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Metal–organic framework-derived hierarchical porous N/Co-doped carbon-supported sponge-like Pd–SnO_2 nanostructures for low-temperature CO oxidation†

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Metal–organic framework-derived porous N/Co-doped carbon (MOF-PNC) nanostructures-supported metal nanoparticles (NPs) are of great importance in multidisciplinary catalytic reactions; however, their catalytic performance toward low-temperature CO oxidation (CO_{Oxid}) is rarely reported. Herein, a MOF-PNC-supported Pd–SnO_2 (Pd–SnO_2/MOF-PNC) was synthesized *via* a microwave-irradiation (MW-I), annealing, and chemical etching approach for thermal CO_{Oxid}. The as-prepared Pd–SnO_2/MOF-PNC had hierarchical porous sponge-like nanostructures composed of porous two-dimensional ultrathin nanosheets (NSs), co-doped with N/Co, with a high specific surface area (185.40 $m^2\ g^{-1}$) and pore volume (0.045 $cm^3\ g^{-1}$), and ornamented with Pd–SnO_2 NPs (7.79 ± 1.42 nm). These merits endowed the Pd–SnO_2/MOF-PNC with excellent thermal catalytic CO_{Oxid} activity at a low complete CO conversion temperature (T_{100} = 65.6 °C) compared to those of Pd(1%)–SnO_2/MOF-PNC (165.2 °C), Pd–SnO_2 (199.1 °C), Pd/MOF-PNC (107.9 °C) and commercial Pd/C catalysts (201.2 °C), due to the augmented electronic interaction and synergy of Pd NPs with oxygen-rich SnO_2 supports and Co–N_x active sites in MOF-PNC. Thus, coupling two supports (*i.e.*, SnO_2/MOF-PNC) is more crucial for promoting the low-temperature CO_{Oxid} activity of Pd NPs.

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Introduction

The global energy demand has increased substantially in the last few decades and is expected to continue to rise owing to the inevitable industrialization and civilization.[1–3] Limitless efforts to solve these issues lie in developing green energy technologies (*i.e.*, fuel cells,[4] batteries,[5] and water splitting[6,7]) and gas conversion reactions.[8–10] CO_{Oxid} is formed during heterogeneous catalysis electrochemically,[11,12] or thermally,[13–16] but the latter is feasible for large-scale applications. Pd-based catalysts are among the most active catalysts for thermal CO_{Oxid}, however, the high cost and earth-rarity of Pd are critical barriers.[17] Using metal oxide supports (SnO_2, SiO_2, Fe_2O_3, TiO_2, and CeO_2) could boost the catalytic performance and stability, and reduce the cost.[18,19] Also, the electronic interaction and synergy of Pd with metal oxide supports enhances the activation/dissociation of CO/O_2 reactants and quickly desorbs intermediate species (*i.e.*, carbonate/formate) and products (*i.e.*, CO_2). For instance, the Pd/MgO-h-BN catalyst showed a lower complete CO conversion temperature (T_{100} = 140 °C) than Pd/MgO (180 °C), but Pd/h-BN could not achieve T_{100}, due to the interaction of Pd with the MgO-h-BN support that enhanced the large amount of adsorbed O_2 and rapidly desorbed the intermediates.[20] Pd@SiO_2-673-CeO_2 catalysts had great thermal CO_{Oxid} at a lower T_{100} (92 °C) than Pd@SiO_2-673 (130 °C), owing to the interaction of Pd with dual supports (*i.e.*, SiO_2 and CeO_2).[21]

Unlike other supports, metal–organic framework-derived porous N/Co-doped carbon (MOF-PNC) nanostructures possess outstanding features (*i.e.* thermal/chemical stability and impressive surface area), and rich metal-N_x active sites,[22–24] which are beneficial for uniform distribution and stabilization of Pd NPs.[25–27] In addition, they make Pd active sites readily accessible and maximize their utilization for thermal CO_{Oxid}.[28–30] For instance, porous C-supported Cu/Cu_2O nanojunctions derived from (Cu-BTC)-MOF had impressive CO_{Oxid} activity achieved at T_{100}

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(155–190 °C),[31] due to a high ratio of Cu metal phases (Cu^0, Cu^+, and Cu^{2+}) and interaction with the porous C support. Noticeably, MOF-PNC-supported metal NPs are not emphasized enough, particularly using SnO_2 as a co-support, for thermal CO_{Oxid}, and their effect remains ambiguous.[24,32–34]

Herein, MOF-PNC-supported Pd–SnO_2 (Pd–SnO_2/MOF-PNC) exhibited hierarchical porous sponge-like nanostructures comprising porous 2D ultrathin MOF-PNC NSs with abundant N/Co dopants, large specific surface area (185.40 m^2 g^{-1}), and encapsulated spherical-like Pd–SnO_2 NPs (7.79 ± 1.42 nm). Coupling the properties of SnO_2 (*i.e.*, ease of adsorption and activation/dissociation of CO/O_2) and the merits of MOF-PNC (*i.e.*, high surface area and rich metal-N_x active sites) can ease CO oxidation on Pd at a low temperature and enhanced durability. The thermal CO_{Oxid} activities of Pd–SnO_2/MOF-PNC, Pd(1%)–SnO_2/MOF-PNC, Pd–SnO_2, SnO_2/MOF-PNC and Pd/MOF-PNC are benchmarked to commercial Pd/C catalysts in order to estimate the effect of the supports.

