Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information.

Cyclohexanone Ammoximation via in-situ H_2O_2 Production Using TS-1 Supported Catalysts

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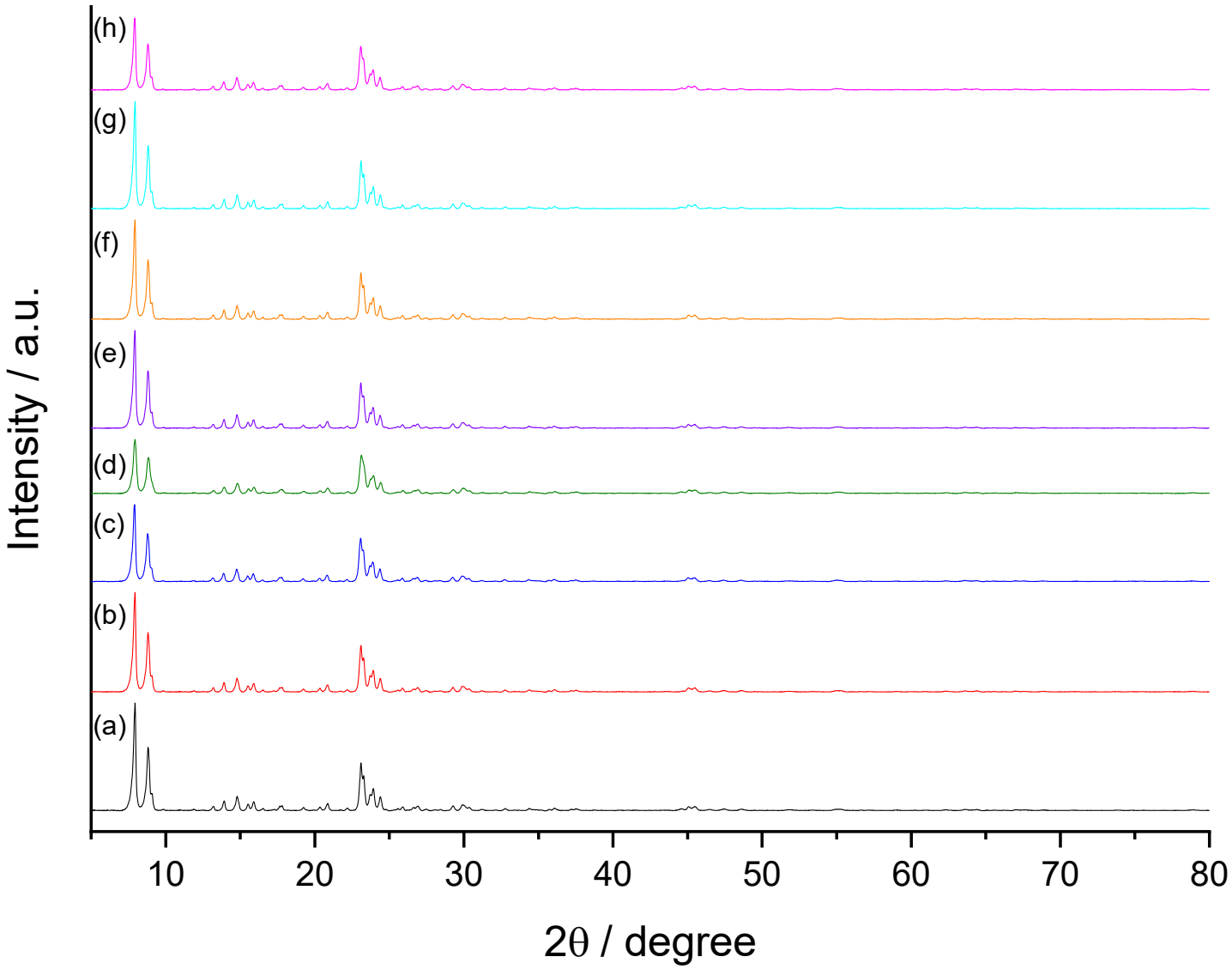

Figure S.1. X-ray diffractograms of 0.66%AuPd/TS-1 catalysts prepared by sol-immobilisation (PVA: metal = 1.2). **(a)** TS-1, **(b)** 0.66%Au/TS-1, **(c)** 0.55%Au-0.11%Pd/TS-1 and **(d)** 0.44%Au-0.22%Pd/TS-1 **(e)** 0.33%Au-0.33%Pd/TS-1, **(f)** 0.22%Au-0.44%Pd/TS-1, **(g)** 0.11%Au-0.55%Pd/TS-1 and **(h)** 0.66%Pd/TS-1. **Note:** TS-1 used as received, all precious metal immobilised catalysts exposed to an oxidative heat treatment (static air, 400 °C, 3 h).

