Supplementary Information

Pt anchored in skeleton of rice husk directed ZSM-5 for excellent catalytic VOCs oxidation: Structure-activity relationship and environmental impact assessment

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Materials

Rice husk powder less than 30 mesh was purchased from Lianyungang, Jiangsu Province, $H_2PtCl_6 \cdot 6H_2O$ (AR, Pt≥37.5 %) was purchased from Aladdin Chemical Reagent Co., Ltd. $Al_2(SO_4)_3 \cdot 18H_2O$ (AR, ≥99.0 %), NaOH (AR, ≥96.0 %), TPABr (AR, 99 %) and HCl (AR, 35-38 %) were purchased from Sinopharm Chemical Reagent Co., Ltd.

Characterization and Catalytic evaluation

The prepared catalysts were characterized by techniques as follows: X-ray diffraction (XRD), N_2 adsorption-desorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), inductively coupled plasm (ICP), temperature-programmed desorption of NH_3 (NH_3-TPD), temperature-programmed desorption of C_7H_8 (C_7H_8-TPD), pyridine adsorption infrared spectrometry (Py-IR), X-ray photoelectron spectroscopy (XPS), in situ diffuse reflectance infrared Fourier spectroscopy (DRIFTs) and life-cycle assessment (LCA).

X-ray powder diffraction (XRD) analysis was performed on Bruker D8 Advance diffractometer with Cu-Kα radiation source in the range of 5-80°. N_2 adsorption-desorption measurements were carried out on the Micromeritics ASAP 2460 instrument at -196 °C and fresh samples were pretreated in vacuum at 120 °C for 2 h. The morphology of the prepared samples was studied by a scanning electron microscope (SEM, Hitachi Regulus 8100, Japanese). High-resolution transmission electron microscopy (HRTEM) and HAADF-STEM images were observed on a FEI Talos F200x microscope operating at 200 kV. The metal content of the samples was determined by Inductively coupled plasma (ICP) on Agilent 5110. Surface elemental valence and concentration were studied under monochromatic Al-Kα radiation (1,486.6 eV) source on Escalab 250 Xi XPS instrument.

NH_3 temperature-programmed desorption (NH_3-TPD), C_7H_8 temperature-programmed desorption (C_7H_8-TPD) and C_7H_8 temperature programmed surface

reactions (C_7H_8-TPSR) of the catalysts were carried out on a Micromeritics apparatus (AutoChem II 2920) connected with a mass spectrometer (Cirrus), where the NH_3, CO_2 and C_7H_8 signals were recorded with m/z =17, 44 and 92, respectively. For NH_3-TPD and C_7H_8-TPD, each 50 mg sample was firstly treated with 10 vol% NH_3/He (NH_3-TPD) and 500 ppm C_7H_8/Ar (C_7H_8-TPD) streams (30 mL/min) at 300 °C for 1 h, and then cooled down to room temperature, the atmosphere was switched to pure He (30 mL/min) and heated to 800 °C at a heating rate of 10 °C/min. For C_7H_8-TPSR, 50 mg of each sample was treated with 3 vol% O_2/He (30 mL/min) at 300 °C for 1 h and cooled down to room temperature. Then, the atmosphere was transferred to C_7H_8/Ar (30 mL/min) and the temperature was heated up to 800 °C at a heating rate of 10 °C/min.

Pyridine adsorption infrared spectrometry (Py-IR) and in situ diffuse reflection infrared Fourier transform spectra (in situ DRIFTs) were carried out to detect the acidity and the adsorbed species on the catalyst surface using a Thermo Scientific Nicolet iS10 equipped with Harrick Praying Mantis diffuse reflectance accessories and a high temperature reaction chamber.

For Py-IR, the catalyst was pretreated at 300 °C for 1 h in a gas flow of He to remove any adsorbed impurities, and then cooled down to 250, 200, 150, 100, 30 °C, respectively. The background spectrum was collected under each temperature. Afterward, He (15 mL/min) carrying Pyridine was introduced to the sample chamber and absorbed to saturation at 30 °C. Subsequently, the pyridine desorption was collected at 30-300 °C. At each temperature, the catalyst was exposed to a flow of He (30 mL/min) for 15 min, and then a series of IR spectra were collected.

