Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary information

Pt nanoparticles entrapped in titanate nanotubes (TNT) for phenol hydrogenation: the confinement effect of TNT

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1. Preparation of Support and Catalysts

Synthesis of Support Materials: Titanate nanotubes (TNT) were synthesized by a previously described method[1]. As-received TiO_2 (Hualisen Corp., China) was mixed with 100 mL concentrated NaOH solution (10 M) in a Teflon container under mild stirring at 140^{o}C for 24 h; the resultant white precipitate was then separated from the mixture and washed with deionized water several times until the conductivity of the solution was below 100 μs/cm and constant.

Mesoporous silica (MS) was synthesized according to the method reported in our previous work[2]. Specifically, dodecylamine was dissolved in a solvent mixture under mild stirring, then TEOS was added drop-wise to the solution, which was stirred for 8 h at room temperature. The white precipitates were then filtered, washed, and dried overnight. Finally, calcination was carried out by increasing the temperature from room temperature to 600°C at a rate of 1^{o}C min^{-1} to completely remove the template.

Hydrophobic modification of TNT: Using methacryloxypropyltrimethoxysilane (KH570) as a silane coupler, the TNT was hydrophobically modified as follows. Pristine TNT and KH570 with a mass ratio of 2:1 were added to a water–ethanol mixed solution under vigorous stirring at 80^{o}C for 5 h. Then the obtained white precipitates were filtered, washed with ethanol to eliminate the extra KH570, and dried at 60°C for 4 hours.

Catalyst preparation: The catalysts were prepared as previously described[2]. First, the selected support, including TNT and MS, was impregnated with an aqueous solution of hexachloroplatinic acid (H_2PtCl_6) at room temperature under stirring. The solvent was then evaporated in a water bath at 60^{o}C, with further vacuum drying at 40^{o}C for 12 h. The supported Pt catalyst was finally prepared by reducing the sample for 2 h under hydrogen flow at 250^{o}C in a tubular furnace with programmed temperature control, at a rate of 3^{o}C min^{-1}. The general properties of the supports and catalysts are given in Table S1.

2. Evaluation of Catalysts

Phenol hydrogenation was used to evaluate the catalysts. A reaction mixture composed of 0.5 g phenol, 20 mg catalyst, and 10 mL dichloromethane was introduced into a stainless-steel autoclave under stirring at 1000 rpm, a value chosen to eliminate the mass transfer limitation. The air in the autoclave was purged with hydrogen for 20 min, then the reaction proceeded at 50^{o}C and 0.5 MPa of 99.99% hydrogen. The quartz turnover frequencies (*qTOFs*) value was defined using the formula below:

$$qTOFs = \frac{m_{phenol}}{m_{Pt}\, t_{react}} \tag{1}$$

where m_{phenol}, m_{Pt}, and t_{react} stand for the mass of phenol converted, the total mass of Pt used, and the reaction time (typically fixed at an initial 30 min).

The products were analyzed using a gas chromatograph (Agilent 6840N, USA) equipped with a FID detector. GC-MS analysis (Shimadzu GCMS-QP5050A, Japan) with a 0.25 mm × 30 m DB-WAX capillary column was used to identify cyclohexanone and cyclohexanol. The column oven temperature was programmed from 120^{o}C (held for 1 min) to 280^{o}C at a rate of 20^{o}C min^{-1}.

3. Characterization of Catalysts and Supports

X-ray diffraction (XRD) patterns were obtained with a D/Max-IIIA X-ray diffractometer (Rigaku, Japan) using Cu Kα radiation.

Transmission electron microscopy (TEM) was carried out with a JEOL JEM2010 microscope (JEOL, Japan) using an accelerating voltage of 200 kV. The filling yield (*Y%*) of the Pt nanoparticles (NPs) confined within the TNT was calculated using the following formula:

$$Y = {V_{confined\ Pt}}\Big/{V_{TNT\ cavity}} = {N \cdot \tfrac{4}{3}\pi r^3}\Big/{\pi R^2 l} = \frac{4Nr^3}{3R^2 l} \tag{2}$$

where *N* and *r* stand for the number and average radius of the Pt NPs confined in the TNT, and *l* and *R* stand for the length and inner radius of the TNT. All data were derived from statistical counts using the TEM images.

