

Supporting Information

The Degradation of Phenol via in-situ H₂O₂ Production Over Supported Pd-based Catalysts.

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Table S.1. Synthesis details of the precursors used in the preparation of mono- and bi-metallic 1% PdX/TiO₂ catalysts.

Catalyst	Pd precursor	Volume of Pd precursor / mL (concentration 6.96 mgmL ⁻¹)	Metal X precursor	Volume of metal X precursor / mL (concentration mgmL ⁻¹)
1%Pd/TiO ₂	PdCl ₂	1.437	-	-
0.5%Pd-0.5%Au/TiO ₂	PdCl ₂	0.718	HAuCl ₄ .3H ₂ O	0.408 (12.25)
0.5%Pd-0.5%Cu/TiO ₂	PdCl ₂	0.718	CuCl ₂	0.981 (5.10)
0.5%Pd-0.5%Co/TiO ₂	PdCl ₂	0.718	CoCl ₂ .6H ₂ O	2.119 (2.36)
0.5%Pd-0.5%Fe/TiO ₂	PdCl ₂	0.718	FeCl ₃ .6H ₂ O	1.046 (4.78)

Note : All catalysts were exposed to a reductive heat treatment (5%H₂/Ar, 400 °C, 4 h, 10 °C min⁻¹) prior to use.

Table S.2. Determination of actual catalyst loading, as determined by MP-AES analysis of aqua-regia digested catalysts.

Theoretical Catalyst Loading / wt. %	Actual Catalyst Loading / wt. %
1%Pd/TiO ₂	0.91%Pd/TiO ₂
0.75%Pd-0.25%Fe/TiO ₂	0.73%Pd-0.27%Fe/TiO ₂
0.5%Pd-0.5%Fe/TiO ₂	0.42%Pd-0.58%Fe/TiO ₂
0.25%Pd-0.75%Fe/TiO ₂	0.24%Pd-0.76%Fe/TiO ₂
1%Fe/TiO ₂	0.81%Fe/TiO ₂

Table S.3. Surface area of as-prepared TiO₂ supported catalysts.

Catalyst	Surface area */ m ² g ⁻¹
TiO ₂ **	61
1%Pd/TiO ₂	56
0.75%Pd-0.25%Fe/TiO ₂	53
0.5%Pd-0.5%Fe/TiO ₂	54
0.25%Pd-0.75%Fe/TiO ₂	56
1%Fe/TiO ₂	59

* Surface area determined from nitrogen adsorption measurements using the BET equation.

