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Hydrodehalogenation of 4-chlorophenol and 4-bromophenol over Pd–Fe/Al_2O_3: influence of catalyst reduction conditions

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SM-1. Preparation of catalysts

The solutions of $Fe(NO_3)_3 \times 9\ H_2O$ (chemically pure, Merck) and $Pd(NO_3)_2$ (pure, Aurat, Russia) in distilled water were used for catalyst preparation. The support (γ-Al_2O_3, Engelhard) was preliminary dried at 150°C for 1 h and the aqueous solutions of calculated amounts of salt(s) in the minimal amount of water were added dropwise, mixed for 2 h and evaporated with a bain-marie for 1.5 h. Then, the catalyst precursors were dried at 150°C for 1 h and calcined in a muffle oven (heating up to 400°C at a rate of 1.6°C min^{-1}, isothermal calcination for 5 h). The bimetallic PdFe/Al_2O_3-c catalyst was synthesized via co-impregnation of the two salts. In the case of PdFe/Al_2O_3-s the sequential impregnations were used: the impregnation with the iron salt was followed by the impregnation with the palladium salt with the intermediate drying at 150°C.

SM-2. Reduction of catalysts before catalytic tests.

The catalysts were reduced with H_2 using three techniques at: (1) severe conditions: treatment in an H_2 flow (0.6 $dm^3\ h^{-1}$) in a tubular quartz reactor for 2 h at 320°C followed by cooling to RT and treatment in a N_2 flow (0.6 $dm^3\ h^{-1}$) containing oxygen traces for 20 mins; then the catalyst was transferred to the catalytic reactor; (2) mild conditions: treatment with a water solution of $NaBH_4$ (p.a., Sigma-Aldrich, USA) (30°C, 1.5 h, molar excess of $NaBH_4$ 2:1 for the reduction of PdO in Pd/Al_2O_3, and 6:1 for the reduction of the bimetallic catalysts) with the simultaneous H_2 supply (0.6 $dm^3\ h^{-1}$); (3) mild conditions: treatment with a water solution of phenol (30°C, 75 mg dm^{-3}, 15 ml) with the simultaneous H_2 supply (0.6 $dm^3\ h^{-1}$). Mild treatments (2) and (3) were performed in the catalytic reactor. After treatment the solution was decanted, the catalyst was washed with distilled water (4 x 15 mL), and then the aqueous solution of the 4-chlorophenol or 4-bromophenol was added, and the catalytic test started.

For XPS analysis the washing water after treatment (3) was decanted and the sample was dried to a free-flowing state in an H_2 flow under a slight heating (less than 50°C).

SM-3. Catalytic tests

Catalysts were tested at 30°C in a glass batch-type reactor equipped with a magnetic stirrer, a thermostatically controlled jacket with the water supply from a thermostat, a reflux condenser with water cooling, a system for supplying hydrogen from a cylinder without purification through a gas flow controller, and a rubber septum for sampling. In the hydrodechlorination of chlorobenzene, 0.1 g of a catalyst and 15 ml of 75 mg dm^{-3}aqueous solution of 4-chlorophenol (99 +%, Lancaster, Germany) were used. The H_2 supply was 0.6 $dm^3\ h^{-1}$. In the hydrodebromination of 4-bromophenol (99 +%, Lancaster, Germany), a 150 mg dm^{-3} solution of

4-bromophenol acidified with a 0.1 M formic acid solution was used and the catalyst weight was 0.05 g. Other test conditions were the same. Before hydrodebromination of 4-bromophenol the catalysts were reduced using technique (3).

SM-4. Product analysis in catalytic tests

Products were analyzed by high-performance liquid chromatography (HPLC) using an Agilent 1100 Series instrument equipped with a Zorbax SB-C18 column (15 cm, 35 °C) and a UV-detector at 278 nm. The mixture of two mobile phases (A – 0.1 M/L formic acid solution in deionized water; B – acetonitrile) at an A:B ratio of 55:45 vol.% was used at a flow rate of 1.0 ml min^{-1}. The aliquots of 0.2 ml were sampled from the reaction mixture through a rubber septum, centrifuged at 2000 rpm for 1 min and 20 μkl probe was injected into the HPLC instrument.