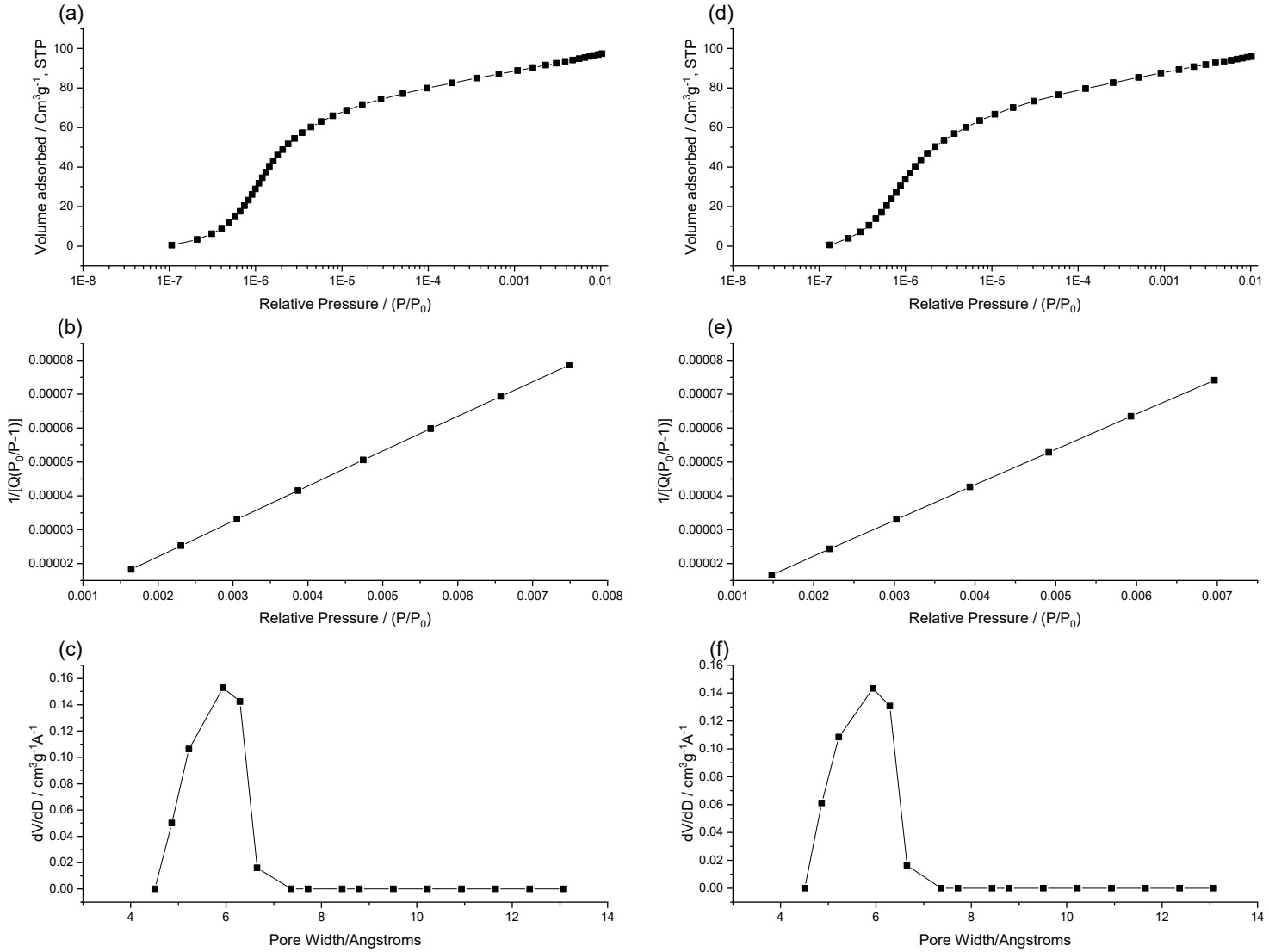

Figure S.2. Summary of porosity and surface area of TS-1 and the fresh 0.33%Au-0.33%Pd/TS-1 (PVA: metal = 1.2) catalyst. **(a)** Nitrogen adsorption isotherm, **(b)** BET analysis plot and **(c)** for the as-received TS-1, with corresponding analysis for the 0.33%Au-0.33%Pd/TS-1 catalyst reported in **(d), (e) and (f)** respectively. Surface areas for the TS-1 and 0.33%Au-0.33%Pd/TS-1 (PVA: metal = 1.2) catalyst were determined to be 425 and 418 m^2g^{-1} respectively, while total pore volumes were determined to be 0.216 and 0.212 cm^3g^{-1} for the as-received TS-1 and 0.33%Au-0.33%Pd/TS-1 (PVA: metal = 1.2) catalyst, respectively. **Note:** The 0.33%Au-0.33%Pd/TS-1 catalyst was exposed to an oxidative heat treatment (static air, 400 °C, 3 h), TS-1 was used as received.

Table S.1. Catalytic activity of 0.66%AuPd/TS-1(PVA: metal = 1.2) catalysts towards H_2O_2 synthesis and its subsequent degradation.

Catalyst	Productivity / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$	Degradation / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$
0.66%Au/TS-1	9	20
0.33%Au-0.33%Pd/TS-1	104	206
0.66%Pd/TS-1	12	42
TS-1	0	0

H_2O_2 direct synthesis reaction conditions: Catalyst (0.01g), H_2O (2.9g), MeOH (5.6g), 5% H_2 / CO_2 (420 psi), 25% O_2 / CO_2 (160 psi), 0.5 h, 2 ˚C 1200 rpm. **H_2O_2 degradation reaction conditions:** Catalyst (0.01 g), H_2O_2 (50 wt.% 0.68 g) H_2O (2.22 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 0.5 h, 2 °C, 1200 rpm. **Note:** All catalysts were exposed to an oxidative heat treatment prior to use (static air, 400 °C, 3 h).

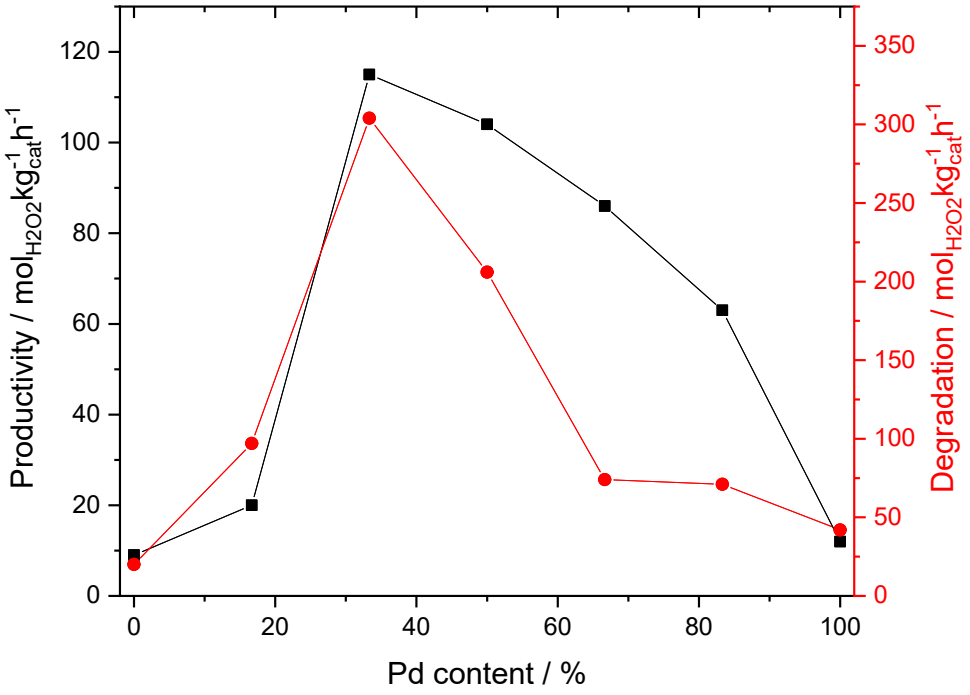

Figure S.3. Catalytic activity of 0.66%AuPd/TS-1(PVA: metal = 1.2) catalysts, prepared via sol-immobilisation towards the direct synthesis and subsequent degradation of H_2O_2. **H_2O_2 direct synthesis reaction conditions:** Catalyst (0.01 g), H_2O (2.9 g), MeOH (5.6 g), 5% H_2 / CO_2 (420 psi), 25% O_2 / CO_2 (160 psi), 0.5 h, 2 ˚C 1200 rpm. **H_2O_2 degradation reaction conditions:** Catalyst (0.01 g), H_2O_2 (50 wt.% 0.68 g) H_2O (2.22 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 0.5 h, 2 °C, 1200 rpm. **Note:** All catalysts were exposed to an oxidative heat treatment prior to use (static air, 400 °C, 3 h).