For in situ DRIFTs, prior to each experiment, the catalyst was pretreated at 300 °C for 1 h in a gas flow of N_2 to remove any adsorbed impurities, and then cooled down to 100 °C. The background spectrum was collected under N_2 and automatically subtracted from the sample spectra. Afterward, 1000 ppm C_7H_8/N_2 (30 mL/min) was introduced for 1 min, and the catalyst was purged by N_2 for the next 2 min to remove adsorbed residuals on the catalyst surface. Subsequently, the reaction gas was switched to O_2 for

30 mL/min at 100 °C, and the DRIFTS spectra of the samples were collected at a specific time. After that, in situ DRIFTs of C_7H_8 oxidation over the catalyst were recorded at 100-175 °C. At each temperature, the catalyst was exposed to a flow of O_2 (30 mL/min) for 3 min followed by N_2 purging for another 2 min, and then a series of IR spectra were collected.

The life-cycle assessment (LCA) was applied using SimaPro 9.0 software and considered the entire life cycle of Pt/ZSM-5, from the extraction of raw materials to the final disposal. Then, an evaluation of the environmental impacts using the ReCipe 2016 Midpoint method was performed.

The activity for C_7H_8 total oxidation was measured in a continuous flow system in a fixed bed reactor at atmospheric pressure. Each Catalyst (100 mg, 30-80 mesh) with 200 mg quartz sand (30-80 mesh) was loaded in the quartz reactor. 1000 ppm C_7H_8/Air was purged into the reactor at a continuous flow 100 mL/min (WHSV = 60,000 mL/(h·g)). After reaching a stable flow, the reactants were passed through the catalyst bed and the temperature was increased from room temperature to 300 °C (5 °C/min). For catalytic activity tests and stability tests with water vapor, a certain fraction of H_2O (1 vol.%, 2 vol.%, 5 vol.%) was fed into the reaction system. The concentrations of the reactants and products were detected online by Agilent-8860 gas chromatograph equipped with a hydrogen flame ionization detector (FID) and a thermal conductivity detector (TCD). Toluene conversion ($X_{Toluene}$, %) was calculated using the following formula:

$$X_{Toluene}\ (\%) = \frac{C_{in}\ -\ C_{out}}{C_{in}} \times 100\%$$

C_{in} and C_{out} are toluene concentrations at the inlet and outlet of the feed flow, respectively.

The CO_2 selectivity (S_{CO2}, %) was defined as the ratio of toluene converted into CO_2 to the total degraded toluene, which was calculated as:

$$S_{CO_2} (\%) = \frac{C_{CO_2}}{\alpha \times X_{Toluene}} \times 100\%$$

where C_{CO2} represents the CO_2 concentration in the outlet gas, α refers to the theoretical CO_2 concentration.

The C_7H_8 reaction rate at 175 °C (R_{175}) was calculated by equation:

$$R_{175} = \frac{C_{175} \times V_{C_7H_8}}{m_{cat}}$$

Where C_{175} is C_7H_8 conversion rate (%) at 175 °C, V_{C7H8} is C_7H_8 flow rate ($\mu mol \cdot s^{-1}$), m_{cat} is the mass of Pt/ZSM-5 in the catalyst (g).

The C_7H_8 specific reaction rate at 175 °C (R_{175}) was calculated by equation:

$$S_{175} = \frac{R_{175}}{S_{BET}}$$

Where S_{BET} is specific surface area of catalyst ($m^2 \cdot g^{-1}$).

Ea was calculated using the Arrhenius equation as follows:

$$\ln k = \ln A - \frac{E_a}{RT}$$

where k is the reaction rate ($mol \cdot s^{-1}$), Ea is the apparent activation energy ($kJ \cdot mol^{-1}$), and A is the pre-exponential factor.