SM-5. Physicochemical study of catalysts - XPS spectra processing

XPS spectra were fitted with the CASAXPS software. The spectra were charge referenced to the Al2p binding energy accepted to be equal to 74.6 eV, which is typical for Al_2O_3.

Fitting of Fe2p spectra.

The U2 Tougaard background was used in the binding energy range between about 704 and 746.5 eV. The second parameter of the background cross section was manually adjusted in the range of −130…−270 to yield the best fit. The Fe2p spectra were fitted with three synthetic components attributed to Fe^0, Fe^{2+} and Fe^{3+} species. Each component represented a set of constrained peaks (see Table S1). The synthetic components were constructed based on the preliminary acquired spectrum of pure metallic iron as a reference of Fe^0 species and the spectra of FeO and Fe_2O_3 oxides[1] as references of Fe^{2+} and Fe^{3+} species. The fitting of all the Fe2p spectra didn't reveal any contribution of Fe^0 species.

Table S1. Parameters of peaks constrained into synthetic Fe2p XPS components of Fe^0, Fe^{2+} and Fe^{3+} species.

Synthetic component	Peak Name	Line Shape	Area	FWHM	Position
Fe^0	A	LA(1.2,4.8,3)	Varied	1.00	Varied
	B	LA(1.2,4.8,3)	A*0.500	A*1.20	A+12.70
Fe^{2+}	C	GL(30)	Varied	(2.2, 2.8) [a)]	Varied [b)]
	D	GL(30)	C*0.500	C*1.00	C+13.54
	E	GL(30)	C*1.45	C*1.40	C+1.50
	F	GL(30)	C*0.689	C*1.40	C+15.11
	G	GL(30)	C*1.51	C*2.20	C+5.35
	H	GL(30)	C*0.747	C*2.20	C+19.37
	I	GL(30)	C*0.392	C*2.20	C+10.52
	J	GL(30)	C*0.164	C*2.20	C+23.82

Fe^{3+}	K	LF(0.3,8,14,100)	Varied	(2.7, 3.2 [a)]	Varied [b)]
	L	LF(0.6,5,10,100)	K*0.568	K*1.42	K+13.77
	M	GL(30)	K*0.243	K * 1.63	K+9.16
	N	GL(30)	K*0.0886	K*1.65	K+23.13
	O	GL(30)	K*0.0289	K*1.03	K+32.37

[a)] Varied within a range.
[b)] The difference between peak K and peak C positions was adjusted to be between 1.1 and 1.3 eV.

Fitting of Pd3d spectra.

The U2 Tougaard background was used in the binding energy range between about 330 and 356 eV. The second parameter of the background cross section was set to −450. The P3d spectra were fitted with two synthetic components attributed to Pd^0 and Pd^{2+} species. Each component represented a set of constrained peaks (see Table S2). The synthetic components were constructed based on the preliminary acquired spectrum of pure metallic palladium as a reference of Pd^0 species and the spectrum of PdO oxide[2] as a reference of Pd^{2+} species. For several samples an additional Ca2p doublet with the $Ca2p_{3/2}$ binding energy of about 348 eV was added to the fitting model because these samples were found to contain the admixture of Ca.

Table S2. Parameters of peaks constrained into synthetic Pd3d XPS components of Pd^0 and Pd^{2+} species.