Materials and methods

Materials

Potassium tetrachloropalladate(II) (K_2PdCl_4 ≥ 98%), tin(II) chloride dihydrate ($SnCl_2{\cdot}2H_2O$ ≥ 98%), cobalt(II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$ ≥ 94.5%), biphenyl-4,4′-dicarboxylic acid (BPDC ≥ 97%), ethylene glycol (EG ≥ 99.8%), triethyleneamine (TEA ≥ 99.5%), dimethylformamide (DMF ≥ 99.8%), and commercial Pd/C catalyst (20 wt%) were purchased from Sigma-Aldrich Chemie GmbH (Munich, Germany).

Preparation of MOF-derived porous Co/N-doped carbon (MOF-PNC)

MOF-PNC was synthesized by mixing $Co(NO_3){\cdot}6H_2O$ (0.44 g), BPDC (0.36 g), TEA (1.5 mL) and DMF (50 mL) under magnetic stirring at 25 °C, then microwave-irradiated at 600 W for 30 min.[33] The obtained precipitates were washed and dried in a vacuum oven at 60 °C, followed by annealing at 800 °C for 5 h. The obtained powder was soaked in an aqueous solution of HCl (3 M) for 24 h, washed, and dried to give MOF-PNC.

Preparation of SnO_2/MOF-PNC

SnO_2/MOF-PNC was prepared by magnetically stirring $SnCl_2{\cdot}2H_2O$ (47.8 mg) in a mixture of EG and water (4 : 1 by volume); then, MOF-PNC (100 mg) was added and the mixture was microwave-irradiated at 600 W for 1 h. The resulting product (SnO_2/MOF-PNC) was washed and dried at 80 °C for 4 h under vacuum.

Preparation of Pd–SnO_2/MOF-PNC

The as-prepared SnO_2/MOF-PNC (100 mg) was mixed with K_2PdCl_4 (61.35 mg) in EG (50 mL) at a pH of 12 with NaOH under magnetic stirring at 25 °C for 30 min, followed by microwave-irradiation at 600 W for 1 h (Anton Paar – Multiwave 3000).[35] Then, the mixture's pH was lowered to 3 using 0.1 M HNO_3, and it was washed thoroughly with deionized H_2O, and dried at 80 °C for 4 h under a vacuum to afford Pd–SnO_2/MOF-PNC. A similar method was used for the preparation of Pd(1%)–SnO_2/MOF-PNC (1 wt% Pd loading) and Pd–SnO_2.

Preparation of Pd/MOF-PNC

Pd/MOF-PNC was prepared by mixing MOF-PNC (100 mg) with K_2PdCl_4 (61.35 mg) in EG (50 mL) under magnetic stirring at 25 °C for 30 min and the pH was adjusted to 12 using NaOH solution (1 M). Then, the solution was placed in a microwave and irradiated at 600 W for 1 h.[35] Finally, the mixture's pH was decreased to 3 using 0.1 M HNO_3, washed with deionized H_2O, and dried at 80 °C for 4 h under vacuum.

Characterisation

The morphology and composition analysis were conducted on a scanning electron microscope (SEM, Hitachi S-4800, Hitachi, Tokyo, Japan) and transmission electron microscope (TEM, TecnaiG220, FEI, Hillsboro, OR, USA) equipped with an energy dispersive spectrometer (EDS). The electronic structure and surface composition were carried out by X-ray photoelectron spectroscopy ((XPS) Ultra DLD XPS Kratos, Manchester, UK). The powder X-ray diffraction pattern (XRD) was measured on an X-ray diffractometer (X'Pert-Pro MPD, PANalytical Co., Almelo, Netherlands). The N_2-physisorption isotherms were measured on a Quanta chrome Autosorb-1 analyzer (Quanta chrome Instrument Corporation). The Fourier transform infrared spectra (FT-IR) were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer (Thermo Scientific).

Thermal CO oxidation reaction

The thermal CO oxidation reaction was carried out in a fixed bed quartz tubular reactor connected to an online gas analyzer (Mass spectra, HIDEN ANALYTICAL the HPR-20 System) using 50 mg of each catalyst at the same Pd loading amount (20 wt%).[36] The catalyst was packed with quartz wool and fixed in the reactor and then pretreated at 200 °C (5 °C min^{-1} heating ramp) under O_2 (5% in Ar) with a flow rate of 20 mL min^{-1} for 1 h and subsequently under H_2 (5% in Ar) with a flow rate of 20 mL min^{-1} for 1 h. After cooling to 25 °C, the catalyst was exposed to the gas mixture (O_2 (20%) + CO (4%) + Ar (76%)) at a flow rate of 20 mL min^{-1} under heating to 300 °C (5° min^{-1} ramping rate).[36] All the catalysts were subjected to the same treatment before the thermal CO oxidation. The percentage of CO conversion (%CO) was calculated using the following (eqn (1)):

$$\%CO = \left(\frac{CO_{in} - CO_{out}}{CO_{in}}\right) \times 100 \quad (1)$$

where CO_{in} is the input amount of CO and CO_{Out} is the output amount of CO estimated from the mass spectra.

The CO temperature-programmed desorption (CO-TPD) was conducted by the initial pretreatment of each catalyst (50 mg) under Ar (50 mL min^{-1} flow rate) at 300 °C (5 °C min^{-1}) for 1 h in a Micromeritics ChemiSorb 2750 analyzer equipped with a thermal conductivity detector (TCD). After cooling to room temperature, the catalysts were exposed to (4% CO + 96% Ar)

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at a flow rate of 30 mL min^{-1} for 30 min under heating to 350 °C (5 °C min^{-1}).[36]

The H_2 temperature-programmed reduction (H_2-TPR) was measured by an initial pretreatment under Ar (50 mL min^{-1}) at 300 °C (10 °C min^{-1}) for 1 h and then exposed to (5% H_2 + 95% Ar) at a flow rate of 30 mL min^{-1} under heating to 350 °C (5 °C min^{-1}).[36]

The O_2 temperature-programmed oxidation (O_2-TPO) was studied by initial treatment under Ar at a flow rate of 50 mL min^{-1} at 300 °C (5 °C min^{-1}) for 1 h and then exposed to (20% O_2 + 80% Ar) at a flow rate of 30 mL min^{-1} under heating to 350 °C (20 °C min^{-1}).

