Appendix A. Supplementary Data

Mesoporous CoO-supported palladium nanocatalysts with high performance for *o*-xylene combustion

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Content

Item	Page
Preparation of KIT-6	3
Catalyst Characterization	3
Elimination of mass transfer limitation	8
Table S1	11
Fig. S1	12
Fig. S2	13
Fig. S3	14
Fig. S4	15
Fig. S5	16

Preparation of KIT-6:

KIT-6 was prepared at a low HCl concentration (0.5 M) in an aqueous solution using tetraethoxysilane (TEOS, Acros 99%) as the silicon source and a blend of Pluronic P123 and *n*-butanol (Aldrich, 99%) as a structure-directing mixture. Briefly, 6 g of Pluronic P123 was dissolved in 217 ml of distilled water and 9.83 ml of HCl (37%) under vigorous stirring. After complete dissolution, 7.41 ml of *n*-butanol was added. The mixture was left stirring at 35 °C for 1 h, after which 13.8 ml of TEOS was slowly added to the homogeneous clear solution. This mixture was further left stirring at 35 °C for 24 h, followed by aging at 100 °C for 24 h under static conditions (this process is referred to as hydrothermal treatment). The solid product was filtered, washed several times with distilled water and alcohol and dried for 24 h at 100 °C. The final KIT-6 template was obtained from above powders after calcined at 550 °C for 4 h under air atmosphere.

Catalyst Characterization:

The real metal contents of Pd in the samples were determined using the ICP−AES technique on a Thermo Electron IRIS Intrepid ER/S spectrometer. Each sample was directly dissolved in a mixture of concentrated HCl (37 wt%) and HNO_3 (75 wt%) aqueous solutions with a volumetric ratio of 3.0 : 1.0 prior to analysis. X-ray diffraction (XRD) patterns of the samples were obtained on a Bruker D8 Advance diffractometer with Cu Kα radiation and nickel filter (λ = 0.15406 nm). BET (Brunauer-Emmett-Teller) surface areas of the samples were determined via N_2 adsorption at −196 °C on a Micromeritics ASAP 2020 analyzer with the samples

being outgassed at 300 $^{\circ}$C for 2.5 h under vacuum before measurement. Transmission electron microscopic (TEM) images and selected-area electron diffraction (SAED) patterns of the samples were obtained using the JEOL-2010 equipment (operating at 200 kV). X-ray photoelectron spectroscopy (XPS, VG CLAM 4 MCD analyzer) was used to determine the binding energies (BEs) of Co 2p, O 1s, Pd 3d, and C 1s of surface species using Mg Kα (hv = 1253.6 eV) as excitation source. In order to remove the adsorbed water and carbonate species on the surface, the samples were pretreated in N$_2$ (flow rate = 20 mL/min) at 300 $^{\circ}$C for 1 h and then cooled to room temperature (RT). The pretreated samples were degassed in the preparation chamber (10^{-5} Torr) for 0.5 h and then introduced into the analysis chamber (3 × 10^{-9} Torr) for XPS spectrum recording. The C 1s signal at 284.6 eV was taken as reference for BE calibration.

Carbon monoxide temperature-programmed reduction (CO–TPR) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics) coupled with mass spectroscopy (MS) (Hiden QGA). Before TPR measurement, ca. 0.03 g of the sample (40–60 mesh) was loaded to a quartz fixed-bed U-shaped microreactor (i.d. = 4 mm) and pretreated in an N$_2$ flow of 30 mL/min at 300 $^{\circ}$C for 1 h. After being cooled at the same atmosphere to RT, the pretreated sample was exposed to a flow (30 mL/min) of 10% CO–90% Ar (v/v) mixture and heated from RT to 900 $^{\circ}$C at a ramp of 10 $^{\circ}$C/min. The alteration in CO concentration of the effluent was monitored online by the chemical adsorption analyzer. The generated CO$_2$ was determined by MS (m/z = 44). The reduction peak was calibrated against

that of the complete reduction of a known standard powdered CuO (Aldrich, 99.995%).

