Electronic Supplementary Informaton

Modulation of support properties in flower-like Pt/Al₂O₃ nanosheet catalysts for dehydrogenation of cycloalkanes

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Experimental Section

Catalyst characterizations

The actual loading of Pt in each reduced Pt/Al_2O_3 catalyst was determined by inductively coupled plasma optical emission spectrometry (Thermo Scientific iCAP6000).

The X-ray diffraction (XRD) analyses were conducted using a Multiflex diffractometer (Bruker D8) equipped with a monochromatic Cu Kα radiation source (λ=1.5406 Å, 40 kV, 40mA). The scanning range of 2θ was set from 10 to 90° at a scan rate of 8°/min.

The textural structures of the catalysts were determined using an ASAP 2460 automated gas sorption analyzer (Micromeritics, USA) through N_2 adsorption-desorption equilibrium at -196 °C. The specific surface area and pore diameter were determined and calculated by Brunauer-EmmettTeller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

The morphology of the supports was examined using a scanning electron microscope (SEM, ThermoFisher Scientific FEI-Apreo SLoVac). The structure and Pt particle size of the reduced/used catalysts were analyzed by using a scanning transmission electron microscopy (JEM-F200) at 200kV.

Solid state ^{27}Al solid state magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy was conducted at room temperature using a JEOL JNM-ECX 600MHz solid-state NMR spectrometer, operating at a magnetic field of 14.1 T.

The pulse chemisorption of CO was conducted on the AMI-300 apparatus to determine the dispersion of metallic Pt particles supported on various supports.

In-situ CO-FT-IR spectra were acquired using a Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific) equipped with a QIRS-A07 Cell and an MCT detector at a resolution of 4 cm^{-1} using 32 scans. Prior to analysis, the sample (0.02 g) underwent pretreatment with $10\%H_2/Ar$ (50 mL/min) at 500 °C for 2 h, followed by purging with N_2 gas (40 mL/min) to remove any H_2 adsorbed during the reduction. After cooling down to 50 °C, a background spectrum was recorded for each sample and automatically subtracted from the subsequent spectra. Each sample was then exposed to a gas mixture of 10% CO/N_2 until adsorption reached saturation, followed by purging with N_2 to remove gaseous CO. The spectra were recorded during both adsorption and desorption of CO.

Hydroxyl groups on the supports were also analyzed by in situ Fourier transform infrared (FTIR) experiments equipped with a QIRS-A07 Cell and an MCT detector at a resolution of 4 cm^{-1} using 32 scans. Prior to analysis, the sample (0.02 g) underwent degas in vacuum at 400 °C for 1 h. After cooling down to 50 °C, the spectra were recorded.

The XPS spectra were collected by using a K-alpha+ X-ray photoelectron spectrometer (Thermo Scientific). Prior to the XPS analysis, all catalysts underwent reduction in flowing H_2 (50 ml/min) at 500 °C for 2h in a reaction chamber and subsequently transferred into the test chamber. Deconvolution of the XPS spectrum was performed by using the Casa XPS software (version2.3.14). The binding energies of all species were referenced to the C 1s feature at 284.8 eV. A standard Shirley background was employed for fitting all the samples. The Pt 4d peak fitting involved symmetrical Gauss-Lorentz curves for Pt^{2+} and Pt^{4+} species and asymmetrical LA(1.2,85,70) curve model for Pt^0 species. Percentages for different states of platinum were estimated based on the area of the curves that provided optimal fitting.

Temperature-programmed desorption of NH$_3$ (NH$_3$-TPD) were performed using an automated chemisorption instrument (Huasi DAS-7200). Typically, the sample (0.1 g) was pretreated in a He flow (30 ml/min) at 400 °C for 30 min at a ramping rate of 5 °C/min. After cooling down to 50 °C in He (30 ml/min) flow, the sample was saturated with 10%NH$_3$/He (50 ml/min) at 50 °C for 1 h. Subsequently, the sample was flushed with flowing He (30 ml/min) for 1 h. Finally, NH$_3$-TPD measurement were recorded by increasing the temperature up to 500 °C at a ramping rate of 10 °C/min. Toluene-TPD analysis was performed following a similar procedure and desorbed toluene was detected by using a mass spectrometry detector (MS, Hiden QIC-20).

The coke deposition on spent catalysts was quantified by using thermogravimetric analysis (TGA) performed on a TA Q500 instrument. The test was conducted in an air stream, with a heating rate of 10 °C/min from 30 to 800 °C.

