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Supporting Information

Modified Mn/ZSM-5 for Non-thermal Plasma Mineralization of VOCs and DFT Simulation Using a Novel Y-type ZSM-5 Model

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1. Catalysts Characterization

1.1. Details of X-ray Diffraction Tests

The X-ray diffraction (XRD) experiments were performed on diffractometer equipment (Bruker, D8 Advance, Germany) in the 2θ range of 5–90 °C with Ni-filtered Cu K Alpha radiation (λ = 0.15418 nm, 40 kV, 40 mA). The XRD phases were identified by comparison with the reference data from Joint Committee on Powder Diffraction Standards (JCPDS) data files.

1.2. Details of N_2 Adsorption-desorption Tests

The N_2 adsorption-desorption isotherms were obtained at −196 °C on a surface area analyzer (Micromeritics, ASAP2020, Norcross, GA, USA). The surface area was estimated by the BET method. The pore size distribution, average pore diameter, and total pore volume were calculated by the BJH method. The samples were outgassed at 100 °C in vacuum for 4 h in pretreatment.

1.3. Details of Scanning Electron Microscope

The morphologies and structure of the catalysts were recorded by a Scanning electron microscope (SEM, ZEISS MERLIN Compact, Jena, Germany) equipped with an energy-dispersive X-ray spectrometer.

1.4. Details of X-ray Photoelectron Spectroscopy Tests

An X-ray photoelectron spectroscopy (XPS) spectrometer (ESCALAB 250XI, Thermo Fisher Scientific, Waltham, MA, USA) equipped with a monochromatic Al K Alpha X-ray source was employed to evaluate the elemental ionic states.

1.5. Raman Spectra

Raman spectra were carried out on a confocal laser micro-Raman spectrometer (Oceanoptics, Raman micro IM-52, Shanghai, China) with laser light of 785 nm.

1.6. Details of H_2 Temperature Programmed Reduction (H_2-TPR)

The H_2-TPR was also performed on the DAS-7000 Chemisorption Analyzer. The sample dosage and pretreatment method were the same as the O_2-TPD procedure. In the process of sample reduction, 5% H_2/N_2 mixture gas was introduced to the reactor and the sample was heated to 850 °C at a flow rate of 8 °C/min.

2. Gas Detection Conditions

Gas samples from the outlet were analyzed online by a gas chromatograph (SHIMADZU Chromatograph, GC-2014C, Kyoto, Japan) equipped with a flame ionization detector, which was for organic compounds detection with a 30 m Rtx-1701 capillary column. A TCD detector was used for carbon dioxide analysis with a 4 m TDX-01 stainless steel column, and a flame ionization detector was used for measuring toluene concentration. The column temperature is 200 °C, the temperature of the flame ionization detector is 220 °C, and the temperature of the TCD detector is 200 °C.

3. Computational Details

All calculations in this work are performed using the CASTEP code, which is based on density functional theory (DFT) calculations with the plane-wave pseudopotential method. Perdew–Burke–Ernzerhof (PBE) functional in the generalized gradient approximation (GGA) is chosen to describe the exchange-correlation potential [1]. The Tkatchenko and Scheffler (TS) scheme is used to correct for the influence of van der Waals (vdW) forces [2]. The plane-wave energy cutoff is set to 480 eV with 1×1×1 Monkhorst-pack k-points grid. The tolerance of self-consistent calculation is set as 5.0×10^{-5} eV/atom. The maximum displacement below 0.05 Å and maximum force on atoms below 0.5 eV/Å are set as the convergence thresholds in geometry optimization.

4. Supplementary Table S1–S2

Table S1. The size parameters of the DDBD reactor.

