

## Electronic supplementary information

The critical roles of hydrophobicity, surface Ru<sup>0</sup> and active O<sub>2</sub><sup>-</sup>/ O<sub>2</sub><sup>2-</sup> sites played for toluene combustion on Ru/ZSM-5 with varied Si/Al ratios

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## 1. Supplementary Experimental Information

### 1.1 Catalyst characterization

The Powder X-ray diffraction (XRD) was carried out on an X-ray diffractometer manufactured by Beijing Puji, with a tube voltage of 40 kV and a tube current of 30 mA, using a CuK $\alpha$  radiation source. The scanning  $2\theta$  range is  $10^\circ - 90^\circ$ , and the scanning step is  $2^\circ \text{ min}^{-1}$ .

X-ray Photoelectron Spectroscopy (XPS) tests were performed with a PerkinElmer PHI1600 system using a single MgK $\alpha$  X-ray source operated at 300 W and 15 kV voltage. The spectra were collected at room temperature with an ultra-high vacuum. The binding energies were calibrated by using the C 1s peak of graphite at 284.6 eV as a standard.

EPR technique has been used to measure the catalysts. The catalysts were pretreated in 100 Torr oxygen at  $750^\circ\text{C}$  for 1 h and then cooled down to room temperature, which was followed by evacuation and then placed in liquid nitrogen of 77K prior to record the EPR signals. Afterwards, the EPR spectra were recorded with a JEOL FA-200 EPR Spectrometer, operating with a field modulation of 100 kHz and microwave frequencies of 9067.558 MHz.

The specific surface areas of the samples were measured by N<sub>2</sub> adsorption-desorption at 77 K on ASAP 2020 instrument. Specific surface areas were calculated using Brunauer-Emmett-Teller (BET) method in the relative pressure ( $p/p_0$ ) range of 0.05-0.25. The pore size distributions of samples were calculated with the cumulative pore volume. The average pore sizes were obtained from the peak positions of the distribution curves. Total pore volumes were accumulated at a relative pressure of  $P/P_0 = 0.99$ .

ICP experiments were conducted on Agilent 700 system to verify the element compositions of the catalysts.

Hydrogen temperature programmed reduction (H<sub>2</sub>-TPR) was performed on the FINESORB 3010C automatic temperature programmed chemical adsorption instrument of Zhejiang Fantai. The amount of catalyst used in the test was 50 mg. First, the catalyst was pretreated in the Ar atmosphere at  $120^\circ\text{C}$  for 30 min and then cooled to room temperature. The treatment gas is switched to a 10% H<sub>2</sub>/Ar mixture. After the baseline is stabilized, the catalyst bed is raised from room temperature to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ , and the tail gas enters the thermal conductivity detector (TCD) to test and record the results of the experiment.

Toluene temperature programmed desorption (Toluene-TPD) was performed on the DAS-7000 temperature programmed chemical adsorption instrument of HUASI. Typically, 50 mg catalyst was pretreated in a 30 mL/min high purity Ar flow at  $400^\circ\text{C}$  1h to remove any possible impurities and H<sub>2</sub>O. Afterwards, the sample

was cooled to 50 °C and adsorb toluene for 1h was followed by purging with a 30 mL min<sup>-1</sup> 99.99% Ar flow to remove any physically absorbed toluene for 30 min. After all these pretreatments, the catalyst was heated from 50 to 800 °C with a rate of 10 °C min<sup>-1</sup>. A TCD was employed to monitor the toluene desorption.

Thermo gravimetric (TGA-DSC) analyses were performed on a STD-Q600 from T A. Each sample was heated between 30 and 500 °C (10 °C min<sup>-1</sup>) under air flow (30 mL min<sup>-1</sup>).

*In-Situ* DRIFTS experiments were carried on a Bruker Vertex equipped with an MCT detector chilled in liquid nitrogen. A micro-size *In Situ* DRIFTS furnace equipped with KBr windows was used. 100 mg powder sample was pretreated at 450 °C for 30min in a high purity 30 mL min<sup>-1</sup> Ar flow and then cooled target temperature. At this stage, the background spectra were collected at a resolution of 4 cm<sup>-1</sup> by accumulating 64 scans in a 30 mL min<sup>-1</sup> Ar flow. All the spectra exhibited in this study were achieved by subtracting the corresponding background spectrum. The spectra were recorded continuously for each series of *in-situ* experiments until the reaction reached equilibrium in a desired gas feed, which is about 2 min.

