

Supplementary Information

Constructing a core-shell Pt@MnO_x/SiO₂ catalyst for benzene catalytic combustion with excellent SO₂ resistance: new insights into active sites

Dan Yang^{a,b}, Fang Dong^{b*}, Jie Wang^{a,b}, Zhicheng Tang^{b*}, Jiyi Zhang^{a*}

*(^a School of Petroleum and Chemical, Lanzhou University of Technology, Lanzhou
730050, 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.)*

*Corresponding author.

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

1.1 Catalyst Characterization

The morphology of the samples was evaluated with transmission electron microscope (TEM). The images of TEM and selected-area electron diffraction patterns were obtained under a microscope of 200 kV using FEI TECNAIG .

The specific surface area and pore diameter of the catalyst was measured on the Micromeritics ASAP 2010 analyzer by the method of low-temperature nitrogen adsorption and desorption.

Power X-ray diffraction (XRD) analysis was finished at 60 kV and 55 mA with a scanning speed of $0.5^{\circ} \text{ min}^{-1}$. The 2θ of wide-angle ranged from 10° to 90° .

Raman scattering was done by using a Laboratory Human Resources Evolution Raman spectrometer (BX41).

The XPS measurement was done on a Thermo Scientific 250Xi Electron Spectrometer (Mg $K\alpha$ radiation; $h\nu = 1253.6 \text{ eV}$).

The FTIR analysis of the sample adopts Fourier infrared spectrometer (Nexus 870, Nicolet), and ATR technology was used for FTIR analysis. Raman scattering was done by using a Laboratory Human Resources Evolution Raman spectrometer (BX41).

In situ diffuse reflectance infrared fourier transform spectroscopy (in situ DRIFTS) was collected on Bruker V70. The powder samples were degassed in N_2 gas with 25 mL/min gas volume at 300°C for 30 min. After that, the samples were cooled to 50°C . Benzene is introduced continuously by a bubbling method with N_2 as a carrier gas at 50°C for 30 min. To remove the weakly adsorbed benzene molecule, the samples were purged with N_2 gas for another 5 min. Thereafter, an air gas and a mixture reaction gas

with air and 30 ppm SO₂ (25 mL/min) were respectively introduced into the in situ cell to react with benzene as requires. Finally, the samples were further heated to 100, 120, 140, 160, 180 and 300 °C to collect the corresponding spectra, respectively.

For H₂-TPR, a 50 mg sample was pre-treated at an atmosphere of nitrogen. The temperature was increased from room temperature to 350 °C with a heating rate of 10 °C min⁻¹. When it cooled down to room temperature, the temperature was increased from room temperature to 800 °C with a heating rate of 10 °C min⁻¹. A reducing gas of 5 % vol. H₂ and 95 % vol. N₂ was passed on the sample at the same time.

For NH₃-TPD, a 100 mg sample was pre-treated at an atmosphere of nitrogen. The temperature was increased from room temperature to 350 °C with a heating rate of 10 °C min⁻¹. And it was treated for 90 min. When it cooled down to room temperature, the temperature was increased from room temperature to 50 °C for 60 min with a gas of 5 % vol. NH₃ and 95 % vol. N₂ passing through. Finally, the temperature was increased from room temperature to 600 °C with a heating rate of 10 °C min⁻¹.

For O₂-TPD, a 100 mg sample was pre-treated at an atmosphere of nitrogen. The temperature was increased from room temperature to 350 °C with a heating rate of 10 °C min⁻¹. And it was treated for 90 min. When it cooled down to room temperature, the temperature was increased from room temperature to 30 °C for 60 min with a gas of 5 % vol. O₂ and 95 % vol. N₂ passing through. Finally, the temperature was increased from room temperature to 800 °C with a heating rate of 10 °C min⁻¹.

1.2 The Calculation of E_a (Activation energy) and R (reaction rate):

Activation energy (E_a) and reaction rate (r) is evaluated according to the Eqs. (3),

(4):

$$\ln r = \frac{-E_a}{RT} + C \quad (3)$$

The r represents the reaction rate ($\text{mol s}^{-1} \text{ g}^{-1}$), the T represents the reaction temperature, the C represents a constant term.

$$r = \frac{F \times \left\{ -\ln \left[\frac{1}{1-x} \right] \right\}}{m} \quad (4)$$

The F represents the feeding rate of benzene (mol s^{-1}), and the m represents the mass of catalyst in the reaction tube. E_a is obtained by the linear relationship between $\ln r$ and $1000/T$ in the above formula.