Finally, cycling tests of the Pt/ZSM-5-T2 catalyst for C_7H_8 oxidation were measured. The test was performed for a continuous five cycles (1000 ppm C_7H_8/Air with the flow rate of 100 mL/min), and in each cycle, the temperature is first increased up to 300 °C then cooled to room temperature. Moreover, for catalytic activity tests and stability tests with water vapor, a certain mass fraction of H_2O was fed into the entire reaction system by the heating belt heating reaction route via a liquid phase pump.
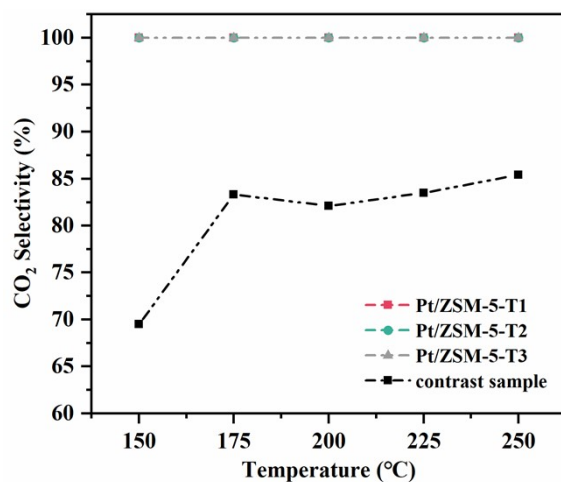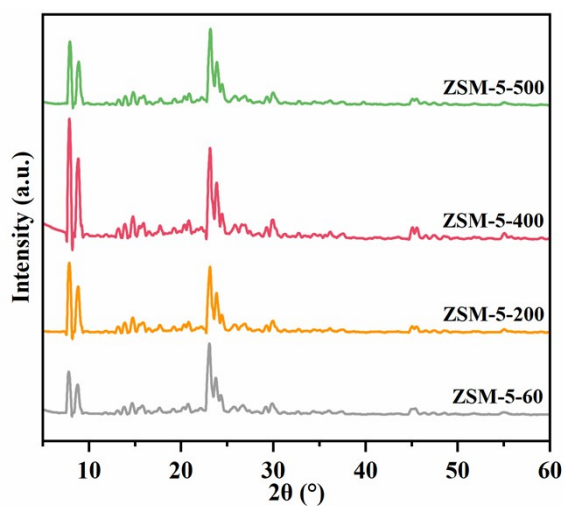
Fig. S1 CO_2 selectivity of all the samples.

Fig. S2 XRD patterns of ZSM-5 molecular sieves with different SiO_2/Al_2O_3 [1].
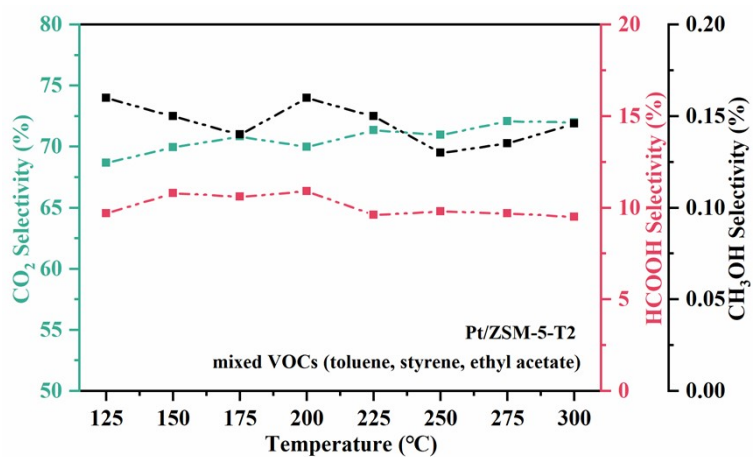
Fig. S3 Products selectivity of VOCs on Pt/ZSM-5-T2 catalyst.

Table S1. The calcination conditions of rice husk powder and corresponding mass values.

Sample	Calcination condition of rice husk powder	Mass of rice husk powder before calcination (g)	Mass after calcination (g)
SiO_2	550 °C, 4 h	6	0.955
SiO_2-8.7 %C	450 °C, 2 h	6	1.045
SiO_2-23.6 %C	450 °C, 1 h	6	1.25

So the carbon content:

(1.045-0.955)/1.045 = 8.7 wt.%

(1.25-0.955)/1.25 = 23.6 wt.%

Table S2. Catalytic testing conditions and comparison of catalytic activities (T_{90}, R_{175}) of as-prepared Pt/ZSM-5 catalysts with previously reported catalysts.

