

## Supporting Information.

### **The Oxidative Degradation of Phenol via in-situ H<sub>2</sub>O<sub>2</sub> Synthesis Using Pd Supported Fe-modified ZSM-5 Catalysts.**

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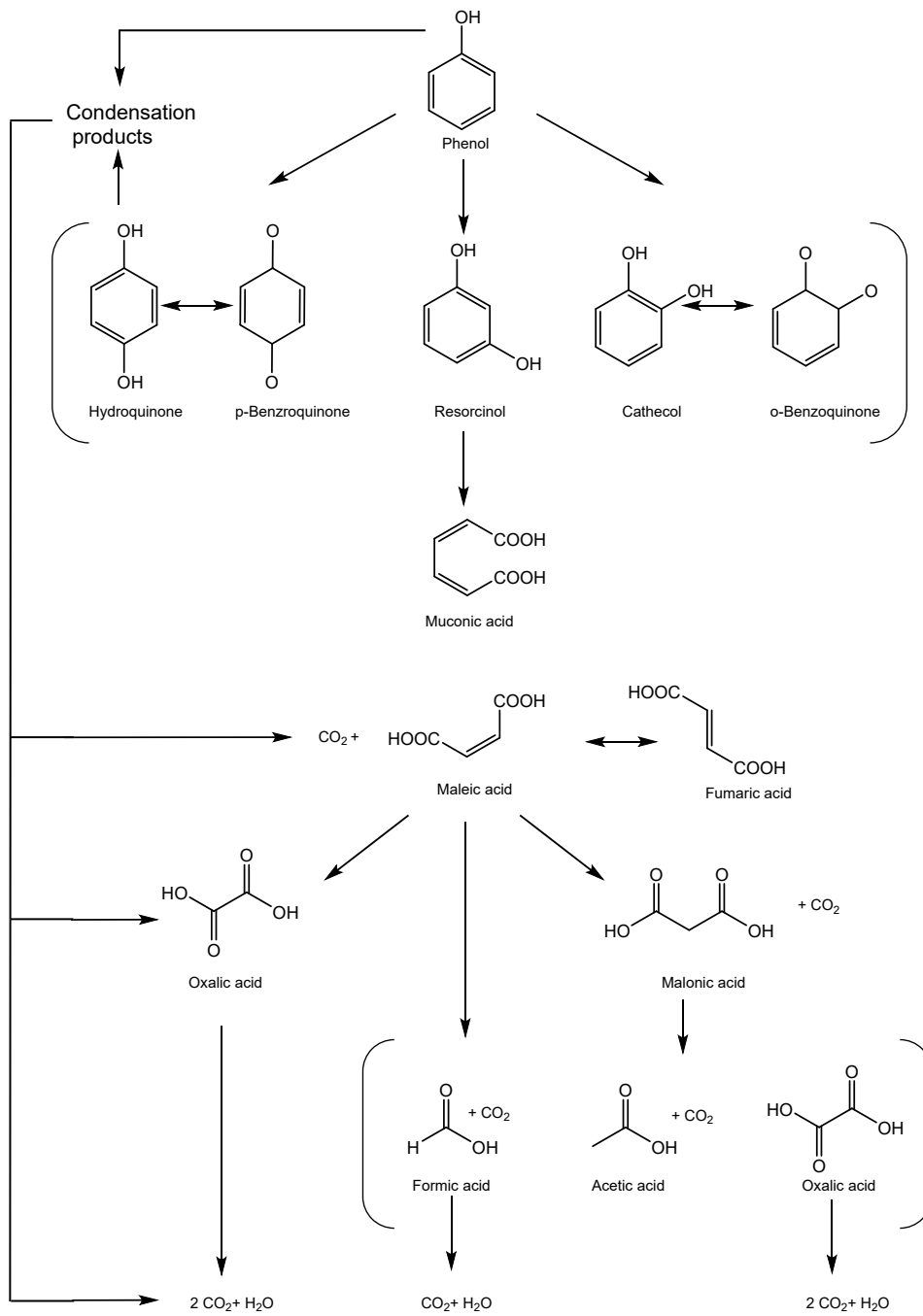
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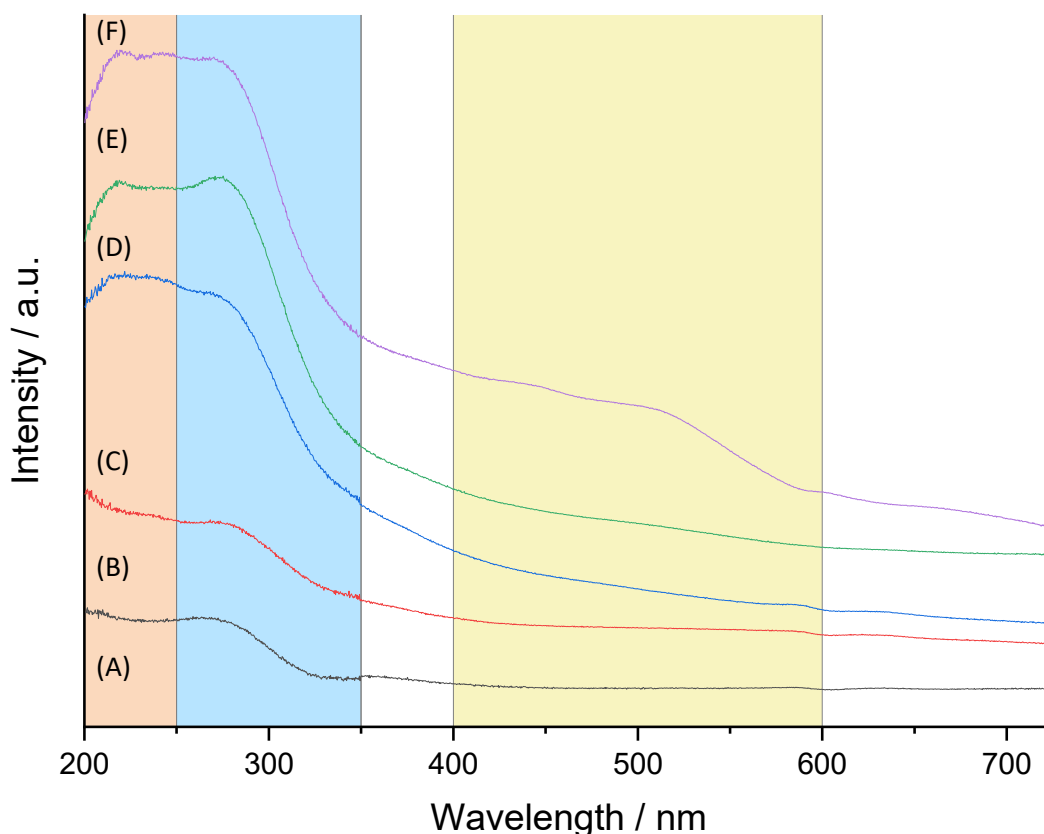