1.3 The Calculation of Turnover Frequency (TOF):

Turnover frequency (TOF), defined as the number of benzene molecules converted per active site per second, is calculated according to the equation:

$$TOF = \frac{F_T * X_T}{\frac{(m_{cat} * w_{Pt})}{M_{Pt}} * d_{Pt}} \quad (5)$$

Where F_T is the benzene flow rate (mol/h), X_T is the conversion of benzene, m_{cat} is the mass of the catalyst (g), w_{Pt} is the mass percentage of Pt in the catalysts, M_{Pt} is the molar mass of Pt (195 g/mol), and d_{Pt} is the Pt dispersion. And d_{Pt} is calculated from the ratio of the active site Pt^0 to the total area of Pt elements in the XPS spectrum.

Table S1 The percentage of oxygen species by O₂-TPD

Samples	O _α (%)	O _α ' (%)	O _β (%)	O _α + O _α ' (%)
Pt/SiO ₂	9.09	68.14	22.77	77.23
Pt@CrO _x /SiO ₂	17.20	54.35	28.45	71.55
Pt@VO _x /SiO ₂	14.18	58.26	27.56	72.44
Pt@MnO _x /SiO ₂	14.92	63.32	21.76	78.24

Table S2 The percentage of surface acid sites by NH₃-TPD

Samples	Weak acid sites (%)	Medium and strong acid sites (%)	Strong acid sites (%)
Pt/SiO ₂	12.87	78.07	9.06
Pt@CrO _x /SiO ₂	14.58	59.34	26.08
Pt@VO _x /SiO ₂	18.58	67.04	14.38
Pt@MnO _x /SiO ₂	24.16	50.89	24.95