To get more insights into the thermal CO oxidation, the CO oxidation rate (r_{CO}) of the catalysts was calculated at different CO conversion temperatures (10, 20, 50, and 80 °C) based on total gas flow (V_{Gas}), initial concentration of CO (X_{CO}), and molar weight of catalyst (M_{Cat}) using eqn (2).

$$r_{CO} = \left[\frac{X_{CO} \times V_{Gas}}{M_{Cat}}\right] \quad (2)$$

The apparent activation energy (E_a) was calculated at varied CO conversion (10–50%), based on the Arrhenius equation (eqn (3)) and the relationship between ln-r_{CO} and 1/T.[36]

$$\ln r = \ln A - \frac{E_a}{RT} + a\ln[CO] + b\ln[O_2] \quad (3)$$

Results and discussion

The Pd–SnO_2/MOF-PNC was synthesized *via* the MW-I of $Co(NO_3)\cdot 6H_2O$ with biphenyl-4,4′-dicarboxylic acid (BPDC) and triethyleneamine (TEA) in dimethylformamide (DMF) solution to form a MOF, which was annealed and etched in HCl solution to afford MOF-PNC NSs (Fig. 1a).[33] This was followed by MW-I with the Sn precursor and then K_2PdCl_4 in ethylene glycol (EG) to give Pd–SnO_2/MOF-PNC.[35] The SEM of Pd–SnO_2/MOF-PNC shows hierarchical porous sponge-like nanostructures (Fig. 1b), composed of porous 2D sheet-supported Pd NPs, with mean size (7.79 ± 1.42 nm), proved by TEM (Fig. 1c and d), which is important for stabilizing the Pd NPs against aggregation during the CO_{Oxid}. The lattice fringe (0.229 nm) of the Pd NPs is assigned to the {111} facet of face-center-cubic (fcc) Pd (Fig. 1e),[35] and the selected area electron diffraction pattern (SAED) reveals the typical rings of Pd (Fig. 1f).[35]

The EDX reveals the presence of Pd/Sn/Co/N/C/O with atomic contents (2.44/4.80/2.74/9.14/66.76/14.11 at%), indicating the successful formation of Pd/SnO_2 over MOF-PNC; however, Pd/MOF-PNC shows the existence of Pd/Co/N/C/O with contents (2.12/4.39/20.54/49.81/23.24 at%) (Fig. 1g) and uniform distribution mapped (Fig. S1, ESI†). Bulk and actual metal contents (Pd/Sn/Co (15.90/18.12/3.16 wt%)) in Pd–SnO_2/MOF-PNC, (Pd/Co (17.70/11.24 wt%)) in Pd/MOF-PNC and (Pd (19.78 wt%)) in Pd/C are confirmed by ICP-OES (Table S1, ESI†). Meanwhile, the existence of Co in both catalysts is attributed to the partial etching by HCl, which is particularly important to coordinate with Pd–SnO_2 and provide additional active sites for thermal CO_{Oxid}. The SEM of Pd/MOF-PNC shows its porous sponge-like structure (Fig. S2a, ESI†), but lower porosity than Pd–SnO_2/MOF-PNC, owing to the possible gas release during the MW-I in the absence of the Sn precursor.

The distribution of Pd NPs (9.07 ± 1.75 nm), the lattice fringe (0.225 nm) for Pd{111} and SAED, but only Pd/Co/C distributed as mapped (Fig. S2b–f, ESI†). The Raman reveals the D- (1358.2 cm^{-1}) and G-bands (1592.0 cm^{-1}), but SnO_2 incorporation induced more defects in Pd–SnO_2/MOF-PNC, proved by its higher I_D/I_G (2.01) than Pd/MOF-PNC (1.77) (Fig. S3a, ESI†).

The XRD of Pd–SnO_2/MOF-PNC and Pd/MOF-PNC at 40°, 46° and 68° is assigned to {111}, {200} and {220} of fcc Pd along with the {002} facet of amorphous C at 26°, but Pd–SnO_2/MOF-PNC has additional peaks of {101}, {200}, {211}, and {110} attributable to the tetragonal SnO_2 (Fig. 2a), compared to Pd/C (Fig. S4, ESI†).[35] The peak assigned to the C{002} facet in Pd–SnO_2/MOF-PNC is broadened with higher full width at half maximum (FWHM) than Pd/MOF-PNC, due to the possible coordination of Pd–SnO_2 with Co–N_x in MOF-PNC. This is also evidenced by the slight positive shifts of fcc Pd in Pd–SnO_2/MOF-PNC and Pd/MOF-PNC relative to Pd/C, implying lattice contraction of Pd. Crystallite sizes (2.8 and 3.0 nm) from the Scherrer equation for Pd–SnO_2/MOF-PNC and Pd/MOF-PNC, respectively.

