Supplementary Information

A novel 3DOM Pt/MeO_x-SiO_2 catalyst for the catalytic oxidation of VOCs

Sha Liu[a,b], Fang Dong[a*], Weigao Han[a], Jiyi Zhang[b*], Zhicheng Tang[a*]

([a] National Engineering Research Center for Fine Petrochemical Intermediates, State Key Laboratory of Low Carbon Catalysis and Carbon Dioxide Utilization, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China. [b] School of Petroleum and Chemical, Lanzhou University of Technology, Lanzhou 730050, China.)

---

[*]Corresponding author.

E-mail address: dongfang@licp.cas.cn (F. Dong), tangzhicheng@licp.cas.cn (Z. Tang), zhangjiyi@lut.edu.cn (J. Zhang).

1. Chemical reagent

Methyl methacrylate (MMA) was purchased from Xilong Scientific Co., Ltd., China. Potassium peroxydisulfate ($K_2S_2O_8$) was purchased from Tianjin Kemiou Chemical Reagent Co. Ltd., China. PEG-PPG-PEG (P123) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd., China. Hydrochloric aicd (HCl) and ethanol (CH_3CH_2OH) were purchased from Leyland Bohua (Tianjin) Pharmaceutical & Chemical Co., Ltd., China. Tetraethyl orthosilicate (TEOS), chloroplatinic acid (H_2PtCl_6), Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) and Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) were purchased from Chengdu Kelong Chemical Co., Ltd., China. Manganese (II) nitrate tetrahydrate ($Mn(NO_3)_2{\cdot}4H_2O$) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd., China.

2. Experimental contents

2.1. Preparation of highly ordered polymethyl methacrylate (PMMA) microspheres

240 mL of deionized water was put into the three-hole round-bottom flask and was heated to 80 ºC with the water bath. At the same time, N_2 was blown in as a protection gas, and water was continuously stirred. A condensation reflux device was fixed to the flask. The other was closed with a stopper. 120 mL of MMA was added to the flask at 80 ºC. 0.6 g of $K_2S_2O_8$ was dissolved in 40 mL of deionized water, and the solution was heated to 80 ºC. After 20 minutes, the solution was poured into a flask and then reacted for 2 hours. The solution was filtered through a microfiltration membrane to obtain a filtrate. The filtrate was centrifuged at 3000 rpm for 10 hours to obtain PMMA

microspheres. Finally, the samples were dried at 60 ºC for 10 hours.

2.2. Preparation of 3DOM SiO_2

0.75 g of P123, 5 mL of ethanol, 2.5 mL of HCl (2 mol/L), and 2.5 mL of H_2O were mixed and stirred in a water bath at 45 ºC for 1 h. Then, 3 g of TEOS was added to the above solution drop by drop. Thereafter, the solution was kept stirring in a water bath at 45 ºC for 3 h and 25 ºC for 2h. 3g of PMMA microsphere template was put on the Buchner funnel and the suction filter pump. Then the solution was poured into the Buchner funnel. The process was repeated 5-6 times. The impregnated PMMA microsphere template was put into the blast drying oven at 40ºC for 12h. The dried samples were calcined in a tube furnace under an air atmosphere. The sample was heated to 310 ºC at a heating rate of 1 ºC/min and held for 3 hours, and then heated from 310 ºC to 650 ºC at a heating rate of 1 ºC/min for 3 hours.

3. Catalyst characterizations

Scanning electron microscopy (SEM) images were obtained by JSM-6701F cold field emission scanning electron microscopy.

The micromorphology and internal structure of the catalysts were observed by transmission electron microscopy (TEM, JEOL-JEM-2010).

The crystal phase of the catalyst was detected by X-ray diffraction instrument (XRD, Japan Smartlabse) under irradiation at λ = 1.5406 nm. The scanning angle is 10^{o}-80^{o}, and the scanning speed is 0.5 ^{o}/min, 60 kV, 55 mA.

Raman scattering was performed on a Laboratory Human Resources Evolution Raman spectrometer (BX41).

Brunauer-Emmett-Teller (BET) surface area, the pore size, and the pore volume of the catalysts were obtained by adsorption and desorption of nitrogen in the ASAP 2020 instrument (America Micromeritics).

