

Electronic Supporting information:

Evaluation of Molecular Poisoning Phenomenon of W Sites in Microporous Materials by Synchrotron X-ray Powder Diffraction

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Materials and Methods:

1 Materials

1.1 H-ZSM-5 pretreatment

H-ZSM-5 (Al:Si=1:19.25) was supplied from Sinopec, China. The elemental analysis of the solid samples was performed using inductively coupled plasma-atomic emission spectroscopy (P-4010/ICP-AES). The sample was calcined in air at 480 °C for 2 h with a ramp rate of 1 °C min⁻¹ before use. In addition, the BET surface area of H-ZSM-5 is 330 m² g⁻¹.

1.2 W modified ZSM-5 sample

W/ZSM-5 was prepared by wet impregnation. Typically, 583mg ammonia metatungstate hydrate ((NH₄)₆H₂W₁₂O₄₀·xH₂O) was dissolved in 20 mL deionized water before 5 g zeolite was added to the solution. After 1 h magnetic stirring, the dispersion was dried in an 80 °C oven overnight. The resulting powder was ground and calcined at 550 °C for 2 h in air. The heating rate was 1 °C min⁻¹.

1.3 W-carbene/ZSM-5 and cis-stilbene adsorbed W/ZSM-5 samples

W-carbene/ZSM-5 was prepared by placing W/ZSM-5 in a flowing stream of 2-butene (2% 2-butene in N₂, 1 bar) at 400 °C for 1 h. The flow rate was 50 ml min⁻¹.

The W/ZSM-5 was heated at 200 °C for 2 hours in vacuum in a round bottle, which pre-attached to a schlenk line in order to remove trace moisture before the cis-butene adsorption. The sample was then exposed to cis-stilbene vapour for 30 minutes at room temperature.

1.4 Catalytic performance evaluation

The reaction between ethene (C₂⁺) and *trans*-2-butene (*trans*-2-C₄⁺, $n(\text{C}_2^+)/n(\text{trans-2-C}_4^+) = 2/1$) was carried out in a stainless steel continuous flow reactor (3/8 inch ID and 15 inch length).

In a typical experiment, 2.1 g catalyst (15–20 cm length) was loaded into the reactor with quartz wool packed at both ends. The catalyst was pretreated in N₂ (16 ml min⁻¹) at 550°C for 1 h. After the reactor cooled down to the reaction temperature, the reactants, 4% C₂⁼/N₂ and 2% *trans*-2-C₄⁼/N₂, were introduced (105 ml min⁻¹ each, WHSV = 0.27 h⁻¹, GHSV = 26–35 h⁻¹). The flow rates were controlled by Brooks mass flow controllers. The reaction temperature was controlled by a custom-made furnace. The reaction pressure was controlled by a Swagelok back pressure regulator. The products were analyzed online by a Shimadzu GC-2014 gas chromatograph equipped with a SGE BP-1 column (100% dimethyl polysiloxane, 30 m length, 0.53 mm ID, 5.0 μm film thickness) and an FID detector. The *trans*-2-butene conversion, propene selectivity, and carbon balance were calculated as follows:

$$\text{Conversion}(trans - 2 - C_4^=) = \frac{n(trans - 2 - C_4^= \text{ in feed}) - n(trans - 2 - C_4^= \text{ remaining})}{n(trans - 2 - C_4^= \text{ in feed})}$$

$$\text{Selectivity}(C_3^=) = \frac{n(C_3^=)}{n(\text{all products})}$$

$$\text{Carbon balance} = \frac{n(C) \text{ in products}}{n(C) \text{ in feed}}$$

2 Laboratory characterization

2.1 Transmission electron microscopy (TEM)

The morphology and microstructure were examined by transmission electron microscopy (TEM) using a JEOL 3000F microscope. TEM specimens were prepared by pipetting 5 μl of the sample dispersion in ethanol onto holey carbon-coated copper mesh grids (400 meshes).