**Figure S.1.** The proposed oxidative degradation products of phenol.

**Table S.1.** Nominal and actual metal loading of 0.5%Pd/Fe-ZSM-5 catalysts, as determined by microwave aqua regia assisted digestion of fresh materials.

Catalyst	Actual Pd loading / wt.%	Actual Fe loading / wt.%
0.5 wt.%Pd/3 %Fe-HZSM-5	0.51	2.69
0.5 wt.%Pd/1%Fe-HZSM-5	0.47	0.73
0.5 wt. %Pd/0.5%Fe-HZSM-5	0.51	0.45
0.5 wt.%Pd/0.125%Fe-HZSM-5	0.48	0.15
0.5 wt.%Pd/0.06%Fe-HZSM-5	0.50	0.05
0.5 wt.%Pd/HZSM-5	0.51	0.00
HZSM-5 (28) (synthesised)	0.0	0.00

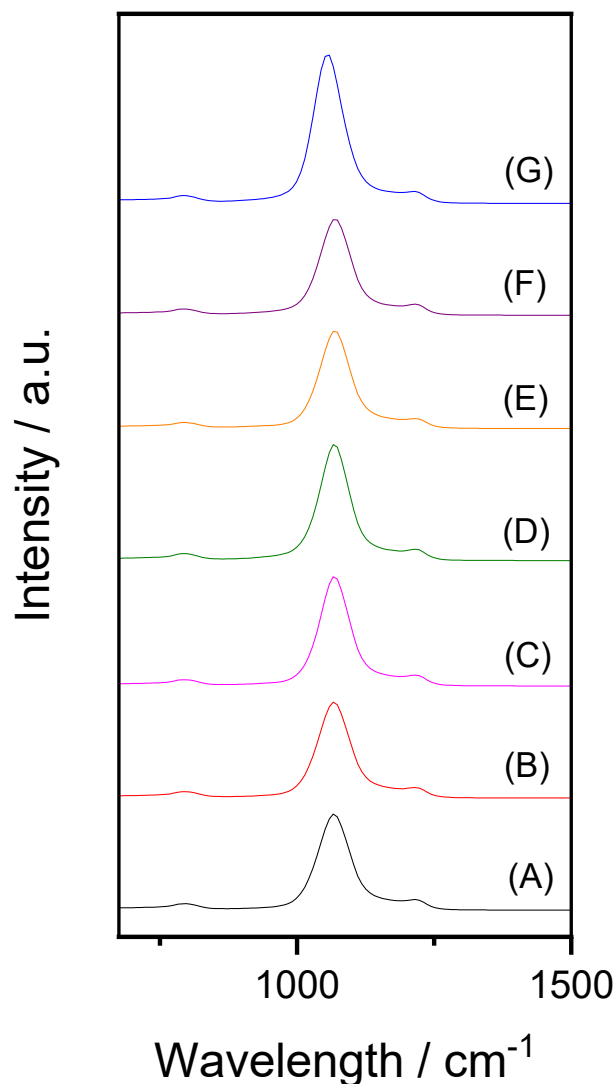
**Note:** All samples exposed to reductive heat treatment (4 h, 500 °C, 10 °C min<sup>-1</sup>, 5%H<sub>2</sub>/Ar).



**Figure S.2.** UV-visible reflectance spectra of 0.5.%Pd/Fe-ZSM-5 catalysts, as a function of total Fe incorporation. **(A)** 0.5%Pd/ZSM-5, **(B)** 0.5%Pd/0.06%Fe-ZSM-5, **(C)** 0.5%Pd/0.125%Fe-ZSM-5, **(D)** 0.5%Pd/0.5%Fe-ZSM-5, **(E)** 0.5%Pd/1%Fe-ZSM-5 and **(F)** 0.5%Pd/3%Fe-ZSM-5 **Note:** All samples exposed to reductive heat treatment (4 h, 500 °C, 10 °C min<sup>-1</sup>, 5%H<sub>2</sub>/Ar).