Oxygen temperature-programmed desorption (O_2–TPD) was carried out on the apparatus same as that used in the CO–TPR experiments. Prior to O_2–TPD experiment, 30 mg of the sample was preheated in an N_2 flow of 30 mL/min at 300 ^oC for 1 h. After cooling to RT, an O_2 flow of 40 mL/min was employed for 60 min, then purging the un-adsorbed O_2 in a He flow of 30 mL/min for another 60 min, and signals were recorded when the sample was heated from RT to 900 ^oC at a ramp of 10 ^oC/min and the same flow. The desorption amounts of oxygen were determined according to an oxygen pulse experiment monitored by a thermal conductivity detector together with MS.

O-xylene temperature-programmed desorption (o-xylene-TPD) was carried out on a mass spectrometer (MS, Hiden QGA). Prior to o-xylene-TPD experiment, ca. 0.03 g of the sample (40−60 mesh) was loaded to a quartz fixed-bed U-shaped microreactor (i.d. = 4 mm) and preheated in an N_2 flow of 30 mL/min at 300 ^oC for 1 h. After cooling to RT, an air flow of 30 mL/min was employed for 60 min, then purging the un-adsorbed O_2 in a N_2 flow of 30 mL/min for another 60 min. Subsequently, an o-xylene flow (1000 ppm) of 30 mL/min was passed through the samples for 1 h, then purging the un-adsorbed o-xylene using a N_2 flow of 30 mL/min for 1 h. Finally, signals were recorded by MS (m/z = 91) when the sample was heated from RT to 900 ^oC at a ramp of 10 ^oC/min and the same flow.

In $situ$ diffuse reflectance Fourier transform infrared spectroscopic (DRIFT)

experiments were carried on a Bruker FT-IR spectrometer (TENSOR II) with a liquid nitrogen-cooling MCT detector. Before the *in situ* DRIFT experiment, 30 mg of the sample was loaded into a high-temperature IR cell with KBr windows (PIKE TECHNOLOGIES). For oxygen adsorption, the samples were preheated in an N_2 flow of 30 mL/min at 300 ^oC for 1 h. Subsequently, the sample was cooled to 40 ^oC and kept for another 30 min, and then the background spectrum was recorded. Finally, an air flow (10.0 mL/min) was used to purge the IR cell, and the DRIFT spectra were recorded after accumulating 32 scans at a spectrum resolution of 4 cm^{-1}. For *o*-xylene adsorption, the samples were preheated in an N_2 flow of 30 mL/min at 300 ^oC for 1 h. After cooling to RT, an air flow of 30 mL/min was employed for 1 h, then purging the un-adsorbed O_2 in a N_2 flow of 30 mL/min for 1 h, and the background spectrum was recorded. Finally, an *o*-xylene flow (1000 ppm) of 10 mL/min was used to pass through the pretreated samples in the IR cell, and the DRIFT spectra were recorded after accumulating 32 scans at a spectrum resolution of 4 cm^{-1}. For water vapor adsorption, the sample was pretreated in an N_2 flow of 30 mL/min at 300 ^oC for 1 h. After the sample was cooled to 190 ^oC, a reactant mixture (1000 ppm *o*-xylene + 20.0 vol% O_2 + N_2 (balance)) flow of 30 mL/min was switched and passed through the sample for 2 h, and then the background spectrum was recorded. Finally, a reactant mixture flow of 30 mL/min with 2.0 vol% water vapor was used to pass through the pretreated samples in the IR cell. The DRIFT spectrum was measured after accumulating 32 scans at a resolution of 4 cm^{-1} until a stable adsorption was achieved.

Elimination of mass transfer limitation

The estimation of the Damköhler number under the most unfavorable conditions reveals that the external diffusion mass transfer resistance was negligible. Making a Weisz–Prater analysis is a facile way to evaluate the absence or presence of internal mass transfer limitation. According to the Weisz-Prater criterion, when the dimensionless Weisz–Prater parameter (N_{W-P}) is less than 0.3, it can be considered as a sufficient condition for the absence of significant pore diffusion limitation [27]. When o-xylene was oxidized at 140 ^{o}C over the Pd/meso-CoO sample, the N_{W-P} value was calculated to be 0.166, which was less than 0.3. Effective diffusivity was calculated according to the Maxwell-Gilliland formula and Nusselt number (details of calculation are placed in the Supplementary material). Damköhler number and Weisz–Prater parameter were calculated under the most unfavorable conditions, and the results reveal that the external and internal diffusion (mass transfer resistance) was negligible under the adopted reaction conditions. In the present work, the concentration of o-xylene was low (1000 ppm), and the kinetic calculation was obtained at low o-xylene conversions (< 10 %). Furthermore, by varying the flow rates and catalyst mass (at the same SV), the same o-xylene conversions were detected over the as-prepared catalysts for o-xylene combustion. Furthermore, the axial dispersion effect can be neglected at a reactor/particle diameter ratio of higher than 10 and a catalyst bed length/particle diameter ratio of higher than 50 [28]. In the present work, the above two ratios were 21 and 65, respectively. There was no significant heat or mass transfer limitation under the adopted reaction conditions.

