

Pt nanoparticles on Ti₃C₂T_x-based MXene as efficient catalysts for selective hydrogenation of nitroaromatic compounds to amines

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Materials and Chemicals

Ti₃AlC₂ powder was obtained from Beijing Hutong Wangyi Commerce & Trade Co., Ltd., China. Sodium borohydride (SB), Ammonia borane (AB), chloroplatinic acid (H₂PtCl₆), ethanol, and concentrated hydrofluoric acid (HF) aqueous solution was purchased from Aladdin, China. All reagents and chemicals were used as received without any purification.

Characterization

Microstructure and particle size characterizations were measured by a transmission electron microscopy (TEM, JEM-2100F, JEOL). The crystal structure of the samples was observed by X-ray diffraction (XRD, Rigaku Co, Cu K α , Japan).. Fourier-Transformed-infrared (FT-IR, Thermo Nicolet, USA) spectroscopy were obtained on IRTracer-100 by using pressed KBr tables. The metal loadings of Pt/Ti₃C₂T_x-D samples were determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Optima 8000).

CO chemisorption (AutoChem II 2920, USA): The dispersion of Pt NPs was calculated on the base of CO chemisorption. Sample (0.1 g) was first pretreated in CO (100 cm³/min) at 150 °C for 1 h and purged with He gas (100 cm³/min) for 1 h. Afterward, the catalyst was cooled to room temperature and CO pluses were injected from a calibrated on-line sampling valve. CO adsorption showed the same peaks areas. A CO/Pt stoichiometry of 1 was used for calculations ¹.

XPS characterization: The tests were carried out by using a surface analysis system (Thermo ESCALAB 250, USA) employing monochromatic Al-K α radiation the surface

samples. Photoelectrons were obtained by an acceptance angle of 90° between the sample surface and the path to the analyzer. Charge neutralization was executed utilizing a co-axial, low-energy electrons and ions beams to avoid shifting in the recorded binding energy (BE). Survey spectra were performed at a pass energy of 100 eV with a step size of 1.0 eV. XPS spectra were collected for Ti 2p, O 1s, C 1s, F 1s and Pt 4f for the as-obtained samples at a pass energy of 20 eV, with a step size of 0.5 eV. The BE scales of all XPS spectra was referenced to the Fermi-edge (E_f), which was set to a BE of 0 eV. The samples were compressed and attached to double-sided tape to acquire the spectra. All teats were operated without Ar ion sputtering. And then, the quantification, using the obtained core-level intensities, and peak fitting of the core-level spectra was performed through a software package (XPSPEAK 4.1). Prior to peak fitting the background contributions were subtracted using a Shirley function. The area ratios of Ti $2p_{3/2}$ and $2p_{1/2}$ peaks were constrained to 2:1; those of Pt $4f_{5/2}$ and $4f_{7/2}$ were constrained to 3:4.

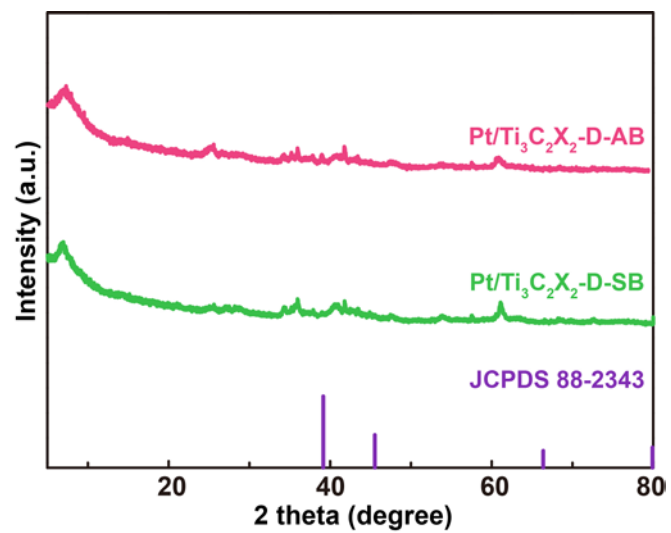


Fig. S1 XRD patterns of Pt/Ti₃C₂T_x-D-AB and Pt/Ti₃C₂T_x-D-SB (Pt JCPDS 88-2343).