**Support material used as received, with no modification prior to metal immobilisation.

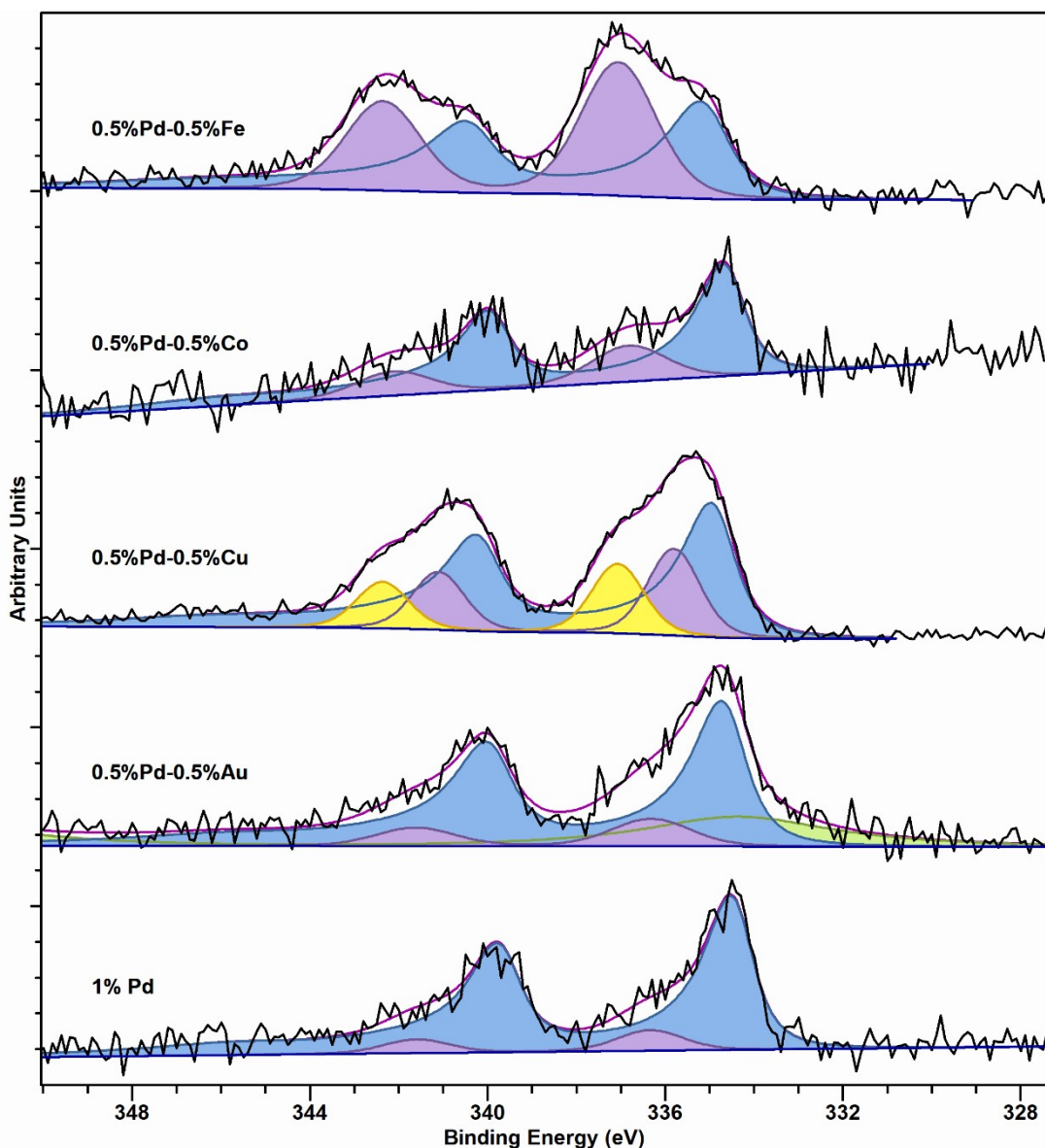


Figure S.1. Pd(3d)/Au(4d) spectra region for as-prepared 1%PdX/TiO₂ catalysts (X = Au, Cu, Co and Fe). **Key:** Metallic Pd (*Blue*), Pd(II) Oxide (*Purple*), Pd(II) Chloride (*Yellow*) and Metallic Au (*Green*). **Note:** all catalysts exposed to a reductive heat treatment prior to use (5%H₂/Ar, 500 °C, 4 h, 10 °C min⁻¹).

Table S.4. The choice of oxidant on the catalytic activity of 0.5%Pd-0.5%Fe/TiO₂ towards the degradation of phenol.

Oxidant	Phenol Conversion / %
H ₂ + O ₂	39.0
H ₂ (N ₂)	6.0
O ₂ (N ₂)	4.0
H ₂ O ₂ (N ₂)*	0.2

Phenol degradation reaction conditions: Catalyst (0.01 g), phenol (1000 ppm, 8.5 g), 5% H₂ / CO₂ (420 psi), 25% O₂ / CO₂ (160 psi), 2 h, 30 °C, 2 h.*Concentration of H₂O₂ (4.5 mmol) used is comparable to that produced if all H₂ in a standard phenol oxidation reaction is converted to H₂O₂. In the case of the O₂ and H₂ only experiments N₂ in parentheses is indicative of gaseous diluent used to maintain total pressure at 580 psi. Similarly, N₂ (580 psi) was used in the experiment, which used commercial H₂O₂ as the oxidant.