Synthetic component	Peak Name	Line Shape	Area	FWHM	Position
Pd^0	A	LF(0.8,1.8,150,150)	Varied	(1.0, 1.3) [a)]	Varied [b)]
	B	LF(0.8,1.8,120,150)	A*0.667	A* 1.00	A + 5.25
	C	GL(30)	A*0.0444	A*1.49	A + 6.35
	D	GL(30)	A* 0.0296	A*1.49	A + 11.60
	E	GL(30)	A*0.0925	A*4.12	A + 8.02
	F	GL(30)	A*0.0616	A*4.12	A + 13.27
Pd^{2+}	G	LF(0.9,1.9,100,300)	Varied	(2.1, 2.5)	Varied [b)]
	H	LF(0.9,1.7,100,300)	G*0.667	G*1.11	G + 5.33
	I	GL(30)	G*0.123	G*1.75	G + 8.79
	J	GL(30)	G*0.0818	G*1.75	G + 13.98

[a)] Varied within a range.
[b)] The difference between peak A and peak G positions was adjusted to be about 2 eV.

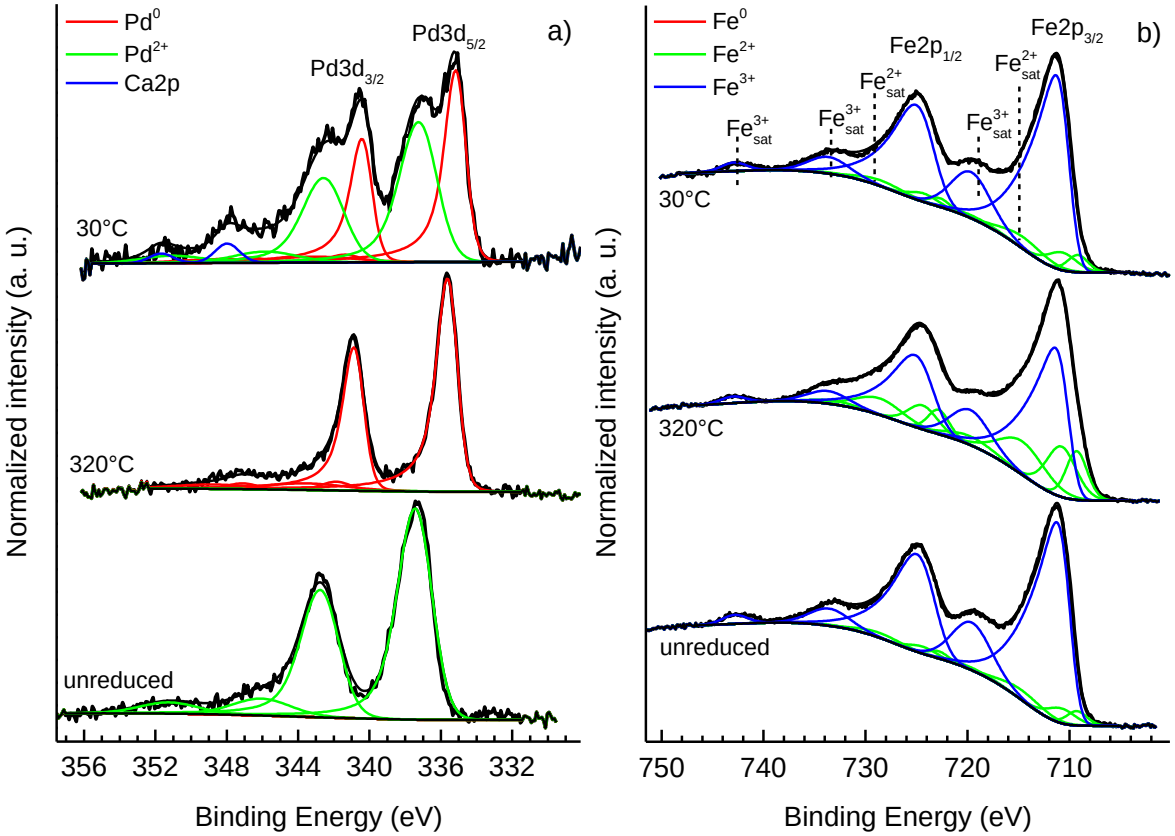

Figure S1. Pd3d (a) and Fe2p (b) XPS spectra of unreduced and reduced FePd/Al_2O_3-c (see reduction conditions in SM-2 and in Table 1 of the article).

