Supporting Information for

Formic Acid Dehydrogenation over Pd NPs Supported on Amine Functionalized SBA-15 Catalysts: Structure-Activity Relationships

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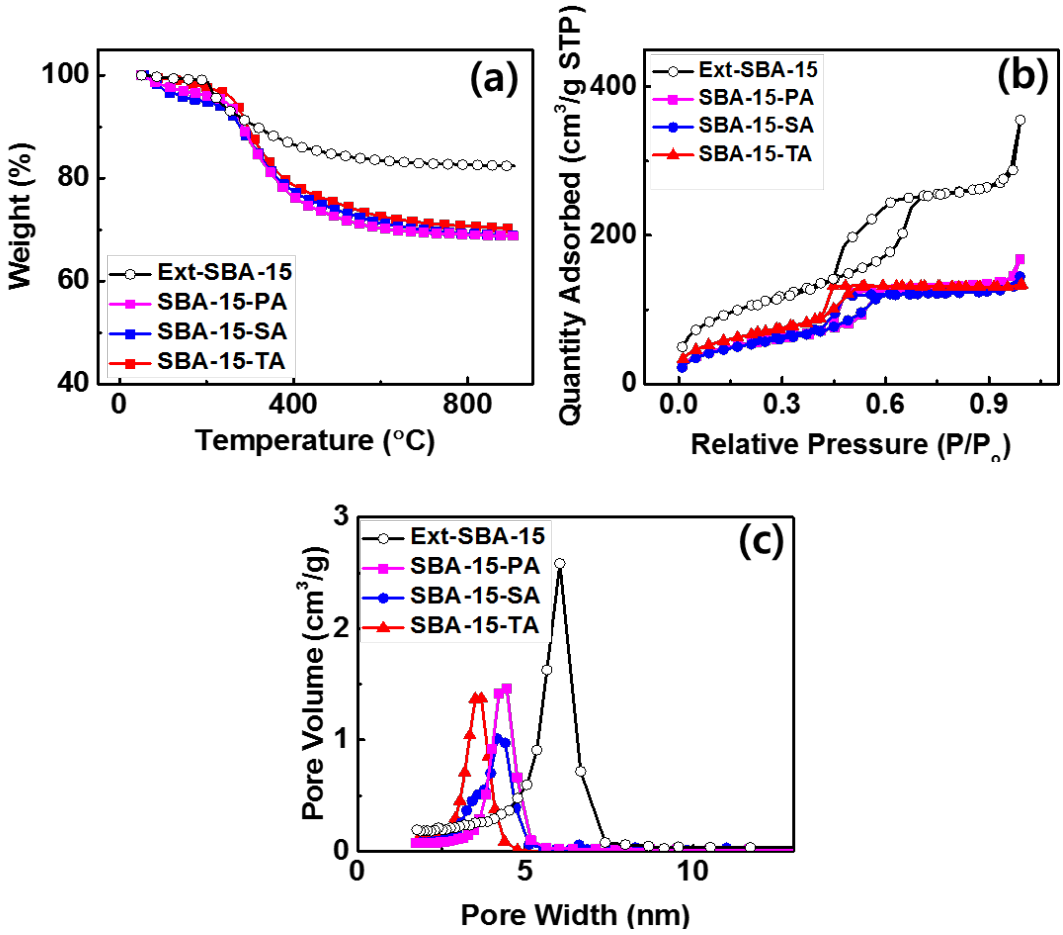

Figure S1. (a) Thermogravimetric analysis (TGA) traces, (b) N_2 Adsorption/desorption profiles, and (c) pore size distribution of three different amine-modified SBA-15 materials (SBA-15-Amine, where Amine is PA, SA, or TA groups) and their precursor Ext-SBA-15.