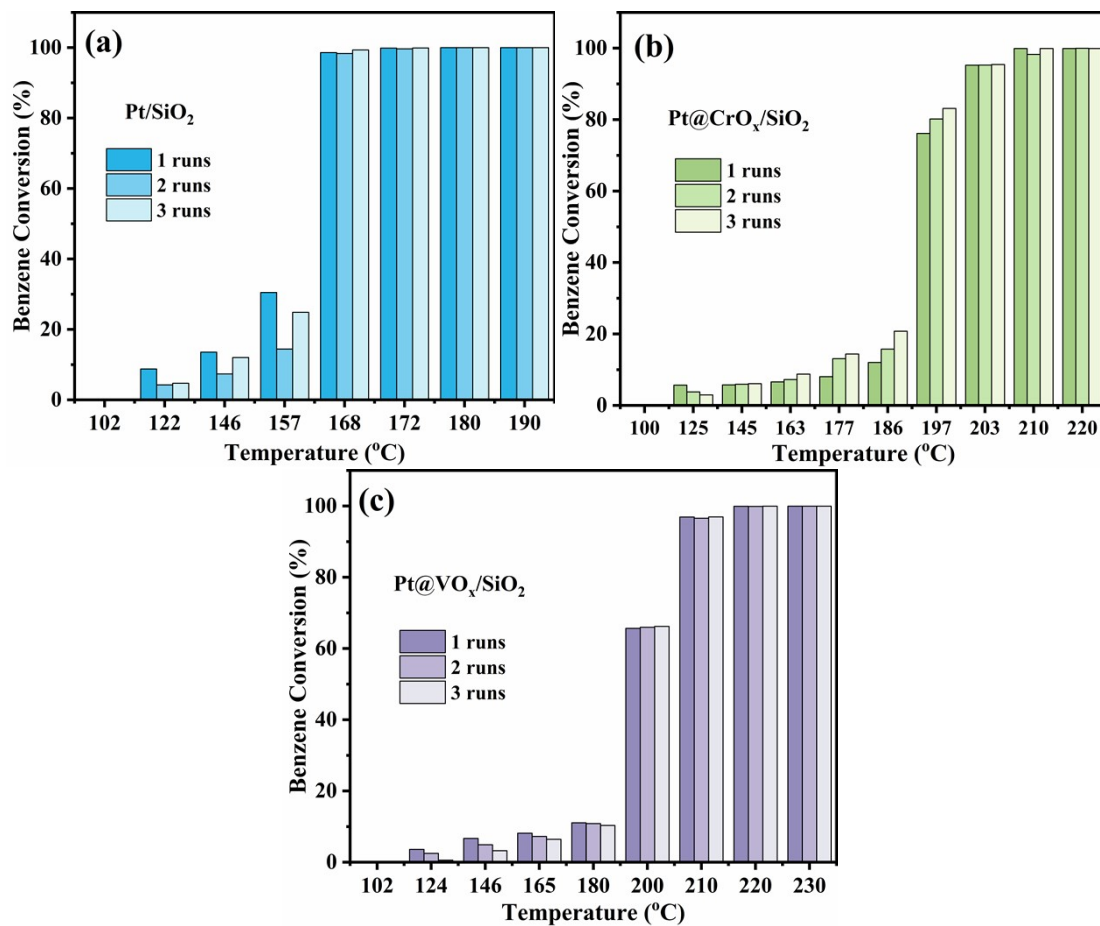


Fig. S1 Cycling stability of benzene oxidation for three consecutive times over Pt/SiO₂ (a), Pt@CrO_x/SiO₂ (b) and Pt@VO_x/SiO₂ (c) catalysts.

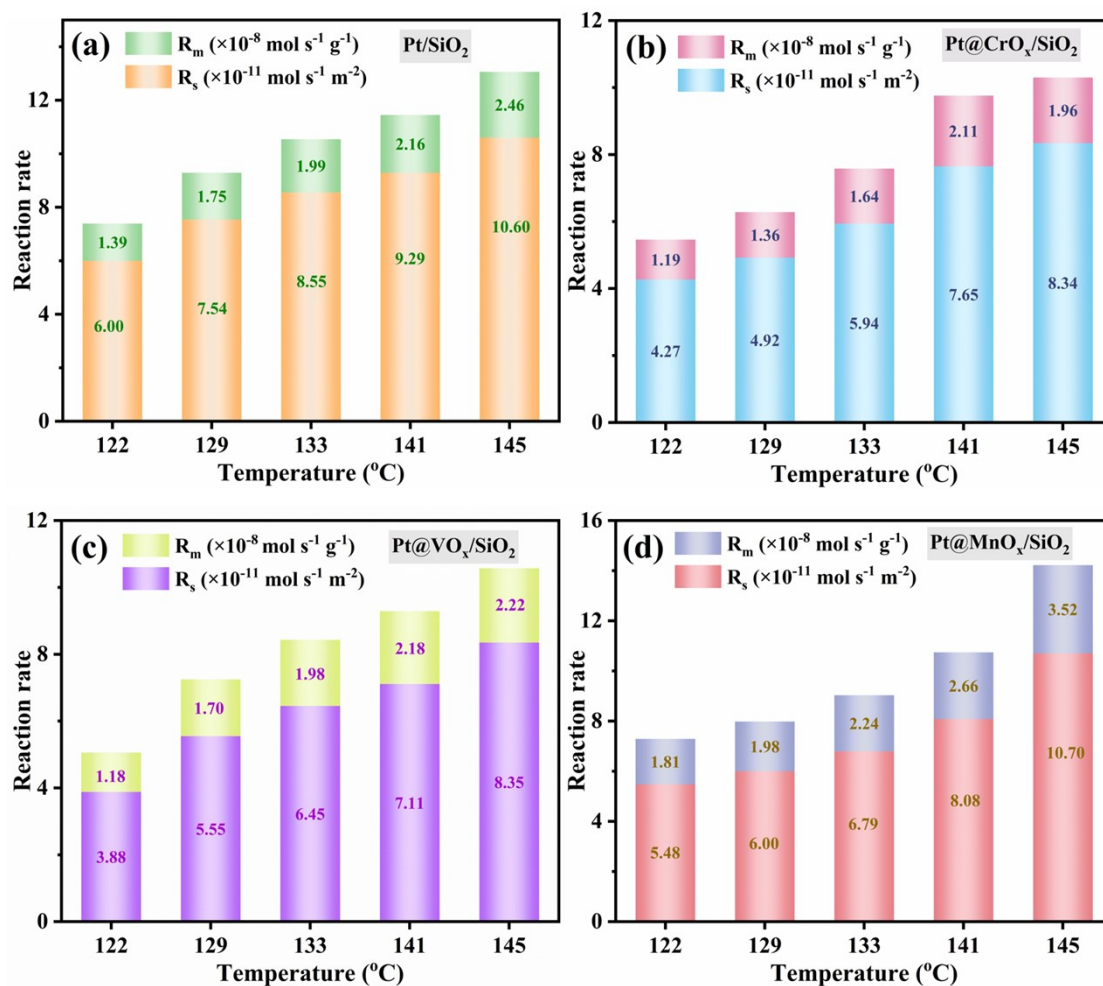


Fig. S2 R_s (reaction rates based on the specific area) and R_m (reaction rates based on the catalyst mass) of Pt/SiO₂ (a), Pt@CrO_x/SiO₂ (b), Pt@VO_x/SiO₂ (c) and Pt@MnO_x/SiO₂ (d) catalysts.

