

Supporting information

Design ordered mesoporous confinement Pt/Ti_{0.1}AlO_y catalysts for the propane catalytic combustion

Liqiong Liu^{a,b}, Weiliang Han^{b*}, Fang Dong^{b,c}, Hua Feng^{a*}, Zhicheng Tang^{b,d*}

(a. College of Chemistry and Chemical Engineering, Northwest Normal University,

Lanzhou, 730070, China.

b. State Key Laboratory for Oxo Synthesis and Selective Oxidation, and National

Engineering Research Center for Fine Petrochemical Intermediates, Lanzhou

Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China.

c. Dalian National Laboratory for Clean Energy, Dalian 116023, China.

d. Shandong Laboratory of Yantai Advanced Materials and Green Manufacturing,

Yantai Zhongke Research Institute of Advanced Materials and Green Chemical

Engineering, Yantai, 264006, China)

**Corresponding author. Tel: +86-931-4968083, Fax: +86-931-4968019, E-mail*

address:

tangzhicheng@licp.cas.cn

(Z.Tang).

1. Catalyst characterizations

The TEM image was carried out on a JEOL JEM-2010 transmission electron microscope equipped operating at 200kV. For TEM analysis, the samples were uniformly dispersed in the ethanol solution, which was further installed on double-sided adhesive tape.

X-ray diffraction (XRD) analysis was conducted to explore the crystal phase of samples, which was recorded on a Rigaku D/MAX-RB X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and run in the range of $0.4-4^\circ$ with 60 kV and 55 mA.

N₂ adsorption-desorption was conducted on a Micromeritics ASAP 2010 instrument, and the specific surface area of the catalyst was determined by nitrogen adsorption in accordance with the Brunauer Emmett and Teller (BET) method. Before measurements, the sample was degassed at 150 °C for 6 h, and BET surface area determination was calculated through six measurements at relative pressures of N₂ in the range of 0.05-1.00.

X-ray photoelectron spectroscopy (XPS) analysis was carried out on a VG ESCALAB 210 Electron Spectrometer using Mg K α radiation ($h\nu = 1253.6 \text{ eV}$) to determine the chemical states of elements in these samples.

To explore the formation of defect structure, A RM 2000 microscope confocal Raman spectrometer (Renishaw PLC) with a 532 nm laser was used.

The Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) was recorded with VERTEX70 having a resolution of 4 cm⁻¹. Each sample was scanned at a range of 1000-3500 cm⁻¹.

Thought Bruker V70 collected in situ DRIFTS (In situ diffuse reflectance infrared fourier transform spectroscopy). Firstly, the 0.3% Pt/Ti_{0.1}AlO_y-EISA catalyst was handled in an N₂ atmosphere at 300 °C for 1h and then cooled to 50 °C. The flow rate was adjusted to 25 mL min⁻¹, and 0.2% propane was introduced continuously at 50 °C for 30 min. Thereafter, pure N₂ gas and a mixed reaction gas of 20% volume O₂ and 80% volume N₂ were introduced into in situ cell and reacted with toluene respectively. Finally, the samples were further heated to 100, 150, 200, 250, 300, and 350 °C to collect the corresponding spectra, respectively.

H₂-temperature program reduction (H₂-TPR) was performed by automatic multi-function adsorption apparatus. The mixed gas of 5 vol.% H₂ and 95 vol.% N₂ was introduced into the quartz tube reactor. After that, 0.1 g catalysts were put in the quartz tube reactor. Before the test, the catalysts were purged with pure N₂ gas at 100 °C for 1 h, and then the test was conducted from 100 °C to 800 °C with a heating rate of 10 °C/min.

O₂-temperature program desorption (O₂-TPD) was used to investigate the types of oxygen species in these samples. Firstly, 0.1 g catalysts were put into the quartz tube reactor, and then they were purged with pure N₂ gas at 100 °C for 1 h. After that, and then the pure He gas was used to remove the unabsorbed O₂ molecules at 30 °C for 1 h. Ultimately, the catalysts were heated from 100 °C to 900 °C.

Besides, to investigate the effect of acidity, NH₃-temperature program desorption (NH₃-TPD) was conducted by automatic multi-function adsorption apparatus. The 0.1 g catalysts were put in the quartz tube reactor and purged with pure N₂ gas at 100 °C

for 1 h, and then the adsorbing gas of 5 vol. % NH₃ and 95 vol. % N₂ was passed into the quartz tube reactor. Finally, the experiment was conducted from 100 °C to 800 °C.

2. Catalytic activity measurements

To evaluate the catalytic activity of the propane oxidation reaction, the experiments were carried out in a continuous-flow fixed-bed quartz tube microreactor. The reaction gas containing propane (2000 ppm) was through the reactor with a weight per hour spatial velocity (WHSV) of 60,000 mL g⁻¹ h⁻¹. The catalysts were first pressed into flakes using a tablet press and then sieved into particles of uniform size using a 40-60 mesh sieve, and then a mixture of 0.2 g catalysts and 0.4 g quartz sand was added to the reactor with an inner diameter of 1 cm and a length of 30 cm. After that, the reaction temperature was increased to 300 °C and each temperature point was stabilized for one hour before sampling. The reactants and products were analyzed with a GC-9190I gas chromatograph and a flame ionization detector.

