) at different scan rate. Rotating ring-disk electrode (RRDE) was employed to measure the electron transfer number (n) per CAL molecule with rotating rate ranges from 400 rpm to 1600 rpm .

All potentials were normalized by the formula below:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.0591 \times \text{pH} \quad (1)$$

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.0591 \times \text{pH} \quad (2)$$

1.5 Product detection

After reaction, the electrolyte was firstly neutralized, and then extracted with diethyl ether. The products were identified by gas chromatography-mass spectrometry (GC-MS, Thermo Fisher Scientific-TXQ Quantum XLS) equipped with a TG-

WAXMS column, and quantitatively analyzed by GC (Shimadzu, GC-2010 Plus) equipped with a flame ionization detector and a KB-WAX capillary column (30 m × 0.25 mm × 0.25 μm, Kromat Corporation, USA).

The conversion of substrate was calculated by the equation below:

$$Conv. = \frac{n_{CAL,0} - n_{CAL}}{n_{CAL,0}} \times 100\% \quad (3)$$

where $n_{CAL,0}$ is primary CAL amount and n_{CAL} is final CAL amount. The FE was calculated by the equation below:

$$FE = \frac{\sum z_i n_i F}{Q} \times 100\% \quad (4)$$

where z is transfer electron number of products per molecule, n is the amount (mole number) of formed chemicals, F is Faraday constant, and Q is the consumed electric quantity. The selectivity was calculated by the equation below:

$$S_i = \frac{k_i n_i}{n_{CAL,0} - n_{CAL}} \times 100\% \quad (5)$$

where k is consumed CAL molecule number of different products (for dimers k is 2, and for other products k is 1), and n is the amount of product.

1.6 Computation method

All the density-functional theory (DFT) calculations with Hubbard-U corrections [1, 2] were performed as implemented in the Vienna Ab-initio Simulation Package (VASP) [3]. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional was used for describing the exchange and correlation

effects [4]. For MoO₃ system, the U-J parameter was set as 6.3 eV [5]. 400 eV was set for plane wave kinetic energy cutoff. The geometry optimization was obtained when the convergence threshold was converged to 10⁻⁴ eV in energy and the force was converged to 0.02 eV Å⁻¹. To minimize the interlayer interactions, the vacuum distance was set to 20 Å [6]. To describe van der Waals (vdW) interactions, DFT-D3 method was also included [7]. The subsequent VASP calculation data results are processed using the VASPKIT code [8]. The models of Pt₃-MoO₃ system indicated that the Pt₃ clusters was located on the MoO₃ (002) surface. The adsorption energy of CAL (E_{ads}) was calculated according to the following equation.

$$E_{\text{ads}} = E_{\text{slab/ads}} - E_{\text{slab}} - E_{\text{ads}} \quad (6)$$

where $E_{\text{slab/ads}}$ was the total energy of cinnamaldehyde adsorption on Pt₃-MoO₃. E_{slab} was the total energy of Pt₃-MoO₃ and the E_{ads} was the total energy of CAL. The more negative the adsorption energy, the stronger the adsorption capacity.

