

Mesoporous Ti-W oxide: synthesis, characterization, and performance in selective hydrogenolysis of glycerol

Yanhua Zhang,^{a,b} Xiao-Chen Zhao,^a Yao Wang,^a Likun Zhou,^a Junying

Zhang,^a Jia Wang,^a Aiqin Wang,^a and Tao Zhang^{a*}

^a*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, Dalian 116023, China;*

Fax: +86-411-84691570; Tel: +86-411-84379015.

^b*Key Laboratory of Green Chemical Technology and High Efficient Energy Saving of
Hebei Province, Hebei University of Technology, Tianjin 300130, China.*

Corresponding author: Tao Zhang

e-mail: taozhang@dicp.ac.cn

Electronic Supplementary Information

Characterization:

Nitrogen adsorption–desorption measurements were performed at $-196\text{ }^{\circ}\text{C}$ with a Micromeritics ASAP2010 instrument. Prior to the measurements, the samples were degassed at $200\text{ }^{\circ}\text{C}$ for at least 4 h. The specific surface areas (S_{BET}) were calculated from the N_2 adsorption isotherm with BET equation. The total pore volumes (V_{p}) were taken at the $P/P_0 = 0.995$. The average pore diameters (D_{p}) and pore size distributions (PSD) were estimated from the adsorption branches of the isotherms based on the Barrett-Joyner-Halenda (BJH) model.

Powder X-ray diffraction (XRD) patterns were collected on a PW3040/60 X' Pert PRO (PANalytical, Inc.) diffractometer equipped with a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.15432\text{ nm}$). A continuous mode was used for collecting data in the 2θ range from 0.65 to 5° operating at 40 kV , 30 mA (low angle) and from 10 to 80° operating at 40 kV , 40 mA (wide angle).

Transmission electron microscopy (TEM) images were obtained on a Tecnai G² Spirit FEI Transmission Electron Microscope and a JEOL 2000EX electronic microscope operating at 120 kV . The samples for TEM were prepared by directly dispersing the fine powders of the products onto a micro-grid carbon polymer supported on a copper grid. The high resolution transmission electron microscopy (HRTEM) images were obtained with Tecnai G² F30 S-Twin Transmission Electron Microscope, operating at 300 kV .

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on a Setaram Setsys 16/18 thermogravimetric analyzer (France). The curves were recorded in flowing air with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ up to $800\text{ }^{\circ}\text{C}$.

The acid properties (strength and concentration) were determined by temperature-programmed desorption of NH_3 (NH_3 -TPD) using a micromeritics Autochem II 2910 chemisorber equipped with a thermocouple detector (TCD) and a quadrupole mass spectrometer. The samples (0.1 g) were loaded in a quartz tube microreactor supported by quartz wool, degassed at $200\text{ }^{\circ}\text{C}$ for 1 h in flowing helium ($20\text{ mL}/\text{min}$), and cooled down to $100\text{ }^{\circ}\text{C}$ ready for measurements. NH_3 adsorption was performed at $100\text{ }^{\circ}\text{C}$ using pulse model. After adsorption saturation, an initiation of heating rate at $10\text{ }^{\circ}\text{C}/\text{min}$ from $100\text{ }^{\circ}\text{C}$ to $900\text{ }^{\circ}\text{C}$ was carried on in a helium flow of $30\text{ mL}/\text{min}$, during which the desorbed NH_3 was monitored by a mass spectrometer system. In the measurement, $m/e = 16$ was monitored to analyze the desorbed NH_3 . This mass number was used instead of $m/e = 17$ to prevent the interference caused by water.

Pyridine adsorption Fourier transform infrared (FT-IR) spectroscopic measurements were used to determine acid types. FT-IR spectra were measured with a Bruker Equinox 55 spectrometer, which is equipped with an extended KBr beam splitting device and a deuterated triglycine sulphate (DTGS) detector, in the absorbance mode with a resolution of 4 cm^{-1} . The samples were pressed into self-supporting disks and loaded into a quartz IR cell with CaF_2 windows. To remove physisorbed water, the sample was pretreated at $200\text{ }^{\circ}\text{C}$ for 30 min in vacuum and then was recorded a background spectrum at room temperature. Then pyridine was introduced into the system and adsorbed on the acid sites. FTIR spectrum of the samples was recorded at room temperature again, after an evacuation at $200\text{ }^{\circ}\text{C}$ for 10 min. The final IR spectra were obtained by subtracting the background spectrum.

