Supporting Information

Ba-doped Pd/Al_2O_3 for continuous synthesis of diphenylamine *via* dehydrogenative aromatization

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Table S1. Dehydrogenative aromatization of the Schiff base over different alkaline-earth metal doped catalyst

Entry	Catalyst	Conv. (%)	Selectivity (%)						DPA **6** yield (%)
			3	**4**	**5**	**6**	**7**	Others[a]	
1	Pd_1/Al_2O_3	89.2±0.2	4.7±0.2	5.5±0.4	16.7±0.5	58.9±1.8	5.4±0.6	8.8±1.1	52.5±1.7
2	Pd_1/Al_3MgO	99.6±0.1	10.9±0.3	3.0±0.3	-	83.2±0.3	1.2±0.2	1.7±0.3	82.9±0.4
3	Pd_1/Al_3CaO	99.4±0.1	15.6±0.9	3.3±0.4	-	80.3±0.4	-	0.8±0.3	79.8±0.5
4	Pd_1/Al_3SrO	98.1±0.4	11.2±0.8	5.9±0.2	-	82.0±0.5	-	0.9±0.2	80.4±0.8
5	Pd_1/Al_3BaO	94.9±0.3	8.1±0.6	1.8±0.4	0.3±0.1	89.3±0.5	-	0.5±0.1	84.7±0.7

Reaction conditions: Cyclohexanone:Aniline:Nitrobenzene (molar ratio) = 1:1:0.66; Temperature = 220°C; N_2 pressure = 2.0 MPa; LHSV = 0.15 h^{-1}; Solvent, m-xylene.

[a] Including contamination in raw material, errors of measurement instrument and trace impurities produced in the reaction.

Table S2. Dehydrogenative aromatization of the Schiff base over different Ba content of Pd_1/Al_yBaO catalyst.

Entry	Catalyst	Conv. (%)	Selectivity (%)						DPA **6** yield (%)	TOF (h^{-1})
			3	**4**	**5**	**6**	**7**	Others[a]		
1	Pd_1/Al_4BaO	96.3±0.5	7.2±0.5	2.0±0.3	1.3±0.3	84.9±0.1	1.5±0.1	3.1±0.2	81.8±0.5	18.6±0.1
2	Pd_1/Al_3BaO	94.9±0.3	8.1±0.6	1.8±0.4	0.3±0.1	89.3±0.5	-	0.5±0.1	84.7±0.5	15.0±0.1
3	Pd_1/Al_2BaO	83.7±0.4	11.5±0.7	5.1±0.3	0.5±0.1	79.8±0.4	-	3.6±0.1	66.8±0.7	19.0±0.2
4	Pd_1/Al_1BaO	71.2±0.3	7.8±0.6	3.2±0.4	11.7±0.8	74.4±0.7	-	2.9±0.3	53.0±0.7	21.2±0.3

Reaction conditions: Cyclohexanone:Aniline:Nitrobenzene (molar ratio) = 1:1:0.66; Temperature = 220°C; N_2 pressure = 2.0 MPa; LHSV = 0.15 h^{-1}; Solvent, *m*-xylene.

[a] Including contamination in raw material, errors of measurement instrument and trace impurities produced in the reaction.

Table S3. Dehydrogenative aromatization of the Schiff base at different temperatures

