

Supporting Information

Metal-support interaction triggered d-p orbital hybridization for efficient electrocatalytic semi-hydrogenation of alkynes

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Materials

Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, powder), palladium(II) chloride (PdCl_2), 1,4 Dioxane, 4-aminophenylacetylene, 4-aminophenylethylene, sodium borohydride (NaBH_4 , powder), tetrabutylphosphonium bromide (Bu_4PBr), ethyl acetate (99.9%), phenylacetylene (>97%), styrene (99%), 4-bromophenylacetylene (98%), 1-bromo-3-ethynyl-benzene (97%), 1-bromo-2-ethynylbenzene (99%), 4-chlorophenylacetylene (98%), 4-chlorostyrene (95%), 4-bromostyrene (95%), 2-bromostyrene (99%), 3-bromostyrene (98%), 1-hexyne (97%), 1-hexene (99%), 2-ethynylpyridine (97%), 2-vinylpyridine (98%), 2-methyl-3-butyn-2-ol (98%), 2-methyl-3-buten-2-ol (98%), 3-hydroxyphenylacetylene (98%), 3-hydroxystyrene (98%), 3-butyn-1-ol (98%), 3-buten-1-ol (98%), potassium hydroxide (powder, 90%) and carbon papers were purchased from Admas Company. Ultrapure water was used throughout all experiments. All chemicals were used without further purification.

Synthesis of Pd/Fe₂O₃ catalysts

The synthesis of Pd/Fe₂O₃ catalysts was performed through a wet-chemical method, with minor adaptations from previously documented procedures. Initially, a solution of PdCl₂ (5 mL, 0.02 M) dissolved in acetonitrile was combined with a measured quantity of FeCl₃·6H₂O in water. This mixture was incrementally introduced into 100 mL of an aqueous tetrabutylphosphonium bromide (Bu_4PBr) solution (0.01 M), and the solution was stirred for 30 minutes to guarantee complete dissolution of the reactants. Subsequently, a NaBH₄ solution (0.4 M in water) was rapidly added to the reaction mixture and stirred. The resultant product was washed multiple times with distilled water and absolute ethanol, then thoroughly dried in an oven at 80°C. The molar ratio

of NaBH₄ to the sum of Pd and Fe (NaBH₄/(Pd+Fe)) was meticulously maintained at 10:1 throughout the reaction.

Synthesis of pure Pd NPs

A solution of PdCl₂ (0.02 M, dissolved in 5 mL of acetonitrile) was gradually introduced into 100 mL of an aqueous Bu₄PBr solution (0.01 M) with constant stirring for 30 minutes to achieve full dissolution. Following this, a NaBH₄ solution (0.4 M, 0.25 mL) was promptly added to the mixture, under continuous stirring to ensure complete reaction. After the addition, the mixture was filtered to separate the solid product. The collected solid was thoroughly washed multiple times with distilled water and absolute ethanol to remove any residual reactants and byproducts. Finally, the washed solid was dried under a vacuum at room temperature to obtain the final product.

Synthesis of pure Fe₂O₃

An aqueous solution of FeCl₃·6H₂O (5 mL, 0.02 M) was gradually added to 100 mL of an aqueous Bu₄PBr solution (0.01 M). The mixture was stirred for 30 minutes to ensure the complete dissolution of the iron chloride. Following this, a NaBH₄ aqueous solution (0.4 M, 0.25 mL) was rapidly introduced into the mixture to initiate the reduction process. After the addition of NaBH₄, the mixture was continuously stirred to ensure a uniform reaction. The resultant product was then collected by filtration, thoroughly washed with distilled water and absolute ethanol to remove impurities, and finally dried in an oven at 80 °C to obtain the final product.

Electrochemical measurements

To prepare the catalyst ink, 1.8 mg of Pd/Fe₂O₃ catalysts were dispersed in a mixture containing water (100 μL), ethanol (100 μL), and Nafion (0.5 wt%, 200 μL). This dispersion process involved sonication for a minimum of 30 minutes to ensure uniformity. Before the application of the catalysts, carbon paper was meticulously cleaned with a series of solvents including acetone, ethanol, and water, each applied multiple times to remove any contaminants. Subsequently, the catalyst ink was uniformly applied onto the carbon paper to achieve a Pd mass loading of 0.5 mg_{Pd} cm²,

targeting a loading area of approximately 1 cm^2 . The coated carbon paper was then left to dry under ambient conditions.