Temperature-programmed reduction (TPR) was carried out on an AutoChem II 2910

chemisorber using 5% H₂ diluted with N₂ (50 mL min⁻¹). 0.05 g of catalyst was programmed heated from -40 °C to 800 °C at a ramping rate of 10 °C min⁻¹. The H₂ and CO chemisorption uptakes of the Pt/Ti₈₀W₂₀-500 catalyst were measured on the same instrument. Prior to pulse chemisorption, the sample was pretreated in H₂ at 180 °C for 1 h to remove the oxide layer on the surface. Both the H₂ and CO pulse chemisorptions were measured at 50 °C under atmospheric pressure.

EPR spectra were recorded at -173 °C with a Bruker EMX spectrometer working in the X-band (9.53 GHz). The powdered samples, without any pretreatment, were placed in the EPR silica tube (i.d. 4 mm) in a weighed amount to fill the resonant cavity completely.

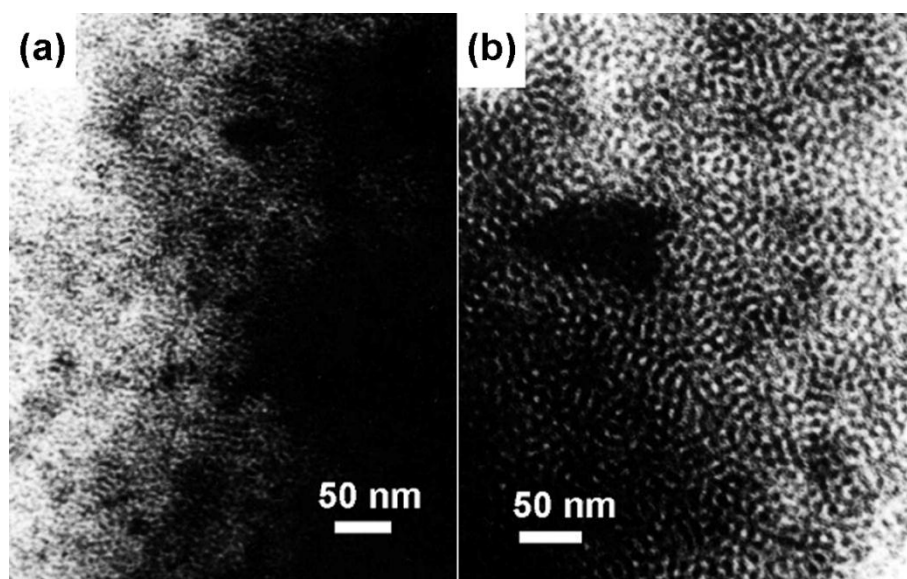


Fig. S1 TEM images of (a) Ti₉₀W₁₀-400 and (b) Ti₈₀W₂₀-400 obtained without the addition of extra HCl.