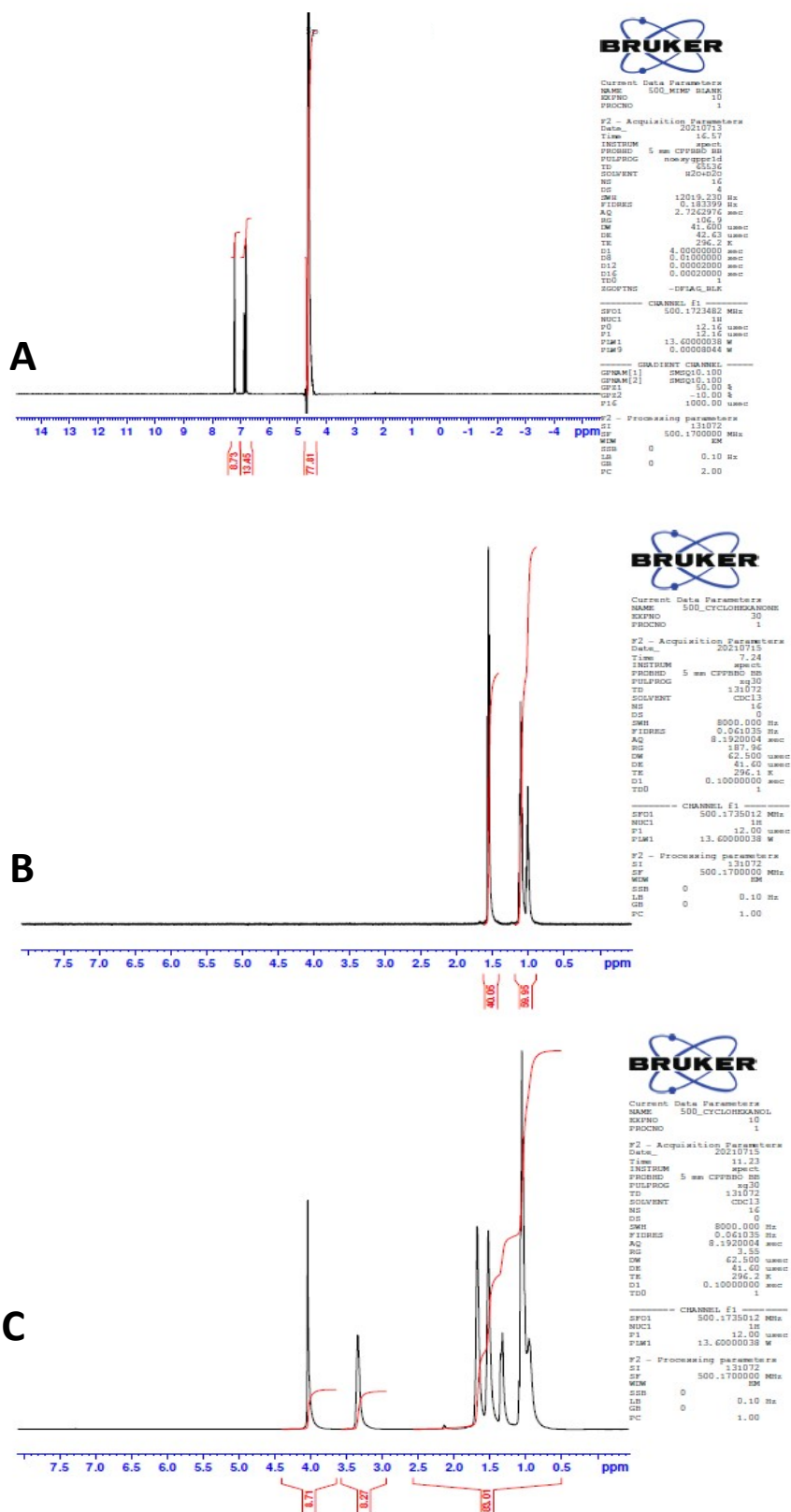


Figure S.2. ^1H NMR spectra of demonstrating the lack of phenol hydrogenation during the oxidative degradation of phenol via in-situ H_2O_2 production. **(A)** post-hydrogenation reaction, **(B)** cyclohexanol and **(C)** cyclohexanone. **Phenol hydrogenation reaction conditions:** Catalyst (0.01 g), phenol (1000 ppm, 8.5 g), 5% H_2 / CO_2 (420 psi), N_2 (160 psi), 2 h, 30 $^\circ\text{C}$, 2 h.

Supplementary Note.