The electrochemical semi-hydrogenation experiments were conducted using an H-type cell, which was arranged to include a platinum wire as the counter electrode, a mercury/mercury oxide (Hg/HgO) reference electrode, and the prepared catalyst-coated carbon paper as the working electrode. The cathode chamber was filled with a solution composed of 1 M KOH (5 mL), dioxane (2 mL), and 0.2 mmol of 4-aminophenylacetylene, ensuring a homogeneous mixture. The anode chamber contained a 1 M KOH solution (7 mL). To purge residual oxygen from the solution, argon gas was bubbled through it for 10 minutes before initiating the reaction.

The electrochemical semi-hydrogenation process was conducted by applying a constant potential ranging from -1.0 V to -1.5 V at ambient temperature. Throughout the reaction, samples were collected from the cathode chamber at various intervals (30 minutes, 1 hour, 2 hours, and 4 hours) and were extracted using ethyl acetate (EA) for analysis. The extracted products dissolved in EA were then analyzed using a gas chromatograph-mass spectrometer (GC-MS), following the protocols outlined in standard calibration curves (referenced as Fig. S8). The yields obtained from GC analysis were calculated using dodecane as an internal standard, based on specific equations (1)-(2) detailed elsewhere in the document. Subsequently, the conversion rates of the alkyne substrates and the selectivity towards alkene products were determined. In this context, "conversion" pertains to the proportion of alkyne substrates transformed during the reaction, while "selectivity" relates to the preference of the reaction towards generating alkene products over other potential outcomes. The comparative performance of various catalysts—including pure Pd, commercially available Pd/C, Fe_2O_3 , and catalysts with varying Pd to Fe_2O_3 molar ratios—was assessed using the same methodology. All catalysts were evaluated to ensure an equivalent Pd loading across the experiments to maintain consistency in the comparison of their electrocatalytic semi-hydrogenation capabilities.

$$\text{conversion}(\%) = \frac{n(\text{consumed alkynes})}{n(\text{initial alkynes})} \times 100\% \quad (1)$$

$$\text{selectivity}(\%) = \frac{n(\text{obtained alkenes})}{n(\text{consumed alkynes})} \times 100\% \quad (2)$$

Characterizations

The characterization of the synthesized products was conducted using a variety of analytical techniques. XRD patterns were obtained with an X'Pert PRO MPD diffraction system, employing a Cu K α radiation source ($\lambda = 1.54056 \text{ \AA}$) over a 2θ range of 10° to 80° , with a scanning rate of 10° per minute. For the analysis of surface chemistry, XPS measurements were carried out on a PHI-5000 VersaProbe III photoelectron spectrometer using a monochromatic Al K α X-ray source (1486.60 eV). The calibration of all XPS peaks was performed using the C1s peak at a binding energy of 284.8 eV as a reference. The morphology of the samples was examined using SEM on a Sigma 300 microscope operated at 3 kV. TEM images were acquired using a JEOL-2100F system, complemented with an EDAX Genesis XM2 for EDX analysis. Additionally, HAADF-STEM images and EDX mapping were conducted with a spherical aberration-corrected electron microscope to obtain detailed structural and compositional information. The Pd and Fe content in the catalysts was quantitatively determined by ICP-OES on a PerkinElmer 8300 instrument. Liquid phase product analysis was performed using GC-MS (Agilent 7890A) equipped with TCD and FID, utilizing an HP-5 MS capillary column (0.25 mm diameter, 30 m length) for separation. NMR spectroscopy was conducted on a JEOL JNM-ECZ400S/L1 instrument, with measurements taken at 400 MHz for ^1H NMR and 101 MHz for ^{13}C NMR, using DMSO- d_6 as the solvent.

In situ Raman spectroscopy.

Raman spectroscopy measurements were conducted using a Labram HR Evolution Raman microscope, utilizing a 785 nm laser for excitation. To optimize signal acquisition, the orientation of the working electrode was adjusted to ensure that the sample's plane was perpendicular to the direction of the incident laser beam. The electrolytic cell was prepared by combining a solution of 2.5 mL of 1.0 M KOH and 1

mL of dioxane (Diox) with 0.1 mmol of 4-aminophenylacetylene. This setup facilitated the electrochemical interaction within the cell. Raman spectra were systematically acquired over a range of potentials, from the OCP down to -1.7 V, with measurements consistently taken at the same spot on the sample to ensure comparability of the data.