The XPS survey of the catalysts displays the valence state of Pd 3d/Co 2p/C 1s/O 1s/N 1s, but Pd–SnO_2/MOF-PNC showed additional spectra of Sn 3d (Fig. S3b, ESI†). The atomic contents of Pd (2.16 at%) in Pd–SnO_2/MOF-PNC and 2.71 at% in Pd/MOF-PNC imply the coherent distribution of Pd on the surface, but the bulk metal contents are given by the ICP-OES (Table S1, ESI†), which is critical for providing enough active sites for thermal CO_{Oxid}. Pd 3d spectra of Pd–SnO_2/MOF-PNC and Pd/MOF-PNC display the phases of Pd^0, Pd^{2+}, and Pd^{4+} (Fig. 2b).[35] The ratio of Pd^0 to Pd^{2+} in Pd–SnO_2/MOF-PNC (0.62) was lower than Pd/MOF-PNC (0.77), due to the incorporation of metal oxide (*i.e.*, SnO_2) signifying more Pd^{2+} in the Pd–SnO_2/MOF-PNC.[35]

The Pd–SnO_2/MOF-PNC had a higher ratio of Pd^{2+} than Pd/MOF-PNC, owing to its possible interaction with SnO_2 during the reduction process, which led to the partial oxidation of Pd to generate more active PdO_x species and slightly decreased the d-band center of Pd, evidenced by the slight positive shift of Pd binding energies of Pd–SnO_2/MOF-PNC than Pd/MOF-PNC (Table S2, ESI†). Norskov *et al.* suggested that a d-band center and d-bandwidth slightly below the Fermi level is optimal for CO chemisorption, so the reduced d-band center of Pd may allow strong interaction and possible poisoning and deactivation.[37,38] However, this did not happen in the case of Pd–SnO_2/MOF-PNC, due to the promotional effect of Pd^0/Pd–O_x and their interfacial interaction with SnO_2 and Co/N-doped porous MOF-derived C. Notably, Norskov and co-workers reported the ability of promoters to balance the CO chemisorption on the metal surface and enhance its activity.[37,38] The C 1s spectra are assigned to sp^3/sp^2 (C–C/C=C) and the C–N bond (Fig. 2c), but shifted positively in Pd–SnO_2/MOF-PNC than Pd/MOF-PNC, due to the reduced electron density on C by the interaction with Pd–SnO_2. The Sn 3d spectra display major Sn^{2+} ($3d_{5/2}$ and $3d_{3/2}$) and minor Sn^0 (Fig. 2d). Meanwhile, Co 2p spectra show Co^{2+} ($3d_{3/2}$ and $3d_{1/2}$) and Co^0 (Fig. 2e). The N 1s spectra are attributed to pyridinic, pyrrolic, and graphitic (Fig. 2f).

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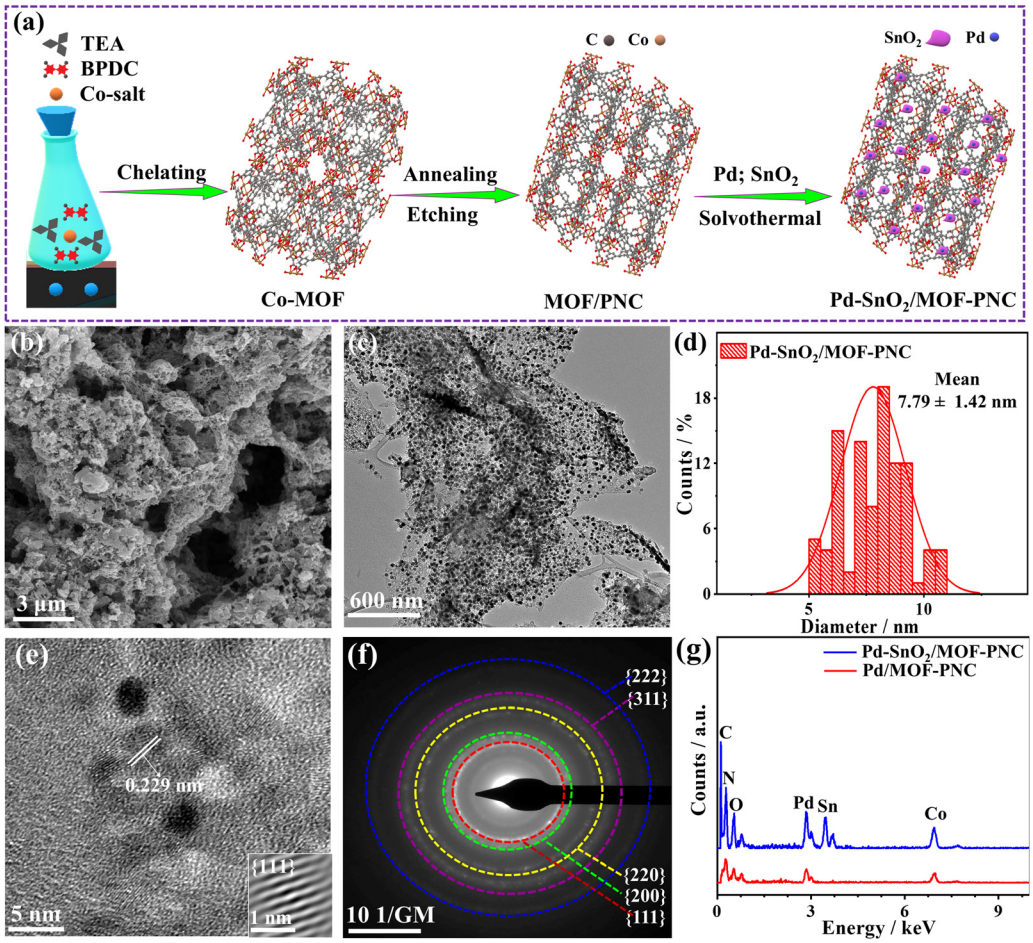

Fig. 1 (a) Schematic synthesis, (b) SEM, (c) TEM, (d) NPs size distribution, (e) HRTEM, (f) SAED of Pd–SnO_2/MOF-PNC and (g) EDX of Pd–SnO_2/MOF-PNC and Pd/MOF-PNC.