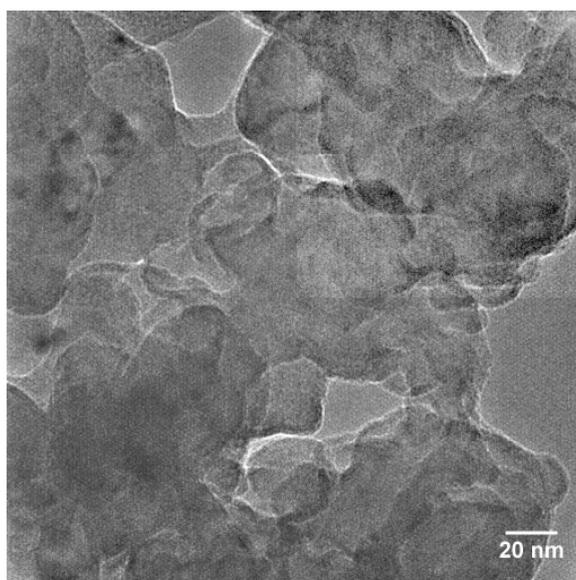


Fig. S1. TEM images of W/ZSM-5.

Figure S1 shows neither detectable WO_x clusters nor WO_3 nanoparticles, indicating WO_x are well dispersed over ZSM-5 catalyst.

2.2 Raman

Raman spectra were measured using a Horiba Jobin Yvon LabRAM HR800 spectrometer with laser excitation at 532 nm (2.33 eV). Measurements were taken with 5 s exposure. The Raman spectrometer was calibrated using a silicon standard beforehand.

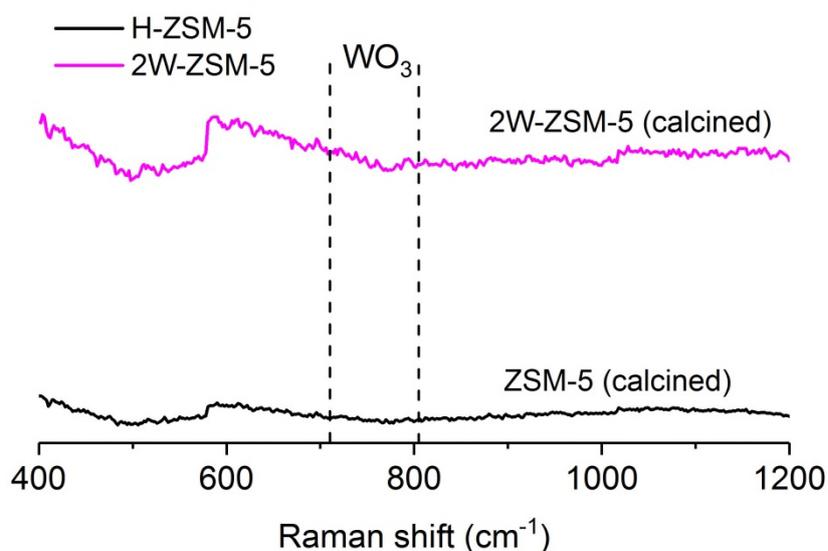
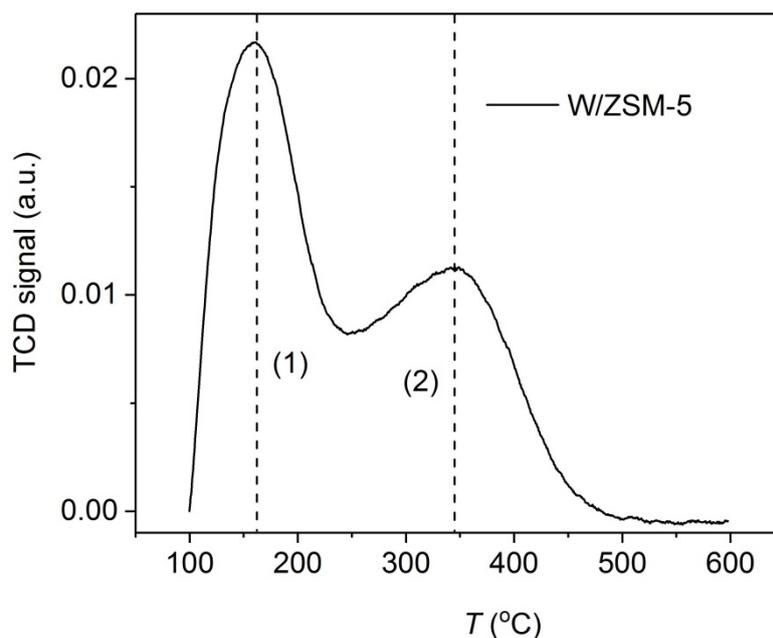