Activity tests

The dehydrogenation of cycloalkanes over Pt/Al$_2$O$_3$ was conducted in a stainless-steel fixed bed flow reactor (O.D.: 30mm, I.D.: 10mm) under atmospheric pressure. Typically, Pt/Al$_2$O$_3$ (20~40 mesh) was diluted with silicon carbide and then positioned at the center of the reactor. Prior to the reaction, the catalyst was in-situ reduced in a flow of 50 ml/min H$_2$ at 500 °C for 2 h. After reduction, the catalyst was cooled down to the desired reaction temperature (350 °C) in a flow of 50 ml/min N$_2$. Once the reaction temperature stabilized, the MCH was pumped into the reactor and vaporized. The evaporated reactants were then passed through the catalyst bed with N$_2$ (50 ml/min) as a carrier gas.

The liquid products were collected with a gas-liquid separator and were analyzed by Shimazu GC-2010 Pro with SH-Rtx-1 capillary column (30 m × 250 μm × 0.25 μm) and Shimadzu GCMS-QP2020 NX with Rxi-5Sil MS capillary column (60 m × 250 μm × 1.00 μm).

The conversion of the cycloalkanes was calculated based on the following equation.

$$X\ [\%] = \frac{\text{mol of initial reactant} - \text{mol of unreacted reactant}}{\text{mole of initial reactant}} \times 100$$

The hydrogen production rate was calculated based on the total Pt loading using following equation:

$$\text{Hydrogen production rate } [mol\ gPt-1min-1] = \frac{m\text{mol of H2 formed after reaction}}{\text{weight of Pt } loading\ \times\ reaction\ time} \times 100$$

The TOF was calculated based on the total Pt loading using following equation:

$$TOF\ [h-1] = \frac{\text{mol of initial reactant} - \text{mol of unreacted reactant}}{\text{mol of } exposed\ \text{Pt } by\ CO\ chemisorption\ \times\ reaction\ time} \times 100$$

The degree of dehydrogenation (DoDH) was defined based on the following equation. The H$_2$ formed after dehydrogenation reaction was determined based on the dehydrogenated products and their compositions. The theoretical H$_2$ production was determined assuming that the reactant converted completely to its dehydrogenated form.

$$\text{Degree of Dehydrogenation } [\%] = \frac{\text{mol of H2 formed after reaction}}{\text{mol of theoretical H2 production in initial reactant}} \times 100$$

$$\text{Hydrogen Yield } [wt\%] = \frac{\text{weight of H2 formed after reaction}}{\text{weight of initial reactant}} \times 100$$

The deactivation rate was defined based on the following equation.