With numerous studies reporting the ability of Pd nanoparticles to catalyse the reduction of phenol to cyclohexanol and cyclohexanone (collectively KA oil)¹ we were motivated to rule out this route to phenol conversion. The ¹HNMR spectra of a post-hydrogenation phenol reaction (Figure S.2.A), where the reaction was carried out under identical conditions to those used for the degradation of phenol via in-situ H₂O₂ production but in the absence of O₂ indicates that under these reaction conditions the formation of KA oil is not a route to phenol conversion, with no chemical shifts attributed to either phenol hydrogenation product observed. The ¹HNMR spectra of the individual products of phenol hydrogenation (cyclohexanol and cyclohexanone) are reported in Figure S.2.B and Figure S.2.C respectively for reference.

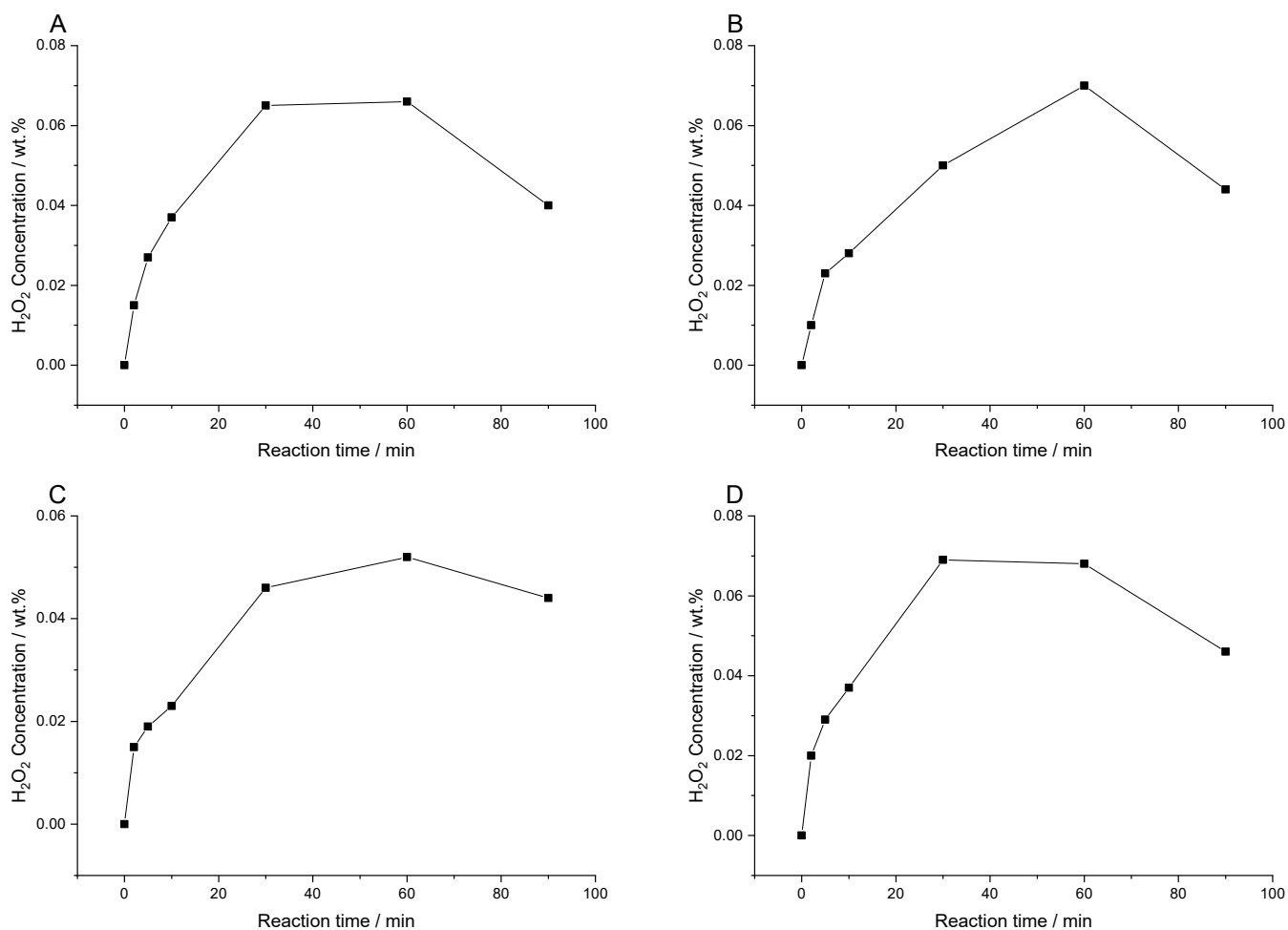


Figure S.3. Catalytic activity of 1%PdFe/TiO₂ catalysts towards the direct synthesis of H₂O₂, as a function of Pd: Fe ratio, under conditions utilised for the in-situ oxidative degradation of phenol. **H₂O₂ direct synthesis reaction conditions:** H₂O (8.5 g) catalyst (0.01 g), 5%H₂/CO₂ (420 psi), 25% O₂/CO₂ (160 psi), 30 °C, 1200 rpm. **H₂O₂ degradation reaction conditions:** H₂O (7.82 g) H₂O₂ (50 wt.%, 0.68 g), catalyst (0.01 g), 5%H₂/CO₂ (420 psi), 25% O₂/CO₂ (160 psi), 30 °C, 1200 rpm.

Table S.5. Catalytic activity towards the direct synthesis and subsequent degradation of H₂O₂, as a function of Pd: Fe ratio, under conditions utilised for the in-situ oxidative degradation of phenol.

Catalyst	H ₂ O ₂ concentration / wt. %	Degradation / %
1%Pd/TiO ₂	0.065	84.4
0.75%Pd-0.25%Fe/TiO ₂	0.050	43.2
0.5%Pd-0.5%Fe/TiO ₂	0.046	32.8
0.25%Pd-0.75%Fe/TiO ₂	0.069	12.2
1%Fe/TiO ₂	0.000	0.01

H₂O₂ direct synthesis reaction conditions: H₂O (8.5 g) catalyst (0.01 g), 5%H₂/CO₂ (420 psi), 25% O₂/CO₂ (160 psi), 30 °C, 0.5 h, 1200 rpm. **H₂O₂ degradation reaction conditions:** H₂O (7.82 g) H₂O₂ (50 wt.%, 0.68 g), catalyst (0.01 g), 5%H₂/CO₂ (420 psi), 25% O₂/CO₂ (160 psi), 30 °C, 0.5 h, 1200 rpm.