The multifunctional dynamic adsorption instrument TP-5080-D was used to analyze the acidity and redox ability of the catalyst surface. For H_2-TPR, a 50 mg sample was pretreated with H_2 for 1 h at 300 ºC. When the temperature dropped to 50 ºC, the sample was heated to 800 ºC in a reducing gas of 5 vol% H_2 and 95 vol% N_2, and the detection signal was continuously recorded.

For O_2-TPD, a 50 mg sample was pretreated with N_2 for 1 h at 300 ºC. When the temperature dropped to 50 ºC, O_2 (5% O_2/N_2) was adsorbed for 1 h. The sample was then heated to 900 ºC in He gas, and the detection signal was continuously recorded.

For NH_3-TPD, a 50 mg sample was pretreated with N_2 for 1 h at 300 ºC. When the temperature dropped to 50 ºC, NH_3 was adsorbed for 1 h. The sample was then heated to 800 ºC in N_2, and the detection signal was continuously recorded.

For SO_2-TPD, it is similar to NH_3-TPD except that NH_3 is replaced with SO_2.

The reaction mechanism was explored by in situ diffuse reflectance infrared Fourier transform spectroscopy (In situ DRIFTS). The results were obtained by a VERTEX 70 spectrometer, which consists of an MCT detector and a CaF_2 window in situ cell. The frequency range of the spectra is mainly from 4000-600 cm^{-1}. The catalyst was pretreated with N_2 at 300 ºC for 30 min. After cooling to 50 ºC, the catalyst continuously adsorbed benzene at 50 ºC for 30 min by the bubbling method with N_2 as the carrier gas. To remove the weakly adsorbed benzene molecule, the catalyst was

purged with N_2 gas for another 5 min. Then, air and SO_2 mixed gas were introduced into the in situ cell and in situ DRIFTS spectra of the catalyst were collected at different temperatures (50 ºC, 100 ºC, 150 ºC, 200 ºC, 250 ºC, 300 ºC).

4. Catalytic activity measurements

To evaluate the activity and stability of these catalysts for the catalytic combustion of VOCs, we selected benzene as the probe molecule. 0.4 g of catalyst (20-40 mesh) and 0.2 g of silica sand (SiO_2) were mixed well and poured into the constant temperature zone of a continuous flow microreactor tube (length of 30 cm, 8 mm of inner diameter), which was stuffed with cotton. The catalyst was exposed to a mixture of benzene (2000 ppm) and the air with a flow rate of 200 mL/min and a weight hourly space velocity (WHSV) of 30 000 mL g^{-1} h^{-1}. An on-line gas chromatograph (FULI, GC9790II) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) was used to detect the concentration of the reactants. Generally, the activity is distinguished by the reaction temperature when the benzene conversion is 90%. The benzene conversion is calculated as follows:

$$X_{benzene} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (1)$$

In equation (1), $X_{benzene}$ represents the benzene conversion. C_{in} and C_{out} represent the benzene conversion at the inlet and outlet of the reactor.

CO_2 selectivity is defined as:

$$CO_2\ selectivity = \frac{[CO_2]_{out}}{([benezene]_{in} - [benezene]_{out}) \times 6} \times 100\% \quad (2)$$

In equation (2), $[benzene]_{in}$ and $[benzene]_{out}$ represent the concentration of

benzene at the inlet and outlet of the reactor, and $[CO_2]_{out}$ represents the concentration of exported CO_2.

5. Kinetic studies

The catalytic performance can also be determined by kinetic studies, such as apparent activation energy (E_a), which is measured as follows:

$$\ln r = \frac{-E_a}{RT} + C \tag{1}$$

In equation (1), r represents the reaction rate (mol s^{-1} g^{-1}), T represents the reaction temperature, and C is a constant term.

$$r = \frac{F \times [-\ln(1-x)]}{m} \tag{2}$$

In equation (2), x represents the conversion rate of benzene, F represents the feeding rate of benzene (mol s^{-1}), and m represents the mass of catalyst. Therefore, the plot of lnr and 1000/T yields E_a values.

The kinetic study also includes specific reaction rates, such as the mass (R_m) and specific surface area (R_s) of the catalyst, and its calculation requires the following equations:

$$R_m = \frac{F \times \eta_{benzene}}{m_{cat}} \tag{3}$$

$$R_s = \frac{F \times \eta_{benzene}}{S_{BET}} \tag{4}$$

$$\eta_{benzene} = \log \frac{1}{1 - \frac{X_{benzene}}{100}} \tag{5}$$

Where F represents the flow rate of benzene (mol s^{-1}), $X_{benzene}$ is the conversion of

benzene, m_{cat} is the mass (g) of the catalyst, S_{BET} is the specific surface area of the catalyst.