Table S.2. Comparison of the catalytic activity of 0.66%AuPd/TS-1(PVA: metal = 1.2) catalysts towards the ammoximation of cyclohexanone via in situ H_2O_2 production, as a function of Au: Pd ratio.

Catalyst	Cyclohexanone Conversion / %	Oxime Selectivity / %	Oxime Yield / %	Carbon balance / %	Apparent rate of reaction / $mol_{oxime}mol_{metal}^{-1}h^{-1}$
0.66%Au/TS-1	3	92	3	100	7.32
0.55%Au-0.11%Pd/TS-1	22	90	20	98	46.00
0.44%Au-0.22%Pd/TS-1	86	89	76	90	158.18
0.33%Au-0.33%Pd/TS-1	80	82	66	90	122.08
0.22%Au-0.44%Pd/TS-1	62	83	52	90	87.10
0.11%Au-0.55%Pd/TS-1	33	85	28	95	43.54
0.66%Pd/TS-1	16	80	13	97	18.35

Ammoximation reaction conditions: Cyclohexanone (2 mmol), NH_4HCO_3 (4 mmol), 5%H_2/N_2 (420 psi), 25%O_2/N_2 (160 psi), catalyst (0.075 g), t-BuOH (5.9 g), H_2O (7.5 g), reaction time 3 h, reaction temperature 80 ˚C, stirring speed 800 rpm. **Note 1:** All catalysts were exposed to an oxidative heat treatment prior to use (static air, 400 °C, 3 h). **Note 2:** Apparent reaction rates are calculated based on theoretical metal content.

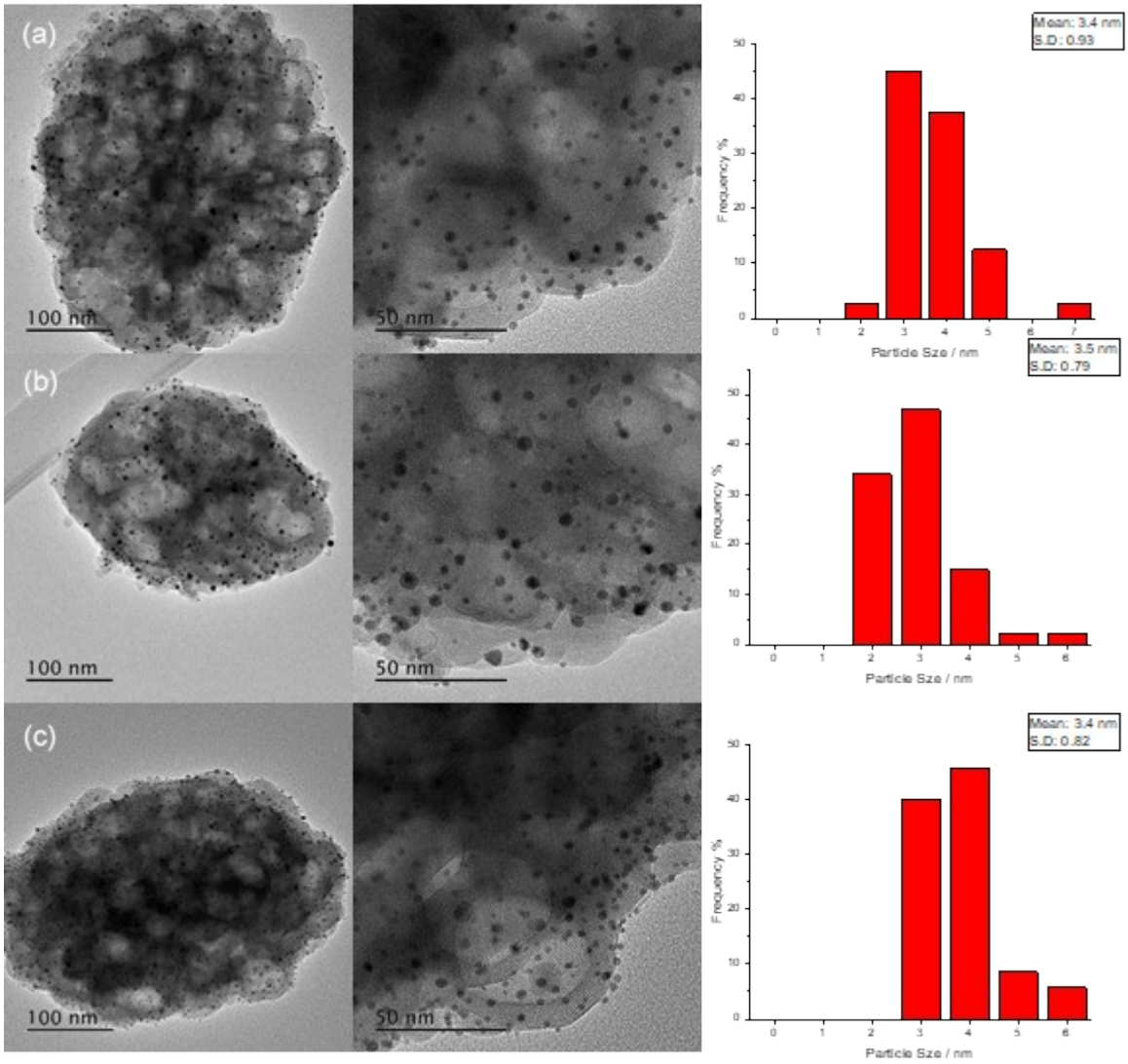

Figure S.4.A Representative bright field transmission electron micrographs and corresponding particle size histograms of 0.66%AuPd/TS-1(PVA: metal = 1.2) catalysts as a function of Au: Pd ratio. **(a)** 0.66%Au/TS-1, **(b)** 0.55%Au-0.11%Pd/TS-1 and **(c)** 0.44%Au-0.22%Pd/TS-1. **Note:** All catalysts were exposed to oxidative heat treatment prior to use (static air, 400 °C, 3 h).