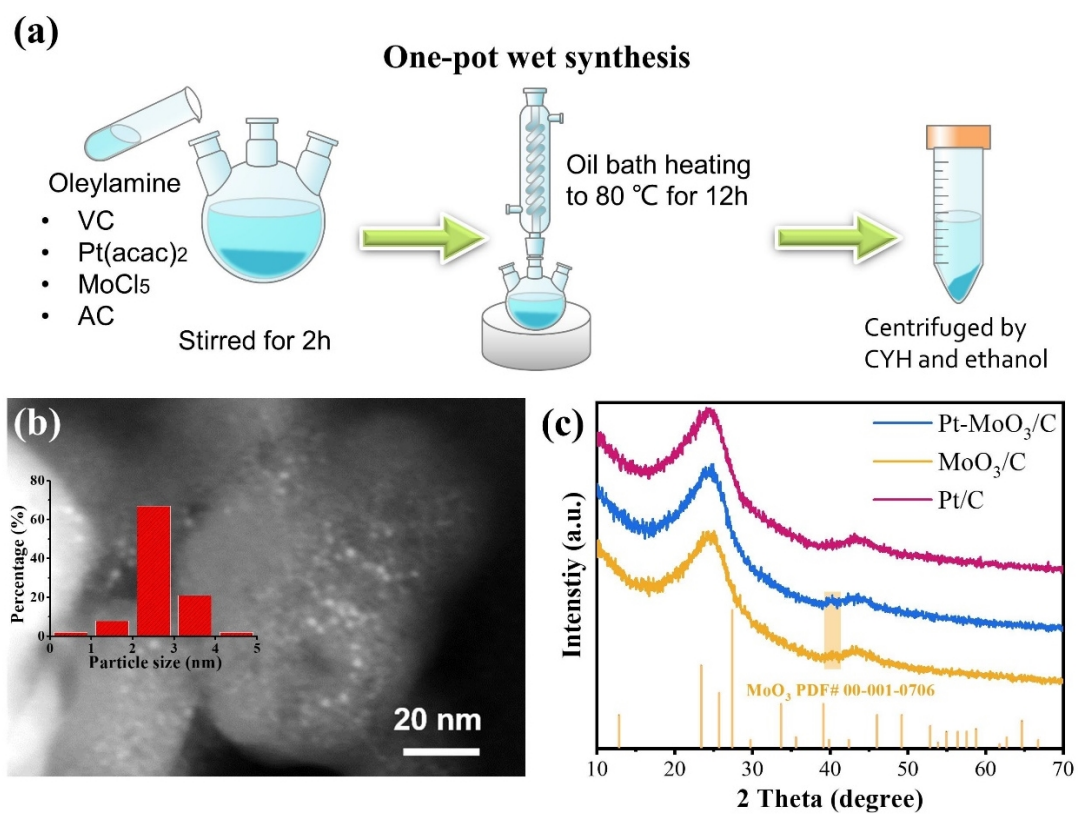


Fig. S1. (a) Schematic of synthesis of Pt-MoO₃/C; (b) particle size distribution of Pt-MoO₃/C; (c) XRD patterns of Pt/C, MoO₃/C, and Pt-MoO₃/C.