Entry	Catalyst	Temp. (°C)	Conv. (%)	Selectivity (%)						DPA **6** yield (%)	TOF (h^{-1})
				3	**4**	**5**	**6**	**7**	Others[a]		
1	Pd_1/Al_2O_3	200	83.3±0.4	2.0±0.1	11.3±0.4	17.9±0.3	61.9±0.9	3.5±0.2	3.4±0.2	51.6±1.0	23.1±0.4
2	Pd_1/Al_2O_3	220	89.2±0.2	4.7±0.2	5.5±0.4	16.7±0.5	58.9±1.8	5.4±0.6	8.8±1.1	52.5±1.7	23.6±0.8
3	Pd_1/Al_2O_3	240	63.1±0.6	4.5±0.3	2.6±0.3	22.9±0.7	56.3±1.1	4.2±0.4	9.5±1.0	35.5±1.0	15.9±0.4
4	Pd_1/Al_4BaO	200	94.1±0.4	9.2±1.0	5.1±0.8	1.2±0.2	80.4±0.4	-	4.1±0.7	75.7±0.7	17.2±0.2
5	Pd_1/Al_4BaO	220	96.3±0.5	7.2±0.5	2.0±0.3	1.3±0.3	84.9±0.1	1.5±0.1	3.1±0.2	81.8±0.5	18.6±0.1
6	Pd_1/Al_4BaO	240	82.8±0.4	6.7±0.4	0.5±0.1	5.7±0.7	75.9±0.6	3.7±0.3	7.5±0.2	62.8±0.8	14.3±0.2
7	Pd_1/Al_3BaO	200	91.7±0.3	12.7±0.3	16.1±0.4	-	69.1±0.1	-	2.1±0.1	63.4±0.3	11.2±0.1
8	Pd_1/Al_3BaO	220	94.9±0.3	8.1±0.6	1.8±0.4	0.3±0.1	89.3±0.5	-	0.5±0.1	84.7±0.7	15.0±0.1
9	Pd_1/Al_3BaO	240	82.4±0.2	6.1±0.8	0.4±0.1	3.3±0.3	75.1±0.7	8.1±0.5	7.0±0.3	61.9±0.7	11.0±0.1
10	Pd_1/Al_2BaO	200	72.3±0.8	13.3±0.7	10.2±0.5	-	70.5±0.6	-	6.0±0.2	51.0±1.0	14.5±0.3
11	Pd_1/Al_2BaO	220	83.7±0.4	11.5±0.7	5.1±0.3	0.5±0.1	79.8±0.4	-	3.6±0.1	66.8±0.7	19.0±0.2
12	Pd_1/Al_2BaO	240	58.5±0.3	15.9±0.7	1.6±0.1	6.2±0.	68.8±0.5	-	7.5±0.2	40.2±0.5	11.4±0.1
13	Pd_1/Al_1BaO	200	55.4±0.2	6.4±0.4	14.8±0.7	6.5±0.6	68.7±0.5	-	3.6±0.1	38.1±0.4	15.2±0.2
14	Pd_1/Al_1BaO	220	71.2±0.3	7.8±0.6	3.2±0.4	11.7±0.8	74.4±0.7	-	2.9±0.3	53.0±0.7	21.2±0.3
15	Pd_1/Al_1BaO	240	63.8±0.4	8.7±0.6	0.5±0.1	13.6	70.9±0.6	2.9±0.1	3.4±0.3	45.2±0.7	18.1±0.3
16	Pd_1/Al_3BaO	210	92.5±0.1	12.0±0.2	8.7±0.6	-	76.2±0.5	-	3.1±0.2	70.5±0.54	12.5±0.1
17	Pd_1/Al_3BaO	230	85.4±0.4	7.4±0.4	0.9±0.1	2.4±0.3	78.4±0.4	4.8±0.4	6.1±0.3	67.0±0.7	11.9±0.1

Reaction conditions: Cyclohexanone:Aniline:Nitrobenzene (molar ratio) = 1:1:0.66; N_2 pressure = 2.0 MPa; LHSV = 0.15 h^{-1}; Solvent, *m*-xylene.

[a] Including contamination in raw material, errors of measurement instrument and trace impurities produced in the reaction.