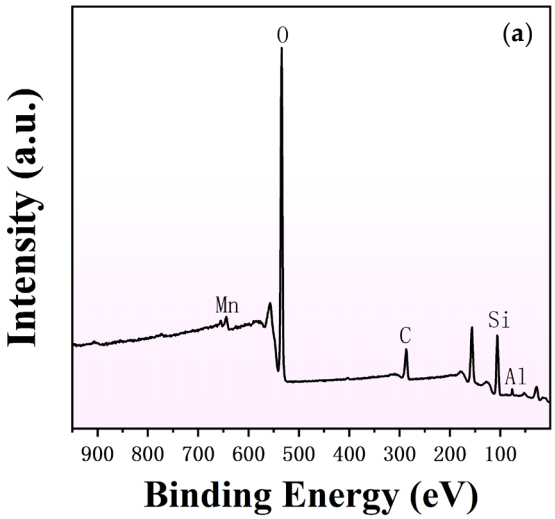
	Length (mm)	Outer Diameter (mm)	Inner Diameter (nm)
exterior dielectric	300	25	20
interior dielectric	300	12	7.5
high voltage electrode	150	—	—
grounded voltage electrode	300	—	—

The cylindrical DDBD reactor contains two layers of crystalline silica dielectric (both 300 mm in length): the exterior one (outer diameter of 25 mm and inner diameter of 20 mm) and interior one (outer diameter of 12 mm and inner diameter of 7.5 mm), resulting in an effective discharge gap of 4 mm. The length of the high-voltage electrode outside the exterior dielectric is 150 mm, while the grounded electrode inside the interior dielectric has a length of 300 mm, resulting in a 150 mm effective discharge length.

Table S2. Correspondence between diffraction angles and related facets.

Diffraction angle	Related Facet
7.9°	{101}
8.9°	{020}
13.9°	{102}
15.5°	{131}
15.9°	{202}
19.3°	{312}
20.4°	{103}
20.9°	{421}
23.2°	{501}
23.9°	{303}
24.5°	{133}
25.9°	{432}
29.8°	{630}
45.0°	{804}

5. Supplementary Figure S1–S2



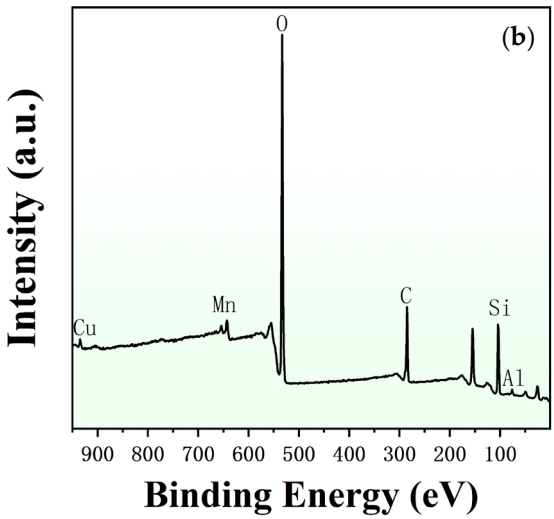


Figure S1. Survey photoemission features from XPS results of samples: (**a**) Mn/ZSM-5 and (**b**) Mn/ZSM-5-D

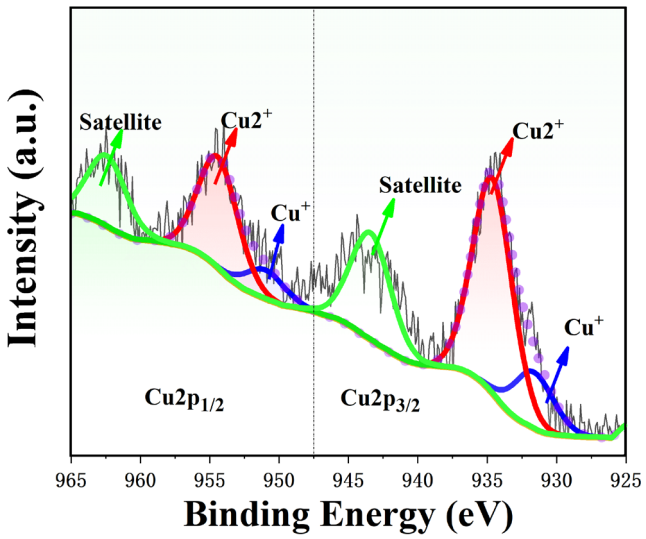


Figure S2. Cu 2p photoemission features from XPS results of Mn/ZSM-5-D.

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