The BET-specific surface area of Pd–SnO_2/MOF-PNC (185.40 m^2 g^{-1}) is slightly higher than that of Pd/MOF-PNC (152.83 m^2 g^{-1}), and Pd/C (107.91 m^2 g^{-1}) (Fig. S5a–c, ESI†); meanwhile, the pore volume of Pd–SnO_2/MOF-PNC (0.045 cm^3 g^{-1}) was slightly higher than that of Pd/MOF-PNC (0.030 cm^3 g^{-1}), and Pd/C (0.012 m^3 g^{-1}), in addition to their multiple pore size range (2–110 nm) with mean pore sizes of 66.78, 56.54, and 12.31 nm for Pd–SnO_2/MOF-PNC, Pd/MOF-PNC, and Pd/C, respectively (Fig. S5d–f, ESI†).

The thermal CO_{Oxid} shows typical light-off curves for the conversion of CO to CO_2 at heating temperatures (25–300 °C) and atmospheric pressure, but a superior activity on Pd–SnO_2/MOF-PNC than Pd/MOF-PNC, and Pd/C (Fig. 3a).[39,40] The T_{100} of Pd–SnO_2/MOF-PNC (65.6 °C) is lower than that of Pd/MOF-PNC (107.9 °C) by 42.3 °C and Pd/C (201.2 °C) by 135.6 °C. This is due to the electronic and synergistic interaction of Pd^0/Pd–O_x active sites with oxygen-enriched SnO_2, Co–N_x and MOF-PNC, which optimizes CO + O_2 adsorption/activation and desorption of CO_2 at low temperatures.

Thus, Pd–SnO_2/MOF-PNC has higher CO_{Oxid} kinetics than Pd/MOF-PNC, and Pd/C, owing to its capacity to oxidize CO at all applied temperatures (Fig. 3b), *i.e.*, 50% of CO to CO_2 (T_{50} = 58.4 °C) on Pd–SnO_2/MOF-PNC was lower than Pd/MOF-PNC (99.9 °C) and Pd/C (186 °C). So, Pd–SnO_2/MOF-PNC completely oxidizes CO within only 13.12 min compared to Pd/MOF-PNC (21.58 min) and Pd/C (40.24 min) (Fig. 3c). The CO_{Oxid} activity of Pd–SnO_2/MOF-PNC was superior to previously reported Pd-based catalysts, *i.e.*, Pd/CeSn, Pd@SiO_2/TiO_2, Pd@CeO_2, Pd/MgO, (Pd@SiO_2-673-CeO_2 (92 °C),[21] Pd/MgO-h-BN (140 °C),[20] Cu/Cu_2O-500 nanojunctions (155 °C),[31] Pd/Cu/gC_3N_4NTs (154 °C),[41] Pd-Cu/gC_3N_4NWs (149 °C),[42] and Au/Pd/gC_3N_4NFs (149 °C)[43]) (Table S3, ESI†). The T_{100} of Pd–SnO_2/MOF-PNC (65.6 °C) is among the lowest values reported for Pd-based catalysts as far as we found. The CO_{Oxid} rate (r_{CO}) of Pd–SnO_2/MOF-PNC was 1.95 and 2.15 times that of Pd/MOF-PNC and Pd/C, respectively (Fig. 3d), indicating maximum utilization of Pd active sites in Pd–SnO_2/MOF-PNC, due to its greater porosity, which makes Pd active sites more accessible during CO_{Oxid}.

This is further seen in the lower activation energy (E_a = 69.5 kJ mol^{-1}) of Pd–SnO_2/MOF-PNC than Pd/MOF-PNC (74.1 kJ mol^{-1}) and Pd/C (89.2 kJ mol^{-1}) (Fig. 3e). The CO_{Oxid} stability of Pd–SnO_2/MOF-PNC at 65.6 °C was shown by a time-on-stream (TOS) for 108 h (Fig. 3f), which reveals excellent durability with insignificant loss in T_{100}. The stability of