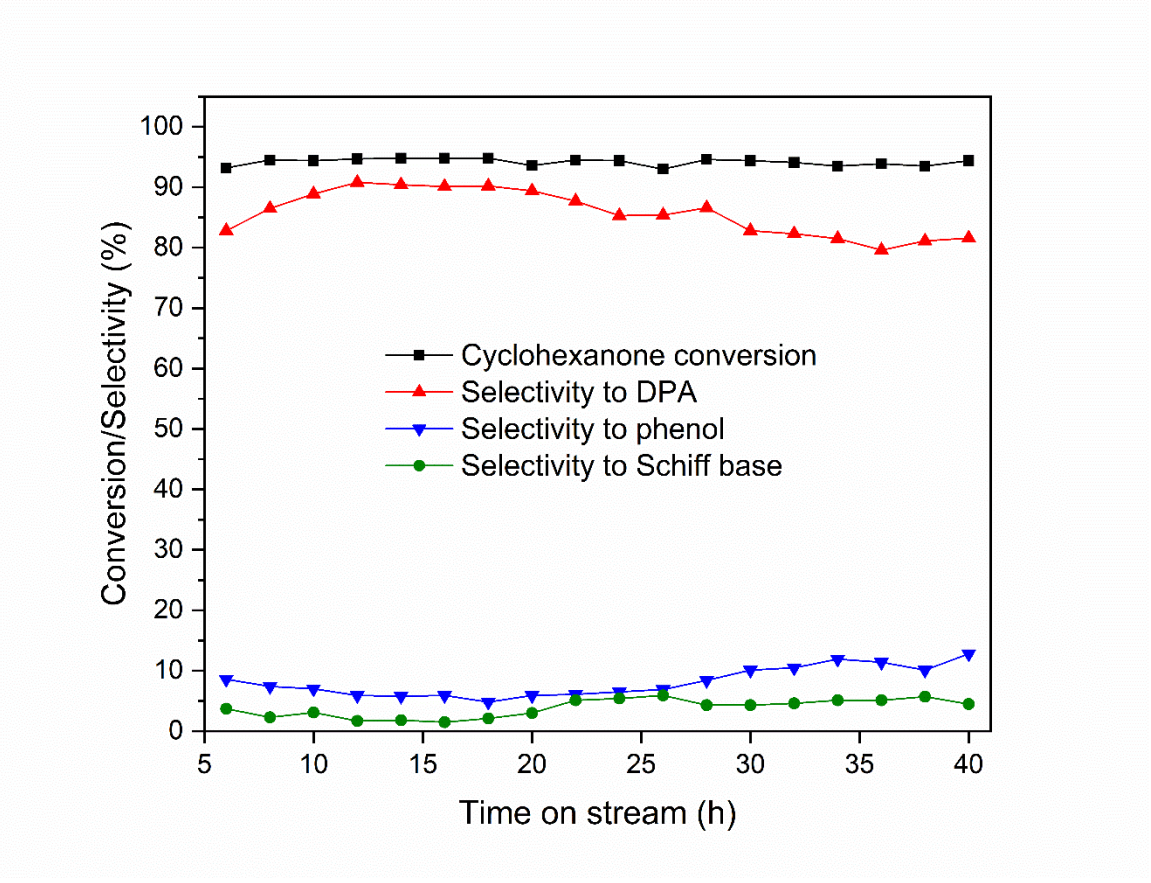

Figure S1. Time on stream performance of Pd_1/Al_3BaO. Reaction conditions: Cyclohexanone:Aniline:Nitrobenzene (molar ratio) = 1:1:0.66; Temperature = 220°C; N_2 pressure = 2.0 MPa; LHSV = 0.15 h^{-1}; Solvent, *m*-xylene.

Table S4 Textural properties of catalysts

Catalyst	Pd loading [a] (wt%)	S_{BET} [b] (m^2 g^{-1})	V_p [c] (cm^3 g^{-1})	d_p [d] (nm)	CO adsorption (μmol/g)	Pd dispersion (%)	Pd Particle size (nm)	
							TEM	CO [e]
Pd_1/Al_2O_3	0.98	325	0.51	33	16.0	17.3	-	6.6
Pd_1/Al_4BaO	0.97	215	0.37	36	31.4	34.4	9.7±3.6	3.4
Pd_1/Al_3BaO	0.99	103	0.25	47	40.3	43.3	7.7±2.7	2.6
Pd_1/Al_2BaO	0.97	92	0.20	43	25.1	27.6	7.0±1.9	4.2
Pd_1/Al_1BaO	0.98	60	0.12	40	17.8	19.4	6.6±2.3	5.9

[a] Metal loading were determined by ICP-OES;

[b] BET surface area;

[c] BJH cumulative desorption pore volume;

[d] Pore size calculated by BJH method.

[e] Calculated by the Pd dispersion which was determined by CO chemisorption.