Calculation of faradaic efficiency

The Faraday efficiencies for the conversion of alkynes to alkenes were determined using the formulas (3) and (4). The total charge transferred, denoted as Q_{all} , was calculated by integrating the current (i) over time (t) curve at the applied fixed voltage. The charge associated with the formation of 4-aminophenylethylene, $Q_{aminophenylethylene}$, was derived from the quantity of 4-aminophenylethylene produced during the reaction. It is important to note that the production of one mole of 4-aminophenylethylene corresponds to the transfer of two moles of electrons, indicating a two-electron process for the conversion.

$$Q_{all} = \int_0^t i dt \quad (3)$$

$$\text{Faradaic efficiency} = \frac{Q_{4\text{-aminophenylethylene}}}{Q_{all}} \times 100\% \quad (4)$$

Theoretical calculations

We have employed the VASP to perform all DFT calculations. The elemental core and valence electrons were represented by the PAW method and plane-wave basis functions with a cutoff energy of 450 eV. GGA with the PBE exchange-correlation function was employed in all the calculations. Geometry optimizations were performed with the force convergency smaller than 0.05 eV/Å. The DFT+U approach was introduced to treat the highly localized Fe 3d states, using parameters of $U-J = 5.3$ eV. Atoms at the bottom were fixed in all the calculations. Monkhorst-Pack k-points of $1 \times 1 \times 1$ were applied for all the calculations of $\text{Co}_3\text{O}_4(110)$. The spin-polarization effect was also considered.

The Gibbs free energy was calculated by the following equation:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$$

Where the value of ΔE , ΔE_{ZPE} , and ΔS denotes the changes of DFT energy, the zero-point energy, and the entropy at 300 K, respectively, Therefore, with overall values, the Gibbs free energy can be calculated as $\Delta G = \Delta E_{H^*} + 0.24 \text{ eV}$, as similarly reported by Nørskov et al. (*Nat. Chem.* **2009**, *1*, 37-46).

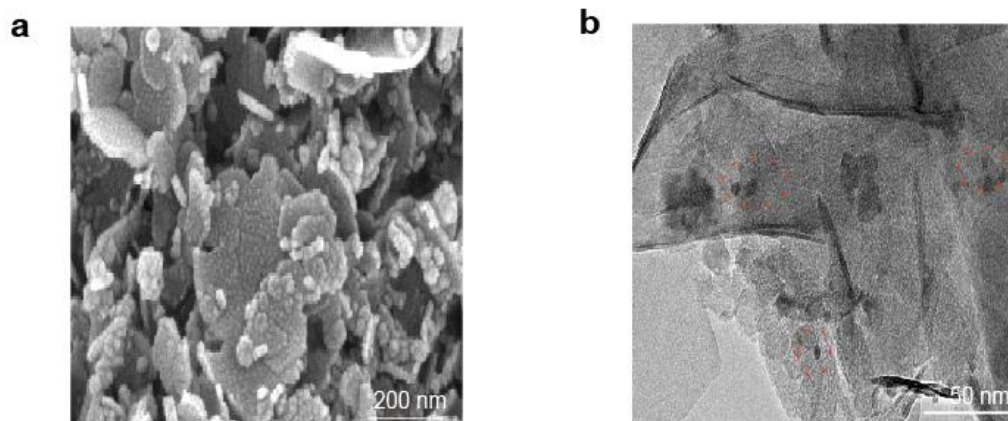


Fig. S1. SEM and TEM images of the Pd/Fe₂O₃.

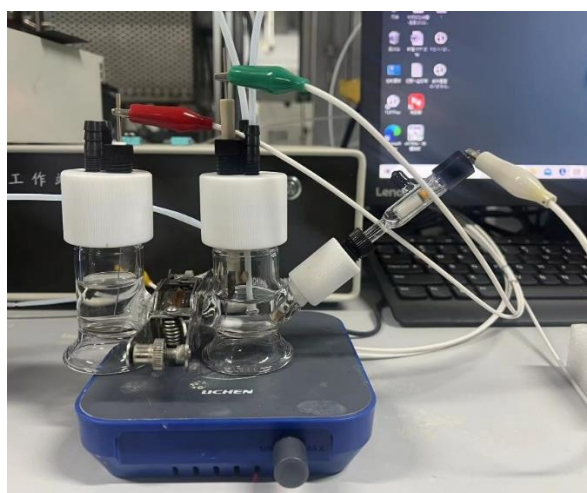


Fig. S2. The electrocatalytic performance of catalysts in an H-type reaction cell consists of the counter electrode (Pt wire), reference electrode(Hg/HgO), and working electrode (catalysts on carbon paper).