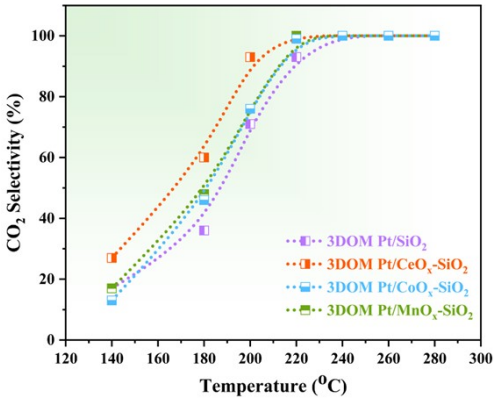

Fig. S1 CO_2 selectivity of the catalysts.

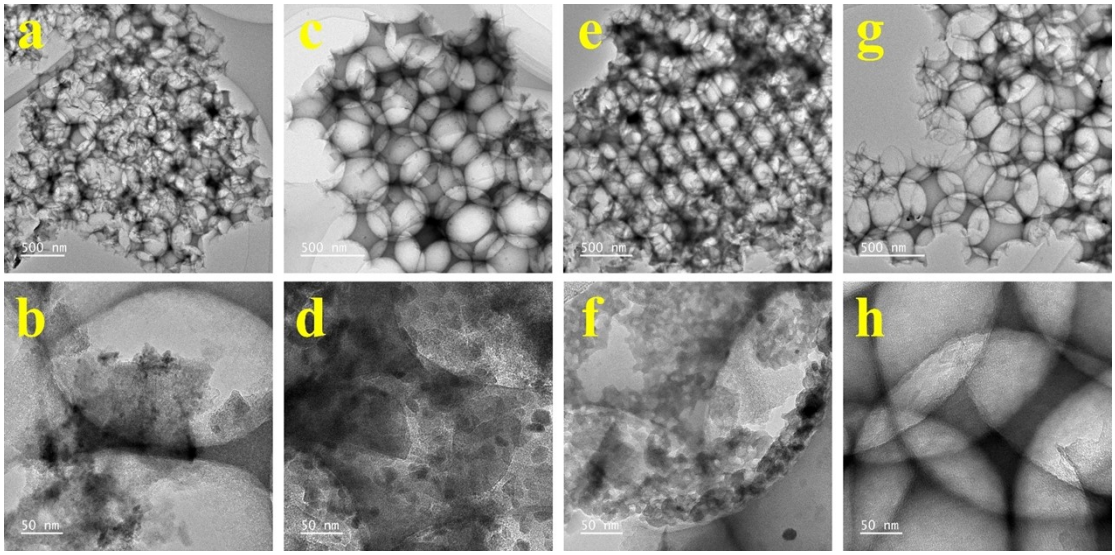

Fig. S2 TEM images of 3DOM Pt/CeO_x-SiO_2 (a and b), 3DOM Pt/CoO_x-SiO_2 (c and d), 3DOM Pt/MnO_x-SiO_2 (e and f) and 3DOM SiO_2 (g and h) catalysts.