### Supplementary Note 1.

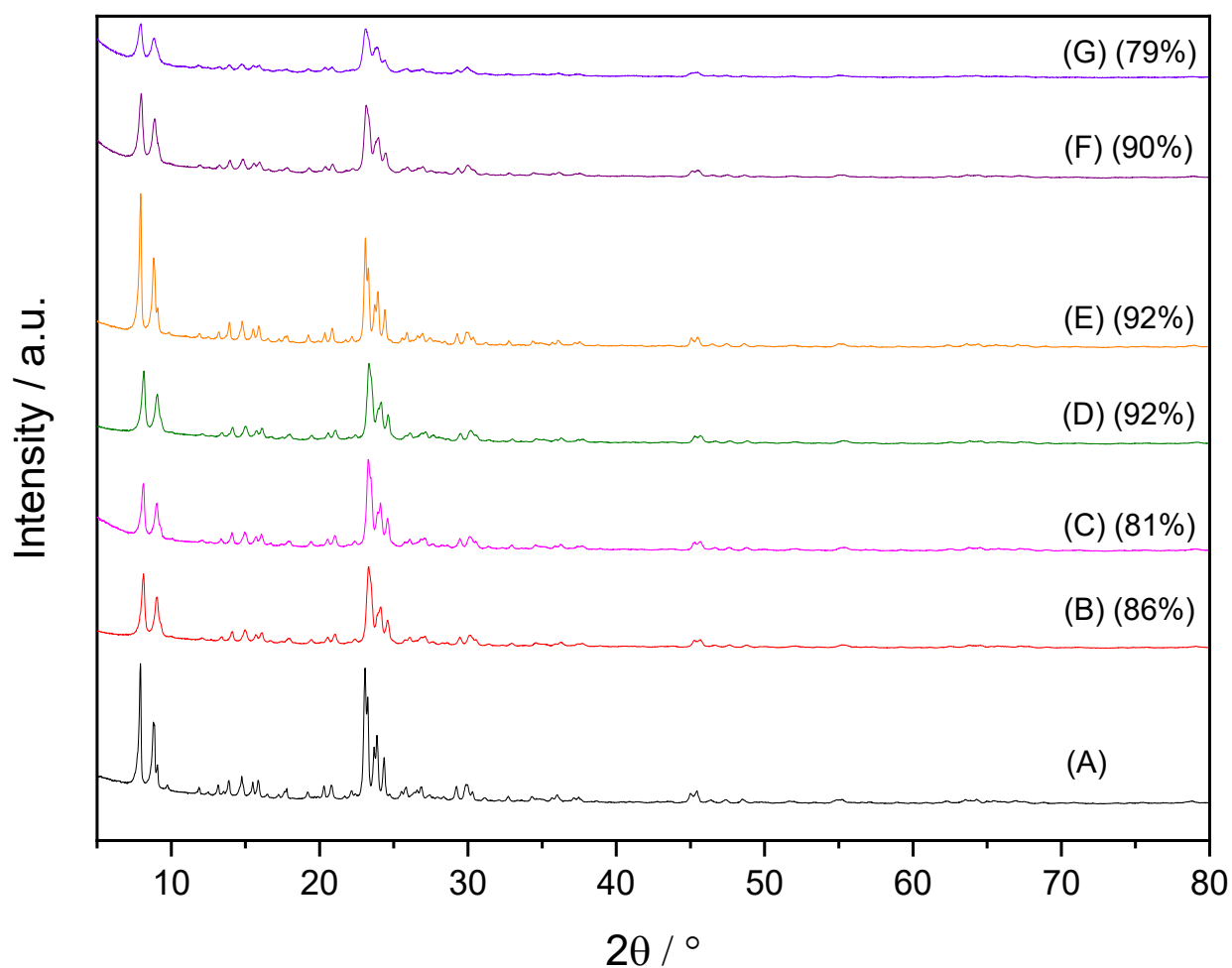
The presence of reflectance bands between 200-250 nm (orange) and 250-350 nm (blue) are considered to be indicative of Fe<sup>3+</sup> tetrahedrally coordinated within the ZSM-5 lattice, in addition to isolated and bi-nuclear Fe species immobilised within the zeolitic framework channels. While the bands observed above 450 nm (yellow) are attributed to the presence of extra-framework Fe<sub>x</sub>O<sub>y</sub> particles (clusters and agglomerates).<sup>1</sup>



**Figure S.3.** FTIR spectra of 0.5.%Pd/Fe-ZSM-5 catalysts, as a function of total Fe incorporation. **(A)** commercial ZSM-5, **(B)** 0.5%Pd/ZSM-5, **(C)** 0.5%Pd/0.06%Fe-ZSM-5, **(D)** 0.5%Pd/0.125%Fe-ZSM-5, **(E)** 0.5%Pd/0.5%Fe-ZSM-5, **(F)** 0.5%Pd/1%Fe-ZSM-5 and **(G)** 0.5%Pd/3%Fe-ZSM-5. **Note:** All samples exposed to reductive heat treatment (4 h, 500 °C, 10 °C min<sup>-1</sup>, 5% H<sub>2</sub>/Ar).