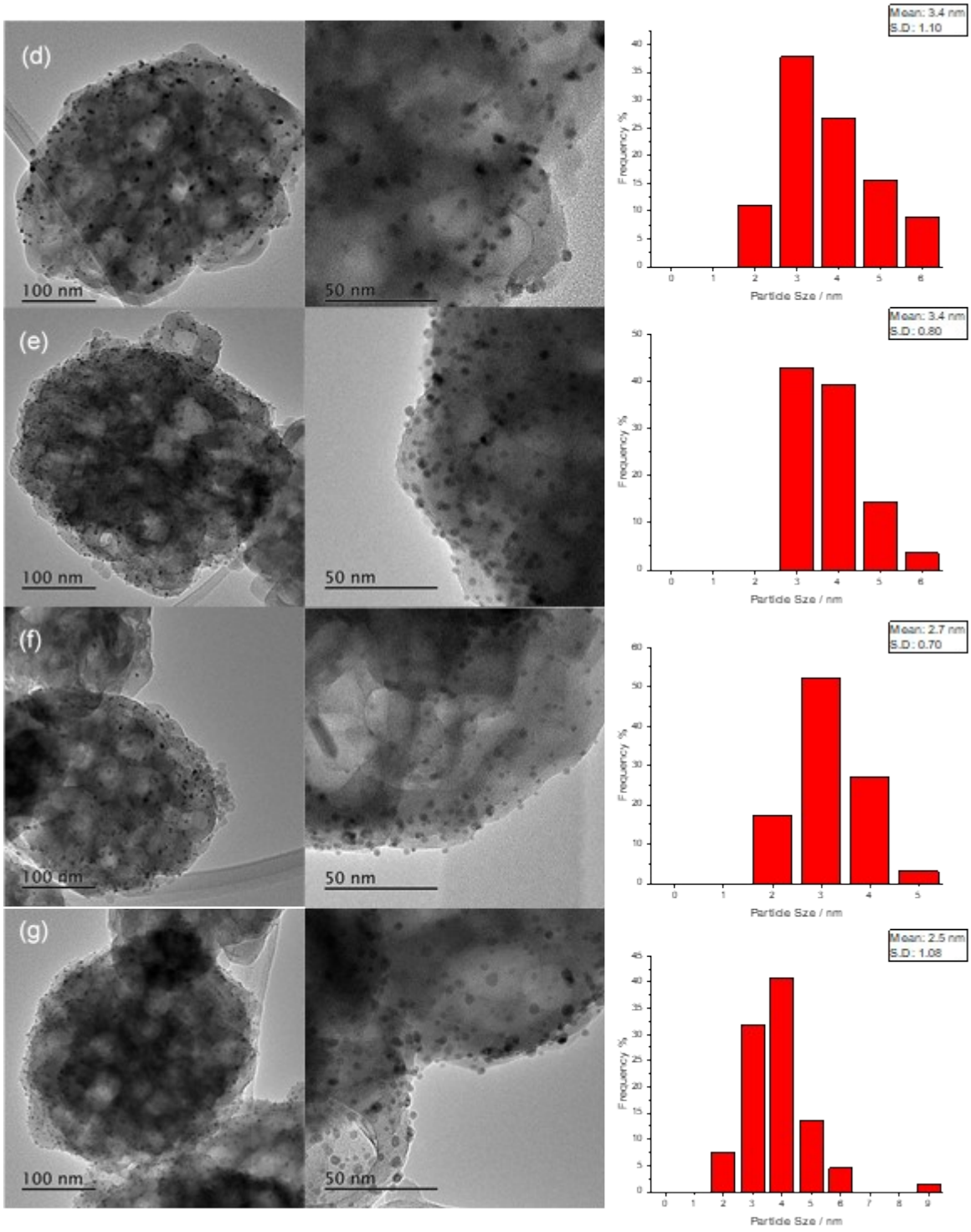

Figure S.4.B Representative bright field transmission electron micrographs and corresponding particle size histograms of 0.66%AuPd/TS-1(PVA: metal = 1.2) catalysts as a function of Au: Pd ratio. **(d)** 0.33%Au-0.33%Pd/TS-1, **(e)** 0.22%Au-0.44%Pd/TS-1, **(f)** 0.11%Au-0.55%Pd/TS-1 and **(g)** 0.66%Pd/TS-1. **Note:** All catalysts were exposed to oxidative heat treatment prior to use (static air, 400 °C, 3h).

Table S.3. The effect of Au: Pd ratio on Au and Pd speciation of 0.66%AuPd/TS-1 catalysts, prepared by sol-immobilisation (PVA: metal =1.2), as determined by XPS analysis.

Catalyst	Pd: Au	Pd^{2+}: Pd^{0}
0.66%Au/TS-1	N.A	N.A
0.55%Au-0.11%Pd/TS-1	0.35	0.00
0.44%Au-0.22%Pd/TS-1	1.16	0.00
0.33%Au-0.33%Pd/TS-1	1.95	0.36
0.22%Au-0.44%Pd/TS-1	3.10	0.43
0.11%Au-0.55%Pd/TS-1	9.25	0.50
0.66%Pd/TS-1	N.A	0.62

Note: All catalysts were exposed to an oxidative heat treatment prior to use (static air, 400 °C, 3h). **N.A:** Not applicable.

Table S.4. Effect of PVA: metal ratio on the catalytic activity of 0.33%Au-0.33%Pd/TS-1 towards H_2O_2 synthesis and its subsequent degradation.

PVA: metal	Productivity / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$	Degradation / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$
0	56	105
0.6	82	166
1.2	104	206
2.4	136	223
5.0	165	239

H_2O_2 direct synthesis reaction conditions: Catalyst (0.01 g), H_2O (2.9 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 0.5 h, 2 °C, 1200 rpm. **H_2O_2 degradation reaction conditions:** Catalyst (0.01 g), H_2O_2 (50 wt.% 0.68 g) H_2O (2.22 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 0.5 h, 2 °C, 1200 rpm. **Note:** All catalysts were exposed to an oxidative heat treatment prior to use (static air, 400 °C, 3 h).