## 1.2 Activity evaluation

The catalysts were evaluated for toluene deep oxidation in a quartz tube (ID=6 mm) reactor with a continuous flow over 0.05g catalyst fix the same weight silica sand. Typically, 0.3-0.4 mm catalyst particles were used for activity evaluation. A K-type thermocouple was placed inside the catalyst bed with the thermocouple head point touching the catalyst bed to monitor the reaction temperature accurately. To measure the light-off behaviors of the catalysts, all data were collected with increasing the temperature. The volume composition of the feed gas is 1000 ppm toluene +air. The flow rate is 30 ml min<sup>-1</sup>, which corresponds to a space velocity of 36,000 ml h<sup>-1</sup> g<sub>cat.</sub><sup>-1</sup>. The 1000 ppm toluene was generated by passing air flow through a bottle containing pure toluene that was chilled in an alcohol low-temperature isothermal bath controlled at -20.4 °C. The reactants and products were analyzed on-line on a SP7890 gas chromatograph equipped with a flame ionization detector (FID) and a TCD, using a SE-30 capillary column (15 m in length) for VOCs separation and a TDX-01 column (3 mm in diameter and 3 m in length) for the separation of O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub>. Before analysis, the reaction was stabilized at each temperature for at least 30 min to get steady state kinetic data. The flow rate of the H<sub>2</sub> carrier gas is 30 ml min<sup>-1</sup>. The selectivity for CO<sub>2</sub> in this study was above 100%, so we identified that the converted toluene at each temperature is completely oxidized.

The reaction rate ( $R_w$  and  $R_s$ ) is calculated with the following formula:

$$R_w = \frac{RF \cdot V\% \cdot X}{22.4 \cdot 60 \cdot m} (\text{mmol g}^{-1} \text{ s}^{-1})$$

$$R_s = R_w / S_{\text{BET}} (\text{mmol m}^{-2} \text{ s}^{-1})$$

RF: flow rate of the reaction gas.

V%: The concentration of Toluene (volume fraction) in the reaction feed.

X: Toluene conversion at a certain temperature.

m: Catalyst weight/mass.

$S_{\text{BET}}$ : The surface areas of the catalysts

## 2. Supplementary Results

### 2.1. Supplementary Figures

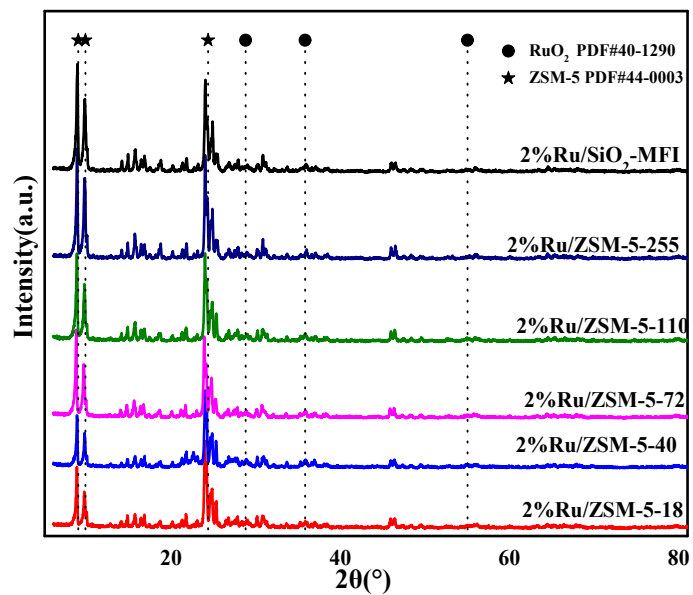
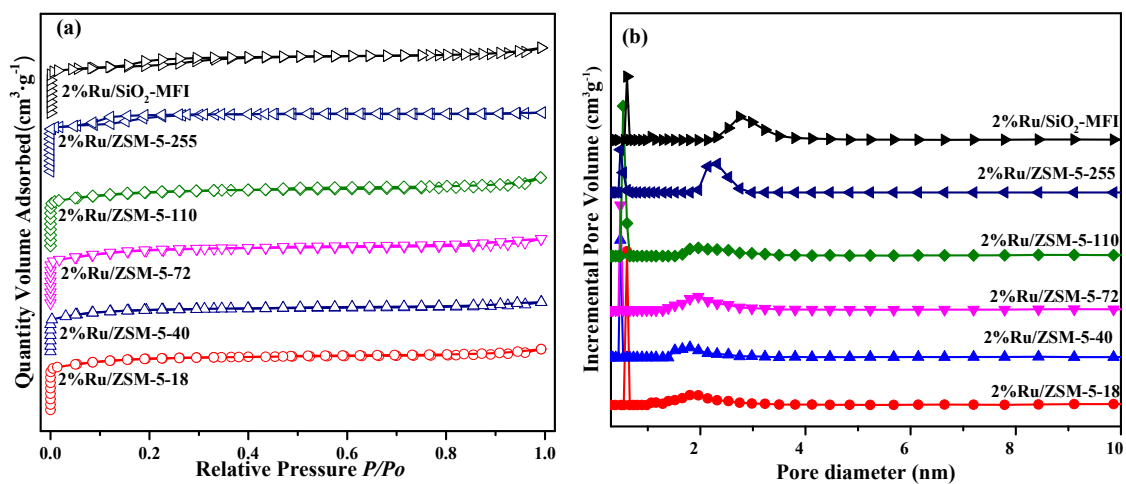
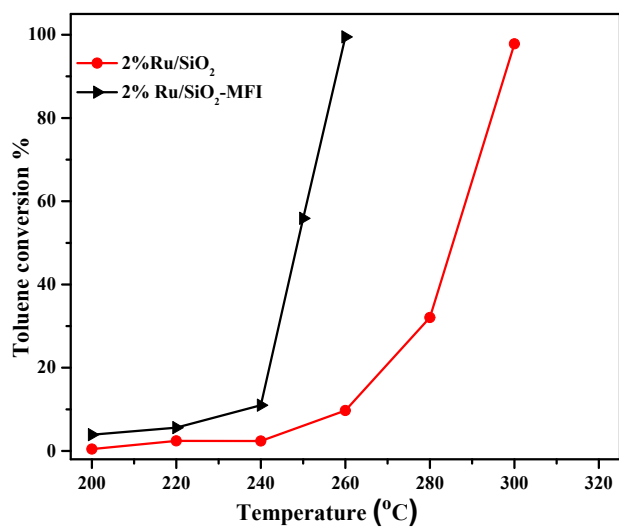