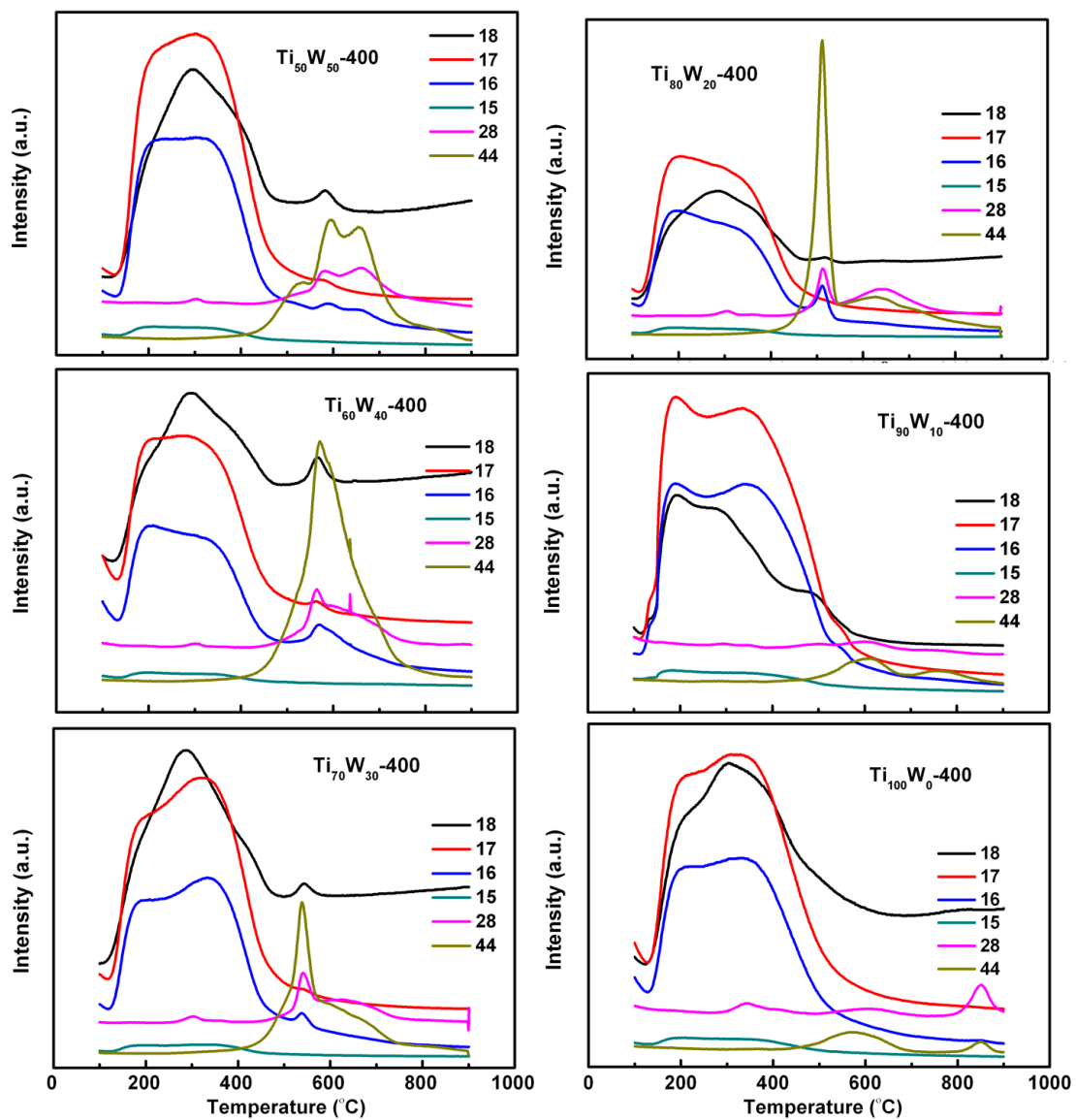


Fig. S2 On-line mass spectrometer signals detected during NH₃-TPD

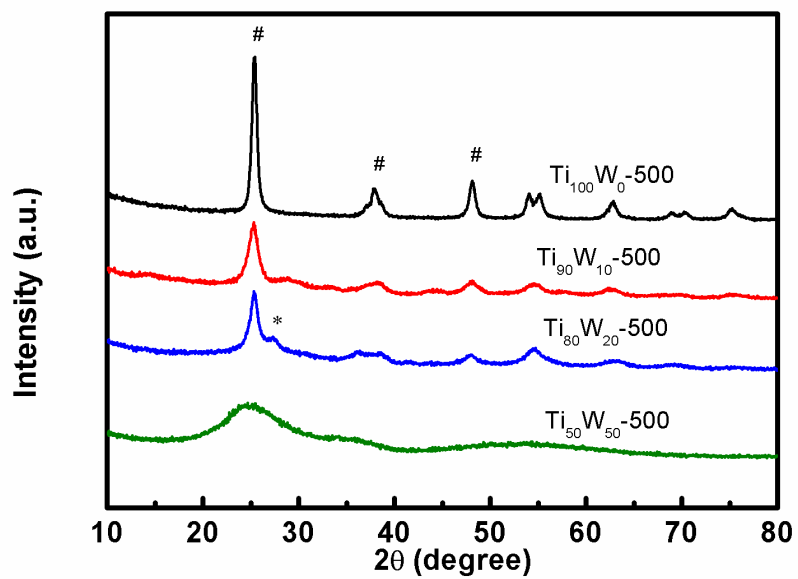


Fig. S3. Wide-angle XRD patterns of mesoporous Ti_{100-n}W_n-500

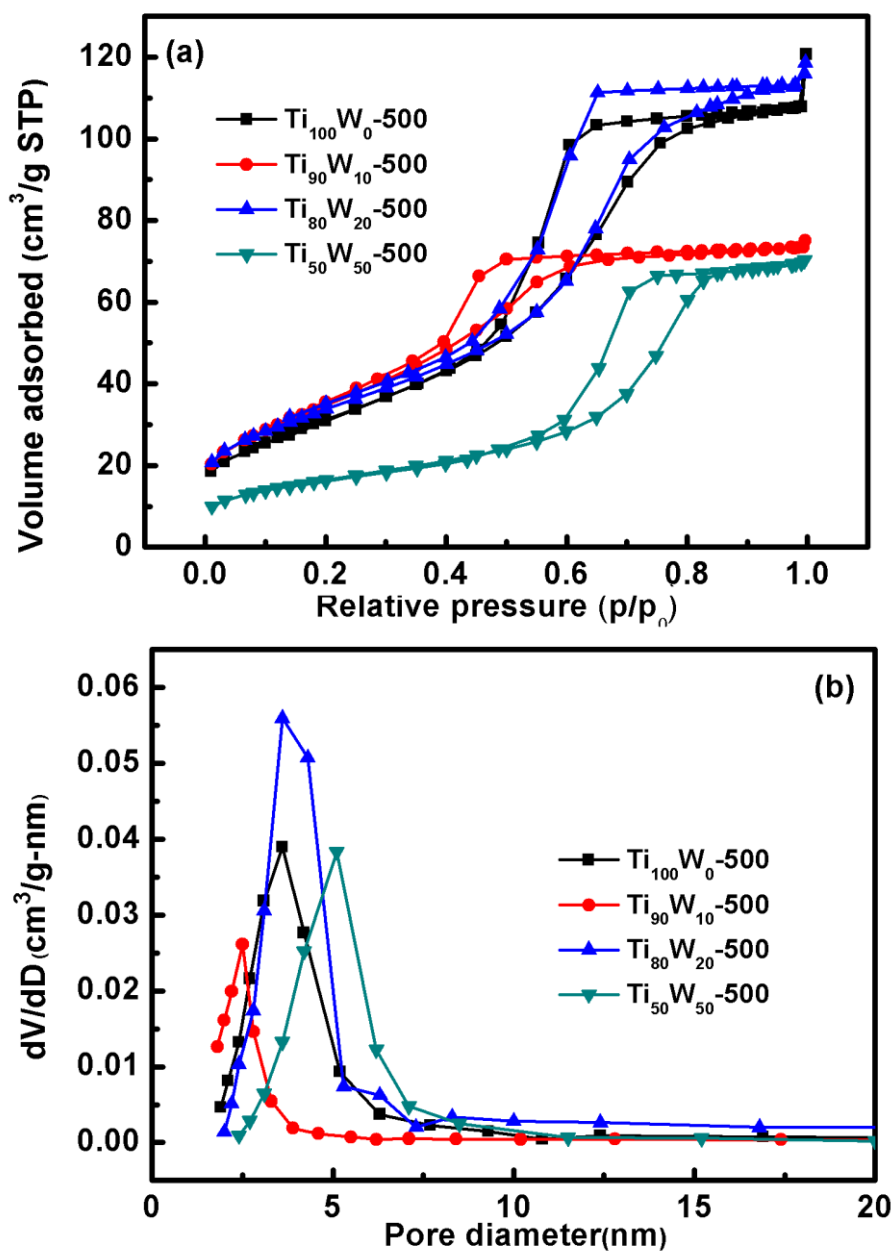