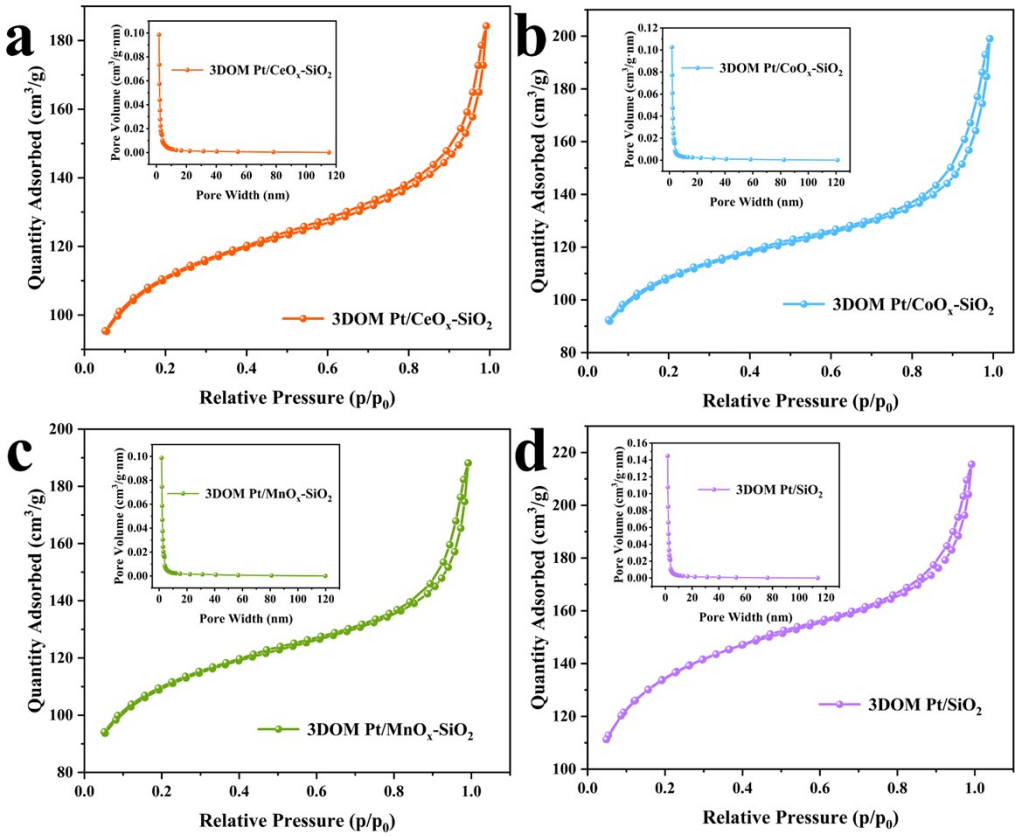

Fig. S3 N_2 adsorption-desorption isotherms and pore-size distribution of 3DOM Pt/CeO_x-SiO_2 (a), 3DOM Pt/CoO_x-SiO_2 (b), 3DOM Pt/MnO_x-SiO_2 (c) and 3DOM Pt/SiO_2 (d) catalysts.

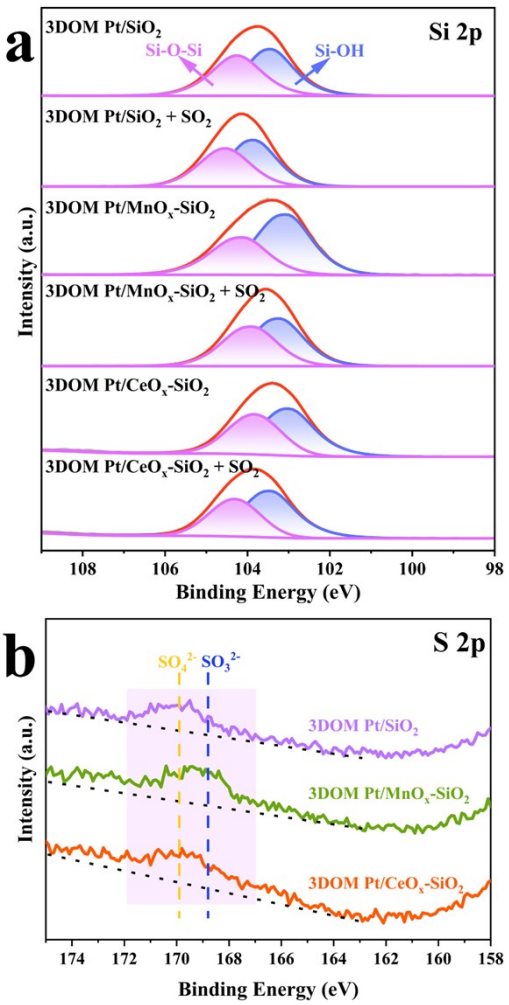

Fig. S4 XPS spectra of Si 2p (a) for fresh and used catalysts of 3DOM Pt/SiO_2, 3DOM Pt/MnO_x-SiO_2 and 3DOM Pt/CeO_x-SiO_2. XPS spectra of S 2p (b) for used catalysts of 3DOM Pt/SiO_2, 3DOM Pt/MnO_x-SiO_2 and 3DOM Pt/CeO_x-SiO_2.