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Supporting Information

Selective oxidation of methane to methanol using supported AuPd catalysts prepared by stabiliser-free sol-immobilisation

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Entry	Total metal loading (wt.%)	Support	Preparation temperature (°C)	Calcination temperature (°C)	Abbreviation
1	1	P25	25	dried	1%AuPd/P25-RT-dried
2	1	P25	25	400	1%AuPd/P25-RT-400
3	1	P25	25	600	1%AuPd/P25-RT-600
4	1	P25	25	800	1%AuPd/P25-RT-800
5	1	P25	70	dried	1%AuPd/P25-70-dried
6	1	P25	70	400	1%AuPd/P25-70-400
7	1	P25	70	600	1%AuPd/P25-70-600
8	1	P25	70	800	1%AuPd/P25-70-800
9	1	rutile	25	dried	1%AuPd/rutile-RT-dried
10	1	rutile	25	400	1%AuPd/rutile-RT-400
11	1	rutile	25	600	1%AuPd/rutile-RT-600
12	1	rutile	25	800	1%AuPd/rutile-RT-800
13	1	rutile	70	dried	1%AuPd/rutile-70-dried
14	1	rutile	70	400	1%AuPd/rutile-70-400
15	1	rutile	70	600	1%AuPd/rutile-70-600
16	1	rutile	70	800	1%AuPd/rutile-70-800
17	0.13	rutile	25	dried	0.13%AuPd/rutile-RT-dried
18	0.13	rutile	25	400	0.13%AuPd/rutile-RT-400
19	0.13	rutile	25	600	0.13%AuPd/rutile-RT-600
20	0.13	rutile	25	800	0.13%AuPd/rutile-RT-800

Table S1: Summary of prepared catalysts and their abbreviations.



Figure S1: Typical ¹H NMR spectrum of post-reaction solution for methane oxidation reaction.



Figure S2: Transmission electron microscopy of 1 wt. % AuPd/TiO₂ prepared at room temperature: (a) Dried, (b) calcined at 400 °C, (c) 600 °C and (d) 800 °C.



Figure S3: Transmission electron microscopy of 1 wt. % AuPd/TiO₂ prepared at elevated temperature (70 °C): (a) Dried, (b) calcined at 400 °C, (c) 600 °C and (d) 800 °C.



Figure S4: Time-on-line analysis for H_2O_2 decomposition for 1 wt. % AuPd/TiO₂ prepared at room temperature.



Figure S5: Time-on-line analysis for H₂O₂ decomposition for 1 wt. % AuPd/TiO₂ prepared at 70 °C.



Figure S6: Powder X-ray diffraction of 1 wt. % AuPd/TiO₂ (P25) catalysts prepared at (a) room temperature and (b) 70 °C. (i) Dried only, (ii) heat treated at 400 °C, (iii) 600 °C, and (iv) 800 °C. \blacktriangle = Rutile; \circ = Anatase.



Figure S7: X-ray photoelectron spectra of Pd 3d region for 1 wt. % AuPd/ TiO_2 prepared at room temperature. Pd^0 = blue line; Pd^{2+} = green line; Au 4d = red line. The dashed lines indicate the peaks due to Pd⁰ and Pd²⁺.



Figure S8: X-ray photoelectron spectra of Pd 3d region of 1 wt. % AuPd/ TiO₂ at elevated 70 °C. $Pd^0 =$ blue line; $Pd^{2+} =$ green line; Au 4d = red line. The dashed lines indicate the peaks due to Pd^0 and Pd^{2+} .