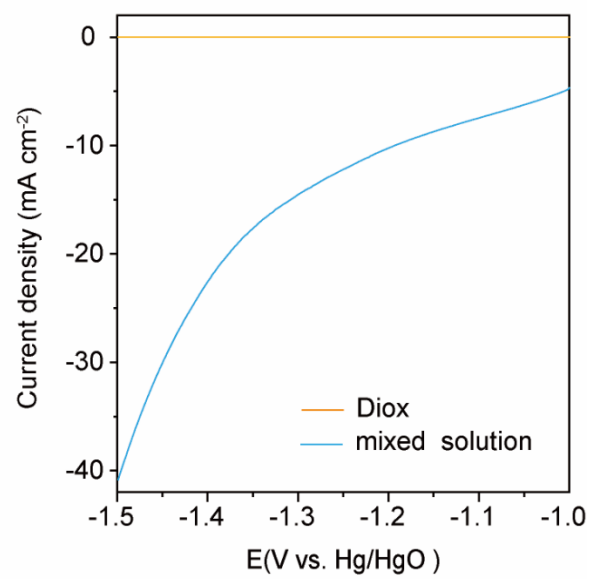


Fig. S3. LSV curves of the Pd/Fe₂O₃ catalysts in the Diox and mixed solution

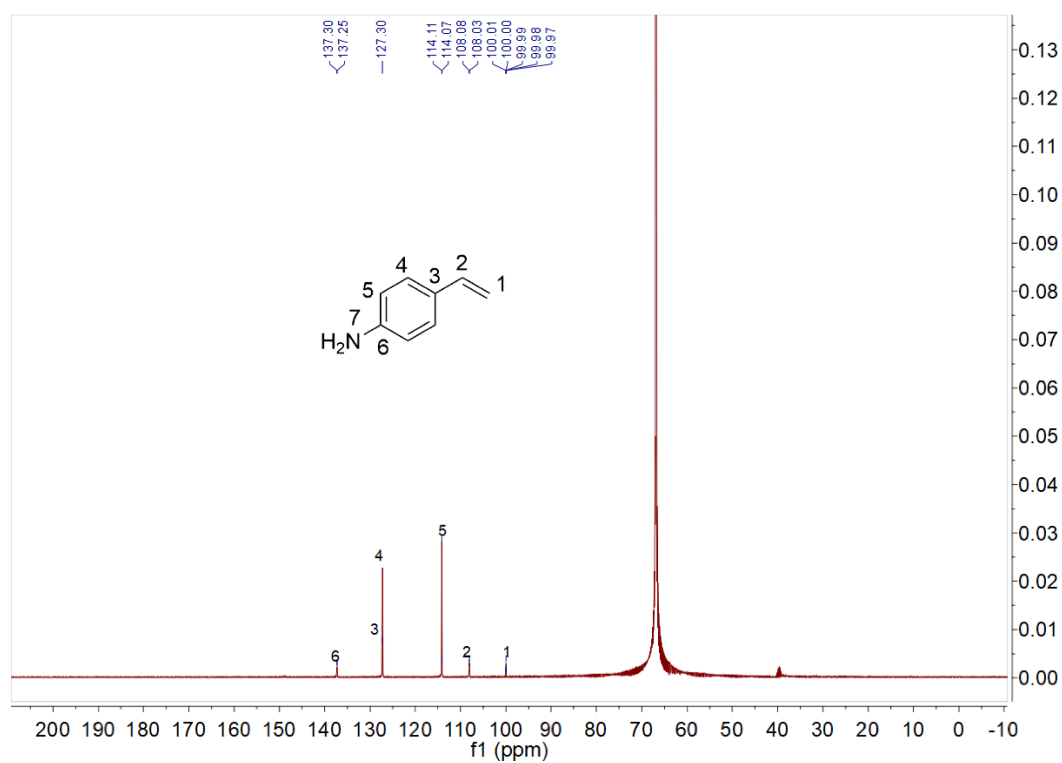
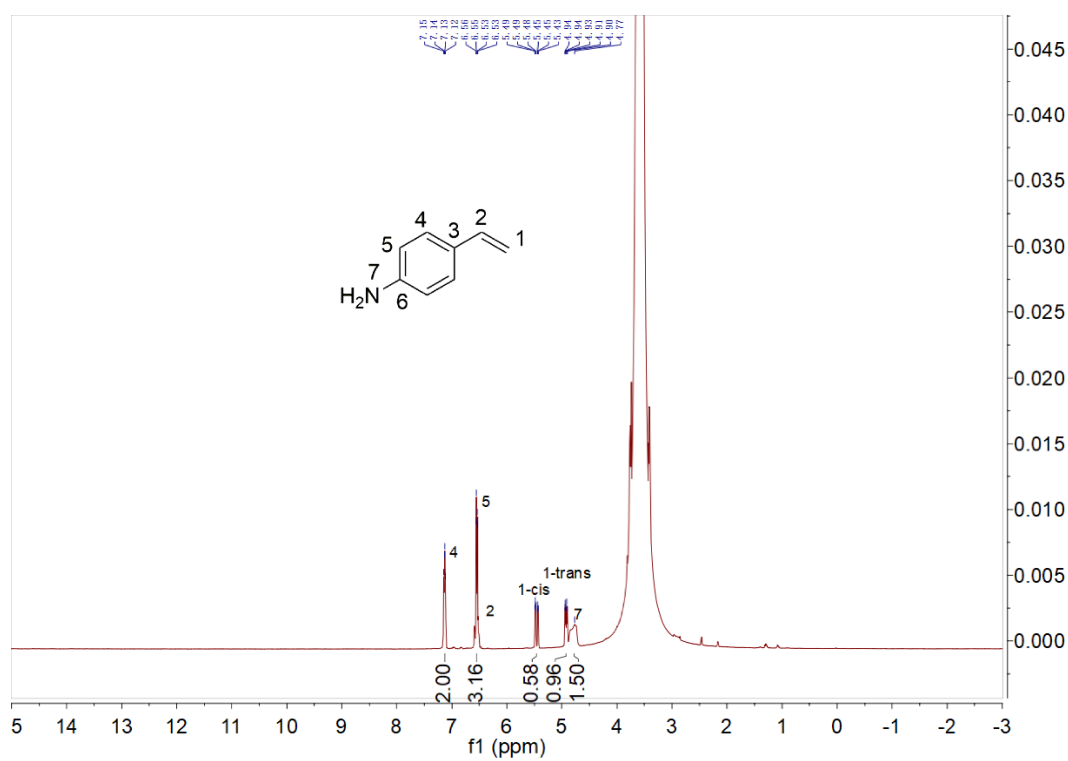


Fig. S4. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6) δ 7.18–7.08 (d, $J = 8.8$ Hz, 2H), 6.62–6.48 (m, 3H), 5.52–5.40 (d, $J = 17.8$ Hz, 1H), 4.91 (ddd, $J = 12.1, 8.7, 3.8$ Hz, 1H), 4.73 (t, $J = 17.3$ Hz, 2H); $^{13}\text{C-NMR}$ (101 MHz, DMSO-d_6) δ 137.28, 127.30, 127.28, 114.09, 108.06, 100.07.

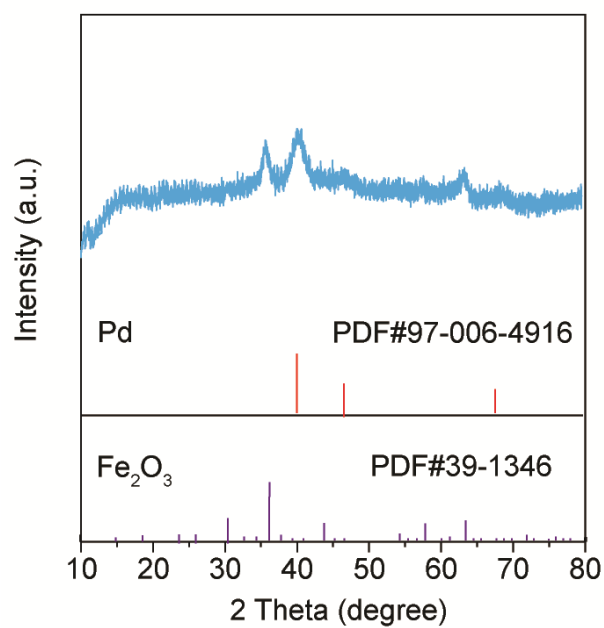


Fig. S5. XRD pattern of Pd/Fe₂O₃ catalysts after reactions.