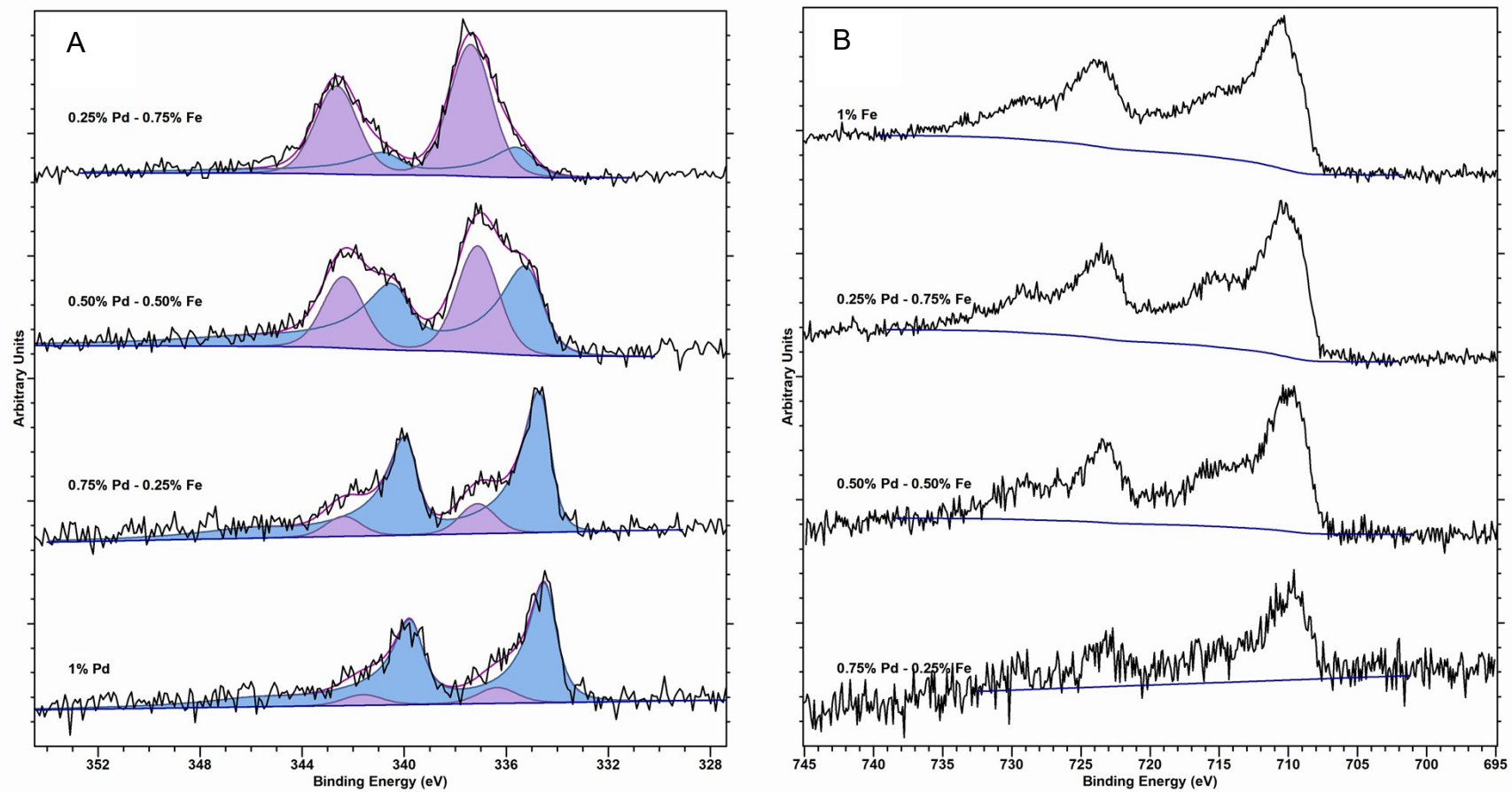


Figure S.4. XPS spectra of **(A)** Pd(3d) and **(B)** Fe (2p) regions for the as-prepared 1%PdFe/TiO₂ catalysts. **Key:** Metallic Pd (*Blue*) and Pd(II) Oxide (*Purple*). **Note:** all catalysts exposed to a reductive heat treatment prior to use (5%H₂/Ar, 500 °C, 4 h, 10 °C min⁻¹).