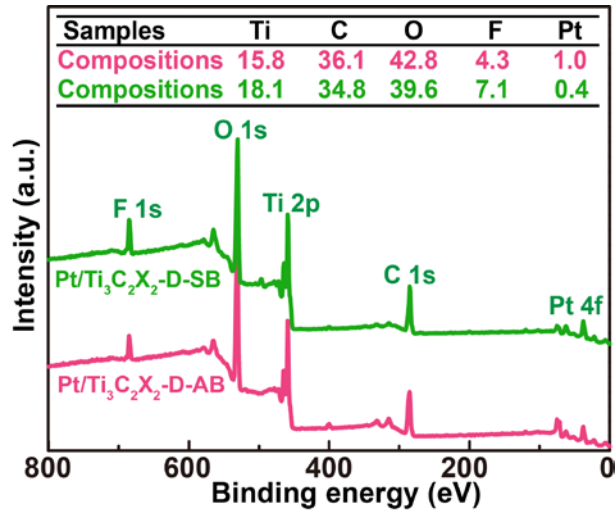


Fig. S2 XPS full scan spectra of Pt/Ti₃C₂T_x-D-AB and Pt/Ti₃C₂T_x-D-SB (inset: the atomic ratio of the detected elements).

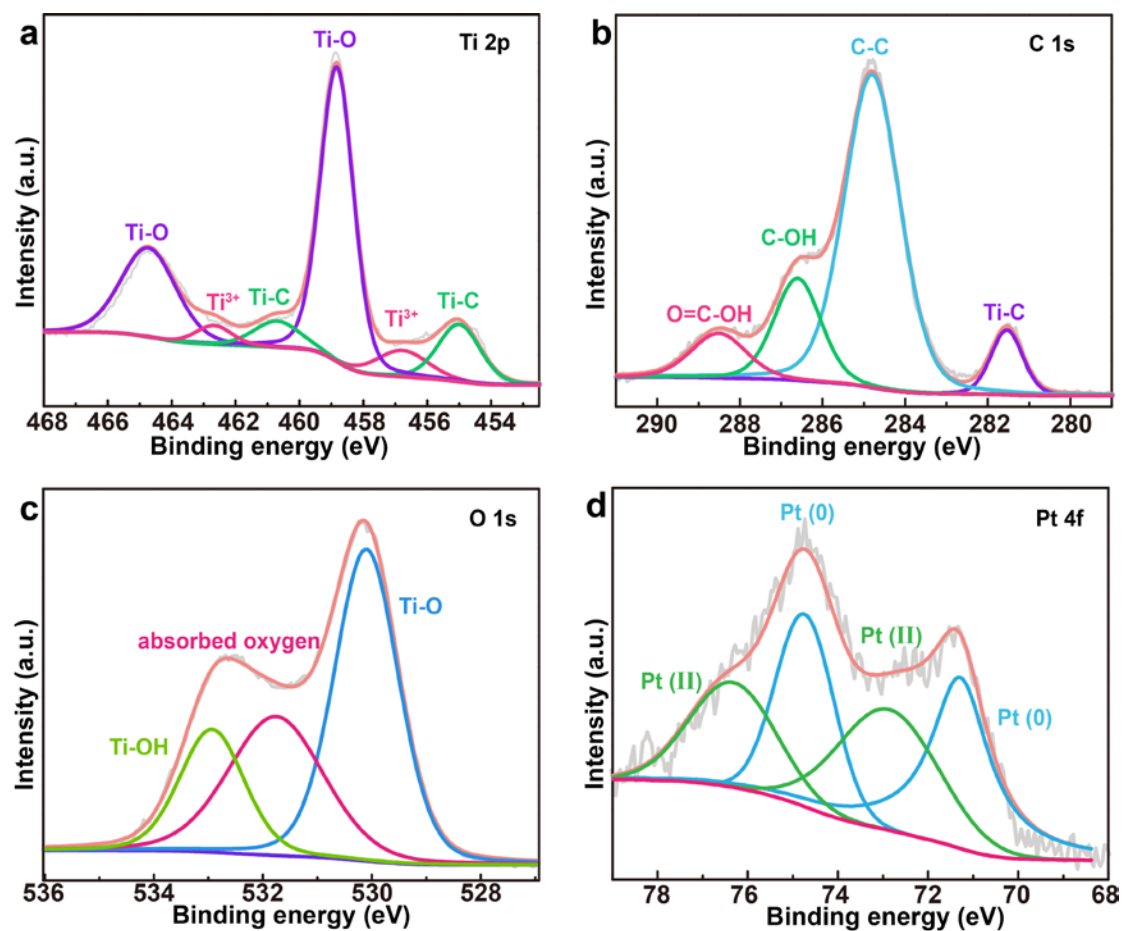


Fig. S3 High resolution XPS spectrum of Ti 2p (a), C 1s (b), O 1s (c) and Pt 4f (d) for Pt/Ti₃C₂T_x-SB, respectively.

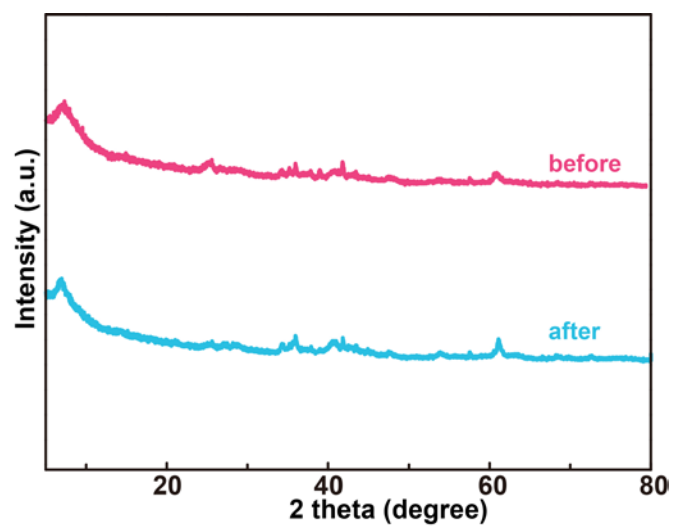


Fig. S4 XRD patterns of Pt/Ti₃C₂T_x-D-AB before and after the sixth run.

Table S1. The ratio of Pt (0) and Pt (II) for all samples by XPS

| Catalyst | Pt (0) | Pt (II) |
|--|--------|---------|
| Pt/Ti ₃ C ₂ T _x -D-AB | 67.4% | 32.6% |
| Pt/Ti ₃ C ₂ T _x -D-SB | 55.1% | 44.9% |

Table S2. Effect of reaction time on catalytic hydrogenation of *p*-CNB to *p*-CAN catalyzed by Pt/Ti₃C₂T_x-AB.

| Reaction time (min) | Conversion (%) | Selectivity (%) | | | |
|------------------------|-------------------|-----------------|----------------|-----|--------|
| | | <i>p</i> -CAN | <i>p</i> -CNSB | AN | others |
| 30 | 79.0 | 91.2 | 7.7 | 0.6 | 0.5 |
| 50 | 92.9 | 93.8 | 5.2 | 0.8 | 0.3 |
| 60 | 100 | 99.5 | 0.4 | 0.1 | 0 |
| 90 | 100 | 97.4 | 1.5 | 0.9 | 0.2 |
| 120 | 100 | 97.6 | 1.2 | 1.0 | 0.2 |

Reaction conditions: catalyst, 5.0 mg; ethanol/water mixture with a volume percent of 28% (total volume: 7.0 mL); the amount of *p*-CNB, 1 mmol; the pressure of hydrogen: 1MPa; reaction temperature: 30 °C.