$$kd\ [\text{h - 1}] = \frac{\text{In}\ [(1\text{ - Xfinal})/Xfinal] - \text{In}\ [(1\text{ - Xinitial})/Xinitial]}{t}$$
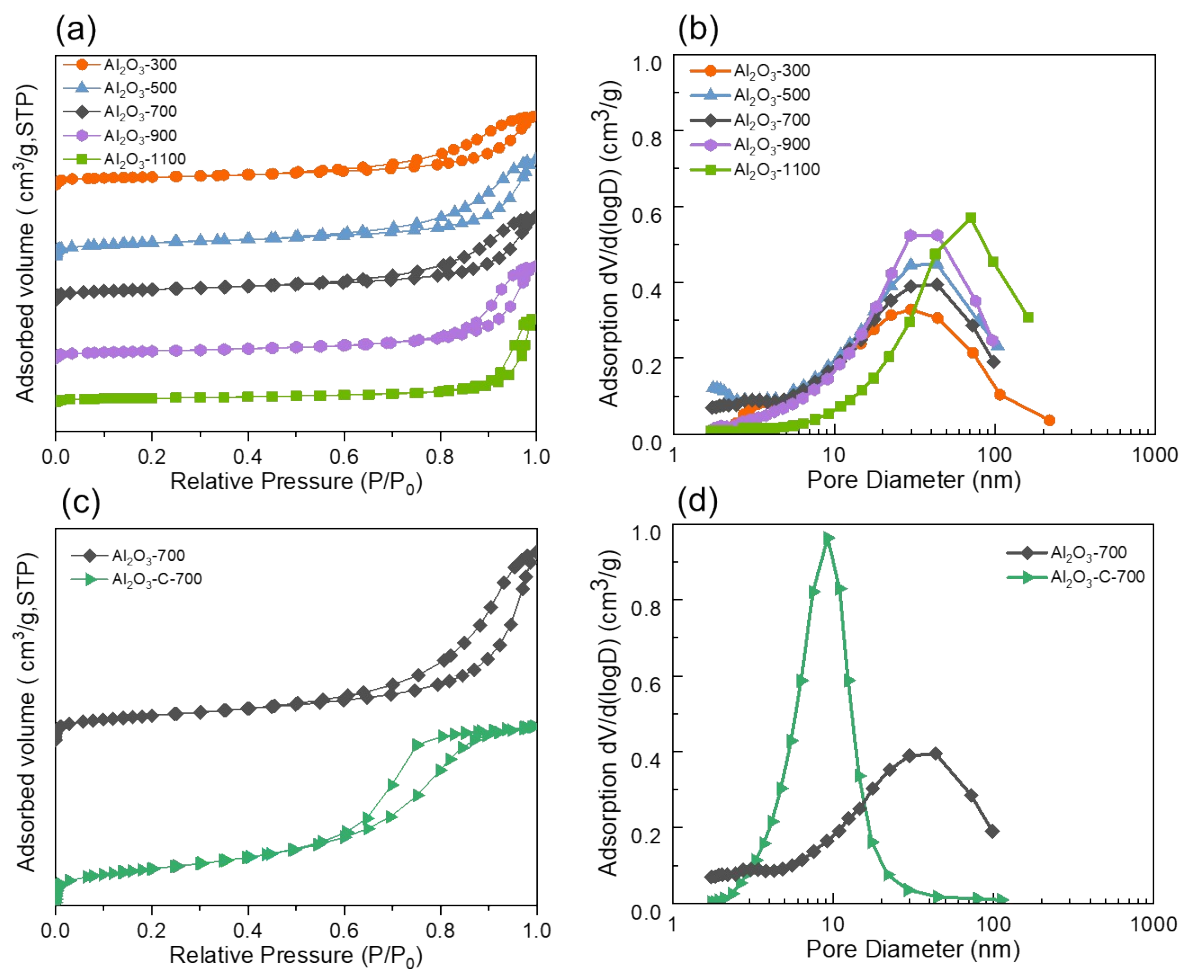

Fig. S1 N_2 adsorption/desorption isotherms (a and c) and pore