### Supplementary Note 2.

It is possible to observe three distinct bands in the FTIR spectra of the 0.5.%Pd/Fe-ZSM-5 catalysts, at approximately 800, 1050 and 1220 cm<sup>-1</sup>, which is characteristic of the SiO<sub>4</sub> tetrahedron units. The adsorption band at 1050 cm<sup>-1</sup> is attributed to the internal asymmetric stretching vibrations of Si-O linkages and has been observed to shift towards higher wavenumbers with increasing SiO<sub>2</sub>: Al<sub>2</sub>O<sub>3</sub> ratios. The adsorption band at 1220 cm<sup>-1</sup> is typically utilised to provide information on the structure of the zeolite and has been assigned to the 5-membered rings present within the framework structure of ZSM-5.<sup>2</sup> The bands at 800 cm<sup>-1</sup> are assigned to the symmetric stretching of the external linkages of the SiO<sub>4</sub> tetrahedron.



**Figure S.4.** X-ray diffractograms of 0.5.%Pd/Fe-ZSM-5 catalysts, as a function of total Fe incorporation. **(A)** commercial ZSM-5, **(B)** 0.5%Pd/ZSM-5 **(C)** 0.5%Pd/0.06%Fe-ZSM-5 **(D)** 0.5%Pd/0.125%Fe-ZSM-5 **(E)** 0.5%Pd/0.5%Fe-ZSM-5 **(F)** 0.5%Pd/1%Fe-ZSM-5 **(G)** 0.5%Pd/3%Fe-ZSM-5. **Note 1:** All samples exposed to reductive heat treatment (4 h, 500 °C, 10 °C min<sup>-1</sup>, 5%H<sub>2</sub>/Ar). **Note 2:** Values in parentheses indicate crystallinity of synthesised materials, as compared to commercial ZSM-5.

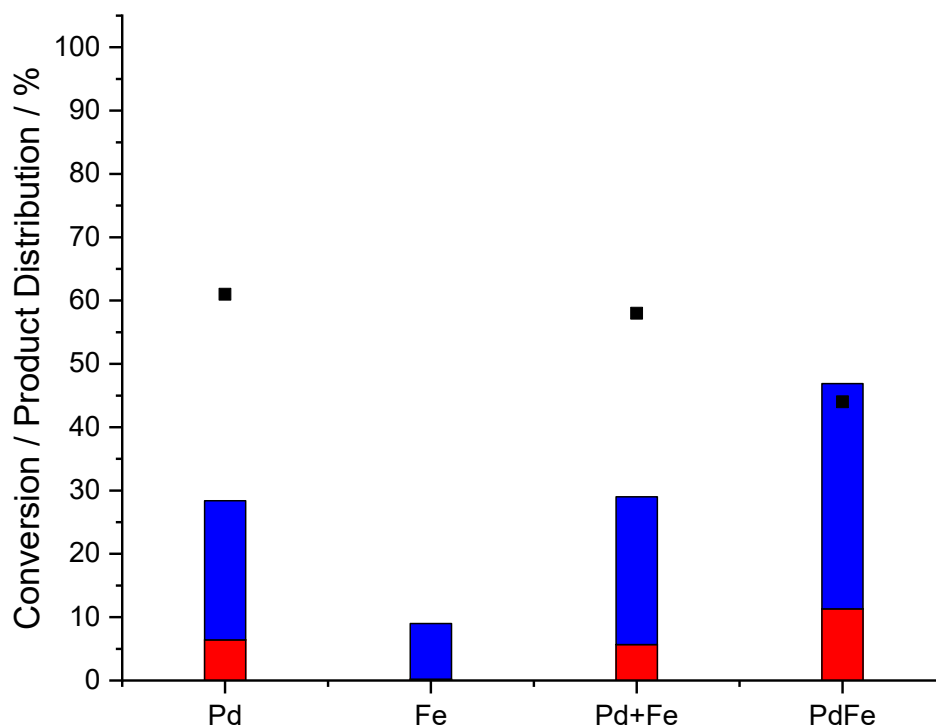
### Supplementary Note 3.

Reflection's characteristic of ZSM-5 can be observed at  $\theta=7-9^\circ$  and  $\theta=23-25^\circ$ .<sup>3</sup>

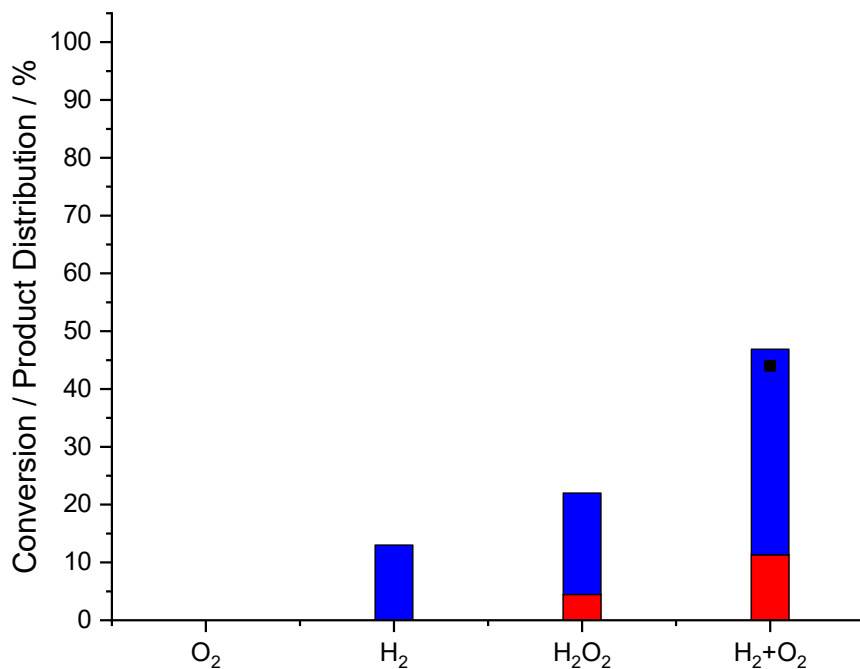
**Table S.2.** Summary of porosity and surface area of 0.5.%Pd-Fe-ZSM-5 catalysts as a function of Fe incorporation.

