Supplementary Information

A supported Au/HZSM-5 catalyst for toluene removal by air plasma

catalytic oxidation using cycled storage-discharge (CSD) mode

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S1. Experimental section

S1.1 Materials

Chloroauric acid (HAuCl₄), >99.8%, (metals basis Au >49%) was purchased from Alfa Aesar. Silver nitrate (AgNO₃) was bought from Sinopharm Chemical Reagent Co., Ltd. Ammonia liquor (NH₃·H₂O) was purchased from Tianjin Kermel Chemical Reagent Co. Ltd. Commercial high-silica HZ molecular sieve (SiO₂/Al₂O₃ = 360, specific surface area of 341 m²/g) was provided by Nankai University Catalyst Co., Ltd.

High purity oxygen (O₂, \geq 99.999%), hydrogen (H₂, \geq 99.999%), and nitrogen (N₂, \geq 99.999%), argon (Ar, \geq 99.999%) were purchased from Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

S1.2 Catalysts characterization

The size and morphology of Au nanoparticles in the Au/HZ catalysts were observed using transmission electron microscopy (TEM-2100, JEOL Ltd., Japan). The elemental chemical composition and valence states of the Au catalyst were characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo VG, USA) using an Al K α target (hv = 1486.6 eV) as the X-ray source, with a tube voltage of 15 kV, power of 300 W, and a scanning step of 0.05 eV. The C1s peak position was calibrated to 284.6 eV as the reference for peak calibration. To confirm the presence of Au⁰ in the samples, UV-vis analysis of HZ and Au/HZ catalysts was conducted using a UV spectrophotometer (UV-2600, SHIMADZU, Japan) for diffuse reflectance spectroscopy (DRS) characterization, with a wavelength range of 200-800 nm. Hydrogen temperature-programmed reduction (H₂-TPR) is applied to analyze the Au^{$\delta+}$ </sup> species in Au/HZ using a chemisorption apparatus (Autochem II 2920, Micromeritics Instrument Corp.,

USA). Moreover, a CO-TPR experiment was also conducted on the Au/HZ catalysts under a 1400 ppm CO/He atmosphere using a mass spectrometer (Agilent 5975C, Agilent Technologies, USA) to investigate the Au^{δ^+} species.

Temperature-programmed-desorption (TPD) technology was applied to analyze C_7H_8 and CO adsorption ability on the catalysts. To determine the carbon balance of the reaction and the surface intermediates on the catalysts, temperature-programmed-oxidation (TPO) technology was adopted. The TPD and TPO experiments are described previously[1].

The adsorption characteristics of CO on the surfaces of the HZ, Au/HZ, and Ag/HZ catalysts were characterized by *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFT). A certain amount of the catalysts was placed in the DRIFT cell, pre-treated at 80 °C under Ar atmosphere for 30 min, then cooled to room temperature. After collecting the background, the atmosphere was switched to 5% CO/He for CO adsorption experiments, followed by infrared spectroscopy data collection.

S1.3 Measurement of the discharge parameters

Input power (P_{in}) is measured by using a wattmeter. The discharge voltage and frequency are measured by using an oscilloscope (DPO4108B, Tektronix) with a high-voltage probe (P6015A, Tektronix). Discharge power (P_{dis}) is calculated from a charge-voltage Lissajous figure measured by a sampling capacitor. At P_{in} of 7 W, P_{dis} in the dry and wet air is about 1.5 W.

S1.4 Definitions of C_7H_8 conversion, CO_x selectivities, carbon balance, and CO conversion C_7H_8 conversion $\begin{pmatrix} X_{C_7H_8} \end{pmatrix}$, CO selectivity (S_{CO}) , CO₂ selectivity $\begin{pmatrix} S_{CO_2} \end{pmatrix}$ for air plasma-catalytic oxidation of C_7H_8 are determined as follows:

$$X_{C_7H_8}(\%) = \left(1 - \frac{n_{C_7H_8}^{unconv}}{n_{C_7H_8}^0}\right) \times 100\%$$
(E1)

$$S_{CO}(\%) = \frac{n_{CO}^{alls}}{7(n_{C_7H_8}^0 - n_{C_7H_8}^{unconv})} \times 100\%$$
(E2)

$$S_{CO_2}(\%) = \frac{n_{CO_2}^{dis}}{7\left(n_{C_7H_8}^0 - n_{C_7H_8}^{unconv}\right)} \times 100\%$$
(E3)

 $n_{C_7H_8}^{0}$ and $n_{C_7H_8}^{unconv}$ are initial amount of C₇H₈ and unconverted C₇H₈, respectively. n_{C0}^{dis} and $n_{C0_2}^{dis}$ are amount of CO and CO₂ generated at discharge stage. n_{TP0}^{TC} is the amount of total carbon produced in TPO process after discharge stage. Therefore, carbon balance (B_C) can be defined as :

$$B_{C}(\%) = \frac{n_{CO_{2}}^{dis} + n_{CO}^{dis} + n_{TPO}^{TC}}{7n_{C_{7}H_{8}}^{0}} \times 100\%$$
(E4)

In this work, no C_7H_8 or other gaseous intermediates were detected in outlet of the reactor, indicating that C_7H_8 conversion attains 100%. Therefore, CO and CO₂ selectivity calculation formula for the plasma oxidation of gaseous C_7H_8 in simulated air are as follows:

$$S_{CO_2} = \frac{C_{CO_2}^{out}}{7C_{C_7H_8}^{in}} \times 100\%$$
(E5)

$$S_{CO} = \frac{C_{CO}^{out}}{7C_{C_7H_8}^{in}} \times 100\%$$
(E6)

S2. Supplementary figures



Fig. S1. CO_x selectivities of C_7H_8 oxidation in CSD mode over the 0.6 wt.% Au/HZ catalysts prepared by air plasma and thermal treatment. Thermal treatment conditions: 100 mL/min of simulated air, calcined at 200 °C for 2 h. Air plasma pretreatment conditions: P_{in} =7 W, 100 mL/min of simulated air, t_{dis} =20 min. Conditions of C_7H_8 oxidation with dry air plasma:

$$n_{C_7H_8}^0 = 23.2 \,\mu\text{mol}, P_{\text{in}} = 7.0 \,\text{W}, t_{\text{dis}} = 20 \,\text{min}, F = 100 \,\text{mL/min}.$$



Fig. S2 UV-vis DRS spectra of Au/HZ and HZ.



Fig. S3 C_7H_8 breakthrough capacities of HZ, Ag/HZ, and Au/HZ. Adsorption conditions: 100

mL·min⁻¹ of dry simulated air with 105 ppm of C_7H_8 , m_{cat}=0.20 g, 25 °C.



Fig. S4 (a) CO₂ concentration in TPO tests, (b) CO₂ produced in TPO and carbon balance (B_C) of Au/HZ catalysts with different Au loadings. Conditions: 100 mL·min⁻¹ of 10%O₂/Ar, 10

°C·min⁻¹.



Fig. S5 CO conversion of HZ, Ag/HZ (1.2 wt.%Ag) and Au/HZ (0.6 wt.% Au) at 100 °C.

Conditions: 100 mL·min⁻¹ of simulated air with 1030 ppm of CO, m_{cat} =0.20 g.

References

[1] A. Zhou, J. L. Liu, B. Zhu, X. S. Li and A. M. Zhu, *Chemical Engineering Journal*, 2022, 433, 134338.