diameter distributions (b and d) of Al_2O_3 supports
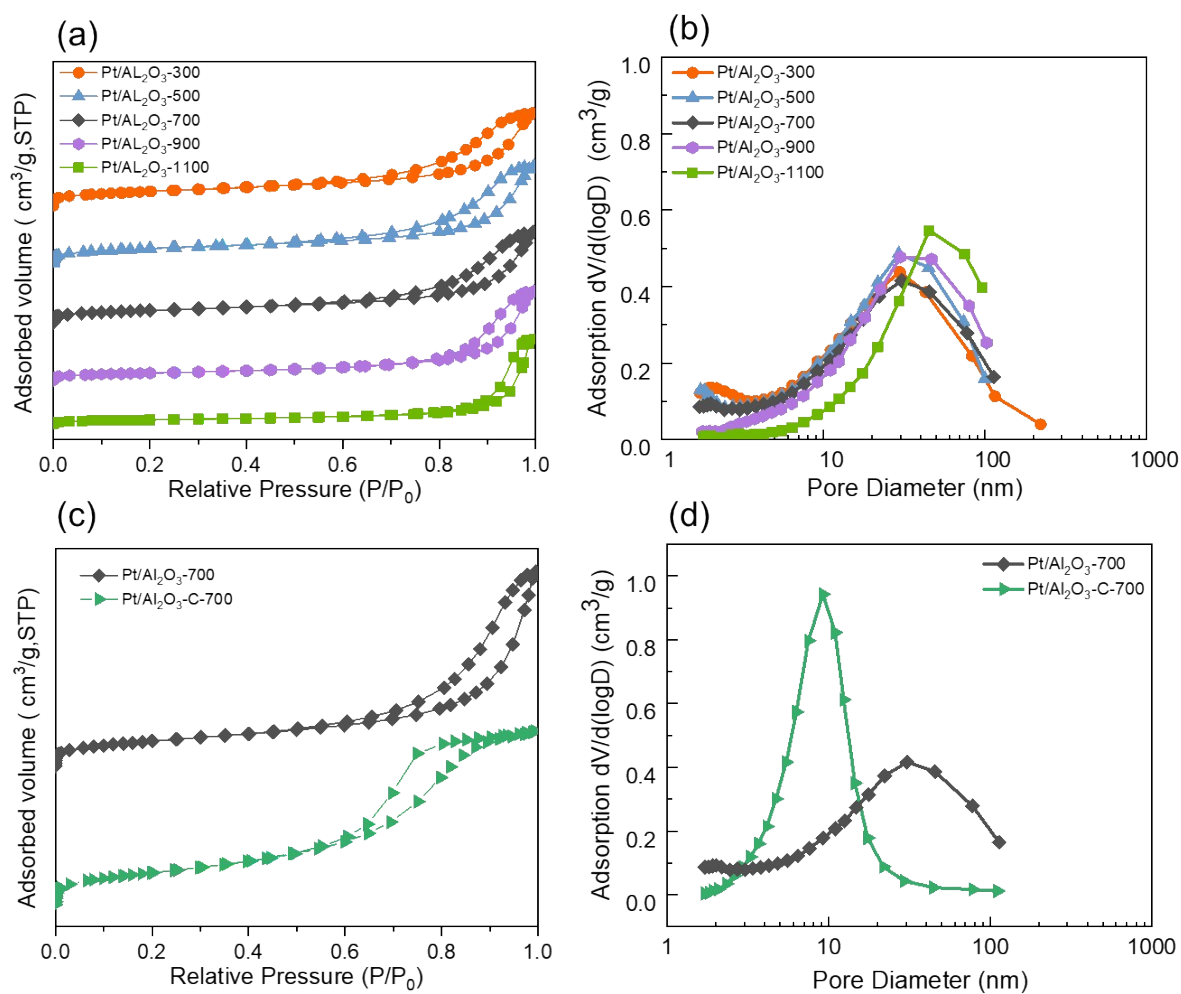
**Fig. S2** N_2 adsorption/desorption isotherms (a and c) and pore diameter distributions (b and d) of reduced Pt/Al$_2$O$_3$ supports