Catalysts	Surface area / m <sup>2</sup> g <sup>-1</sup> [a]	V <sub>micropore</sub> cm <sup>3</sup> g <sup>-1</sup>
0.5 wt.%Pd/3 %Fe-HZSM-5	259	0.04
0.5 wt.%Pd/1%Fe-HZSM-5	281	0.05
0.5 wt.%Pd/0.5%Fe-HZSM-5	345	0.07
0.5 wt.%Pd/0.125%Fe-HZSM-5	348	0.08
0.5 wt.%Pd/0.06%Fe-HZSM-5	399	0.07
0.5 wt.%Pd/HZSM-5	407	0.09
	491	0.11
HZSM-5 (28) (synthesised)	516	0.12
HZSM-5 (30) (commercial)	413	0.15

[a] Surface area determined from nitrogen adsorption measurements using the BET equation. **Note:** Synthesised and commercial ZSM-5 materials were exposed to an oxidative heat treatment (flowing air, 550 °C, 3 h, 1 °Cmin<sup>-1</sup>), while metal immobilised catalysts were exposed to an oxidative heat treatment (static air, 550 °C, 3 h, 10 °Cmin<sup>-1</sup>), prior to a subsequent reductive heat treatment (5%H<sub>2</sub>/Ar, 400 °C, 4 h, 10 °Cmin<sup>-1</sup>).