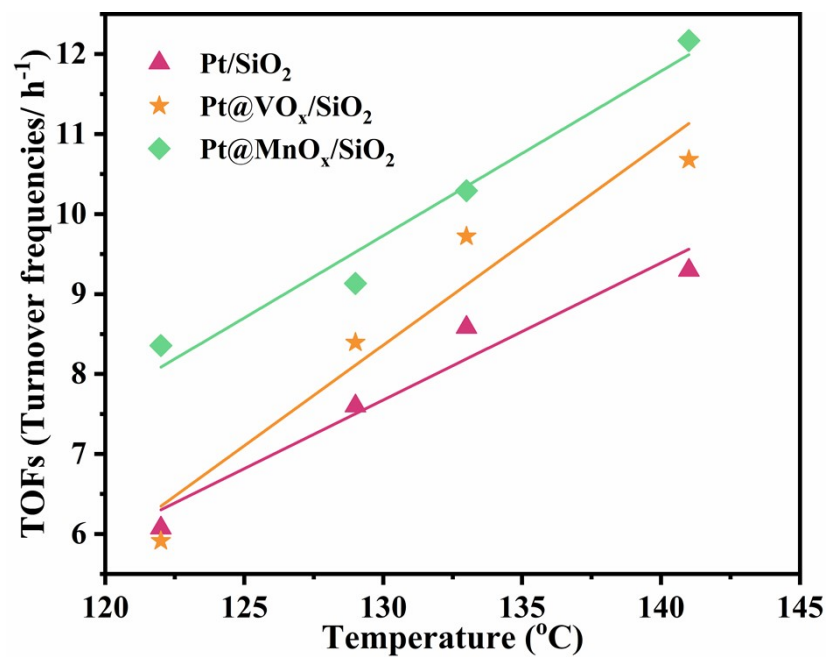


Fig. S3 Reaction rates of Pt/SiO₂, Pt@VO_x/SiO₂ and Pt@MnO_x/SiO₂ catalysts for benzene oxidation reaction: on basis of TOF value.

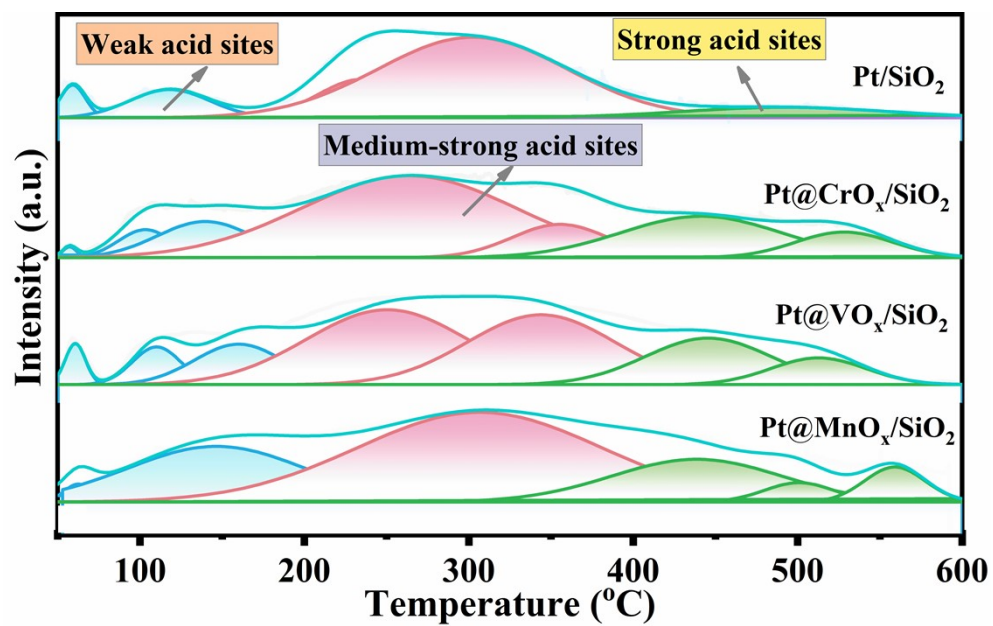


Fig. S4 NH₃-TPD analysis of Pt/SiO₂, Pt@CrO_x/SiO₂, Pt@VO_x/SiO₂ and Pt@MnO_x/SiO₂ catalysts.