Calculation of Damköhler number (D_a):

The absence of external diffusion mass transfer resistance was checked by the Damköhler number (D_a).

$$D_a = kC_0^{n-1}\tau$$

Where k = reaction rate constant,

C_0 = initial concentration of reactant,

n = reaction order, τ = stay time.

According to the activity data obtained over Pd/meso-CoO at o-xylene concentration = 1000 ppm and SV = 120,000 mL/(g h), the k, C_0, and τ were 0.1349 at 170 °C, 1.362 × 10^{-6} mol/(g s), and 0.0314 s, respectively. The oxidation of o-xylene at an o-xylene/O_2 molar ratio of 1/200 would follow a first-order reaction mechanism with respect to o-xylene concentration. Hence the value of n was 1.

$k = 0.1349$, $C_0 = 1.362 \times 10^{-6}$ mol/(g s), $n = 1$, $\tau = 0.0314$ s

$D_a = 0.1349 \times (1.362 \times 10^{-6})^{1-1} \times 0.0314 = 0.0042 < 1$

Calculation of Weisz-Prater Criterion (N_{W-P}):

The absence of internal mass diffusion transport resistance was checked by the Weisz-Prater Criterion (N_{W-P}).

$$N_{w-p} = \frac{r_a \cdot R_p^2}{C_s \cdot D_{eff}}$$

Where r_a = reaction rate per volume of catalyst, mol/(m^3 s)

R_p = catalyst particle radius, m

D_{eff} = effective diffusivity, m^2/s

C_s = reactant concentration at the external surface of the catalyst, mol/m^3

D_{eff} was determined from Maxwell-Gilliland formula ($D_{A,B}$) and Nusselt number (D_K):

$$D_{A,B} = 4.36 \times 10^{-5} \cdot T^{3/2} \cdot P^{-1} \cdot (1/M_A + 1/M_B)^{1/2} \cdot (V_A^{1/3} + V_B^{1/3})^{-2}$$

$$D_K = 9700r \cdot (T/M)^{1/2}$$

$$D_{eff} = 0.25 \, D_{A,B} \cdot D_K \cdot (D_{A,B} + D_K)^{-1}$$

Where T is temperature, P is pressure, M (M_A and M_B) is molar mass of reactant, V_A and V_B are molecule volume of reactants, and r is average pore diameter of catalyst.

For o-xylene oxidation, a total gas flow rate of 33.2 mL/min and an average catalyst particle size of 0.282 mm were employed for the kinetic study. The concentration of o-xylene employed in the feed was 1000 ppm. For the Pd/meso-CoO sample, the pore diameter was 3.8 nm, and the reaction rate was 0.034 mol/(m^3 s) at 140 ^{o}C.

$r_a = 0.034$ mol/(m^3 s); $R_p = 1.41 \times 10^{-4}$ m

$D_{eff} = 15.05 \times 10^{-8}$ m^2/s; $C_s = 0.027$ mol/m^3

$$N_{w-p} = \frac{r_a \cdot R_p^2}{C_s \cdot D_{eff}} = 0.166 < 0.3$$

Therefore, the internal diffusion effect could be neglected for the kinetic study of o-xylene oxidation.