Fig. S1. The XRD patterns of the catalysts.



**Fig. S2.** (a)  $N_2$  adsorption-desorption isotherms of the catalysts (b) pore size distributions.



**Fig. S3.** Comparing the reactivity of 2%Ru/SiO<sub>2</sub>-MFI with 2%Ru/SiO<sub>2</sub>.

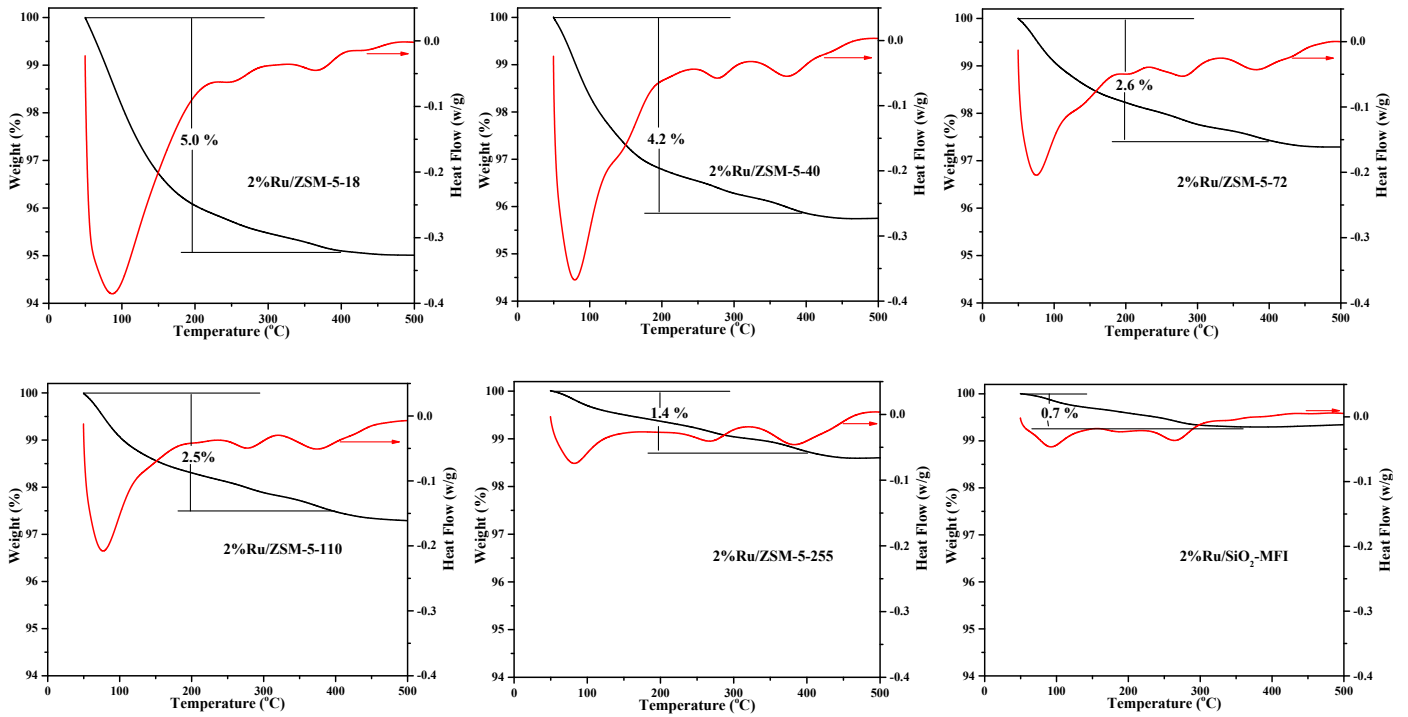


Fig. S4. TGA-DSC profiles of the catalysts.

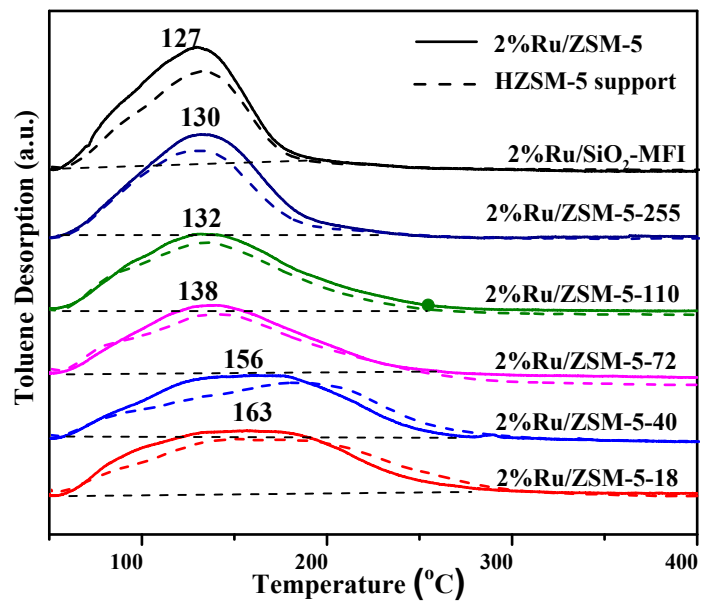
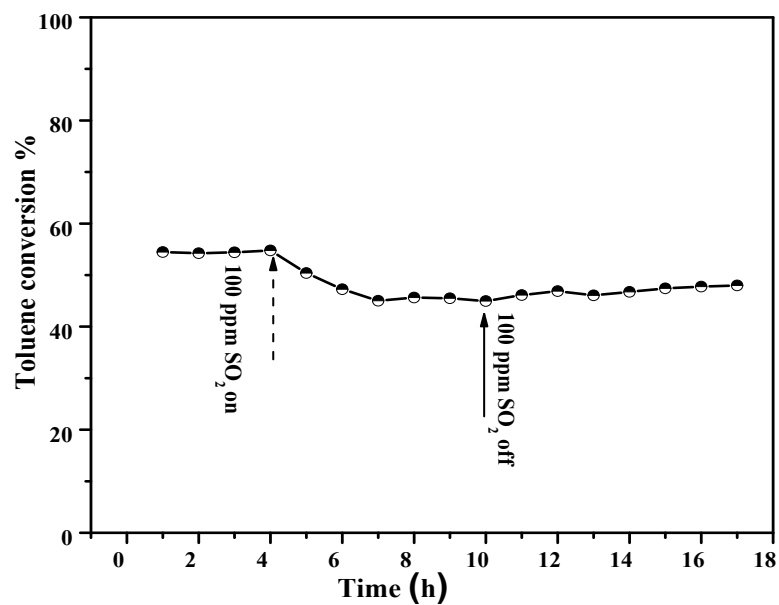


Fig. S5. Toluene-TPD results of the catalysts.



**Fig. S6.** Stability test of 2%Ru/SiO<sub>2</sub>-MFI in the presence of 100 ppm SO<sub>2</sub> at 250 °C

## 2.2. Supplementary Tables

**Table S1** Reaction Results of the catalysts.

Sample	T <sub>10</sub> (°C)	T <sub>50</sub> (°C)	T <sub>100</sub> (°C)
2%Ru/ZSM-5-18	270	293	320
2%Ru/ZSM-5-40	271	291	300
2%Ru/ZSM-5-72	258	282	290
2%Ru/ZSM-5-110	256	270	280
2%Ru/ZSM-5-255	243	256	270
2%Ru/SiO <sub>2</sub> -MFI	235	248	260

T<sub>10</sub>: 10% toluene conversion temperature

T<sub>50</sub>: 50% toluene conversion temperature

T<sub>100</sub>: 100% toluene conversion temperature