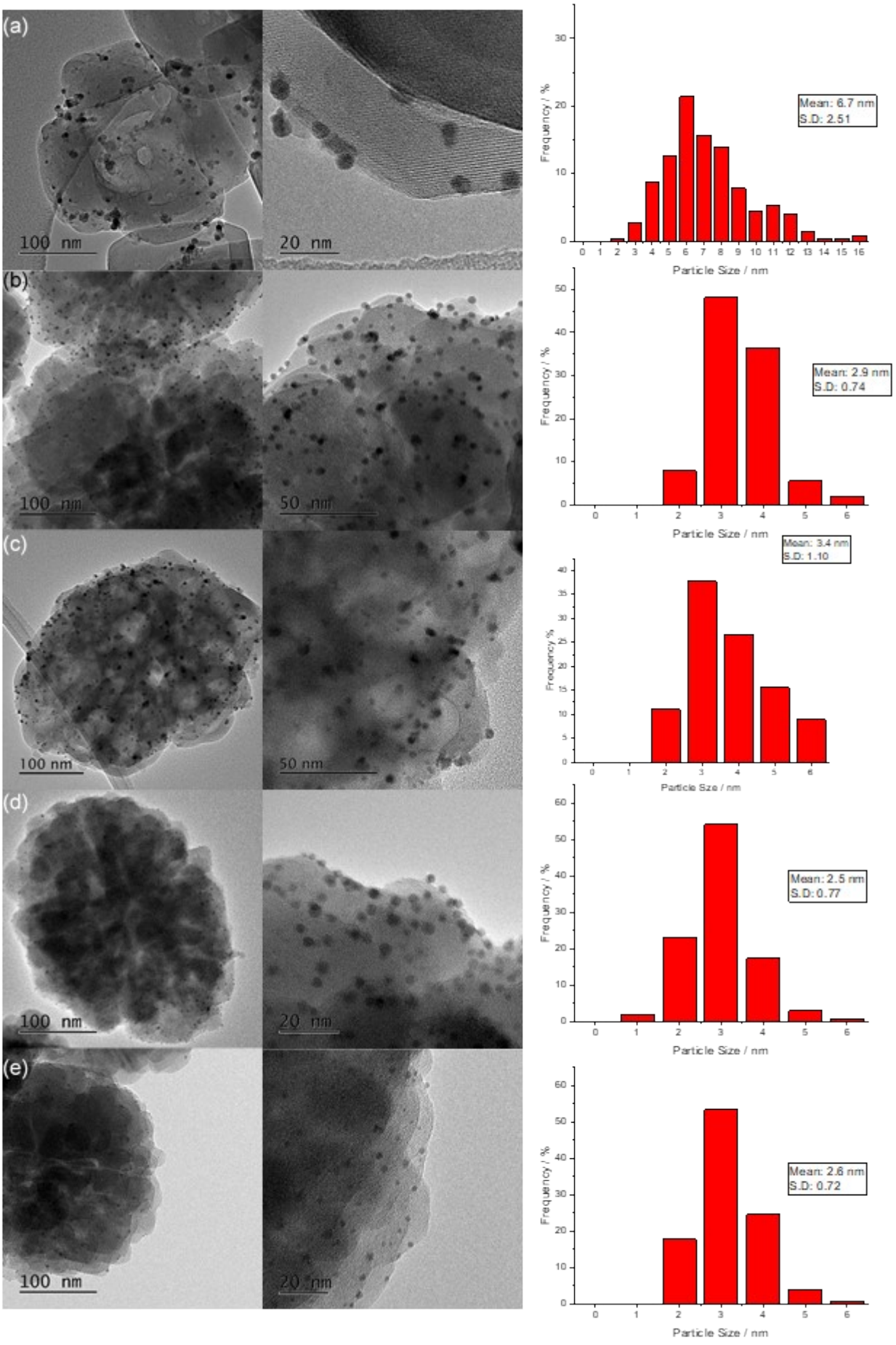

Figure S.5. Representative bright field transmission electron micrographs and corresponding particle size histograms of 0.33%Au-0.33%Pd/TS-1 catalysts as a function of PVA: metal ratio **(a)** PVA: metal = 0 **(b)** PVA metal = 0.6, **(c)** PVA: metal = 1.2, **(d)** PVA: metal = 2.4, **(e)** PVA: metal = 5.0. **Note:** All catalysts exposed to oxidative heat treatment prior to use (static air, 400 °C, 3 h).

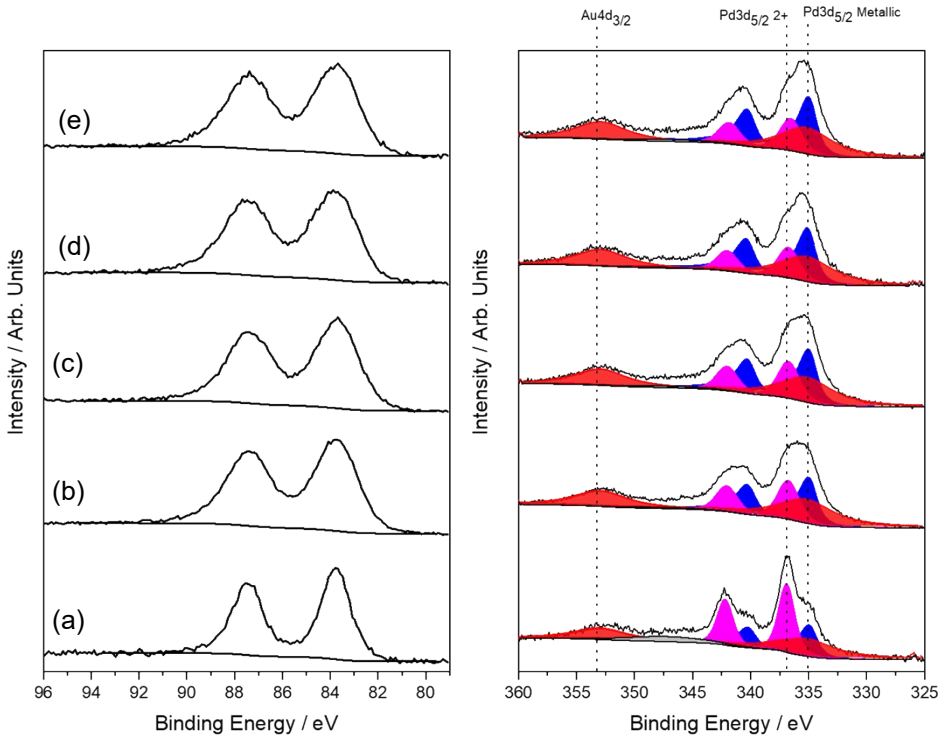

Figure S.6. X-ray photoelectron spectra of Au(4f) and Pd(3d)/Au(4f) spectra of 0.33%Au-0.33%Pd/TS-1 catalysts as a function of PVA: metal ratio during colloid formation. **(a)** PVA: (Au+Pd) = 0 **(b)** PVA: (Au+Pd) = 0.6, **(c)** PVA: (Au+Pd) = 1.2, **(d)** PVA: (Au+Pd) = 2.4, **(e)** PVA: (Au+Pd) = 5.0. ***Key:*** Au^0 (red*)*, Pd^{2+} (*pink*) and Pd^0 (*blue*). **Note:** All catalysts were exposed to oxidative heat treatment prior to use (static air, 400 °C, 3 h).