			Pd spe	cies [%]	Binc	ling Energ	y [eV]	SEM-	EDX	MP-AI	ES
Entry	Heat Treatment	AuPd/TiO₂	Pd ²⁺	Pd ^o	Pd ²⁺	Pd ⁰	Au (4f)	Total metal loading (wt. %)	Au content (wt. %)	Total metal loading (wt. %)	Au content (wt. %)
1	Dried	0.009	0	100	-	334.7	82.9	0.92	0.44	0.97	0.49
2	400 °C	0.006	100	0	336.3	-	83.1				
3	600 °C	0.004	100	0	336.5	-	83.1				
4	800 °C	0.022	100	0	336.6	-	83.3				
5	Dried	0.005	0	100	-	334.3	82.8	0.85	0.44	0.89	0.44
6	400 °C	0.004	100	0	336.4	-	83.1				
7	600 °C	0.004	100	0	337.0	-	83.8				
8	800 °C	0.011	100	0	337.0	-	83.3				

Table S2: Surface elemental composition of 1 wt. % AuPd/ TiO₂ (P25) catalysts. Entries 1-4: prepared at room temperature, Entries 5-8: prepared at 70 °C.



Figure S9: Powder X-ray diffraction of 1 wt. % AuPd/rutile TiO₂ catalysts prepared at (a) room temperature and (b) 70 °C. (i) Dried only, (ii) heat treated at 400 °C, (iii) 600 °C, and (iv) 800 °C. \blacktriangle = Rutile; \circ = Anatase.



Figure S10: Transmission electron microscopy of 1 wt. % AuPd/rutile TiO_2 prepared at room temperature: (a) Dried, (b) calcined at 400 °C, (c) 600 °C and (d) 800 °C.



Figure S11: Transmission electron microscopy of 1 wt. % AuPd /rutile TiO₂ prepared at 70 °C: (a) Dried, (b) calcined at 400 °C, (c) 600 °C and (d) 800 °C.



Figure S12: Time-on-line analysis for H_2O_2 decomposition for 1 wt. % AuPd/rutile TiO₂ prepared at room temperature.



Figure S13: Time-on-line analysis for H_2O_2 decomposition for 1 wt. % AuPd/rutile TiO₂ prepared at 70 °C.



Figure S14: X-ray photoelectron spectra of Pd 3d region for 1 wt. % AuPd/rutile TiO₂ prepared at room temperature. Pd^0 = blue line; Pd^{2+} = green line; Au 4d = red line. The dashed lines indicate the peaks due to Pd⁰ and Pd²⁺.



Figure S15: X-ray photoelectron spectra of Pd 3d region of 1 wt. % AuPd/rutile TiO₂ prepared at 70 °C. Pd^0 = blue line; Pd^{2+} = green line; Au 4d = red line. The dashed lines indicate the peaks due to Pd^0 and Pd^{2+} .

	Hoat	Aupd/	Pd spe	cies [%]	Binding Energy [eV]			SEM-	-EDX	MP-	-AES Au content (wt.%) 0.49 0.48
Entry	Treatment	Ti	Pd ²⁺	Pd ⁰	Pd ²⁺	Pd ⁰	Au (3d)	Total metal loading (wt. %)	Au content (wt.%)	Total metal loading (wt. %)	Au content (wt.%)
1	Dried	0.065	0	100		334.6	334.5	1.03	0.52	1.00	0.49
2	400 °C	0.059	52.1	47.9	336.4	334.4	334.3				
3	600 °C	0.038	58.4	41.6	336.5	334.4	334.3				
4	800 °C	0.027	52.7	47.3	336.5	334.4	334.3				
5	Dried	0.040	0	100		334.6	334.5	0.74	0.41	0.91	0.48
6	400 °C	0.037	37.1	62.9	336.4	334.4	334.6				
7	600 °C	0.029	39.6	60.4	336.4	334.3	334.6				
8	800 °C	0.019	40.5	59.5	336.4	334.3	334.5				

Table S3: Surface elemental composition of 1 wt. % AuPd/rutile TiO₂ catalysts. Entries 1-4: prepared at room temperature, Entries 5-8: prepared at 70 °C.