The conversion of propane was calculated by the following equation:

$$X_{propane} = \frac{[C]_{in} - [C]_{out}}{[C]_{in}} \times 100 \% \quad (S1)$$

$X_{propane}$ indicates the conversion rate of propane.

$[C]_{in}$ indicates the inlet concentration of propane.

$[C]_{out}$ indicates the outlet concentration of propane.

The kinetic calculation of catalysts

The catalytic combustion of propane over mPt/Ti_{0.1}AlO_y-EISA and 0.3%Pt/Ti_{0.1}AlO_y-VI catalysts were passed for as a first-order reaction, and the activation energy can be calculated via the Arrhenius equation and the calculation

process is as follows:

$$r = \frac{F}{W} [-\ln(1 - X_{propane})] \quad (S2)$$

In which $X_{propane}$, W and F represent the conversion rate of propane, catalyst weight, and the feed rate of propane, respectively. Eq. S5 is obtained from Eq. S3 and Eq. S4.

$$r = kC_{propane} \quad (S3)$$

Where $C_{propane}$ and k denote the concentration in feed flow and the dynamics.

$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (S4)$$

Where R , T , and E_a indicate gas constant, reaction temperature, and activation energy.

$$\ln r = -\frac{E_a}{RT} + B \quad (S5)$$

where B means the constant. On the basis of Eq. S2 and Eq. S5, the relation between $\ln r$ and $1/T$ can be obtained, as shown in Fig. S3. The Values of the four samples are listed in Table S1.

The selectivity of CO_2 was calculated as follows:

$$CO_2 \text{ selectivity} = \frac{[CO_2]_{out}}{3 \times ([C]_{in} - [C]_{out})} \times 100 \% \quad (S6)$$

$[CO_2]_{out}$ indicated the outlet concentration of CO_2 .

Table S1 The catalytic performance results of mPt/Ti_{0.1}AlO_y-EISA catalysts.

Catalysts	T ₁₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)	Ea (kJ·mol ⁻¹)
0.2%Pt/Ti _{0.1} AlO _y -EISA	353	425	534	84.37
0.3%Pt/Ti _{0.1} AlO _y -EISA	340	412	494	60.76
0.5%Pt/Ti _{0.1} AlO _y -EISA	343	454	579	85.21

Table S2 The number of surface acids over mPt/Ti_{0.1}AlO_y-EISA catalysts.

Catalysts	Weak acid area	Medium acid area	Strong acid area	Total acid area
0.2%Pt/Ti _{0.1} AlO _y -EISA	263	301	478	1042
0.3%Pt/Ti _{0.1} AlO _y -EISA	322	341	571	1234
0.5%Pt/Ti _{0.1} AlO _y -EISA	254	854	229	1337

Table S3 Surface area, pore volume, and average pore size of 0.3%Pt/Ti_{0.1}AlO_y-EISA, 0.3%Pt/Ti_{0.1}AlO_y-VI, and the Ti_{0.1}AlO_y support.

Catalysts	BET surface area (m ² ·g ⁻¹)	Average pore size (nm)	Pore volume (cm ³ ·g ⁻¹)
0.3%Pt/Ti _{0.1} AlO _y -EISA	228.6	11.3	0.64
0.3%Pt/Ti _{0.1} AlO _y -VI	311.4	6.5	0.51
Ti _{0.1} AlO _y support	253.7	9.9	0.62

Table S4 The catalytic performance results of 0.3%Pt/Ti_{0.1}AlO_y-EISA
and 0.3%Pt/Ti_{0.1}AlO_y-VI catalysts.

Catalysts	T ₁₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)	Ea (kJ·mol ⁻¹)
0.3% Pt/Ti _{0.1} AlO _y -EISA	340	412	494	60.76
0.3% Pt/Ti _{0.1} AlO _y -VI	348	462	548	85.04

Table S5 The number of surface acids over 0.3%Pt/Ti_{0.1}AlO_y-EISA and0.3%Pt/Ti_{0.1}AlO_y-VI catalysts.

Catalysts	Weak acid area (percentage)	Medium acid area (percentage)	Strong acid area (percentage)	Total acid area (percentage)
0.3%Pt/Ti _{0.1} AlO _y -EISA	322 (26.10%)	341 (27.63%)	571 (46.27%)	1234 (100%)
0.3%Pt/Ti _{0.1} AlO _y -VI	314 (26.04%)	318 (26.37%)	574 (47.59%)	1206 (100%)

Table S6 XPS analysis of 0.3%Pt/Ti_{0.1}AlO_y-EISA and 0.3%Pt/Ti_{0.1}AlO_y-VI catalysts.