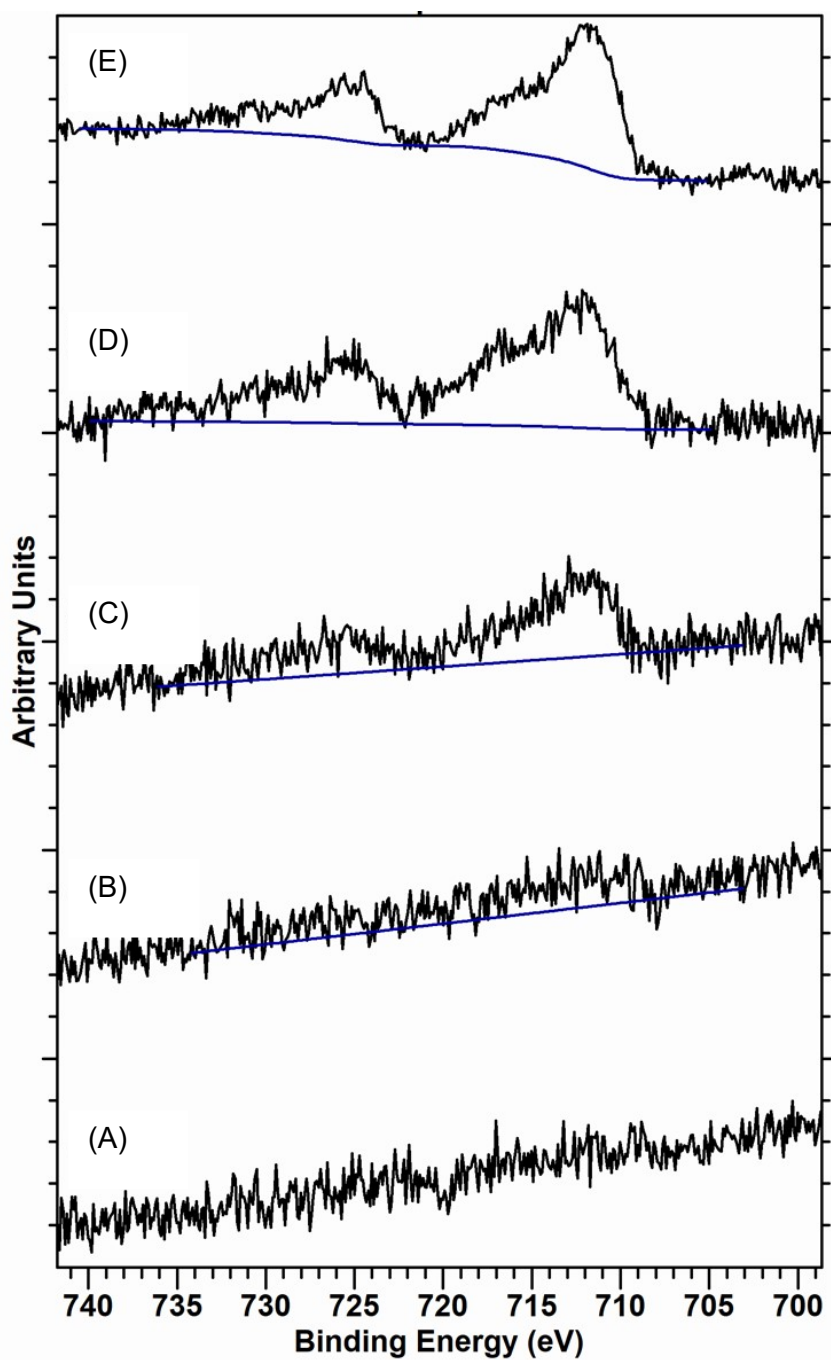


**Figure S.5.** Catalytic performance of ZSM-5 based catalysts towards the oxidative degradation of phenol via in-situ H<sub>2</sub>O<sub>2</sub> synthesis. **Key:** Selectivity towards phenolic derivatives (Red bar), Selectivity towards organic acids (Blue bar), H<sub>2</sub> conversion (Black squares). **Phenol oxidation reaction conditions:** Catalyst (0.01 g), Phenol (1000 ppm), 5% H<sub>2</sub>/CO<sub>2</sub> (420 psi), 25% O<sub>2</sub>/CO<sub>2</sub> (160 psi), 1200 rpm, 30 °C, 2 h. **Note 1 :** Total metal loading is identical in all cases. **Note 2:** All samples exposed to reductive heat treatment (4 h, 500 °C, 10 °C min<sup>-1</sup>, 5%H<sub>2</sub>/Ar).



**Figure S.6.** The effect of oxidant on the catalytic activity of 0.5%Pd/0.5%Fe-ZSM-5 catalyst towards the oxidative degradation of phenol. **Key:** Selectivity towards phenolic derivatives (Red bar), Selectivity towards organic acids (Blue bar),  $H_2$  conversion (Black squares). **Phenol oxidation reaction conditions:** Catalyst (0.01 g), Phenol (1000 ppm), 5%  $H_2/CO_2$  (420 psi), 25%  $O_2/CO_2$  (160 psi), 1200 rpm, 30 °C, 2 h. **Note 1:** The concentration of preformed  $H_2O_2$  utilised is comparable to that produced if all  $H_2$  in a standard in-situ reaction is converted to  $H_2O_2$ . **Note 2:** All samples exposed to reductive heat treatment (4 h, 500 °C, 10 °C  $min^{-1}$ , 5% $H_2/Ar$ ).