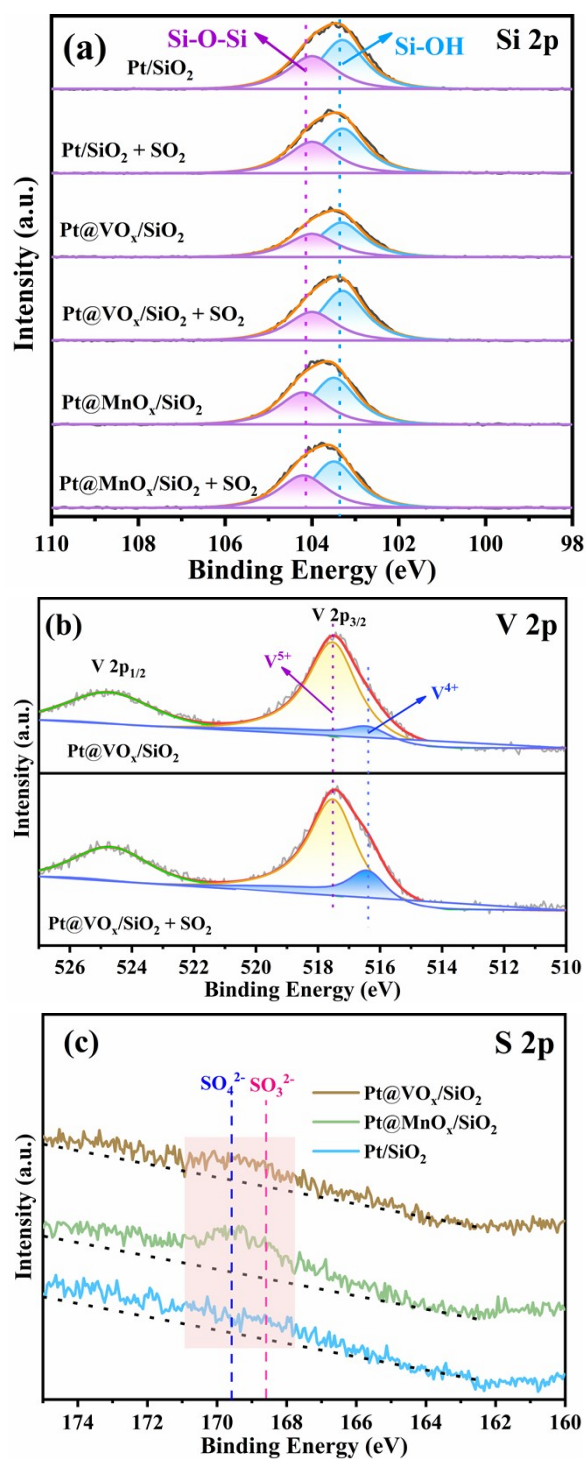


Fig. S5 XPS spectra of Si 2p (a) for fresh and used catalysts of Pt/SiO₂, Pt@VO_x/SiO₂ and Pt@MnO_x/SiO₂; XPS spectra of V 2p (b) for fresh and used catalysts of Pt@VO_x/SiO₂; XPS spectra of S 2p (c) for Pt@VO_x/SiO₂, Pt@MnO_x/SiO₂ and Pt/SiO₂ catalysts.