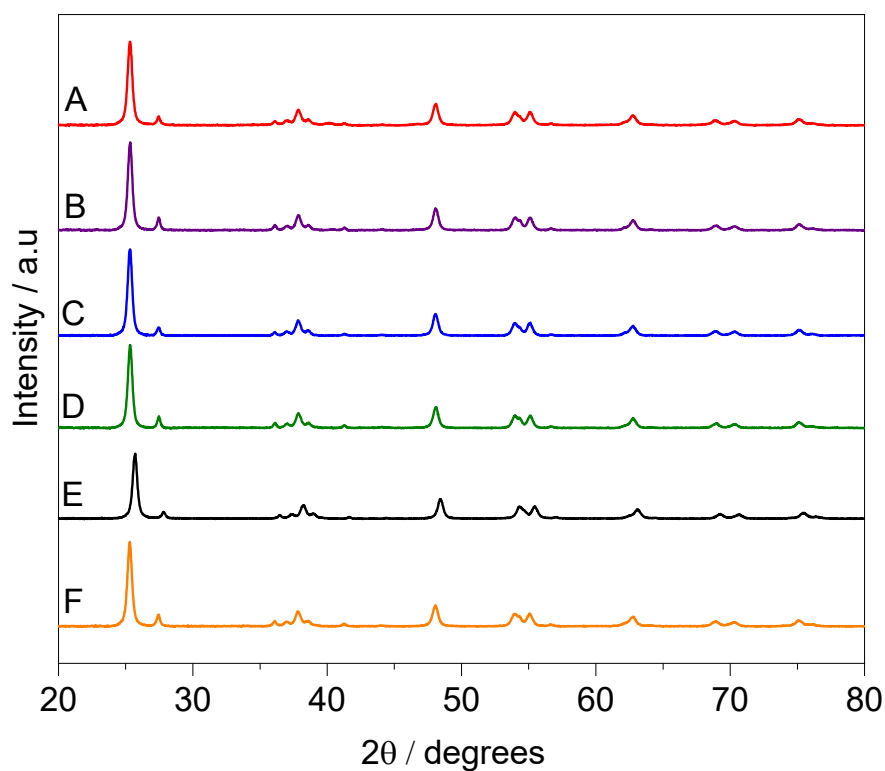


Figure S.5. X-ray diffractograms of 1%PdFe/TiO₂ catalysts, prepared via an excess chloride methodology. **(A)** 1%Pd/TiO₂, **(B)** 0.75%Pd-0.25%Fe/TiO₂, **(C)** 0.5%Pd-0.5%Fe/TiO₂, **(D)** 0.25%Pd-0.75%Fe/TiO₂, **(E)** 1%Fe/TiO₂ and **(F)** TiO₂. **Note:** all catalysts exposed to a reductive heat treatment prior to use (5%H₂/Ar, 500 °C, 4 h, 10 °C min⁻¹).