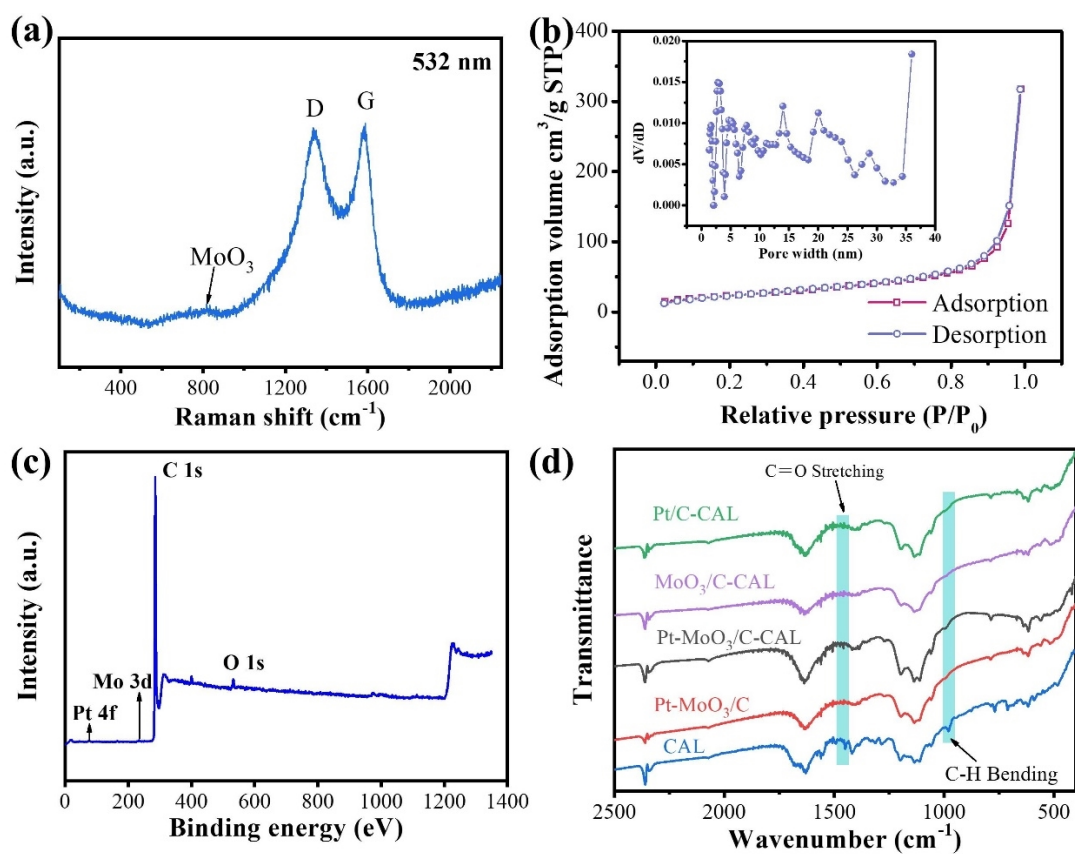


Fig. S2. (a) Raman spectrum of Pt-MoO₃/C; (b) nitrogen adsorption-desorption isotherm and DFT pore size distributions of Pt-MoO₃/C; (c) XPS survey spectrum and (d) FT-IR spectra of Pt-MoO₃/C, CAL and CAL adsorbed Pt-MoO₃/C.