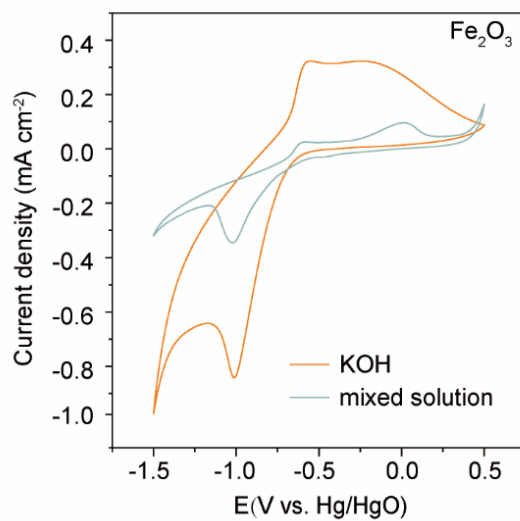


Fig. S6. Cyclic voltammetry curves for Fe₂O₃.

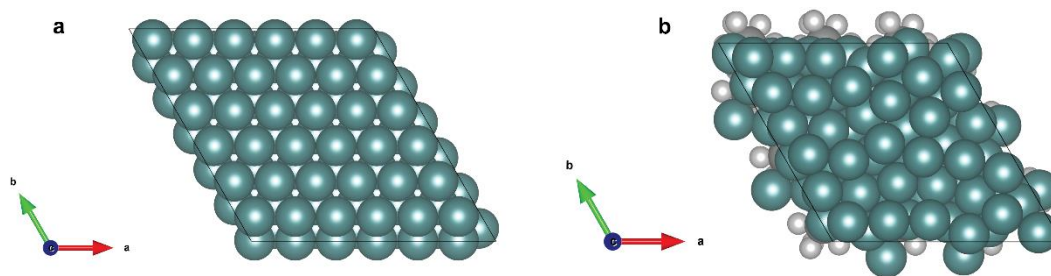


Fig. S7. The atomic structure comparison of Pd in (a) pure Pd and (b) Pd/Fe₂O₃ catalysts, respectively.

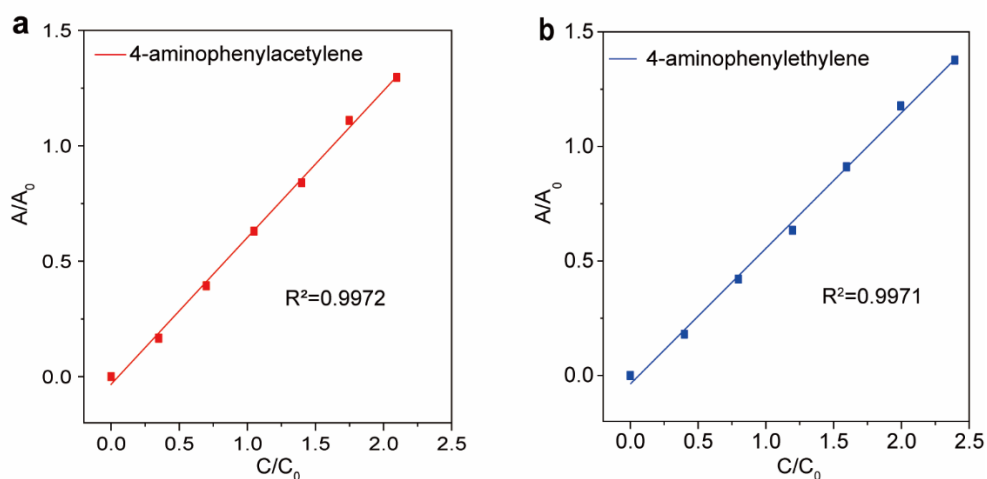


Fig. S8. The correct calibration curves with an internal standard dodecane for quantitative analysis. (a) the curve of 4-aminophenylacetylene. (b) the curve of 4-aminophenylethylene.