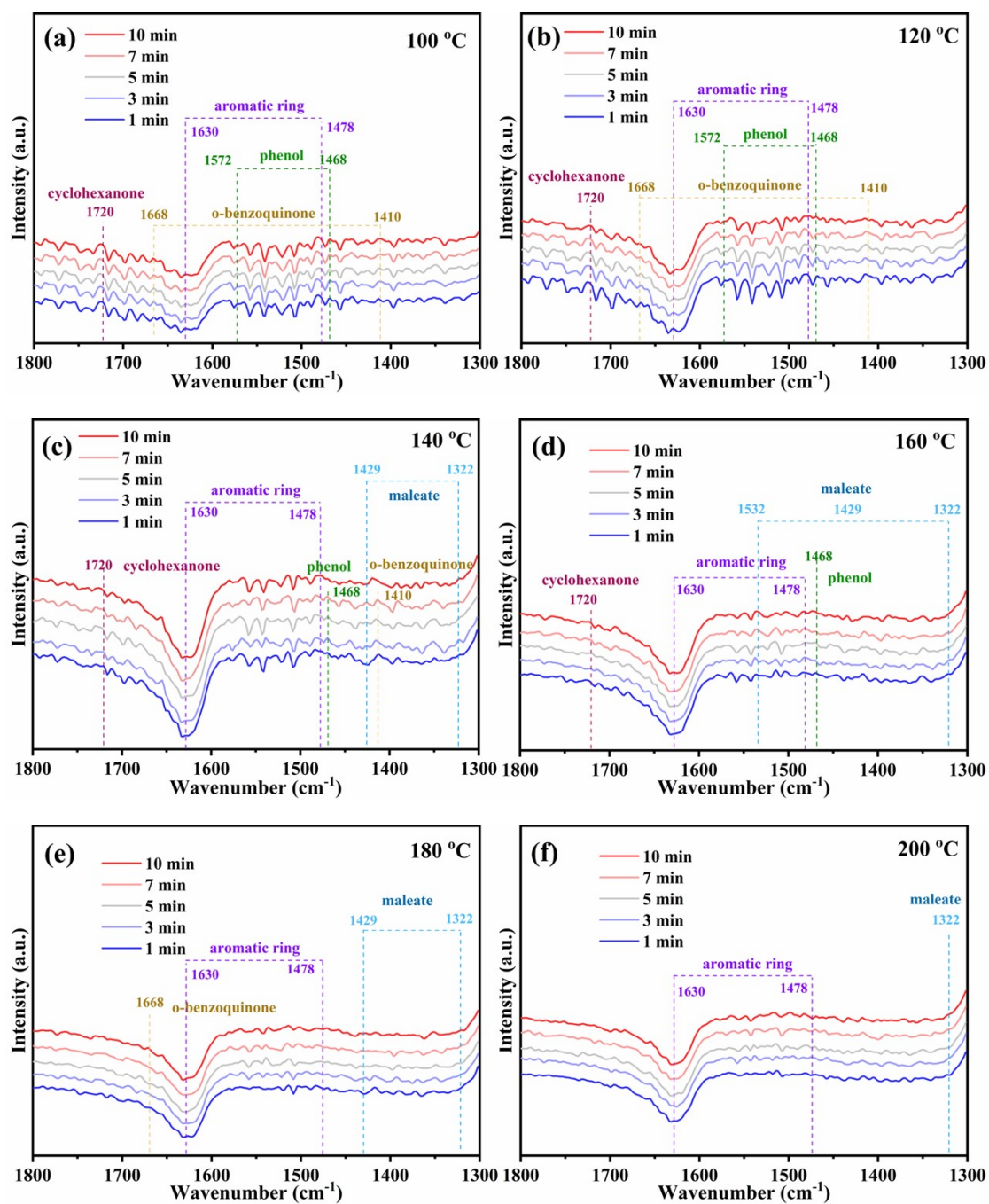


Fig. S6 In situ DRIFT spectra of Pt@MnO_x/SiO₂ catalyst exposed to air flow at different temperature for different times (a-f).