Table S1. The fractions of Pt^0, Pt^{2+} and Pt^{4+} on Pt/Al_2O_3 catalysts by XPS

Catalysts	Pt^0 fraction	Pt^{2+} fraction	Pt^{4+} fraction
Pt/Al_2O_3-300	78.3%	17.4%	4.3%
Pt/Al_2O_3-500	79.2%	12.5%	8.3%
Pt/Al_2O_3-700	81.1%	10.8%	8.1%
Pt/Al_2O_3-900	89.3%	5.9%	4.8%
Pt/Al_2O_3-1100	90.4%	5.8%	3.8%

(a)

(b)

(c)

(d)

d$_{TEM}$=1.8nm

20 nm
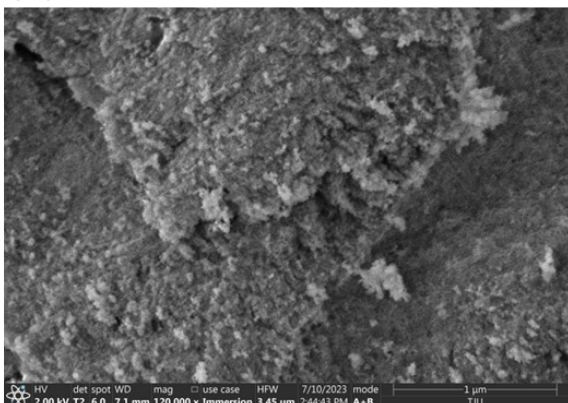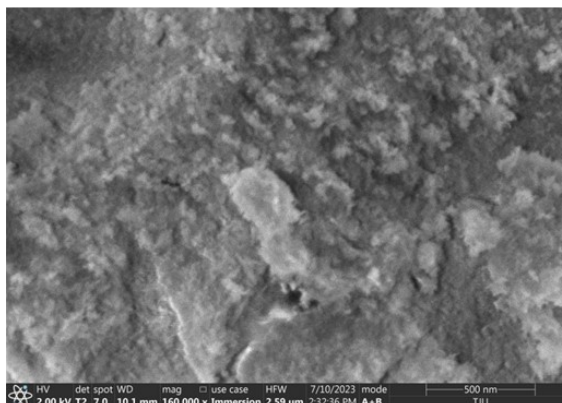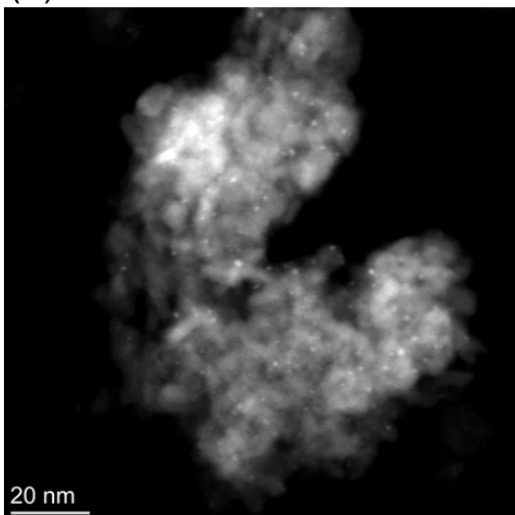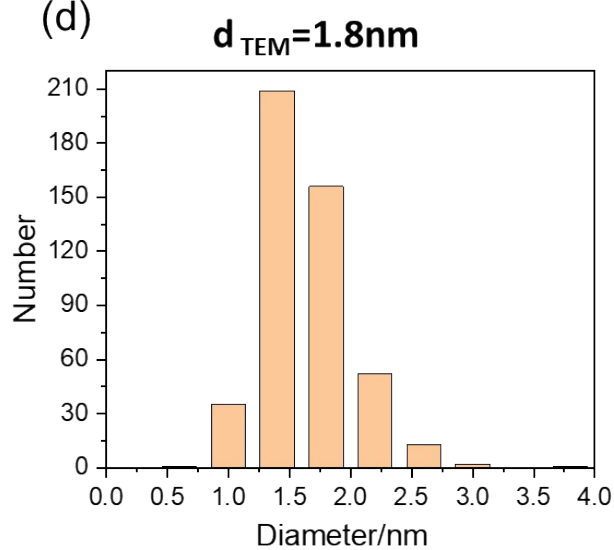
Fig. S3 SEM images of Al$_2$O$_3$-C-700 support (a&b). HAADF-STEM image (c) and particle size distribution (d) of the reduced Pt/Al$_2$O$_3$-C-700 catalyst
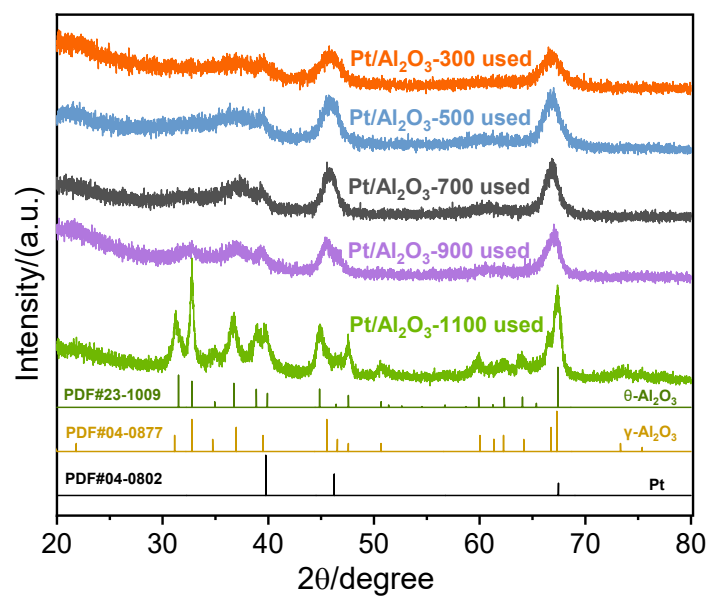
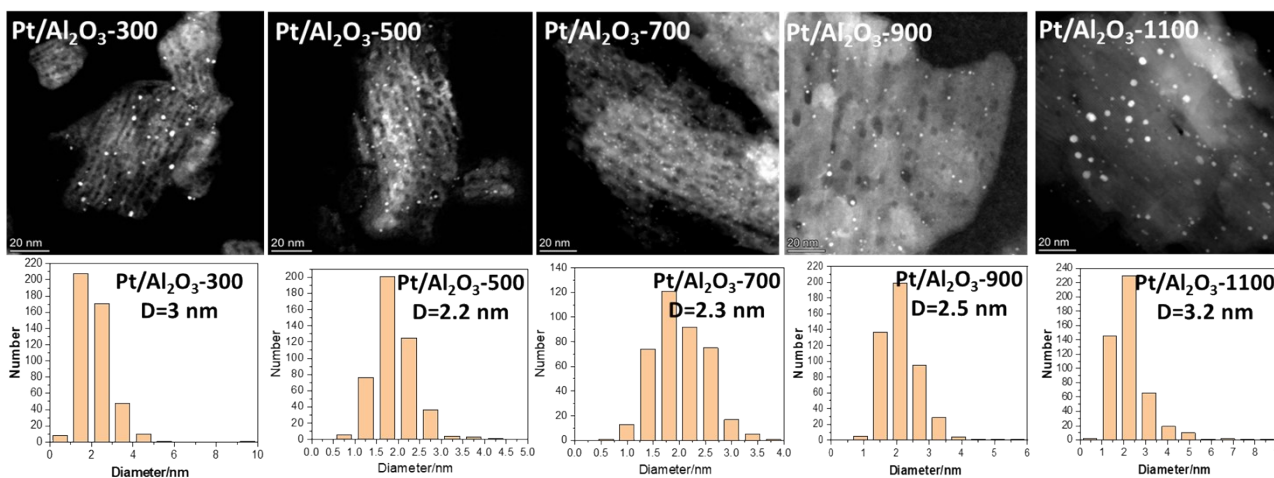**Fig. S4** XRD patterns of spent Pt/Al₂O₃ catalysts