Fig. S4. (a) Nitrogen adsorption isotherms and (b) the corresponding PSD curves for Ti_{100-n}W_n-500 (n = 0, 10, 20, 50).

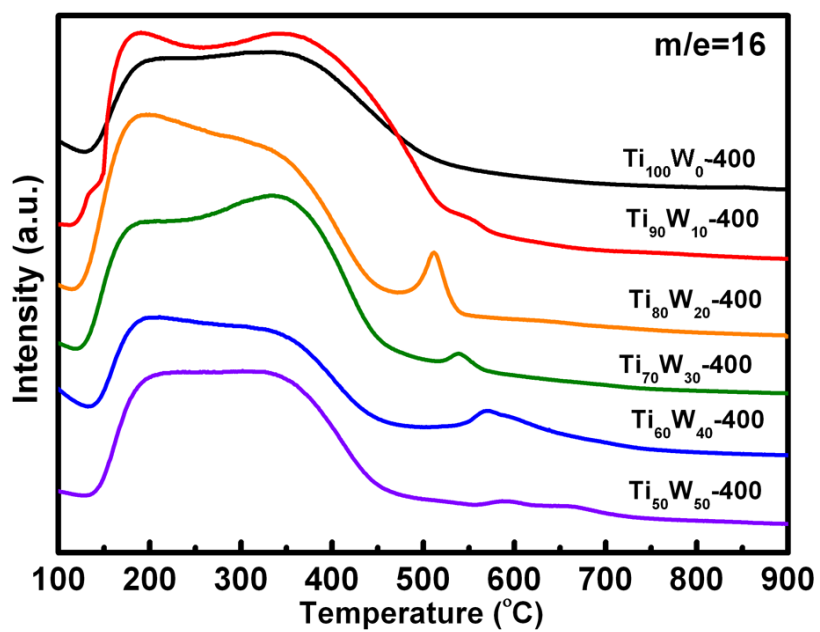


Fig. S5. NH_3 -TPD ($m/e=16$) curves of $\text{Ti}_{100-n}\text{W}_n$ -400s