Table S.5. Effect of calcination temperature on the catalytic activity of 0.33%Au-0.33%Pd/TS-1(PVA: metal = 1.2) towards H_2O_2 synthesis and its subsequent degradation.

Calcination temperature / °C	**Initial Productivity / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$**	**Re-use Productivity / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$**	**Initial Degradation / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$**
Dried only*	212	88	637
200	176	106	522
300	138	115	401
400	104	104	206
500	98	98	183

*Catalyst dried 16 h, 110 °C, static air. **H_2O_2 direct synthesis reaction conditions:** Catalyst (0.01 g), H_2O (2.9 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 0.5 h, 2° C, 1200 rpm. **H_2O_2 degradation reaction conditions:** Catalyst (0.01 g), H_2O_2 (50 wt.% 0.68 g) H_2O (2.22 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 0.5 h, 2 °C, 1200 rpm.

Table S.6. Effect of calcination temperature on the catalytic activity of 0.33%Au-0.33%Pd/TS-1(PVA: metal = 1.2) towards H_2O_2 synthesis and its subsequent degradation.

Calcination temperature / °C	Productivity / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$	Au leaching / %	Pd leaching / %
Dried only*	212	4.0	15.4
200	176	0	12.6
300	138	0	4.1
400	104	0	1.2
500	98	0	0.3

*Catalyst dried 16 h, 110 °C, static air. **H_2O_2 direct synthesis reaction conditions:** Catalyst (0.01 g), H_2O (2.9 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 0.5 h, 2° C, 1200 rpm. **H_2O_2 degradation reaction conditions:** Catalyst (0.01 g), H_2O_2 (50 wt.% 0.68 g) H_2O (2.22 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 0.5 h, 2 °C, 1200 rpm.

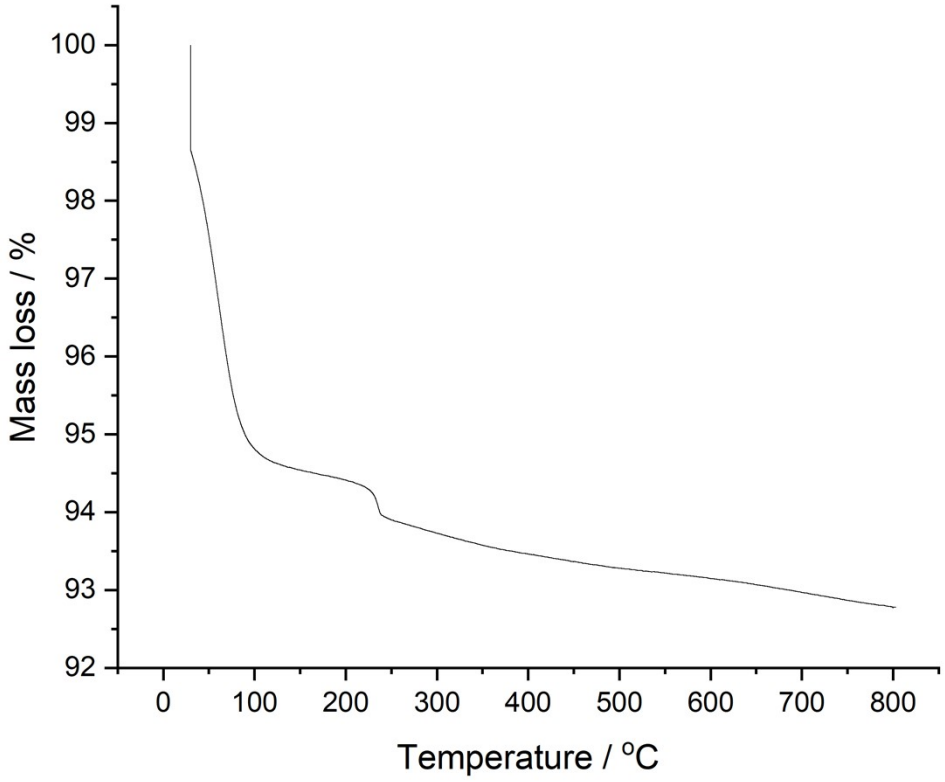

Figure S.7. Thermal gravimetric analysis of the as-prepared (dried) 0.33%Au-0.33%Pd/TS-1(PVA: metal = 1.2) catalyst. The sample was heated to a temperature of 800 °C at a ramp rate of 5 °$Cmin^{-1}$, under a flow of air (50 $mLmin^{-1}$).