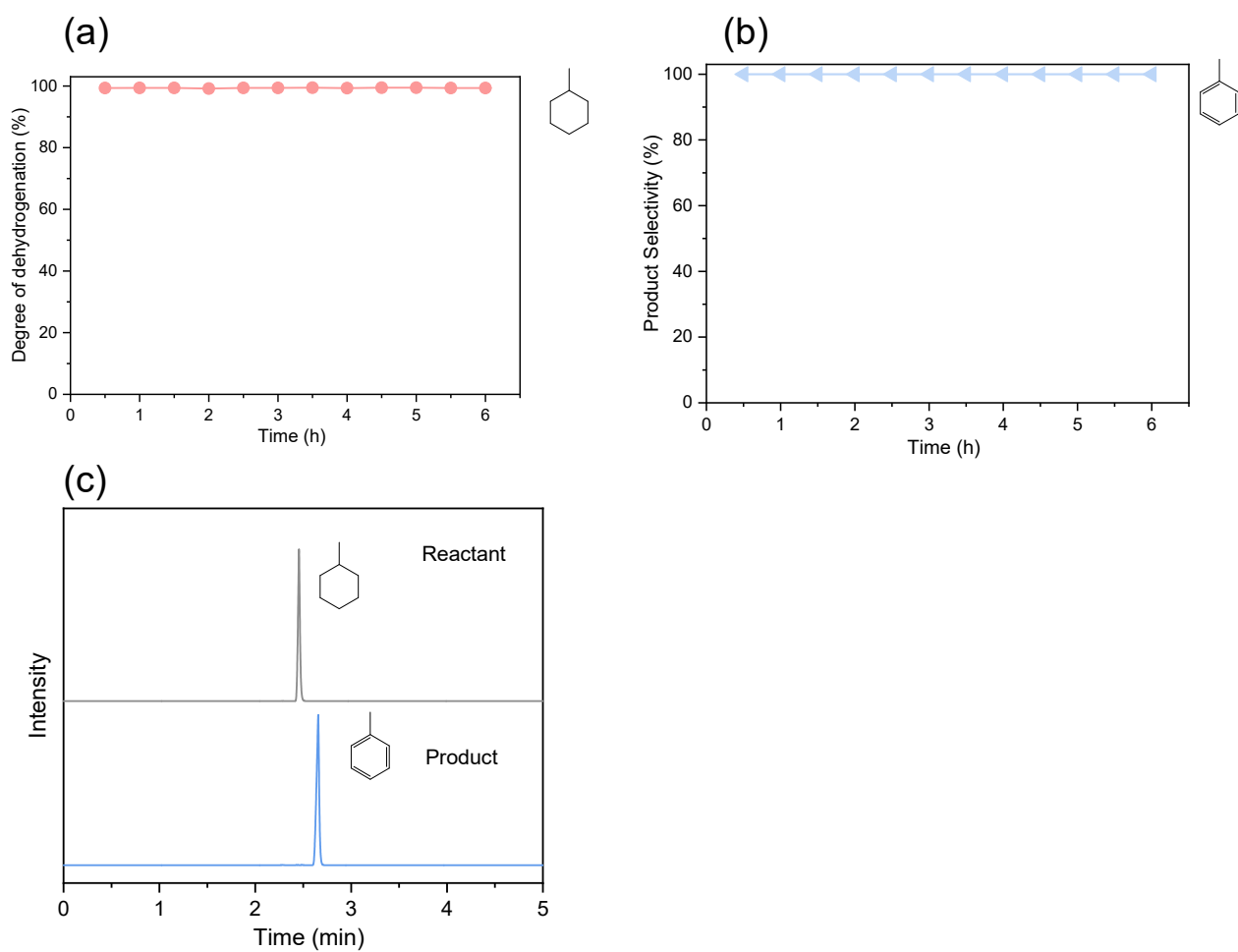**Fig. S5** HAADF-STEM images and particle size distribution of spent Pt/Al$_2$O$_3$ catalysts