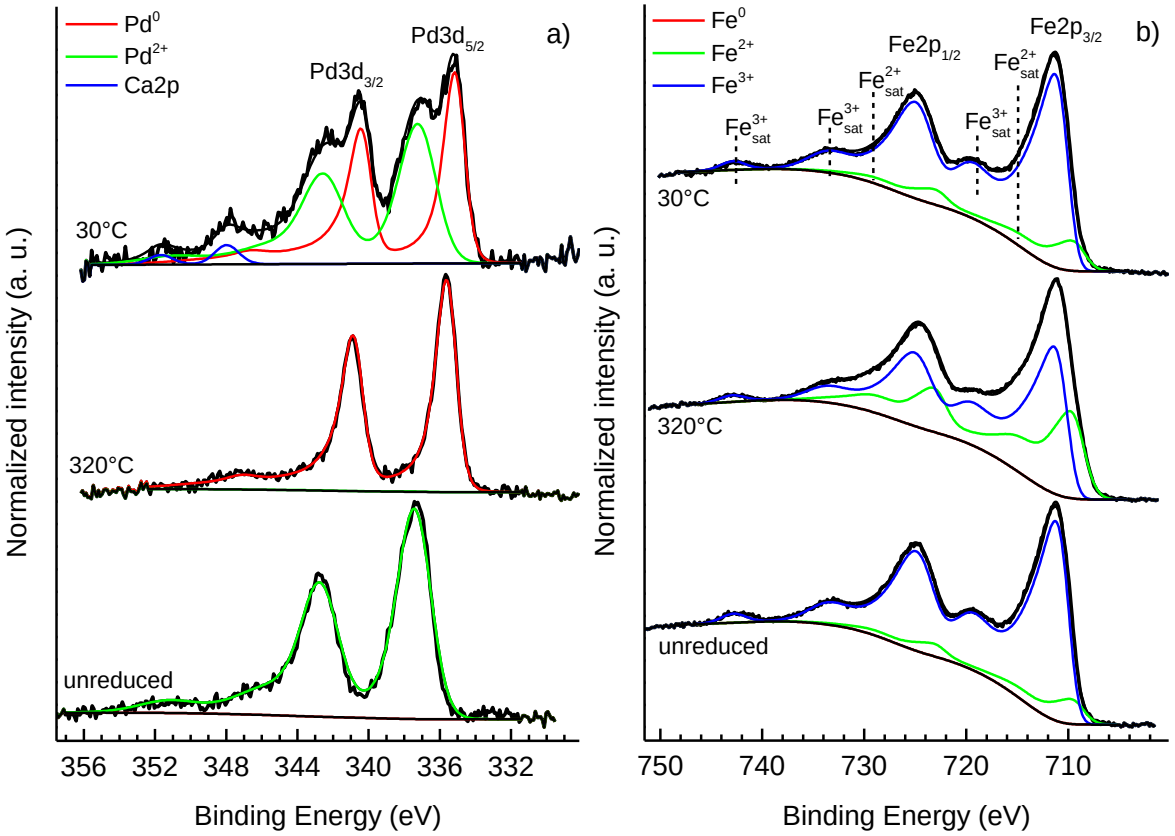

Figure S2. Pd3d (a) and Fe2p (b) XPS spectra of unreduced and reduced FePd/Al_2O_3-c (see reduction conditions in SM-2 and in Table 1 of the article). Peaks attributed to each species are combined into synthetic components.