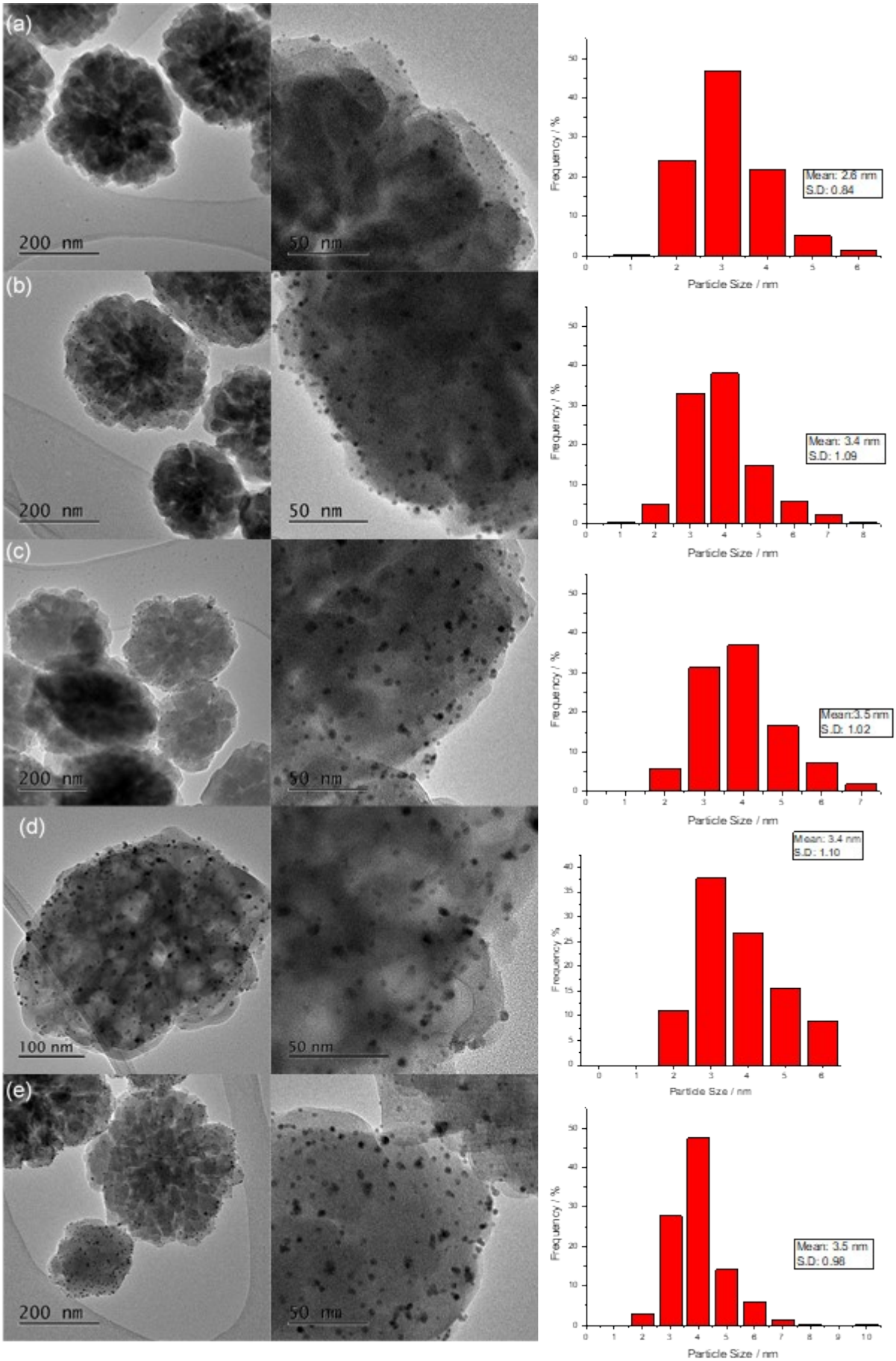

Figure S.8. Representative bright field transmission electron micrographs and corresponding particle size histograms of 0.33%Au-0.33%Pd/TS-1(PVA: metal = 1.2) catalysts as a function of calcination temperature **(a)** dried only, 110 ˚C, 16h **(b)** 200 ˚C, **(c)** 300 ˚C and **(d)** 400 ˚C, **(e)** 500 ˚C.

Table S.7. Effect of calcination temperature on Au and Pd speciation of 0.33%Au-0.33%Pd/TS-1 catalysts, prepared by sol-immobilisation (PVA: metal = 1.2), as determined by XPS analysis.

Calcination temperature / °C	Pd: Au	Pd^{2+}: Pd^{0}
Dried only*	2.04	Pd^{0} only
200	1.90	0.38
300	2.25	0.30
400	2.48	0.54
500	2.26	0.41

Table S.8. Effect of Pt incorporation on the catalytic activity of 0.66%AuPd/TS-1(PVA: metal = 1.2) towards H_2O_2 synthesis and its subsequent degradation.

Catalyst	Productivity / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$	Degradation / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$
0.33%Au-0.33%Pd/TS-1	104	206
0.275%Au-0.275%Pd-0.11%Pt/TS-1	135	172
0.22%Au-0.22%Pd-0.22%Pt/TS-1	106	320
0.11%Au-0.11%Pd-0.44%Pt/TS-1	72	364
0.66%Pt/TS-1	58	386

H_2O_2 direct synthesis reaction conditions: Catalyst (0.01 g), H_2O (2.9 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 0.5 h, 2° C, 1200 rpm. **H_2O_2 degradation reaction conditions:** Catalyst (0.01 g), H_2O_2 (50 wt.% 0.68 g) H_2O (2.22 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 0.5 h, 2°C, 1200 rpm. **Note:** All catalysts exposed to oxidative heat treatment prior to use (static air, 400 °C, 3 h).

Table S.9. Comparison of the catalytic activity of 0.66%AuPdPt/TS-1(PVA: metal = 1.2) catalysts towards the ammoximation of cyclohexanone via in situ H_2O_2 production, as a function of Pt content.

Catalyst	Cyclohexanone Conversion (%)	Oxime Selectivity (%)	Oxime Yield (%)	C-balance (%)	Apparent rate of reaction / $mol_{oxime}mol_{metal}^{-1}h^{-1}$ ($mol_{oxime}mol_{metal}^{-1}h^{-1}$)
0.33%Au-0.33%Pd/TS-1	80	82	66	90	122.08
0.275%Au-0.275%Pd-0.11%Pt/TS-1	88	86	76	88	148.04
0.22%Au-0.22%Pd-0.22%Pt/TS-1	75	80	60	85	123.69
0.11%Au-0.11%Pd-0.44%Pt/TS-1	52	75	39	87	90.10
0.66%Pt/TS-1	30	62	20	90	48.87

Ammoximation reaction conditions: Cyclohexanone (2 mmol), NH_4HCO_3 (4 mmol), 5%H_2/N_2 (420 psi), 25%O_2/N_2 (160 psi), catalyst (0.075 g), t-BuOH (5.9 g), H_2O (7.5 g), reaction time 3 h, reaction temperature 80 ˚C, stirring speed 800 rpm. **Note 1:** All catalysts were exposed to oxidative heat treatment prior to use (static air, 400 °C, 3 h). **Note 2:** Apparent reaction rates are calculated based on theoretical metal content.