Figure S2. Raman spectra of W/ZSM-5 and H-ZSM-5

It is well-reported that Raman peaks attributable to O–W(–O) of WO_3 crystals at around 710 and 810 cm^{-1} with the assigned W–O–W vibrations in the range from 200 to 300 cm^{-1} , which are not seen in W/ZSM-5. That means that there is no polymerization of monotungstate at 8 wt% W loading.

2.3 Temperature-programmed desorption of NH_3 (NH_3 -TPD)

Temperature-programmed desorption of NH_3 (NH_3 -TPD) was performed on a Micromeritics AutoChem II 2920 to evaluate the acidity of the catalysts. Prior to NH_3 adsorption at 100 $^\circ\text{C}$, the catalysts were heated at 600 $^\circ\text{C}$ under N_2 (30 ml min^{-1}) for 40 min with a heating rate of 10 $^\circ\text{C min}^{-1}$ so that all the adsorbed and undesired species were removed from the surface. After 30 min NH_3 adsorption (10% NH_3/He , 30 ml min^{-1}), NH_3 was switched to N_2 (30 ml min^{-1}) for 30 min to remove the physisorbed NH_3 . The analysis was conducted with He (50 ml min^{-1}) as the carrier gas in the temperature range of 100–600 $^\circ\text{C}$ with a heating rate of 10 $^\circ\text{C min}^{-1}$.



Peak	T (°C)	$n(\text{NH}_3)$ (mmol/g)
(1)	160	0.65
(2)	349	0.47

Fig. S3. NH_3 -TPD of W/ZSM-5

3 Synchrotron X-ray diffraction (SXR D)

High-resolution SXR D data were collected at beamline I11, Diamond Light Source, Harwell, UK. The energy of the incident X-ray was set at 15 keV. The wavelength and the 2θ zero point were determined by fitting the diffraction data of high-quality silicon powder (SRM640c). Before data collection, W/ZSM-5 were treated under vacuum at 300 °C for 2 h. Adsorbed water should have been removed completely. W-carbene/ZSM-5 and cis-stilbene adsorbed W/ZSM-5 were prepared as described previously. All samples were loaded into borosilicate glass capillaries (0.7 mm ID) in a glove box. Glass wool was packed on top of the sample. The SXR D data were collected in a Debye-Scherrer geometry using multi-analyzer crystals (MAC) detectors in the 2θ range of 0–150° with 0.001° data binning. Each data set was collected for 1 h for good statistics.

Rietveld refinement was performed using TOPAS-Academic. ZSM-5 zeolite starting model is obtained from reference from Heo et al¹. All SXR D peaks appear at below $2\theta = 55^\circ$, thus data at 3–55° were used for Rietveld refinement. In total, there are 4186 hkl reflections measured within this 2θ range, of which at least 300 independent ones were observed. From a mathematical perspective, the number of variables should not exceed the number of observables. In the Rietveld refinement performed in this work, the number of varied structural parameters has not exceeded 300. Thus, the resulting crystallographic models are reliable. The background was described by a shifted Chebyshev function. A Thompson-Cox-Hastings pseudo-Voigt peak function was used to describe the shape of diffraction peaks. The scale factor and lattice parameters were allowed to vary at all times. Refined structural parameters include the fractional coordinates (x , y , z), isotropic displacement factors (B_{eq}), site occupancy factors (SOFs), the translation and rotation of the axes of the rigid bodies describing the guest molecules within the zeolite framework. The rigid bodies were described by Z-matrix. The quality of the refinement was assured by a small weighted-profile R -factor (R_{wp}), a small goodness-of-fit (GOF) factor and