Table S3. Binding energies (eV) of $Pd3d_{5/2}$ and $Fe2p_{3/2}$ components in XPS spectra of unreduced and reduced catalysts

Catalyst	Reduction	$Pd3d_{5/2}$		$Fe2p_{3/2}$	
		Pd^0	Pd^{2+}	Fe^{2+}	Fe^{3+}
Fe/Al_2O_3	no reduction	–	–	N/D***	710.6
	in-situ, 320°C*	–	–	N/D	710.7
Pd/Al_2O_3	no reduction	–	337.0	–	–
	in-situ , 320°C	335.1	N/D	–	–
	ex-situ, 30°C **	334.9	336.9	–	–
$PdFe/Al_2O_3$ -c	no reduction	–	337.4	709.8	711.2
	in-situ, 320°C	335.7	N/D	709.9	711.4
	ex-situ, 30°C	335.2	337.3	709.6	711.4
$PdFe/Al_2O_3$ -s	no reduction	–	337.3	709.4	711.0
	in-situ, 320°C	335.5	336.8	709.7	711.3
	ex-situ, 30°C	335.2	337.3	709.6	711.3

* In-situ reduction using technique (1) (Ar+5%H_2, 1 atm., 320°C, 2 h, heating rate of 5°C min^{-1})
** Ex-situ reduction using technique (3) (30°C, H_2 flow of 0.6 dm^3 h^{-1}, 1 h, 75 mg dm^{-3} aqueous phenol solution, washing with water, drying at 50°C under H_2 flow).
*** Component was not detected.

SM-6. Physicochemical study of catalysts (XRD, TEM)

The conditions of physical-chemical analysis were described earlier[3]. X-ray powder diffraction patterns were recorded on a MiniFlex 300/600 (Rigaku, Japan) diffractometer (CuKα radiation, 1.5418 Å).

The high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEM 2100F-UHR instrument (JEOL, Japan) at accelerating voltage of 200 kV equipped with an EDX accessory.

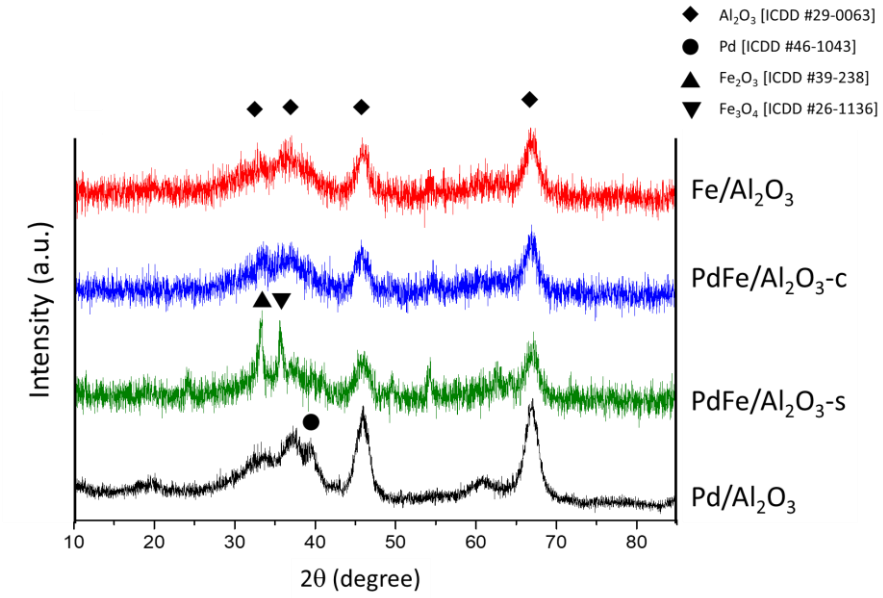

Figure S3. XRD profiles of catalysts pre-reduced under severe conditions (H_2, 320°C).