N_2 adsorption-desorption isotherms were measured with a Tristar 3010 isothermal nitrogen-sorption analyzer (Micromeritics, USA) using a continuous adsorption procedure.

X-ray photoelectron spectroscopy (XPS) with an Axis Ultra DLD (Kratos, Britain) was used to examine the electronic properties of the catalysts.

Hydrogen temperature programmed reduction (H_2-TPR) was performed on homemade equipment. A 50 mg sample was heated at 10^{o}C min^{-1} from room temperature to 800^{o}C in 5% H_2/Ar (40 mL min^{-1}, STP).

Inductively coupled plasma atomic emission spectrometry (ICP-AES) was conducted using a Perkin Elmer Optima 3300 DV ICP-AES (Perkin Elmer, Canada) to determine the catalysts' Pt content.

4. Some Important Results

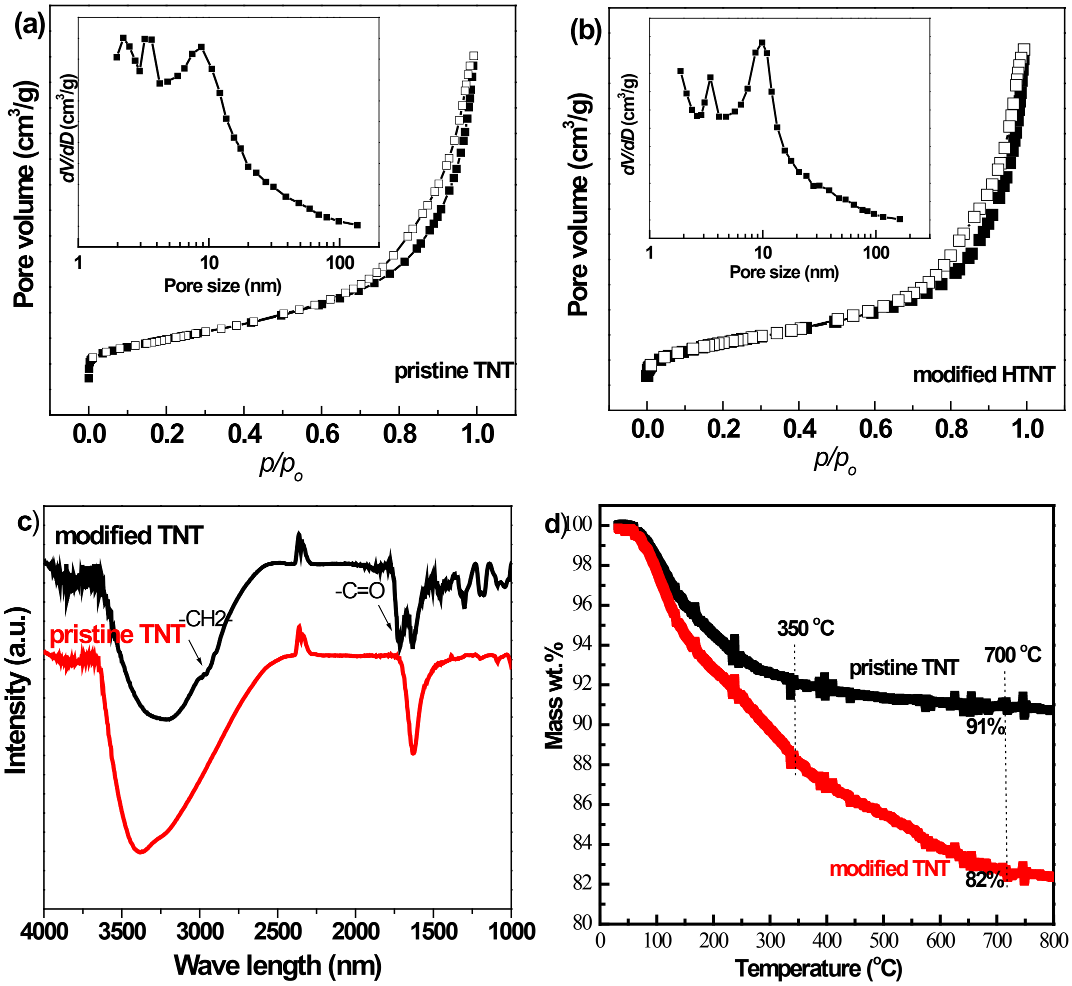

Fig. S1 Nitrogen-sorption curves with inset pore-size distribution plots (a–b), FTIR patterns (c), and TG curves (d) of pristine TNT and modified TNT.