Table S1. Catalytic performance for *o*-xylene combustion over the catalysts reported in the literature.

| Catalyst	Reaction condition	$T_{10\%}$ (°C)	$T_{90\%}$ (°C)	Ref.
0.8 wt% Pd/HFAU(17)	1700 ppm *o*-xylene, O_2 concentration = 20 %; SV = 18,000 h^{-1}	210	218	34
0.30 wt% Pt/HBEA(50)-reduced	1700 ppm *o*-xylene, O_2 concentration = 20 %; SV = 18,000 h^{-1}	185	195	5
1 wt% Pd/Co$_3$O$_4$ (3DL)	150 ppm *o*-xylene, O_2 concentration = 20 %; WHSV = 60,000 mL/(g h)	204	254	8
1 wt% Pd/Co$_3$O$_4$ (3D)	150 ppm *o*-xylene, O_2 concentration = 20 %; WHSV = 60,000 mL/(g h)	178	204	6
1.94 wt% Au–Pd–0.22Fe/3DOM Mn$_2$O$_3$	1000 ppm *o*-xylene, O_2 concentration = 20 %; WHSV = 40,000 mL/(g h)	140	213	35
0.96 wt% Pd/meso-CoO	1000 ppm *o*-xylene, O_2 concentration = 20 %; WHSV = 40,000 mL/(g h), SV = 38,200 h^{-1}	140	173	This work
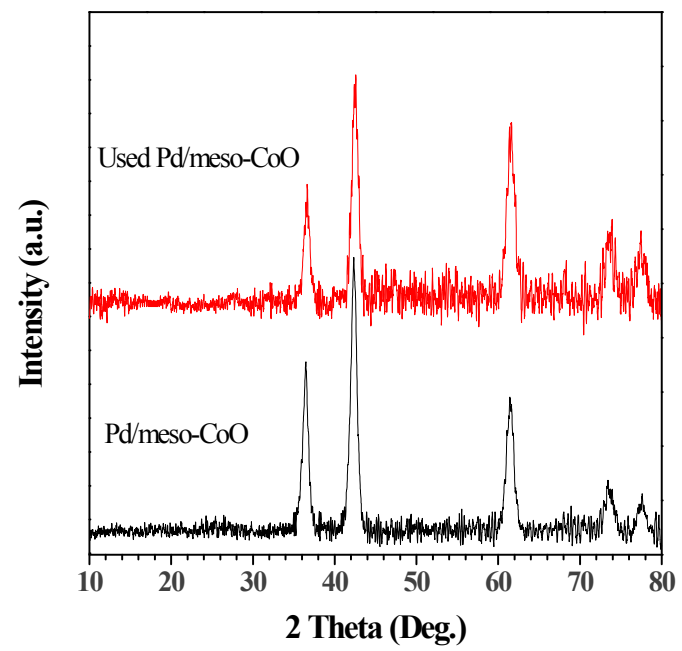
Fig. S1. XRD patterns of Pd/meso-CoO before and after on-stream reaction in the presence of 2.0 vol% H_2O.
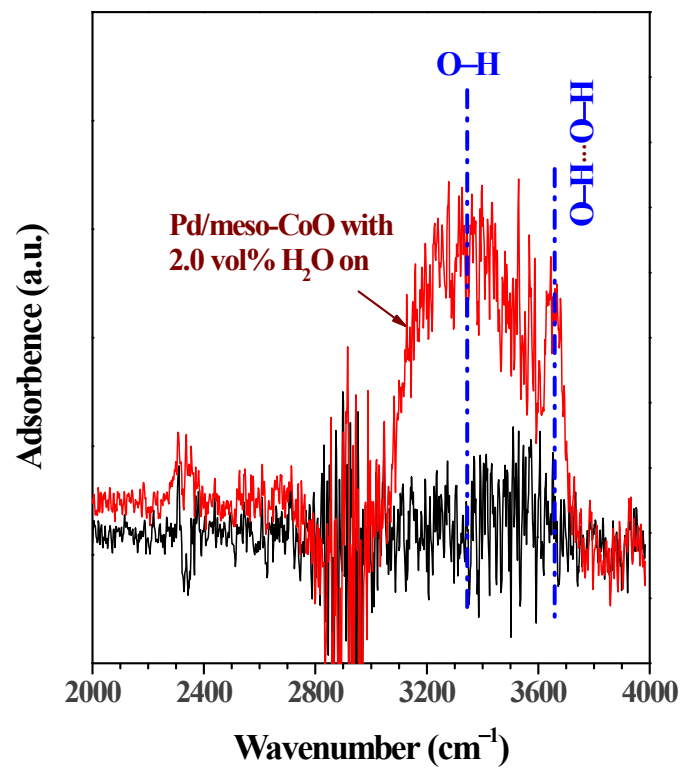
Fig. S2. *In situ* DRIFT spectra of the Pd/meso-CoO sample before (black line) and after (red line) exposure to 2.0 vol% H_2O.