	Temperature of reduction (°C)		Product	s [μmol]		Oxygenate	Methanol	Total		H ₂ O ₂ Remaining [%]
Entry		Methanol	Formic Acid	Methyl hydroperoxide	CO ₂	selectivity [%]	Selectivity [%]	Productivity [mol kg _(cat) -1 h ⁻¹]	TOF [h⁻¹]	
1	400	0.0	0.0	0.0	0.4	0.0	0.0	0.077	1.07	1.3
2	800	0.1	0.0	0.1	0.4	40.6	20.2	0.127	1.75	2.9

Table S4. The effect of reducing 1 wt.% AuPd/TiO₂ (P25) before reaction.^[a]

[a] Standard reaction conditions: time: 30 minutes, temperature: 50 °C, P_{CH4}: 30.5 bar, stirring rate: 1500 rpm, all catalysts (1 wt. % total): 7.24x10⁻⁷ mol of metals equal to 10 mg for solid catalysts, volume: 10 mL of H₂O.[H₂O₂]: 0.5 M.. Catalysts were prepared by SI at room temperature (entries 2-5) or at 70 °C (entries 6-9). Catalyst is dried at 110 °C, 10 °C min⁻¹, 16 h, before reduction: Various temperatures, flowing 5 % H₂/Ar, 3 h, 20 °C min⁻¹ [b] Analysed by ¹H NMR spectroscopy with 1 % TMS in CDCl₃ internal standard. [c] Analysed by gas chromatography using an FID methaniser. Values obtained using CO₂ calibration curve. [d] Oxygenate selectivity calculated as (moles oxygenates/total moles of products) x 100. [e] Total productivity calculated as (moles(products) / weight(catalyst))/time). [f] TOF: Turn-over frequency, calculated as (moles(products) / total moles(metal)) / time (h). [g] Remaining H₂O₂ assayed by Ce⁴⁺(aq.) titration. Calculated as (moles(initial)/moles(final) x100. [h] Determined by transmission electron microscopy.[i] H₂O₂ decomposition reaction conditions: time: 30mins, temperature: 24 °C, atmospheric pressure, stirring rate: 1000 rpm, all catalysts (1 wt. % total): 7.24x10⁻⁷ mol of metals equal to 10 mg for solid catalysts, volume: 10 mL of H₂O.[H₂O₂]: 0.5 M



Figure S16: Transmission electron microscopy of 0.13 wt. % AuPd/rutile TiO_2 prepared at room temperature: (a) Dried, (b) calcined at 400 °C, (c) 600 °C and (d) 800 °C.





Figure S17: Time-on-line analysis for H_2O_2 decomposition for 0.13 wt. % AuPd/rutile TiO₂ prepared at room temperature.



Figure S18: X-ray photoelectron spectra of Pd (3d) region for 0.13 wt. % AuPd/rutile TiO₂ prepared at room temperature. Pd^0 = blue line; Pd^{2+} = green line; Au 4d = red line. The dashed lines indicate the peaks due to Pd^0 and Pd^{2+} .

	Heat	AuPd/Ti	Pd speci	es [%]	Binding Energy [eV]				MP-AES		
Entry	Treatment		Pd ²⁺	Pd ⁰	Pd ²⁺	Pd ⁰	Au (4f)	Au (3d)	Total metal loading (wt. %)	Au content (wt. %)	
1	Dried	0.015	0	100		334.8	83.2	334.0	0.15	0.10	
2	400 °C	0.009	52.0	48.0	336.6	334.8	83.4	334.0			
3	600 °C	0.010	58.4	41.5	336.6	334.7	83.3	334.0			
4	800 °C	0.008	52.7	47.3	336.4	334.7	83.2	334.0			

Table S5: Surface elemental composition of 0.13 wt. % AuPd/rutile TiO₂ SI catalysts prepared at room temperature.



Figure S19: Powder X-ray diffraction of 0.13 wt. % AuPd/rutile TiO₂ catalysts prepared at room temperature. (i) Dried only, (ii) heat treated at 400 °C, (iii) 600 °C, and (iv) 800 °C. \blacktriangle = Rutile; \circ = anatase.