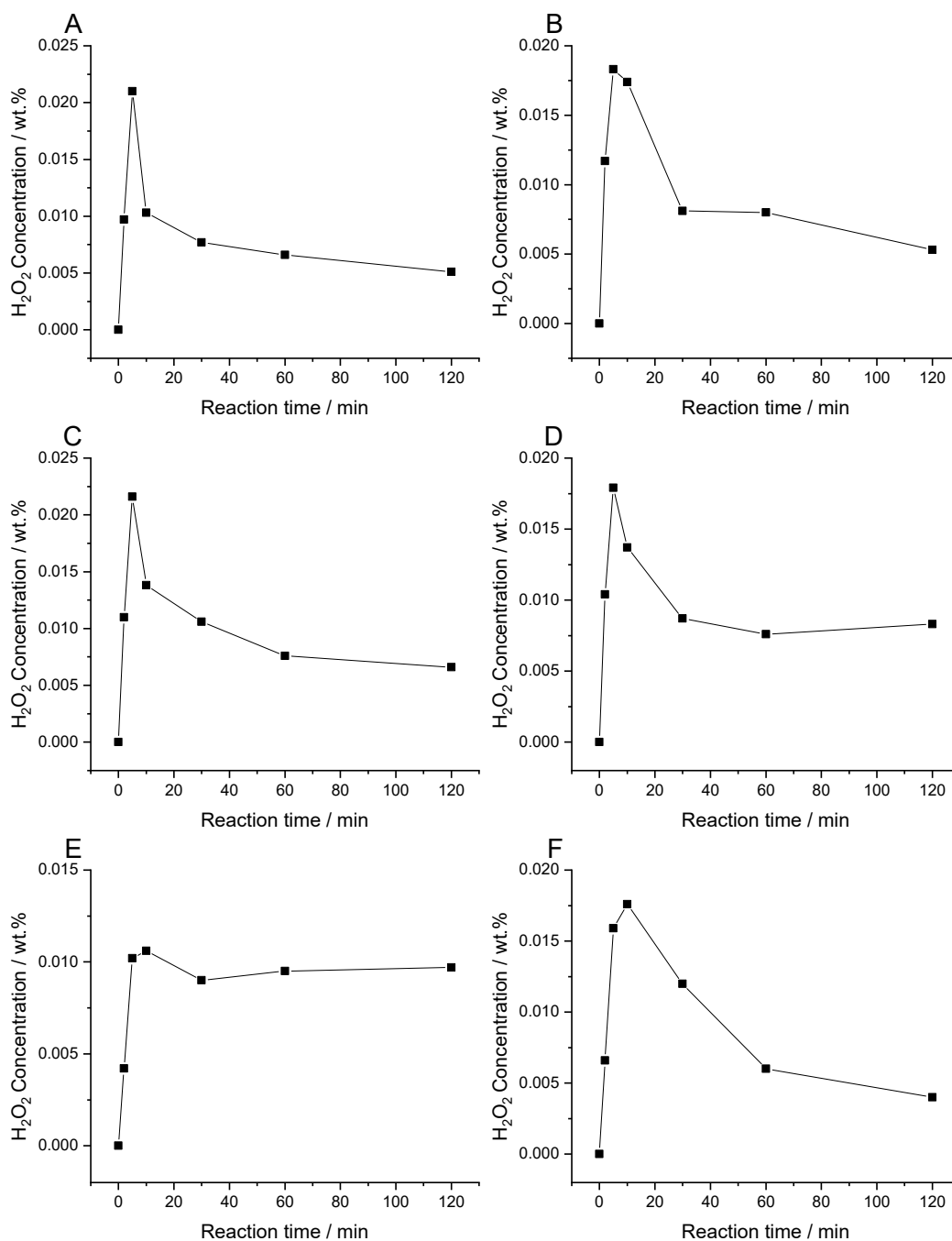


**Figure S.7.** Fe(2p) core levels spectra for **(A)** 0.5%Pd/0.06%Fe-ZSM-5, **(B)** 0.5%Pd/0.125%Fe-ZSM-5, **(C)** 0.5%Pd/0.5%Fe-ZSM-5, **(D)** 0.5%Pd/1%Fe-ZSM-5 and **(E)** 0.5%Pd/3% Fe-ZSM-5. **Note:** All samples exposed to reductive heat treatment (4 h, 500 °C, 10 °C min<sup>-1</sup>, 5%H<sub>2</sub>/Ar).

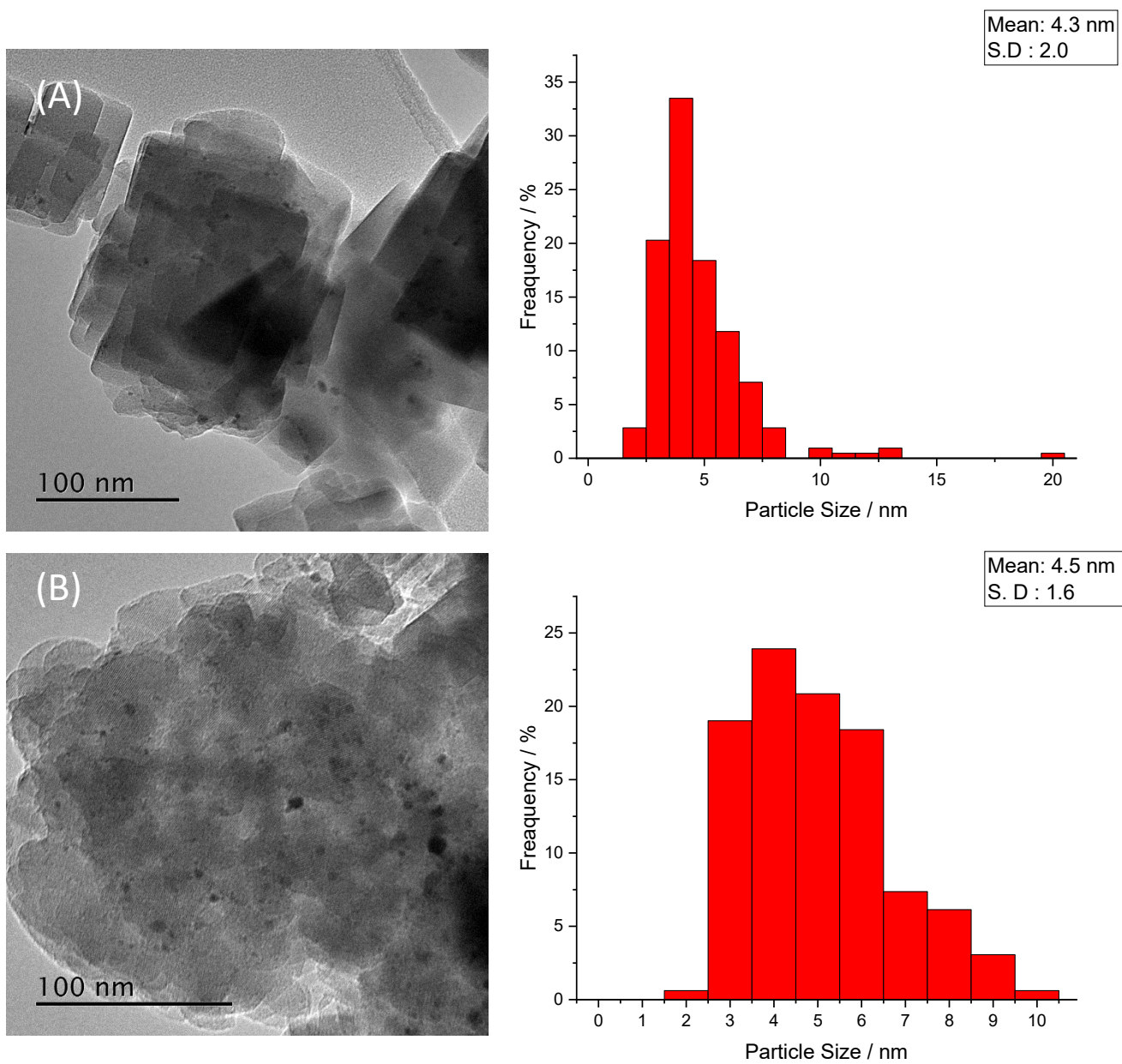
**Table S.3.** Atomic ratios of key catalytic species, as determined by XPS.