Catalysts	Pt ²⁺ /(Pt ²⁺⁺ Pt ⁴⁺)	Pt ⁴⁺ /(Pt ²⁺⁺ Pt ⁴⁺)	O _{latt} /O _{total}	O _{ads} /O _{total}
	(%)	(%)	(%)	(%)
0.3% Pt/Ti _{0.1} AlO _y -EISA	56.24	43.76	53.84	46.16
0.3% Pt/Ti _{0.1} AlO _y -VI	55.23	44.77	82.40	17.60

Table S7 XPS analysis after sulfur resistance of 0.3%Pt/Ti_{0.1}AlO_y-EISA and0.3%Pt/Ti_{0.1}AlO_y-VI catalysts.

Catalysts	Pt ²⁺ /(Pt ²⁺ +Pt ⁴⁺) (%)	Pt ⁴⁺ /(Pt ²⁺ +Pt ⁴⁺) (%)	O _{latt} /O _{total} (%)	O _{ads} /O _{total} (%)
0.3%Pt/Ti _{0.1} AlO _y -EISA	57.97	42.03	59.51	40.49
0.3% Pt/Ti _{0.1} AlO _y -VI	55.24	44.76	69.40	30.60

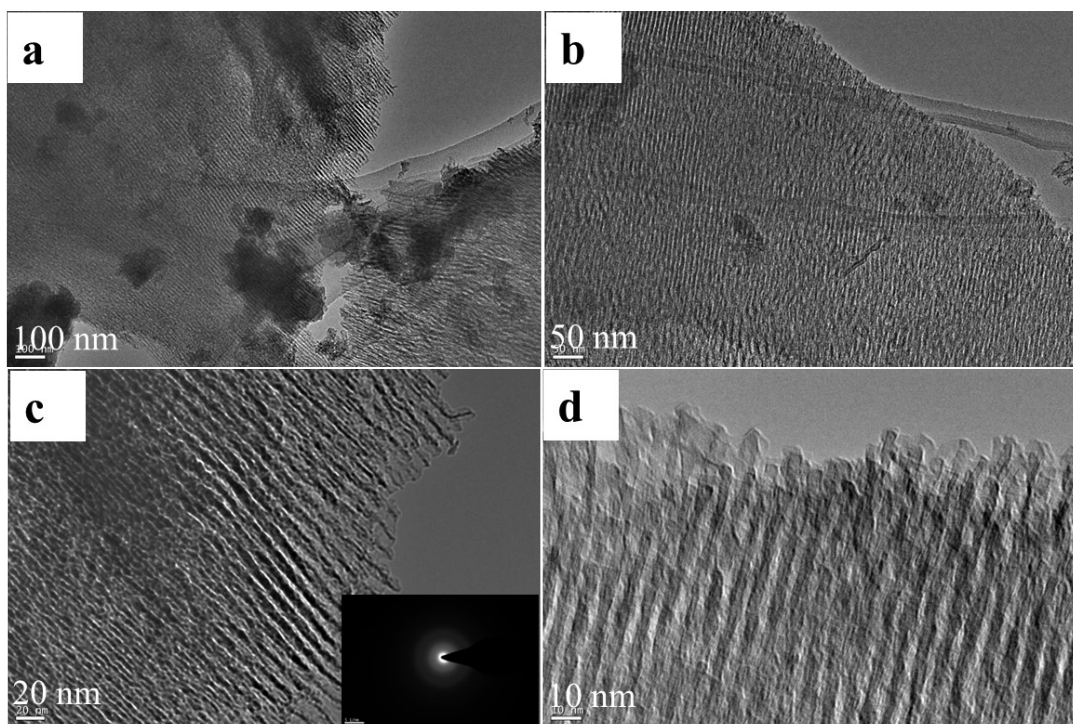


Fig. S1 TEM images of the $\text{Ti}_{0.1}\text{AlO}_y$ support: 100 nm (a), 50 nm (b), 20 nm (c), 10 nm (d).

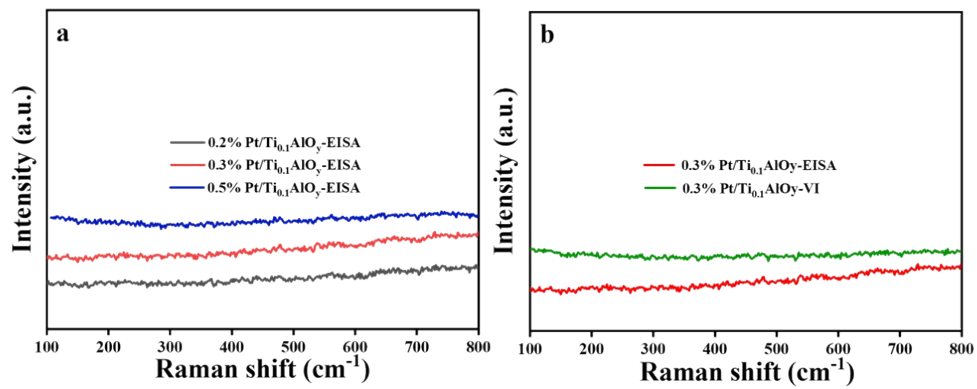


Fig. S2 Raman spectra of mPt/Ti_{0.1}AlO_y-EISA (a), 0.3%Pt/Ti_{0.1}AlO_y-EISA and 0.3%Pt/Ti_{0.1}AlO_y-VI catalysts (b).