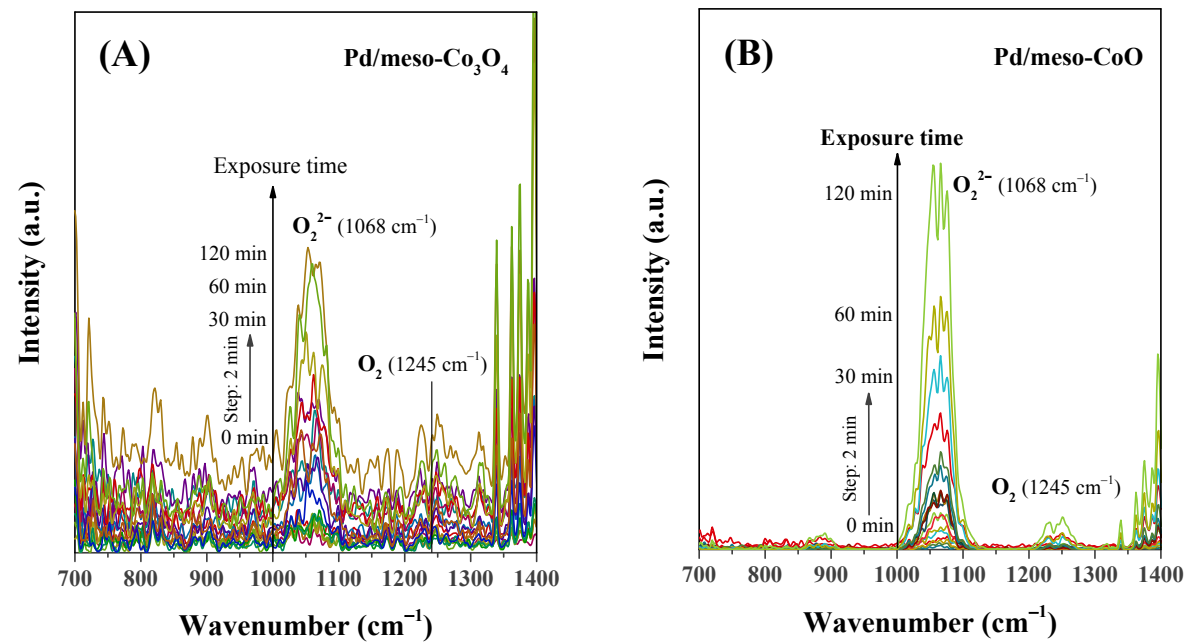
Fig. S3. *In situ* DRIFT spectra of (A) Pd/meso-Co$_3$O$_4$ and (B) Pd/meso-CoO after exposure to the air flow (10 mL/min) at 40 °C for different time.
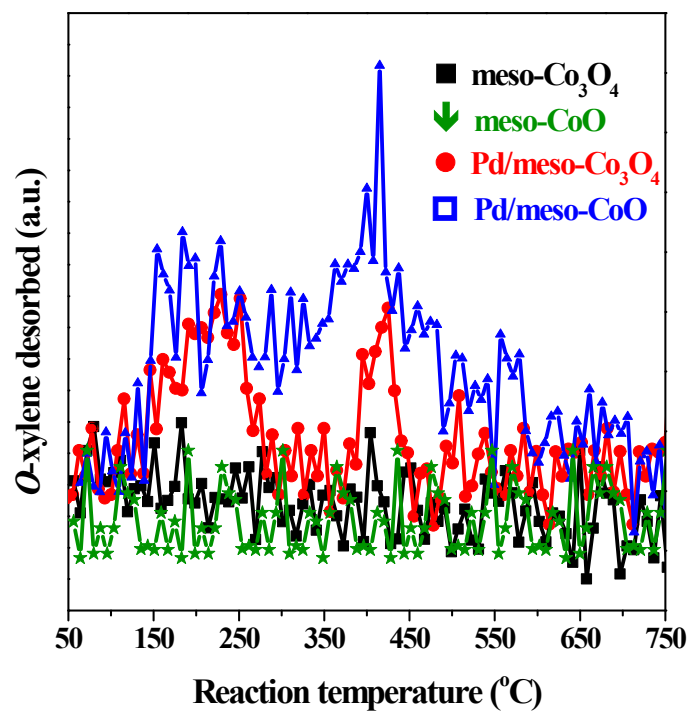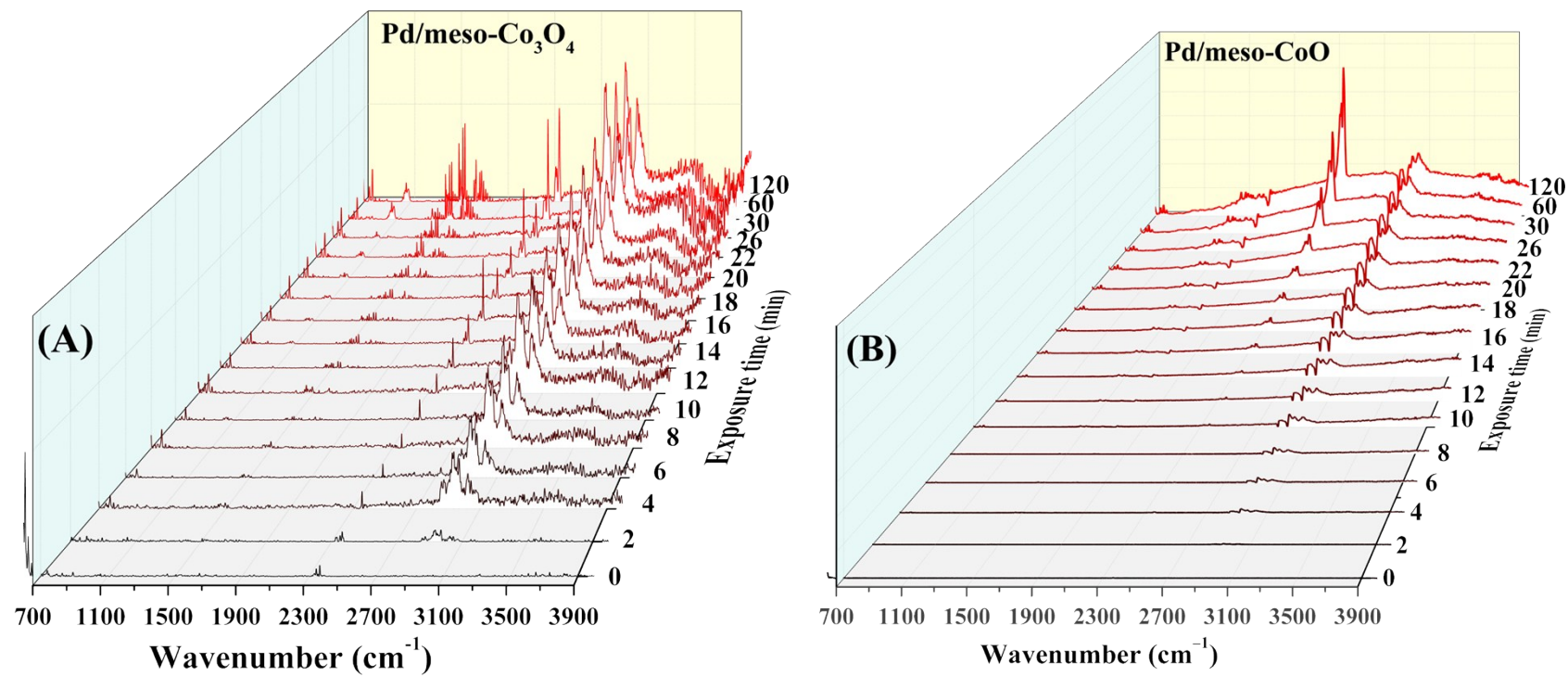
Fig. S4. *O*-xylene–TPD profiles of the samples.

Fig. S5. *In situ* DRIFT spectra of (A) Pd/meso-Co$_3$O$_4$ and (B) Pd/meso-CoO after exposure to the 1000 ppm *o*-xylene flow (10 mL/min) at 40 °C for different time.