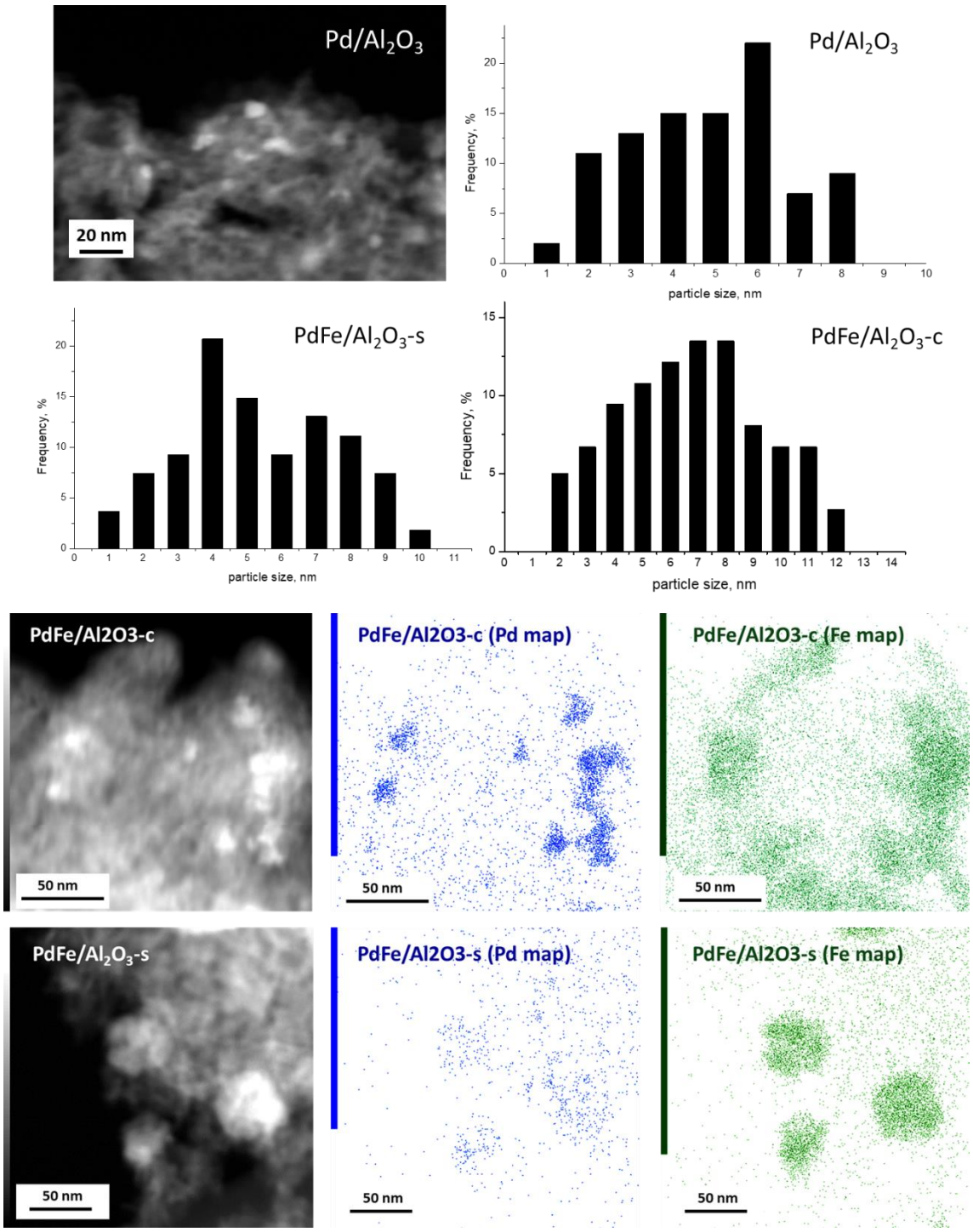

Figure S4. TEM images and EDX maps of catalysts reduced under severe conditions (H_2, 320°C).

References

1. S. Gota, E. Guiot, M. Henriot and M. Gautier-Soyer, *Phys. Rev. B*, 1999, **60**(20), 14387.
2. T. Pillo, R. Zimmermann, P. Steiner and S. Hüfner, *J. Phys.: Condens. Matter*, 1997, **9**(19), 3987.
3. E.S. Lokteva, V.V. Shishova, N.N. Tolkachev, A.N. Kharlanov, K.I. Maslakov, A.O. Kamaev, I.Y. Kaplin, I.N. Savina and E.V. Golubina, *Molecules*, 2021, **26**(1), 141.