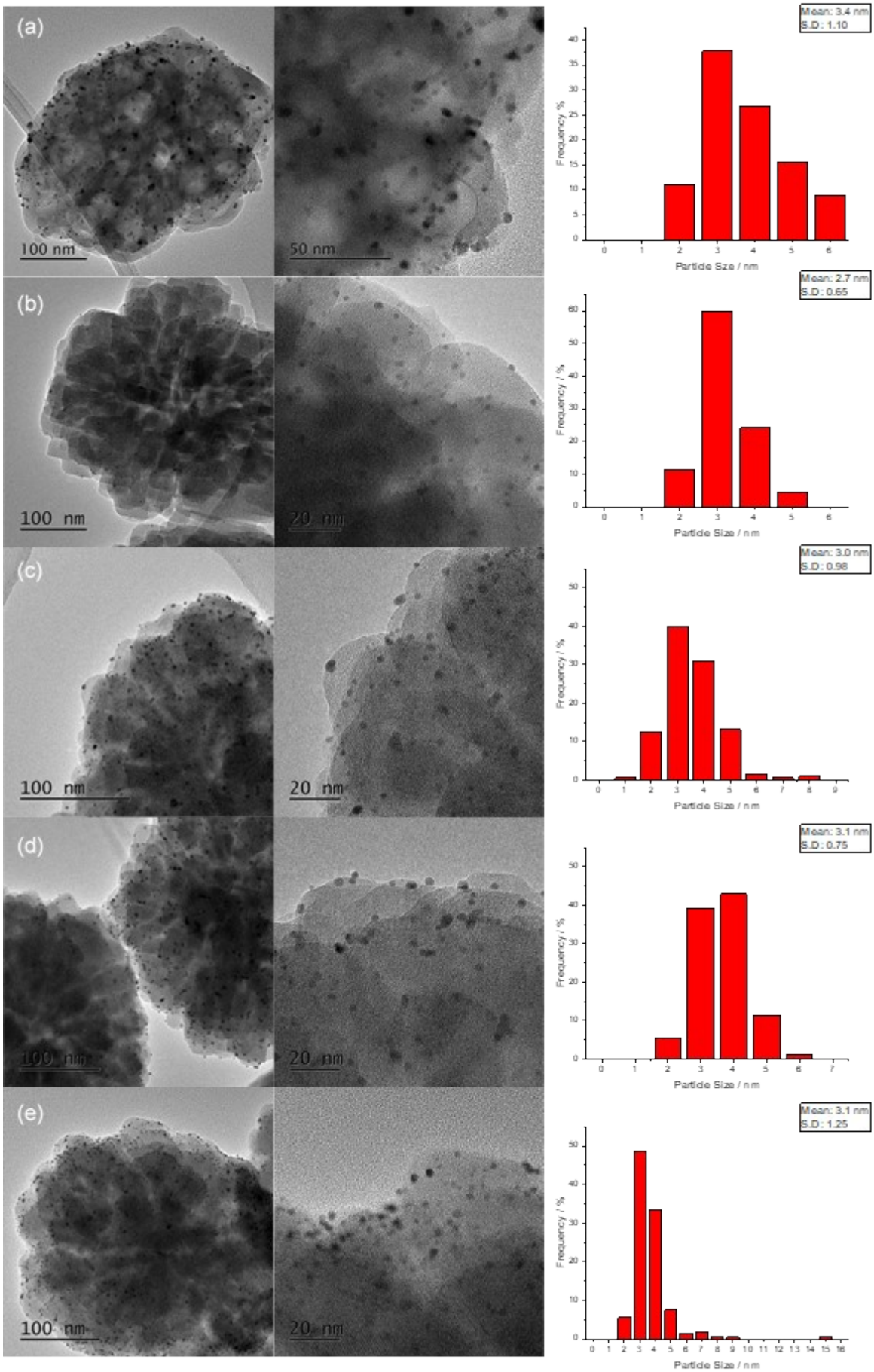

Figure S.9. Representative bright field transmission electron micrographs and corresponding particle size histograms of 0.66%AuPdPt/TS-1(PVA: metal = 1.2), as a function of Pt content **(a)** 0.33%Au-0.33%Pd/TS-1 **(b)** 0.275%Au-0.275%Pd-0.11%Pt/TS-1, **(c)** 0.22%Au-0.22%Pd-0.22%Pt/TS-1, **(d)** 0.11%Au-0.11%Pd-0.44%Pt/TS-1, **(e)** 0.66%Pt/TS-1. **Note:** All catalysts were exposed to oxidative heat treatment prior to use (static air, 400 °C, 3 h).

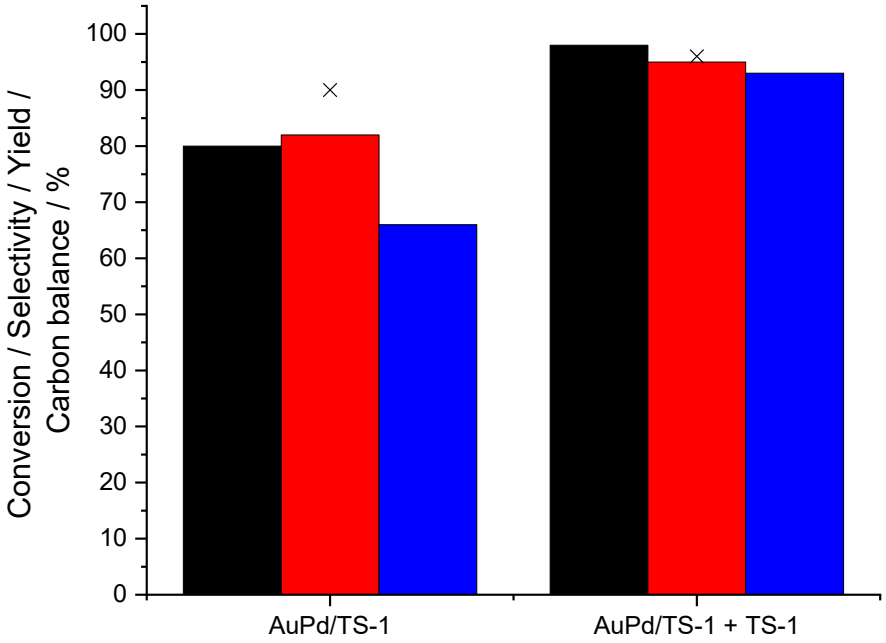

Figure S.10. The effect of TS-1 addition to the 0.33%Au-0.33%Pd/TS-1(PVA: metal = 1.2) catalyst. **Ammoximation reaction conditions:** Cyclohexanone (2 mmol), NH_4HCO_3 (4 mmol), 5%H_2/N_2 (420 psi), 25%O_2/N_2 (160 psi), catalyst (0.075 g), TS-1 (0.075 g), t-BuOH (5.9 g), H_2O (7.5 g), 3 h, 80 ˚C 800 rpm. ***Key:*** Cyclohexanone conversion (*black bar*), Selectivity towards oxime (*red bar*), Cyclohexanone oxime yield (*blue bar*), Carbon balance (*cross*es). **Note:** The AuPd-supported catalyst was exposed to an oxidative heat treatment prior to use (static air, 400 °C, 3 h), and the bare TS-1 was used as received.