Catalysts	Pollutant Type	Concentration (ppm)/Flow rate	WHSV ($mL \cdot g^{-1} \cdot h^{-1}$)	T_{90} (°C)	R_{175} ($\mu mol \cdot g^{-1} \cdot s^{-1}$)	Ref
Pt/ZSM-5-T1				194	0.387	This work
Pt/ZSM-5-T2	C_7H_8	1000 ppm C_7H_8, air	60,000	170	0.733	
Pt/ZSM-5-T3				174	0.692	
Pt/PZN-2	C_7H_8	1000 ppm C_7H_8, air	60,000	176	0.618	[2]
Pt/CZ-500				202	0.015	
Pd_8Cu_2/MZ	C_7H_8	50 ppm C_7H_8, air	3,6000	152	0.022	[3]
$Co_{3-x}O_{4-y}$	C_7H_8	300 ppm C_7H_8, air	7,2000	146	0.192	[4]
$Co_{3-x}O_4$				180	0.113	
Pt NPs@Co_3O_4				179	0.261	
Pt-Co_3O_4	C_7H_8	1000 ppm C_7H_8, 20 %O_2/N_2	60,000	185	0.106	[5]
Pt ion@Co_3O_4				194	0.063	
Pt/ZSM-5-T2	C_8H_8	200 ppm C_8H_8, air	60,000	196	0.091	This work
CeO_2-C	C_8H_8	600 ppm C_8H_8, air	15,000	350	0.020	6
CeO_2-O				221	0.049	
TS-1	C_8H_8	200 ppm C_8H_8, air	75,000	326	0.000	7
Pt/ZSM-5-T2	$C_4H_8O_2$	1000 ppm $C_4H_8O_2$, air	60,000	325	0.084	This work
1Ru/TiO_2	$C_4H_8O_2$	500 ppm $C_4H_8O_2$, air	60,000	237	0.047	8
MnO_x-CeO_2-h	$C_4H_8O_2$	500 ppm $C_4H_8O_2$, air	60,000	224	0.050	9

Table S3. Input and output of Pt/ZSM-5 catalysts in a LCA analysis.

Pt/ZSM-5-T1 in This work		
Input/Output	Quantity	Unit
Step1：Rice husk powder Pre-treatment		
Input		
Rice husk powder	6.965	KG
Energy（heating）	20.3	KWh
Output		
SiO$_2$ template（T1）	1.19567	KG
Step2：ZSM-5 Synthesis		
Input		
T1	1.19567	KG
Al$_2$(SO$_4$)$_3$·18H$_2$O	0.03303	KG
NaOH	0.18308	KG
TPABr	0.26467	KG
H$_2$O	14.328	L
Energy（stirring and heating）	67.8	KWh
Output		
ZSM-5-T1	0.995	KG
Step3：Pt/ZSM-5 Preparation		
Input		
Pt	0.005	KG
ZSM-5-T1	0.995	KG
Energy（stirring and heating）	40.2	KWh
Output		
Pt/ZSM-5-T1	1	KG

Pt/ZSM-5-T2 in This work		
Input/Output	Quantity	Unit
Step1：Rice husk powder Pre-treatment		
Input		
Rice husk powder	6.965	KG
Energy（heating）	12.25	KW-h
Output		
SiO_2-8.7% C template（T2）	1.3134	KG
Step2：ZSM-5 Synthesis		
Input		
T2	1.3134	KG
$Al_2(SO_4)_3 \cdot 18H_2O$	0.03303	KG
NaOH	0.18308	KG
TPABr	0.26467	KG
H_2O	14.328	L
Energy（stirring and heating）	67.8	KWh
Output		
ZSM-5-T2	0.995	KG
Step3：Pt/ZSM-5 Preparation		
Input		
Pt	0.005	KG
ZSM-5-T2	0.995	KG
Energy（stirring and heating）	40.2	KWh
Output		
Pt/ZSM-5-T2	1	KG

Pt/ZSM-5-T3 in This work		
Input/Output	Quantity	Unit
Step1：Rice husk powder Pre-treatment		
Input		
Rice husk powder	6.965	KG
Energy（heating）	8.75	KW-h
Output		
SiO_2-23.6% C template（T3）	1.56414	KG
Step2：ZSM-5 Synthesis		
Input		
T3	1.56414	KG
$Al_2(SO_4)_3 \cdot 18H_2O$	0.03303	KG
NaOH	0.18308	KG
TPABr	0.26467	KG
H_2O	14.328	L
Energy（stirring and heating）	67.8	KWh
Output		
ZSM-5-T3	0.995	KG
Step3：Pt/ZSM-5 Preparation		
Input		
Pt	0.005	KG
ZSM-5-T3	0.995	KG
Energy（stirring and heating）	40.2	KWh
Output		
Pt/ZSM-5-T3	1	KG

Catalyst A: Pt/ZSM-5-C		
Input/Output	Quantity	Unit
Step1：ZSM-5 Synthesis		
Input		
TEOS	4.2188	KG
NaAlO$_2$	0.00816	KG
NaOH	0.18308	KG
TPAOH	0.48556	KG
H$_2$O	10.746	L
Energy（stirring and heating）	67.8	KWh
Output		
ZSM-5-C	0.995	KG
Step2：Pt/ZSM-5 Preparation		
Input		
Pt	0.005	KG
ZSM-5-C	0.995	KG
Energy（stirring and heating）	40.2	KWh
Output		
Pt/ZSM-5-C	1	KG

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