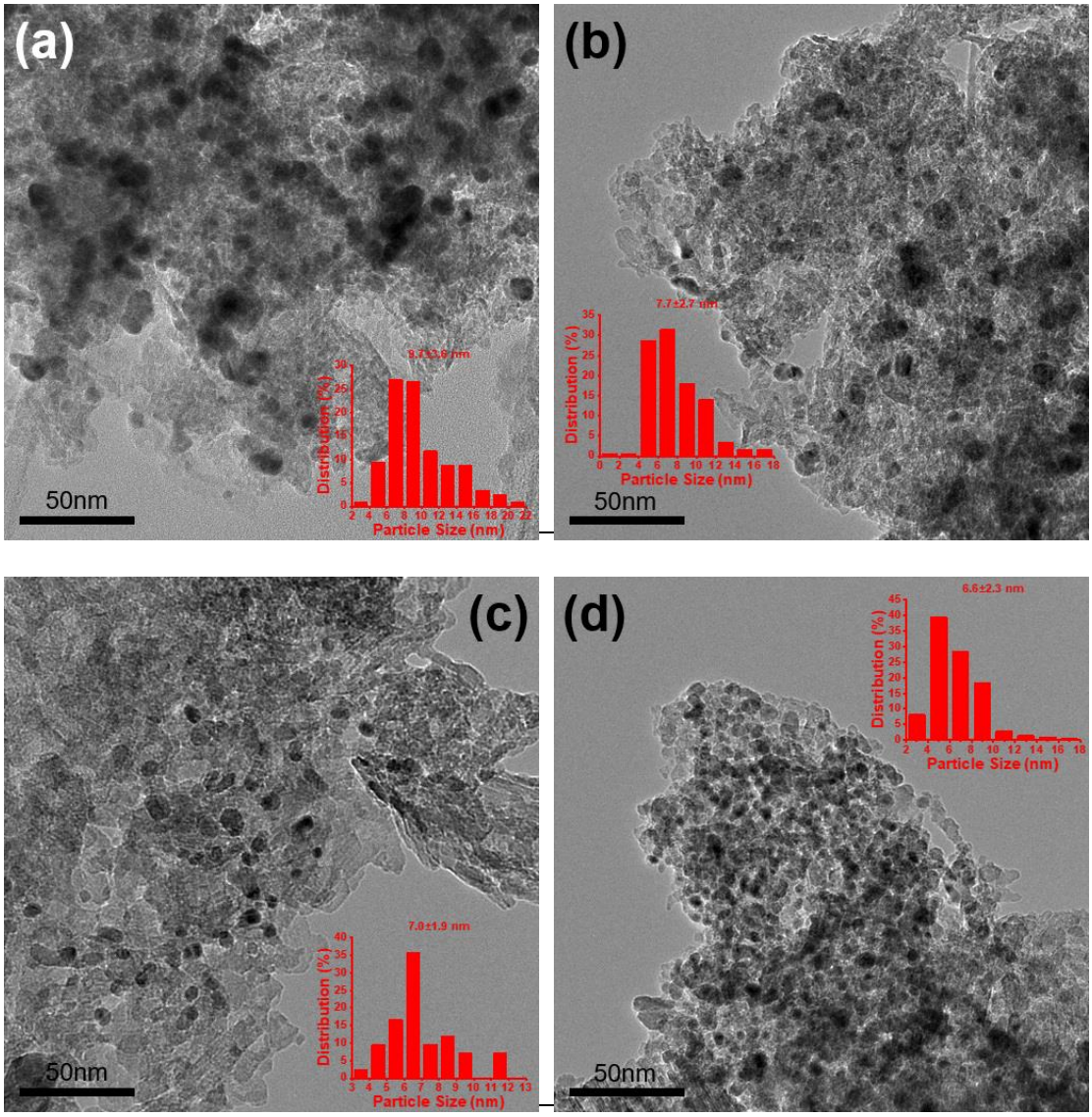

Figure S2. TEM images of (a) Pd_1/Al_4BaO, (b) Pd_1/Al_3BaO, (c) Pd_1/Al_2BaO and (d) Pd_1/Al_1BaO.