Fig. S6 Dehydrogenation of methylcyclohexane over Pt/Al$_2$O$_3$-700. (a) Catalyst stability; (b) Product selectivity; (c) Gas chromatogram trace of reactants and the products. Reaction conditions: WHSV$_{cycloalkanes}$ = 10 h^{-1}, 350 °C, Carrier gas: N$_2$ 50 ml/min
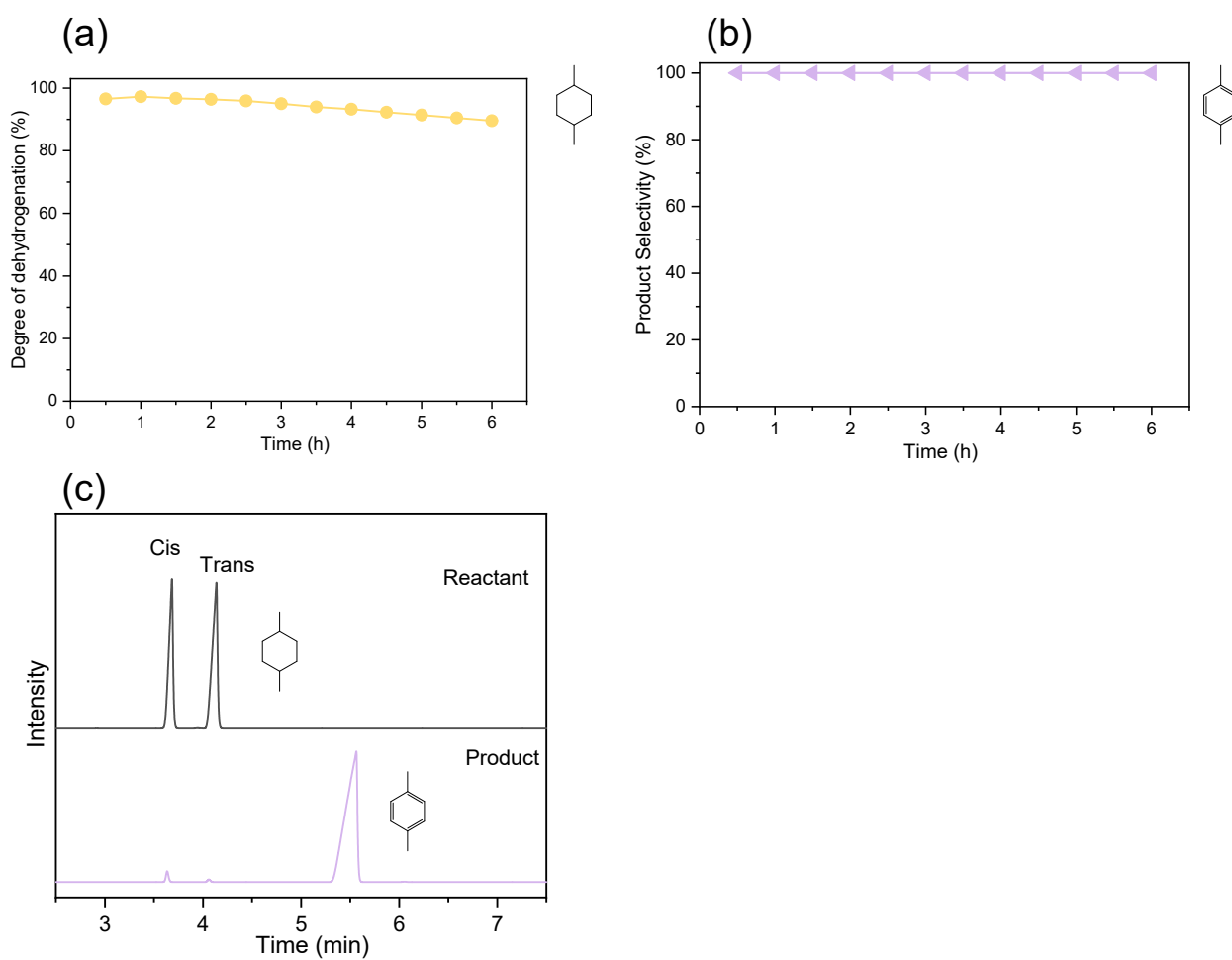
Fig. S7 Dehydrogenation of 1,4-dimethylcyclohexane over Pt/Al$_2$O$_3$-700. (a) Catalyst stability; (b) Product selectivity; (c) Gas chromatogram