Table S3. Effect of temperature on catalytic hydrogenation of *p*-CNB to *p*-CAN catalyzed by Pt/Ti₃C₂T_x-AB.

| Reaction temperature (°C) | Conversion (%) | Selectivity (%) | | | |
|---------------------------|----------------|-----------------|--------|-----|--------|
| | | p-CAN | p-CNSB | AN | others |
| 25 | 70.3 | 89.9 | 9.0 | 0.5 | 0.6 |
| 30 | 100 | 99.5 | 0.4 | 0.1 | 0 |
| 40 | 100 | 97.8 | 1.3 | 1.6 | 0.2 |
| 50 | 100 | 95.8 | 0.5 | 3.4 | 0.3 |

Reaction conditions: catalyst, 5.0 mg; ethanol/water mixture with a volume percent of 28% (total volume: 7.0 mL); the amount of *p*-CNB, 1 mmol; the pressure of hydrogen: 1MPa; reaction time: 1 h.

Table S4. Effect of hydrogen pressure on catalytic hydrogenation of *p*-CNB to *p*-CAN catalyzed by Pt/Ti₃C₂T_x-AB.

| H ₂ pressure ^c (MPa) | Conversion (%) | Selectivity (%) | | | |
|---|-------------------|-----------------|----------------|-----|--------|
| | | <i>p</i> -CAN | <i>p</i> -CNSB | AN | others |
| 1.0 | 100 | 99.5 | 0.4 | 0.1 | 0 |
| 1.5 | 100 | 96.5 | 2.9 | 0.5 | 0.1 |
| 2.0 | 100 | 96.3 | 2.9 | 0.8 | 0.1 |
| 2.5 | 100 | 95.8 | 2.8 | 1.3 | 0.1 |

Reaction conditions: catalyst, 5.0 mg; ethanol/water mixture with a volume percent of 28%(total volume: 7.0 mL); the amount of *p*-CNB, 1 mmol; reaction time: 1 h; reaction temperature: 30 °C.

Table S5. The catalytic performance for different catalysts

| Catalysts | Solvent | P (MPa) | T (°C) | Time (min) | Conv. (%) | Sel. (%) | Ref. |
|--|------------|------------|-----------|---------------|--------------|-------------|------|
| Pt/Al ₂ O ₃ @NC-15 | EtOH | 1 | 80 | 60 | 100 | 98.6 | 2 |
| Pt@Cu(0.23)/TiO ₂ | EtOH | 1 | 80 | 90 | 50.4 | 100 | 3 |
| PVP-Pt | MeOH | 0.1 | 30 | 30 | 100 | 68.8 | 4 |
| Ru/CNT | MeOH | 4 | 60 | 30 | 100 | 90.3 | 5 |
| Pt/CMK-3 | EtOH | 4 | 25 | 5 | 100 | 56.8 | 6 |
| PtNi/CNTs | EtOH | 0.1 | 30 | 160 | 99.6 | 98.2 | 7 |
| Pt/ZrO ₂ | EtOH | 0.1 | 30 | 210 | 99.4 | 90.9 | 8 |
| Pt-SA/C | EtOH | 1 | 40 | 60 | >99 | >99 | 9 |
| PtCeO _x /CNTs | EtOH | 0.1 | 30 | 67 | 99.4 | 98.1 | 10 |
| Pt–NiO@mSiO ₂ | EtOH | 1 | 45 | 120 | 87.9 | 95.3 | 11 |
| Ru5/NPC(NB) | MeOH | 1.5 | 140 | 150 | 98 | 98 | 12 |
| Pt/Ti ₃ C ₂ T _x -D-AB | EtOH/water | 1 | 30 | 60 | 100 | 99.5 | This |
| Pt/Ti ₃ C ₂ T _x -D-SB | EtOH/water | 1 | 30 | 60 | 40.4 | 84.3 | Work |

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