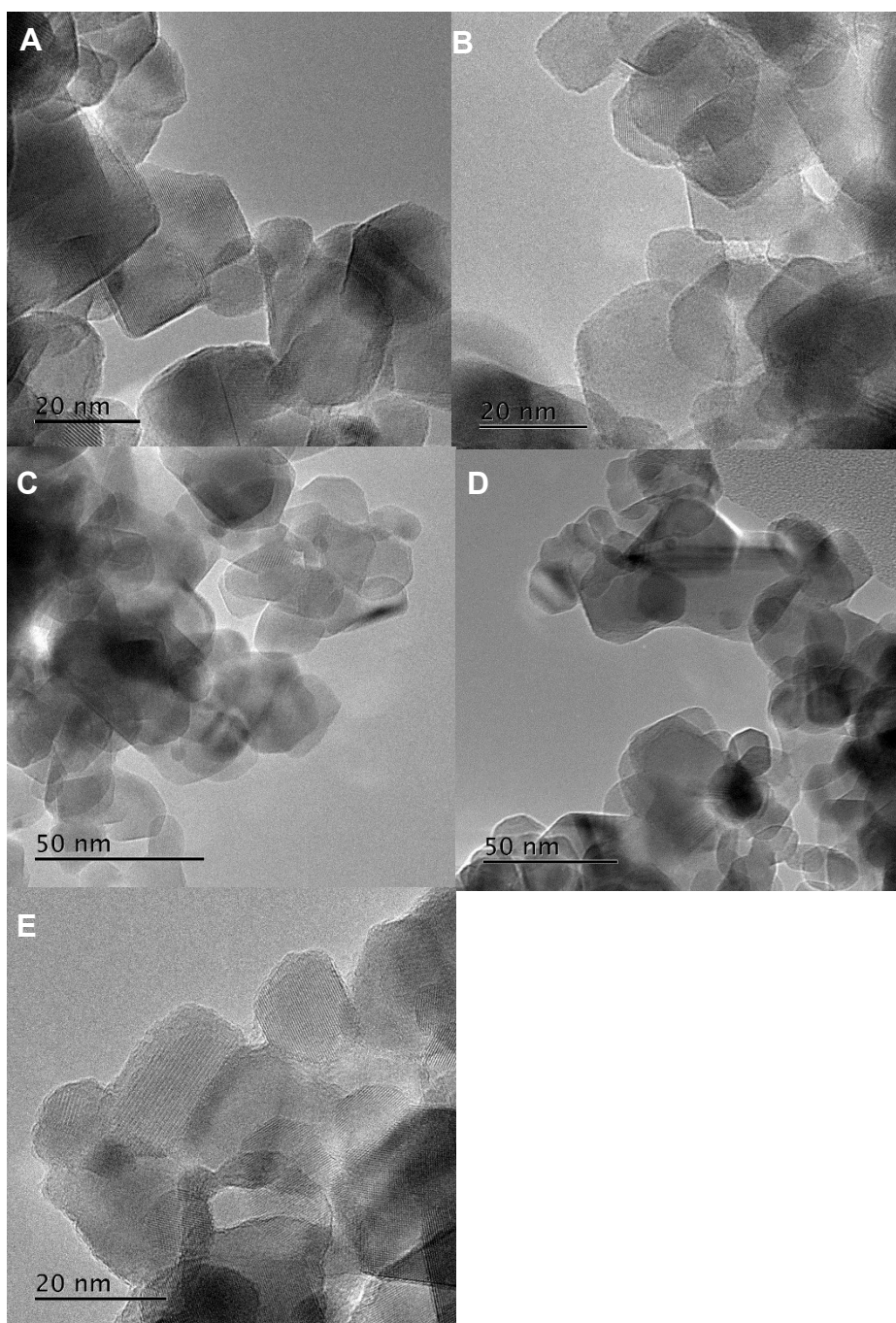


Figure S. 6 Transmission electron microscopy of the 1%PdFe/TiO₂ catalysts prepared by an excess chloride methodology. **(A)** 1%Pd/TiO₂, **(B)** 0.75%Pd-0.25%Fe/TiO₂, **(C)** 0.5%Pd-0.5%Fe/TiO₂, **(D)** 0.25%Pd-0.75%Fe/TiO₂ and **(E)** 1%Fe/TiO₂ **Note:** all catalysts exposed to a reductive heat treatment prior to use (5%H₂/Ar, 500 °C, 4 h, 10 °C min⁻¹).

Table S.6. MP-AES analysis of post reaction solutions of the degradation of phenol utilising 1% PdFe/TiO₂ as a function of Pd: Fe ratio.

Catalyst	Phenol Conversion / %	Selectivity towards phenolic derivatives / %	Selectivity towards organic acids / %	Fe leaching / ppm (%)	Pd leaching / ppm (%)
1%Pd/TiO ₂	11.0	11.0	89.0	-	0.0 (0)
0.75%Pd-0.25%Fe/TiO ₂	32.0	30.0	70.0	1.35 (46)	0.17 (2)
0.5%Pd-0.5%Fe/TiO ₂	39.0	31.0	69.0	2.44 (42)	0.08 (1)
0.25%Pd-0.75%Fe/TiO ₂	46.0	29.0	71.0	3.22 (36)	0.05 (1)
1%Fe/TiO ₂	3.0	0.0	100.0	0.0 (0)	-