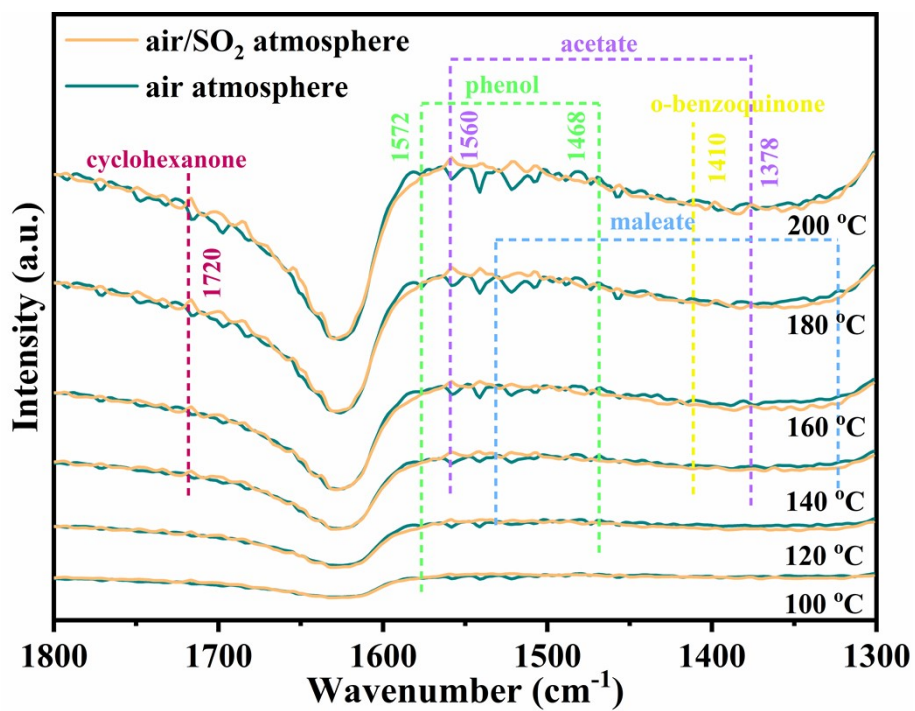


Fig. S7 In situ DRIFT spectra diagram of Pt/SiO₂ catalyst reaction at different temperatures under two atmospheres.

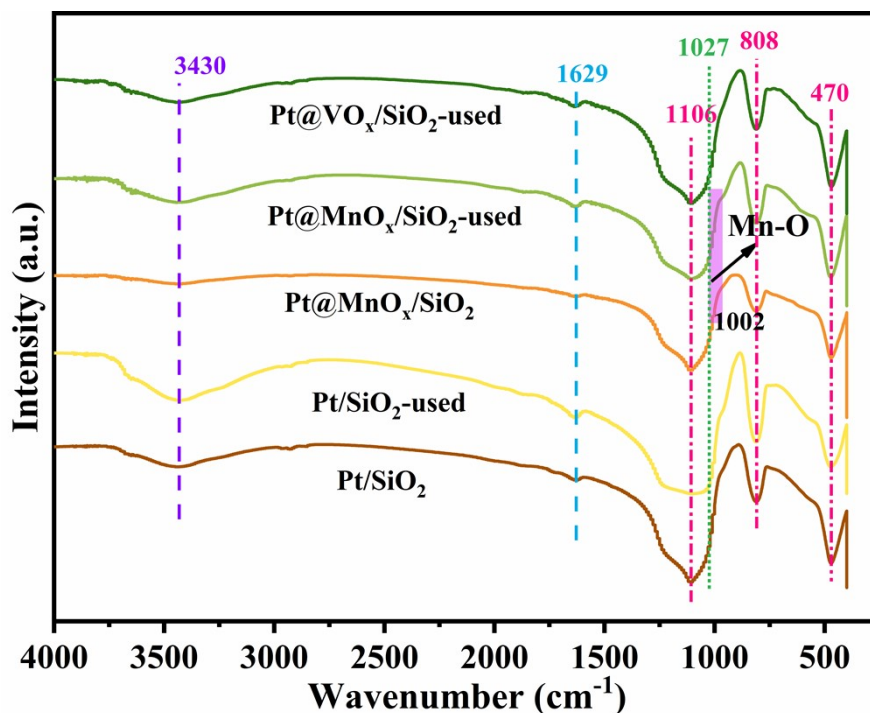


Fig. S8 FTIR spectra of fresh and used samples of Pt/SiO₂, Pt@MnO_x/SiO₂ and used Pt@VO_x/SiO₂ catalysts.

The peaks at 470 and 808 cm⁻¹ belong to the symmetric stretching vibration of Si-O-Si bond in SiO₂ carrier, and the characteristic peak nears 1106 cm⁻¹ can be attributed to the antisymmetric stretching vibration of siloxane bond. Besides, the spectral band at 1027 cm⁻¹ is associated with Si-O bond, while the bands at 3430 and 1629 cm⁻¹ are attributed to the O-H bond stretching vibrations of molecular water. Moreover, in the Pt@MnO_x/SiO₂ catalyst, the band at 1002 cm⁻¹ is due to the vibration of the Mn-O bond, and the intensity of this peak increases in the used catalyst, which may be related to the re-dispersion of Mn species after the reaction.