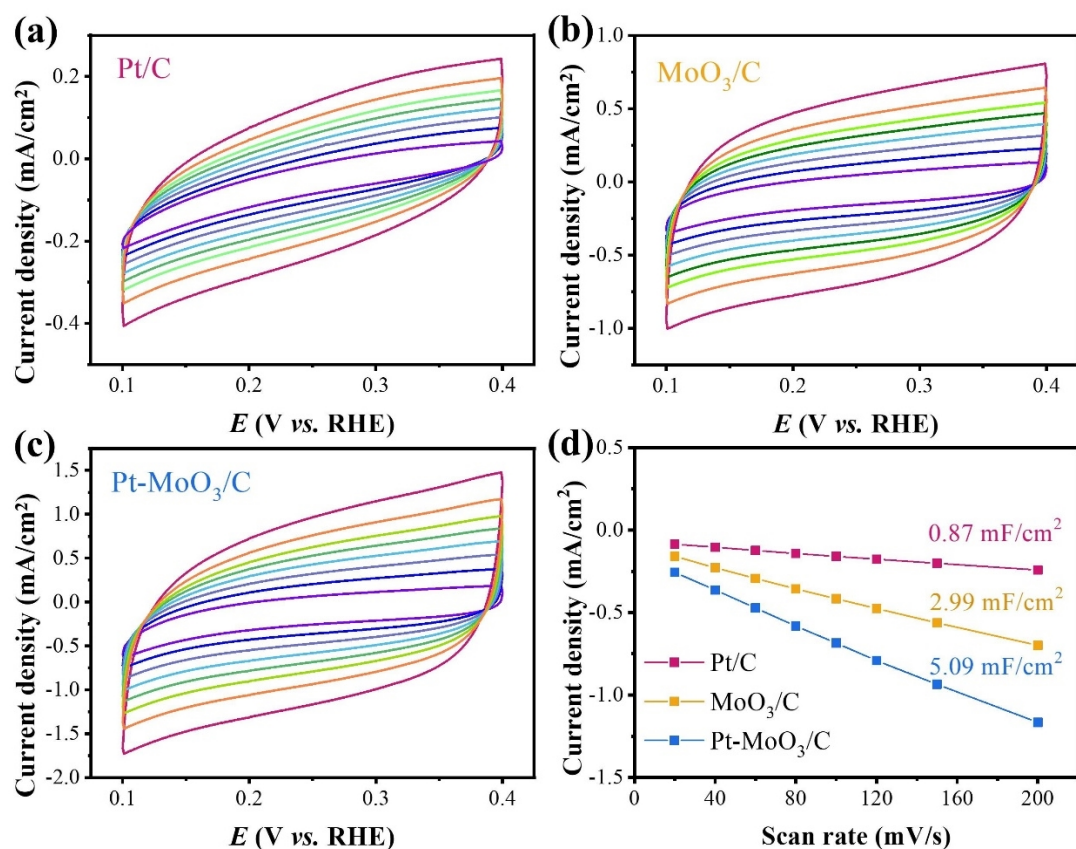


Fig. S3. ECSA calculated by double-layer capacitance measure. CV curves of (a) Pt-MoO₃/C, (b) Pt/C, and (c) MoO₃/C at different scan rates of 20 mV/s, 40 mV/s, 60 mV/s, 80 mV/s, 100 mV/s, 120 mV/s, 150 mV/s, and 200 mV/s; (d) the corresponding current collected at 0.25 V (vs. RHE) as a function of the scan rate.

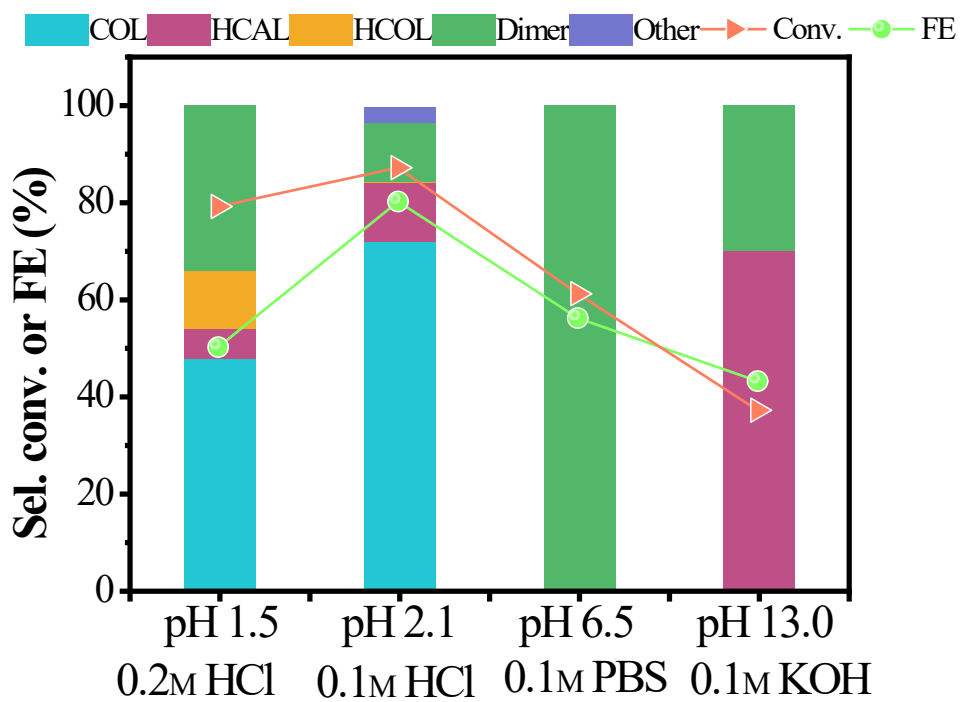


Fig. S4. Selectivity, conversion, and FE of CAL ECH in different electrolyte. (CAL concentration: 20 mM, catalyst: Pt-MoO₃/C, reaction time: 6 h, potential: -0.4 V vs. RHE)