trace of reactants and the products. Reaction conditions: WHSV$_{cycloalkanes}$ = 10 h^{-1}, 350 °C, Carrier gas: N$_2$ 50 ml/min
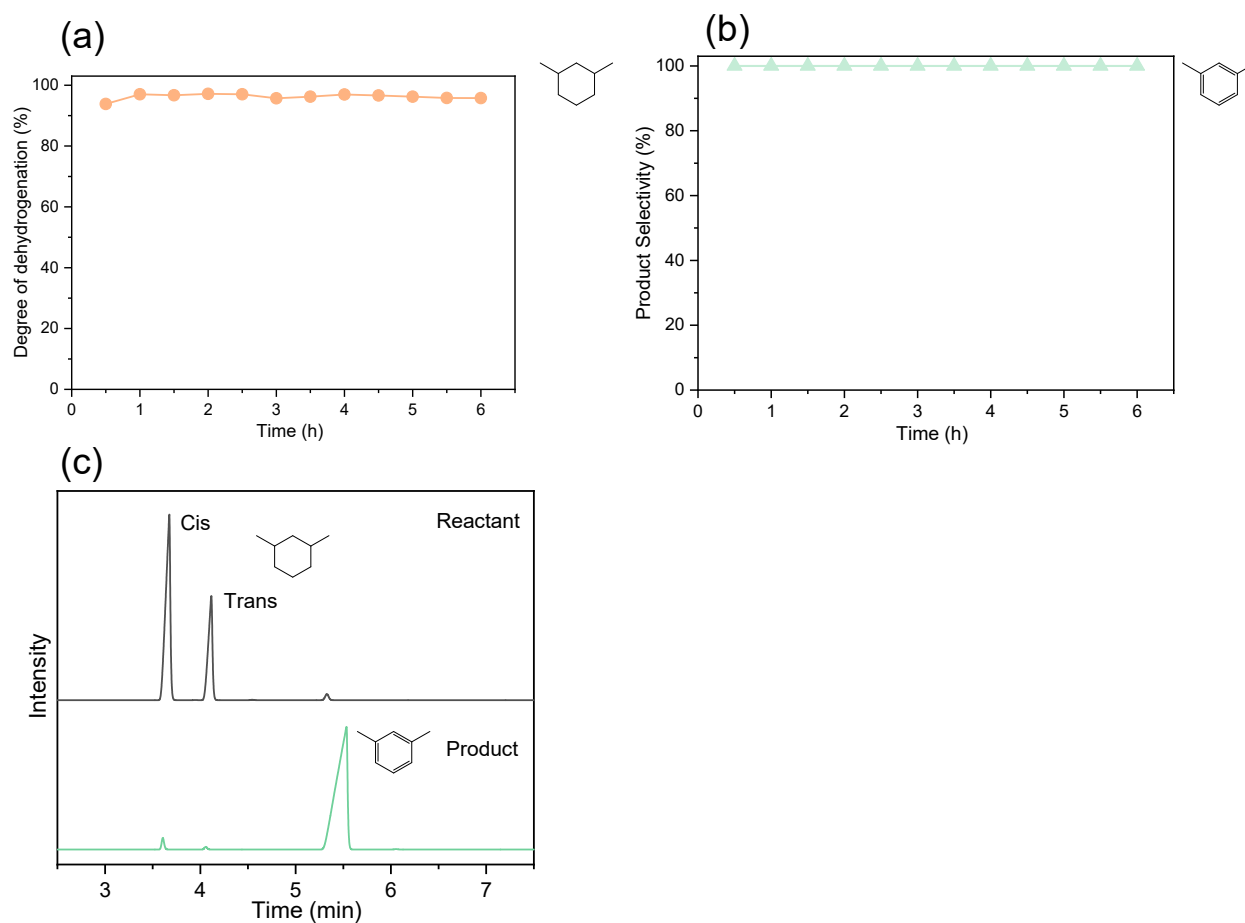
Fig. S8 Dehydrogenation of 1,3-dimethylcyclohexane over Pt/Al$_2$O$_3$-700. (a) Catalyst stability; (b) Product selectivity; (c) Gas chromatogram trace of reactants and the products. Reaction conditions: WHSV$_{cycloalkanes}$ = 10 h^{-1}, 350 °C, Carrier gas: N$_2$ 50 ml/min