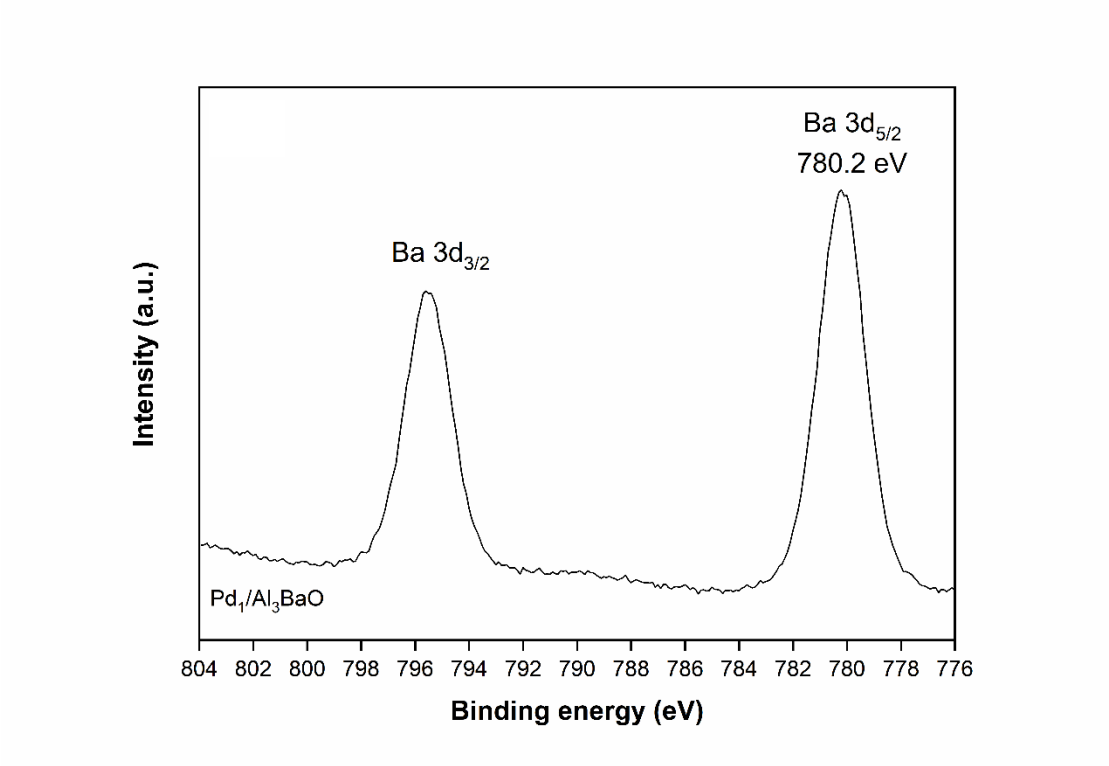

Figure S3. Ba 3d XPS spectrum of Pd_1/Al_3BaO

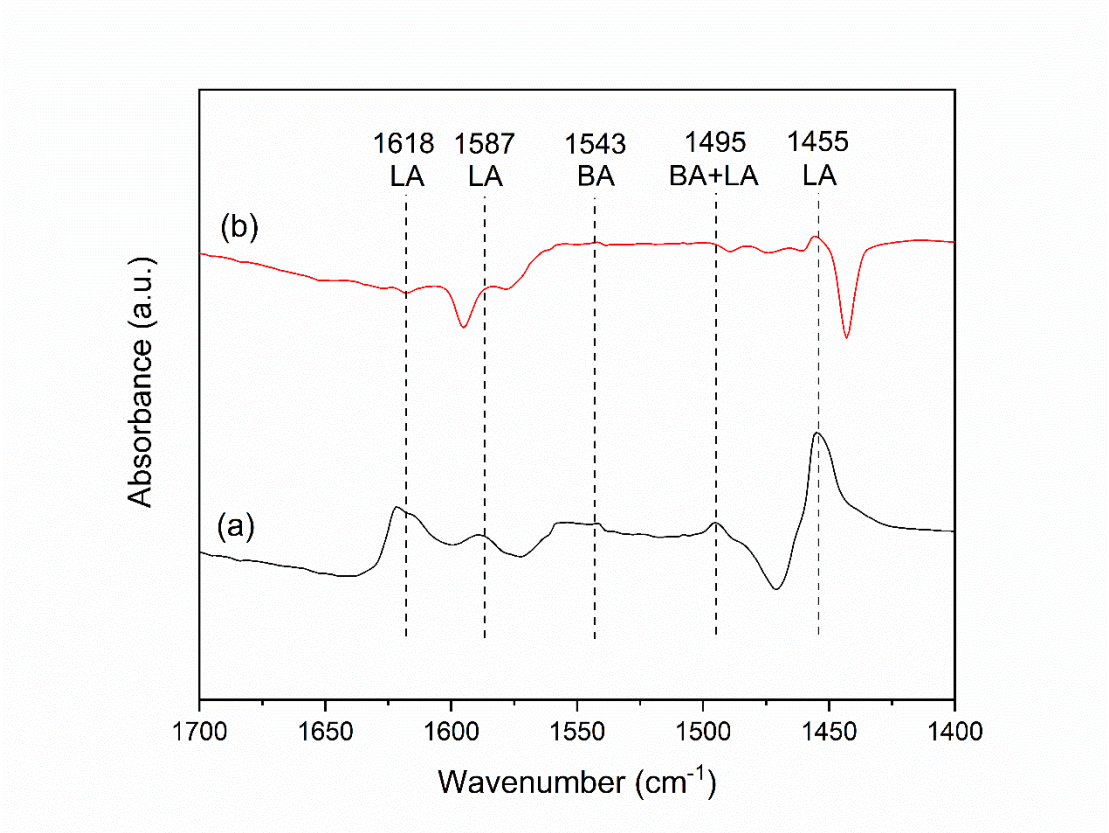

Figure S4. FTIR of pyridine adsorption of (a) Pd_1/Al_2O_3 and (b) Pd_1/Al_3BaO.