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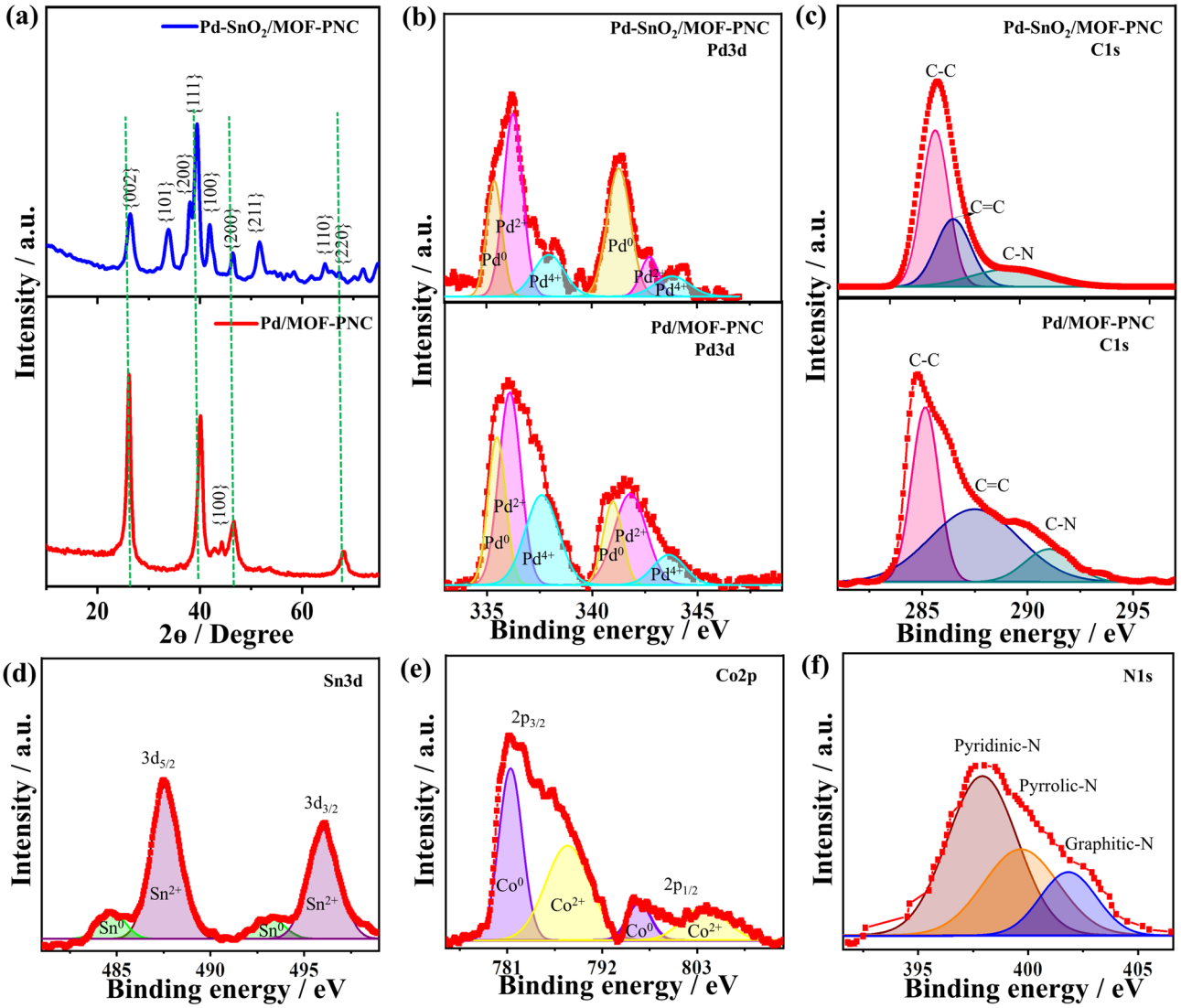

Fig. 2 (a) XRD, and high-resolution XPS (b) Pd 3d, (c) C 1s (d) Sn 3d, (e) Co 2p and (f) N 1s of Pd–SnO_2/MOF-PNC and Pd/MOF-PNC. The green lines in (a) refer to the positions of pure Pd NPs on C, which were taken from the JCPDS database.

Pd–SnO_2/MOF-PNC is further provided by TEM, which displayed the good dispersion of Pd nanoparticles over SnO_2/MOF-PNC without any obvious aggregation, indicating the architecture durability (Fig. S6a, ESI†). The XPS full-scan showed the presence of C 1s, Pd 3d, Co 2p, O 1s, N 1s, and Sn 3d without significant degradation for Pd (2.13 at%), implying compositional stability (Fig. S6b, ESI†). The BET maintained the same isotherm adsorption/desorption features before stability with an inferior loss in the surface area and pore volume (Fig. S6c and d, ESI†). This implies the reservation of the physiochemical properties of Pd–SnO_2/MOF-PNC after the durability test, as also proved by measuring the CO_{Oxid} after the stability test, which displayed a minimal loss in the T_{100} (only 5 °C) (Fig. S4b, ESI†).

The active sites and CO_2 production rate of Pd–SnO_2/MOF-PNC are proved by its higher turnover number (TON = 14.8 μmol g_{Cat}^{-1}) and turnover frequency (TOF = 61.97 h^{-1}) relative to Pd/MOF-PNC (11.5 μmol g_{Cat}^{-1}; 45.75 h^{-1}) and Pd/C (7.86 μmol g_{Cat}^{-1}; 31.49 h^{-1}) (Fig. 4a and b). The recyclability of Pd–SnO_2/MOF-PNC reveals that the catalyst remained active for 5 consecutive cycles with no degradation. The CO-TPD gave sharp peaks for Pd–SnO_2/MOF-PNC (74.5 °C) and Pd/MOF-PNC (72.6 °C), compared to a broad peak for Pd/C (174.2 °C) (Fig. 5a). This implies more accessible Pd active sites in Pd–SnO_2/MOF-PNC and its capacity to adsorb/oxidize CO at a lower temperature due to the presence of an oxygen-rich SnO_2 support, higher surface area, and abundant active sites.[36]

The O_2-TPO displays a sharp oxygen-uptake peak on Pd–SnO_2/MOF-PNC (66.8 °C) relative to broad peaks on Pd/MOF-PNC (116.3 °C) and Pd/C (197.6 °C) (Fig. 5b), implying ease of O_2 adsorption (O_{ads}) on Pd–SnO_2/MOF-PNC, due to the interfacial interaction of Pd with SnO_2 and MOF-PNC. This leads to rapid turnover of the adsorbed CO/O_2, which is important for inducing a reaction between the active O_{ads} and CO_{ad} on the Pd surface to allow quick CO_{Oxid} kinetics.[36] Also, the oxygenated species (*i.e.*, SnO_2) in Pd–SnO_2/MOF-PNC enables a lower energy barrier for