Catalyst	Al 2p	Si 2p	C 1s	Fe 2p	O 1s	Pd 3d (Metallic)	Pd 3d (2+)	Pd <sup>2+</sup> /Pd <sup>0</sup>	Pd/Si
0.5wt.%Pd/3.0wt.%Fe/ZSM-5	1.9	33.4	4.8	0.3	59.6	0.03	0.01	0.33	0.0012
0.5wt.%Pd/1.0wt.%Fe/ZSM-5	1.5	33.1	6.4	0.2	58.8	0.04	0.02	0.50	0.0018
0.5wt.%Pd/0.5wt.%Fe/ZSM-5	1.4	35.0	2.3	0.1	61.2	0.07	0.02	0.29	0.0026
0.5wt.%Pd/0.125wt.%Fe/ZSM-5	1.6	33.2	6.2	0.0	59.0	0.02	0.02	1.00	0.0012
0.5wt.%Pd/0.06wt.%Fe/ZSM-5	1.5	32.7	8.2	n/d	57.6	0.03	0.02	0.67	0.0015
0.5wt.%Pd/ZSM-5	1.4	33.0	7.2	0.0	58.4	0.02	0.01	0.50	0.0009

**Note:** All samples exposed to reductive heat treatment (4 h, 500 °C, 10 °C min<sup>-1</sup>, 5%H<sub>2</sub>/Ar).



**Figure S.8.** Comparison of catalytic activity towards the direct synthesis of  $H_2O_2$ , as a function of reaction time. **(A)** 0.5%Pd/ZSM-5, **(B)** 0.5%Pd/0.06%Fe-ZSM-5, **(C)** 0.5%Pd/0.125%Fe-ZSM-5, **(D)** 0.5%Pd/0.5%Fe-ZSM-5, **(E)** 0.5%Pd/1%Fe-ZSM-5, **(F)** 0.5%Pd/3%Fe-ZSM-5.  **$H_2O_2$  direct synthesis reaction conditions:** Catalyst (0.01 g),  $H_2O$  (8.5 g), 5% $H_2/CO_2$  (420 psi), 25% $O_2/CO_2$  (160 psi), 30 °C, 1200 rpm. **Note:** All samples exposed to reductive heat treatment (4 h, 500 °C, 10 °C min<sup>-1</sup>, 5% $H_2/Ar$ ).



**Figure S.9.** Transmission electron micrographs and corresponding particle size histograms of the as-prepared (A) 0.5%Pd/ZSM-5 and (B) 0.5%Pd/3%Fe-ZSM-5 catalysts. **Note:** All samples exposed to reductive heat treatment (4 h, 500 °C, 10 °C min<sup>-1</sup>, 5% H<sub>2</sub>/Ar).

**Table S.4.** Metal leaching during the oxidative degradation of phenol via in-situ H<sub>2</sub>O<sub>2</sub> synthesis

Catalyst	Phenol Conversion / %	Selectivity towards Phenolic Derivatives / %	Selectivity towards Organic Acids / %	Metal Leached / ppm (%)	
				Pd	Fe
0.5%Pd/ZSM-5	39	29	71	0.3 (4.4%)	-
0.5%Pd/3%Fe-ZSM-5	70	29	71	0.2 (3.0%)	2.3 (6.4%)

**Phenol oxidation reaction conditions:** Catalyst (0.01 g), Phenol (100ppm), 5% H<sub>2</sub>/CO<sub>2</sub> (420 psi), 25% O<sub>2</sub>/CO<sub>2</sub> (160 psi), 1200 rpm, 2 h, 30 °C. **Note:** All samples exposed to reductive heat treatment (4 h, 500 °C, 10 °C min<sup>-1</sup>, 5%H<sub>2</sub>/Ar).

**Table S.5.** Product distribution in the oxidative degradation of phenol via in-situ H<sub>2</sub>O<sub>2</sub> synthesis.

Catalyst	Time / h	Phenol Conversion / %	Selectivity towards Phenolic Derivatives / %	Selectivity towards Organic Acids
				/ %
0.5%Pd/ZSM-5	1	32.0	26.0	74.0
	2	38.0	30.0	70.0
0.5%Pd/3%Fe-ZSM-5	1	56.0	35.0	65.0
	2	72.0	26.0	74.0
0.5%Pd/3%Fe-ZSM-5 (hot filtration)	2	58.0	29.0	71.0
0.5%Pd/3%Fe-ZSM-5 (hot filtration) with 0.5%Pd/ZSM-5	2	72.0	16.0	84.0
0.5%Pd/3%Fe-ZSM-5 (hot filtration) with H <sub>2</sub> O <sub>2</sub> *	2	65.0	22.0	78.0

**Phenol oxidation reaction conditions:** Catalyst (0.01 g), Phenol (1000ppm), 5% H<sub>2</sub>/CO<sub>2</sub> (420 psi), 25% O<sub>2</sub>/CO<sub>2</sub> (160 psi), 1200 rpm, 30 °C. \*During the second 1 h hot-filtration experiment a concentration of H<sub>2</sub>O<sub>2</sub> was used that was identical to that if all the H<sub>2</sub> in a standard in-situ reaction was converted to H<sub>2</sub>O<sub>2</sub>, an atmosphere of 25%O<sub>2</sub>/CO<sub>2</sub> (580 psi) was used. **Note:** All samples exposed to reductive heat treatment (4 h, 500 °C, 10 °C min<sup>-1</sup>, 5%H<sub>2</sub>/Ar).

## References.

1. J. Xu, R. D. Armstrong, G. Shaw, N. F. Dummer, S. J. Freakley, S. H. Taylor and G. J. Hutchings, *Catal. Today*, 2016, **270**, 93-100.
2. L. Shirazi, E. Jamshidi and M. R. Ghasemi, *Cryst. Res. Technol.*, 2008, **43**, 1300-1306.
3. R. J. Lewis, A. Bara-Estaun, N. Agarwal, S. J. Freakley, D. J. Morgan and G. J. Hutchings, *Catal. Lett.*, 2019, **149**, 3066-3075.