Phenol degradation reaction conditions: Catalyst (0.01 g), phenol (1000 ppm, 8.5 g), 5% H₂ / CO₂ (420 psi), 25% O₂ / CO₂ (160 psi), 2 h, 30 °C, 2 h. **Note:** Values in parentheses indicate the extent of Fe and Pd leaching as a percentage of metal loading.

Table S.7. Pd and Fe leaching of 1%PdFe/TiO₂ catalysts exposed to phenol oxidation reaction conditions in the absence of phenol or under conditions where phenol oxidation through H₂O₂ generation is not possible.

Catalyst	Fe leaching / ppm (%)	Pd leaching / ppm (%)
1%Pd/TiO ₂	-	0.0 (0)
0.75%Pd-0.25%Fe/TiO ₂	0.0 (0)	0.0 (0)
0.5%Pd-0.5%Fe/TiO ₂	0.0 (0)	0.0 (0)
0.25%Pd-0.75%Fe/TiO ₂	0.0 (0)	0.0 (0)
1%Fe/TiO ₂	0.0 (0)	-
0.5%Pd-0.5%Fe/TiO ₂ (phenol)*	0.0 (0)	0.0 (0)

Phenol degradation reaction conditions: Catalyst (0.01 g), H₂O (1000 ppm, 8.5 g), 5% H₂ / CO₂ (420 psi), 25% O₂ / CO₂ (160 psi), 2 h, 30 °C, 2 h.*Conditions as outlined above, in the presence of phenol (1000 ppm) under N₂ atmosphere (580 psi). **Note:** Values in parentheses indicate the extent of Fe and Pd leaching as a percentage of metal loading.

References.

1. H. Zhou, B. Han, T. Liu, X. Zhong, G. Zhuang and J. Wang, *Green Chem.*, 2017, **19**, 3585-3594.