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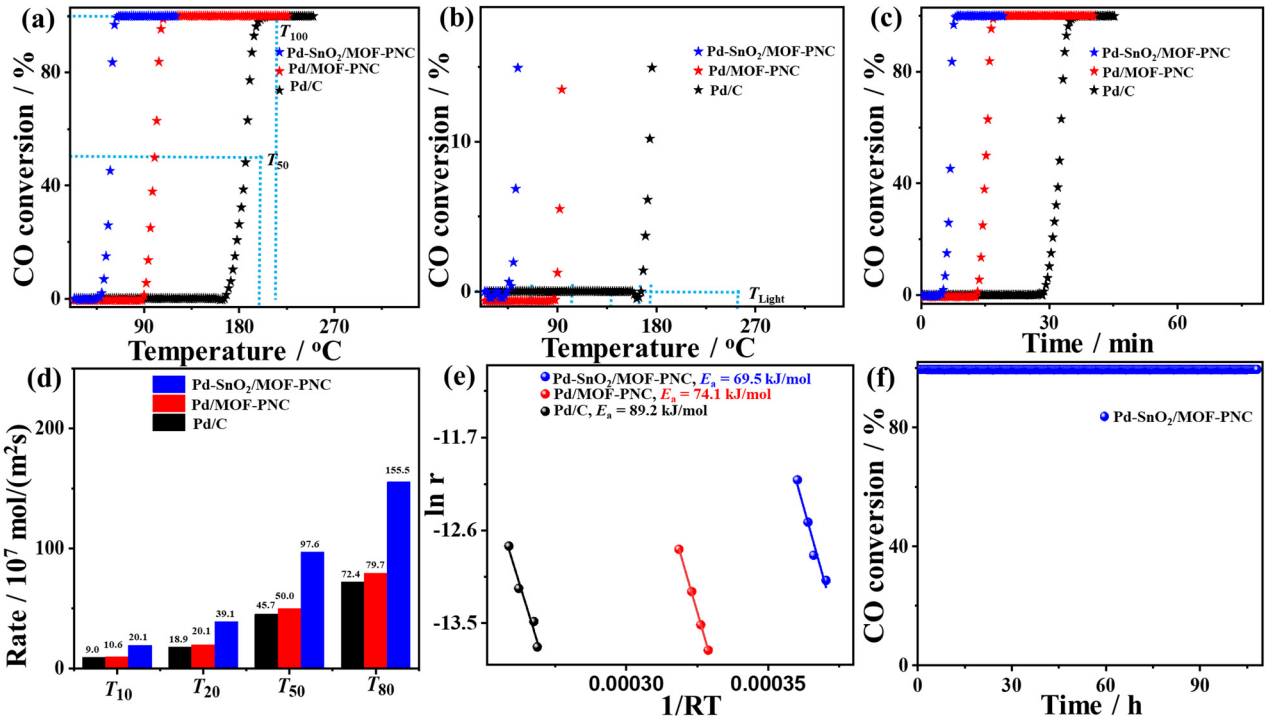

Fig. 3 (a, b) Temperature-dependent CO conversion, (c) time-dependent CO conversion, (d) rate at different CO conversion temperatures, (e) Arrhenius plots, and (f) time on stream (TOS) of Pd–SnO_2/MOF-PNC, Pd/MOF-PNC, and Pd/C.

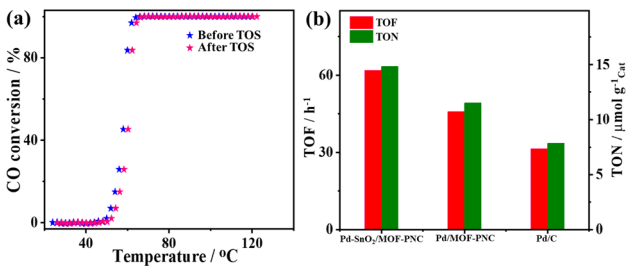

Fig. 4 (a) Temperature of CO conversion before and after the TOS test and repetitive CO conversion after H_2-TPR and O_2-TPO of Pd–SnO_2/MOF-PNC. (b) Turnover number (TON) and turnover frequency (TOF) of Pd–SnO_2/MOF-PNC, Pd/MOF-PNC and Pd/C.

CO/O_2 uptake/activation, thereby accelerating the complete CO_{Oxid} kinetics.[24,33] The H_2-TPR confirms the reducibility of the catalysts,[36] where Pd–SnO_2/MOF-PNC, Pd/MOF-PNC, and Pd/C show a broad H_2 adsorption at 62.3, 184.1, and 199.9 °C, respectively, which implies that Pd–SnO_2/MOF-PNC got reduced fast, owing to the interaction of SnO_2, Pd^{2+}, and Co^{2+} (Fig. 5c). This may serve as evidence for its exposed metal active sites.

The H_2-TPR, O_2-TPO, and CO-TPD reveal that coupled Pd, SnO_2, and MOF-PNC enhance the CO redox properties and CO_{Oxid} activity of Pd–SnO_2/MOF-PNC. Hence, the CO_{Oxid} mechanism on Pd–SnO_2/MOF-PNC could follow Langmuir–Hinshelwood,[36] *i.e.*, co-adsorption of CO/O_2 on Pd–SnO_2/MOF-PNC, followed by dissociation of O_2 to form O lattice and O adsorbed (O_{ads}) (eqn (R1) and (R2)), which then oxidizes CO_{ads} to CO_{2ads} (*i.e.*, the rate determining step (eqn (R3))) and CO_2 desorbed from Pd–SnO_2/MOF-PNC (eqn (R4)).

$$O_{2g} + \text{Pd–SnO}_2\text{/MOF-PNC} \rightarrow 2O_{ads}\text{–Pd–SnO}_2\text{/MOF-PNC} \quad \text{(R1)}$$

$$CO_g + \text{Pd–SnO}_2\text{/MOF-PNC} \rightarrow CO_{ads}\text{–Pd–SnO}_2\text{/MOF-PNC} \quad \text{(R2)}$$

$$O_{ads}\text{–Pd–SnO}_2\text{/MOF-PNC} + CO_{ads}\text{–Pd–SnO}_2\text{/MOF-PNC} \rightarrow CO_{2ads}\text{–Pd–SnO}_2\text{/MOF-PNC} \quad \text{(R3)}$$

$$CO_{2ads}\text{–Pd–SnO}_2\text{/MOF-PNC} \rightarrow CO_2 + \text{Pd–SnO}_2\text{/MOF-PNC} \quad \text{(R4)}$$