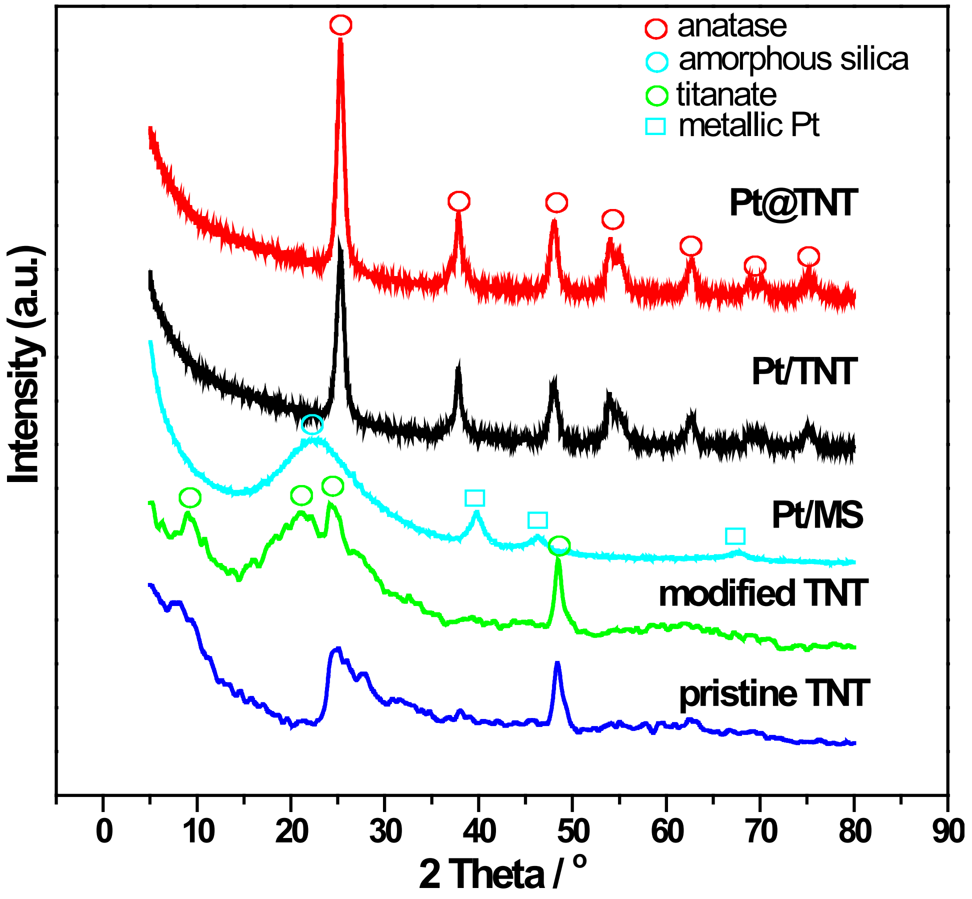

Fig. S2 XRD patterns of supports and catalysts

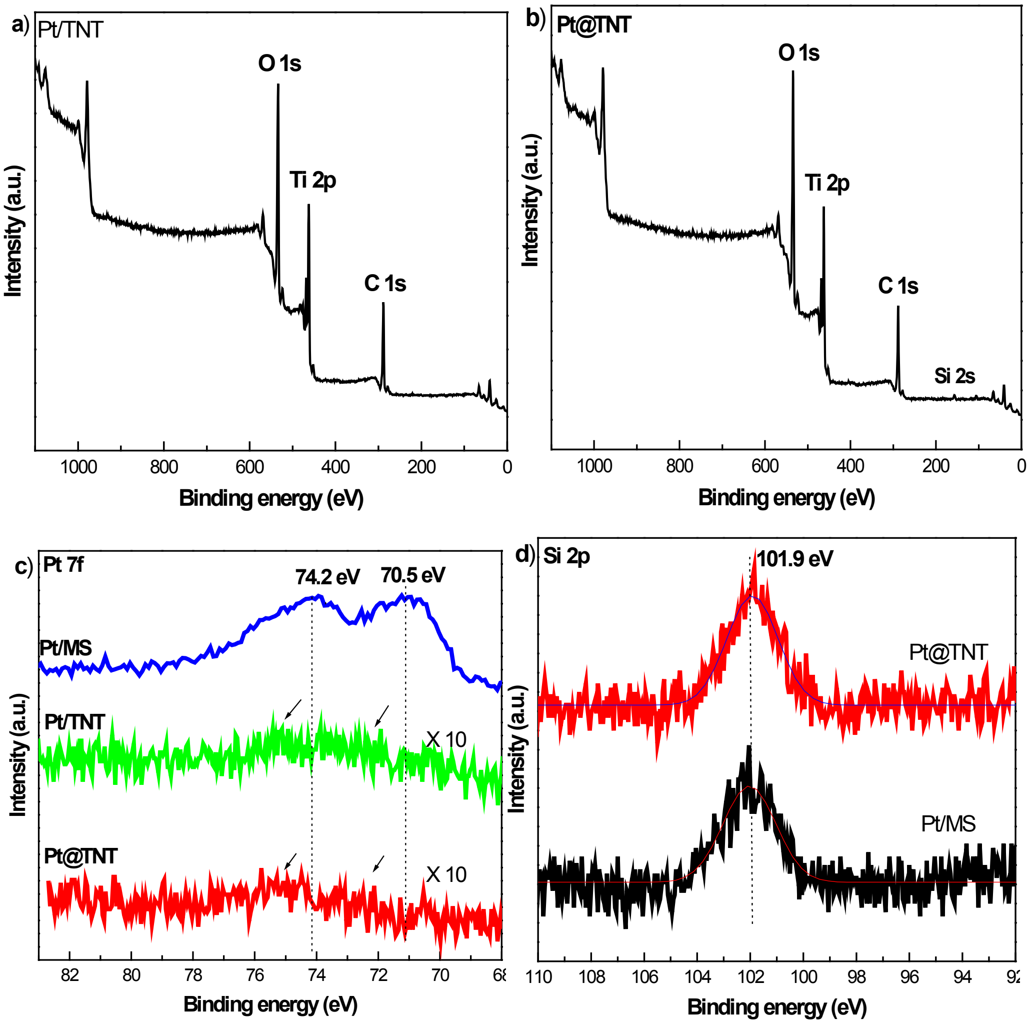

Fig. S3 XPS plots of various catalysts

Table S1 Specifications of different supports and catalysts

Sample	S_{BET} (m^2 g^{-1})	Pore size (nm)	Pore volume (cm^3 g^{-1})	[a]Metal content (wt.%)	[b]Metal particle size (nm)
TNT	344	9.5	0.38	-	-
Modified TNT	300	10	0.30	-	-
MS	813	3.7	0.87	-	-
Pt/TNT	287	9.4	0.31	1.0	3.6
Pt@TNT	290	10	0.30	0.95	2.8
Pt/MS	702	3.8	0.84	1.1	6.4

[a] Determined by ICP.

[b] Observed from TEM images, except for Pt/MS, which was determined from the XRD pattern using Jada software.

Reference

1. X. Sun and Y. Li, *Chemistry-A European Journal*, 2003, **9**, 2229-2238.
2. X. Yang, L. Du, S. Liao, Y. Li and H. Song, *Catalysis Communications*, 2012, **17**, 29-33.