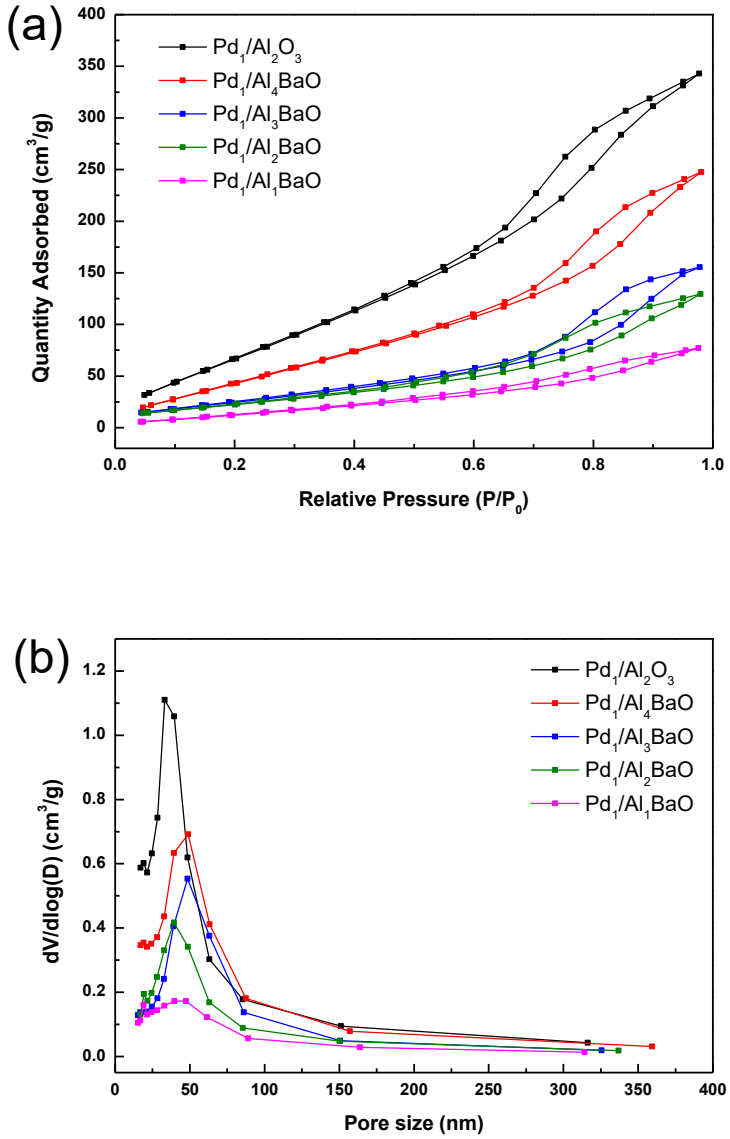

Figure S5. (a) The N_2 Adsorption-desorption isotherms of reduced Pd-based catalysts samples and (b) pore size distribution of Pd-based catalysts calculated from the absorption data with BJH model.