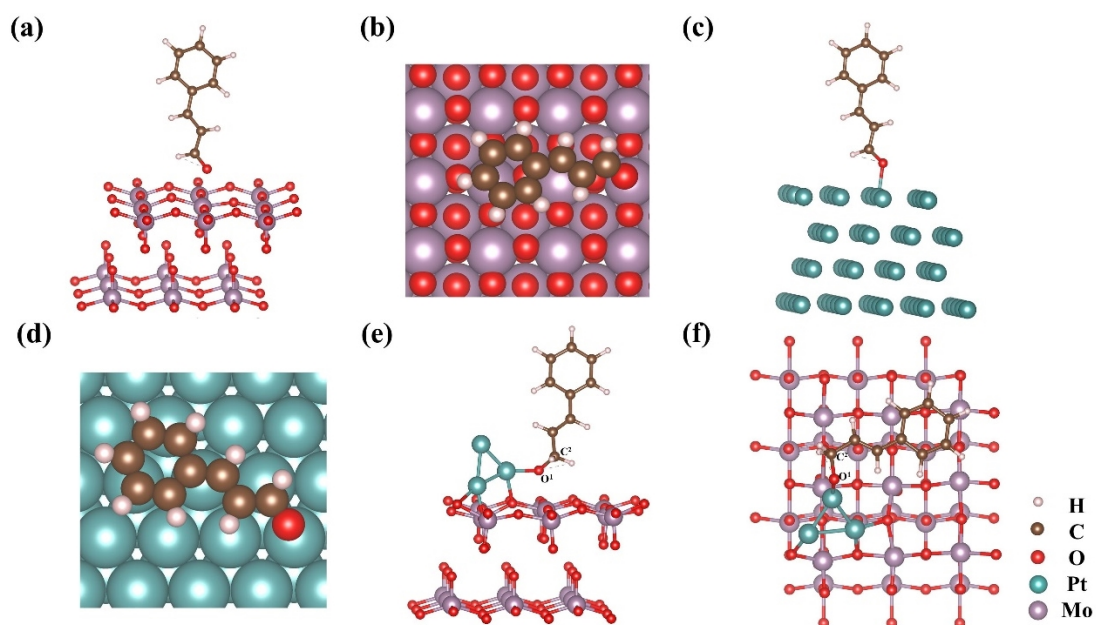


Fig. S5. (a-d) Vertical and parallel adsorption configurations of CAL over MoO₃(002) and Pt(111) plane, respectively; (e, f) first hydrogenation of CAL on C₂ over Pt₃-MoO₃ via vertical and parallel adsorption configuration, respectively.

In regard to the detailed C=O hydrogenation approach, two possible pathways involved: carbonyl O (O¹) then carbonyl C (C²) or C² then O¹ [9]. However, the first step cannot occur on the O₁ owing to strong depriving force of H_{ads} by lattice oxygen. Therefore, the C² will be firstly hydrogenated then O¹. Considering that hydrogen bond to O¹ will also interact with lattice O on MoO₃, the corresponding energy barrier will be low. Thus, the first hydrogenation of C² will be the rate-determining step, and we compared the C² hydrogenation energy on the Pt₃-MoO₃ with different CAL adsorption configurations. The energy barrier of CAL first hydrogenation on Pt₃-MoO₃ *via* vertical adsorption was only 0.35 eV, much lower than that of Pt-MoO₃ *via* parallel adsorption (0.62 eV). Therefore, the vertical adsorption would be beneficial for enhancing the CAL hydrogenation selectivity.

Table S1. Metallic composition of Pt-MoO₃/C before and after test by different methods.

		XPS		ICP	
		at. %	wt. %	at. %	wt. %
Before reaction	Pt	0.01	/	/	0.87
	Mo	0.02	/	/	2.16
After reaction	Pt	0.01	/	/	0.71
	Mo	0.02	/	/	2.03

Table S2. Comparison of the reported catalysts and Pt-MoO₃/C catalysts in this work for cinnamaldehyde electrochemical hydrogenation.

	Catalyst	Selectivity (%)	FE (%)	Conversion (%)
Wei [9]	RuO ₂ -SnO ₂ - TiO ₂ /Ti	88.86	17.47	58.00
Gao [10]	MoS ₂ -DMA	90	68	~55
This work	Pt-MoO ₃ /C	~78	~50	~99

Table S3. Summary of DFT calculations results.

	Pt ₃ -MoO ₃ (002)		Pt(111)		MoO ₃ (002)	
	Parallel adsorption	Vertical adsorption	Parallel adsorption	Vertical adsorption	Parallel adsorption	Vertical adsorption
Adsorption energy (eV)	-1.61	-1.88	-0.93	-1.11	-0.34	-0.47
First hydrogenation barrier (eV)	0.62	0.35	/	/	/	/
C=O bond length (Å)	1.234	1.266	/	/	/	/

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