To investigate the effect of Pd nanoparticles loaded with a lower content (*i.e.*, 1 wt%) decorated on SnO_2/MOF-PNC, Pd(1%)–SnO_2/MOF-PNC was prepared and tested for thermal CO oxidation, which showed significantly higher T_{100} (165.2 °C) than Pd–SnO_2/MOF-PNC (65.6 °C) (Fig. S7a, ESI†). Meanwhile, in the absence of Pd nanoparticles, SnO_2/MOF-PNC could not attain T_{100} even at 300 °C, implying that Pd is the main active site for the thermal CO oxidation. Also, to get more insights into the effect of the support, Pd–SnO_2 was examined for CO_{Oxid} and achieved T_{100} (199.1 °C) which was greater than Pd–SnO_2/MOF-PNC (65.6 °C) and even Pd/MOF-PNC (107.9 °C) (Fig. S7a–c, ESI†), which indicates that using a co-support of SnO_2/MOF-PNC is crucial for promoting the CO_{Oxid} activity and kinetics as further seen in the lower rate (r_{CO}) of Pd–SnO_2 than that of Pd–SnO_2/MOF-PNC, and Pd(1%)–SnO_2/MOF-PNC (Fig. S7d, ESI†). Also, the estimated E_a of Pd–SnO_2 was greater than that of Pd(1%)–SnO_2/MOF-PNC, Pd/MOF-PNC, and Pd–SnO_2/MOF-PNC (Fig. S7e, ESI†). These results clarify the importance of combining mixed Pd phases (Pd^0/Pd–O_x) and an oxygen-rich SnO_2 support for excellent CO_{Oxid} activity as

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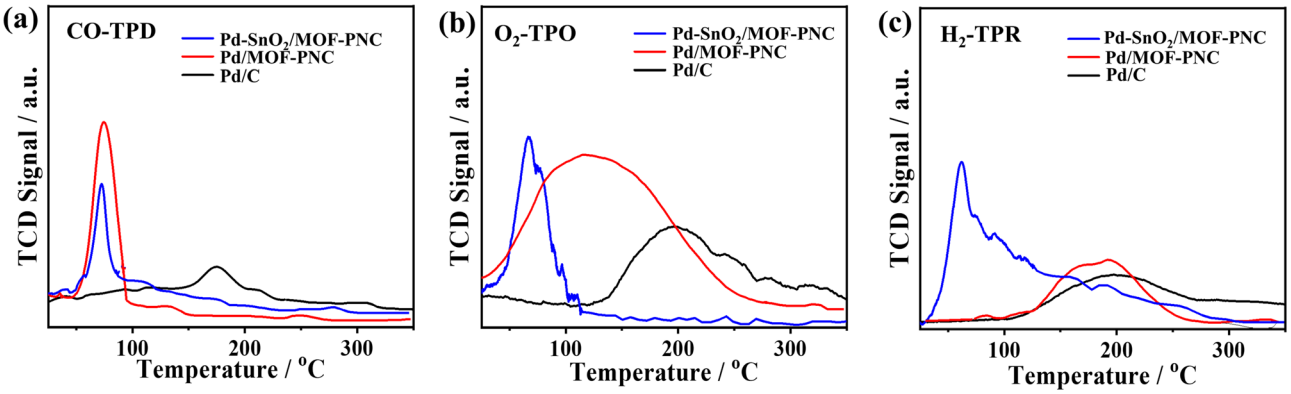

Fig. 5 (a) CO-temperature-programmed desorption (CO-TPD), (b) O_2-temperature-programmed oxidation (O_2-TPO), and (c) H_2-temperature-programmed reduction (H_2-TPR) of Pd–SnO_2/MOF-PNC, Pd/MOF-PNC and Pd/C.

shown by low T_{100}, but high kinetics, TON and TOF of Pd–SnO_2/MOF-PNC. Thus, coupling Pd with a metal oxide support is preferred for promoting the CO_{Oxid}, due to the optimal CO/O_2 adsorption and ease of activation/dissociation at low temperatures.

Conclusion

In brief, hierarchical porous sponge-like Pd–SnO_2/MOF-PNC was prepared by the MW-I, annealing, and chemical etching approach to initially form MOF-PNC, mixed with SnO_2 and Pd and then MW-I. Pd–SnO_2/MOF-PNC comprises porous 2D ultrathin MOF-PNC NSs with monodispersed Pd–SnO_2 NPs (7.79 ± 1.42 nm), a large specific surface area (185.40 $m^2\ g^{-1}$), and pore volume (0.045 $cm^3\ g^{-1}$). Thus, the CO_{Oxid} at T_{100} of Pd–SnO_2/MOF-PNC (65.6 °C) was lower than those of Pd/MOF-PNC (107.9 °C), Pd(1%)–SnO_2/MOF-PNC (165.2 °C), Pd–SnO_2 (199.1 °C), and Pd/C (201.2 °C), and also superior to most previously reported Pd-based catalysts. This originated from the electronic interaction and synergism of Pd NPs with oxygen-rich SnO_2 supports and Co-N_x active sites in MOF-PNC to deliver low energy barriers and high kinetics. These results indicate that using two supports, SnO_2/MOF-PNC is preferred for promoting the thermal CO_{Oxid} activity of Pd NPs.

Conflicts of interest

We declare no conflicts of interest.

Acknowledgements

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