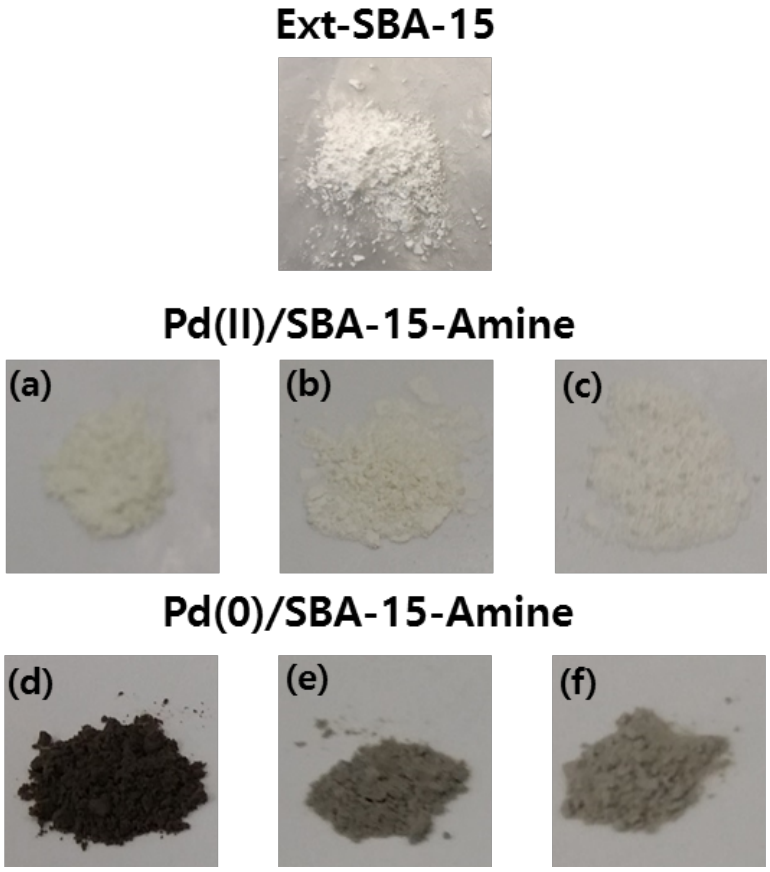

Figure S2. Photographs of Ext-SBA-15 (1st row), Pd(II)/SBA-15-Amine (2nd row), and Pd(0)/SBA-15-Amine (3rd row). (a) Pd(II)/SBA-15-PA, (b) Pd(II)/SBA-15-SA, (c) Pd(II)/SBA-15-TA, (d) Pd(0)/SBA-15-SA, (e) Pd(0)/SBA-15-SA, and (f) Pd(0)/SBA-15-TA materials.

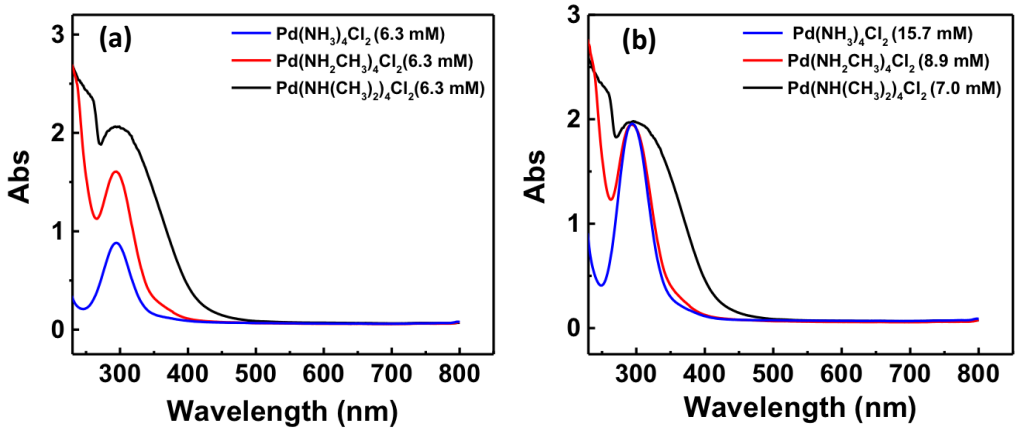

Figure S3. The UV-Vis spectra of the aqueous solutions containing three different tetraamine palladium(II) complexes, $[Pd(NH_3)_4Cl_2]$, $[Pd(NH_2CH_3)_4Cl_2]$, and $[Pd(NH(CH_3)_2)_4Cl_2]$: (a) with the same concentration and (b) with similar absorbance using different concentrations.

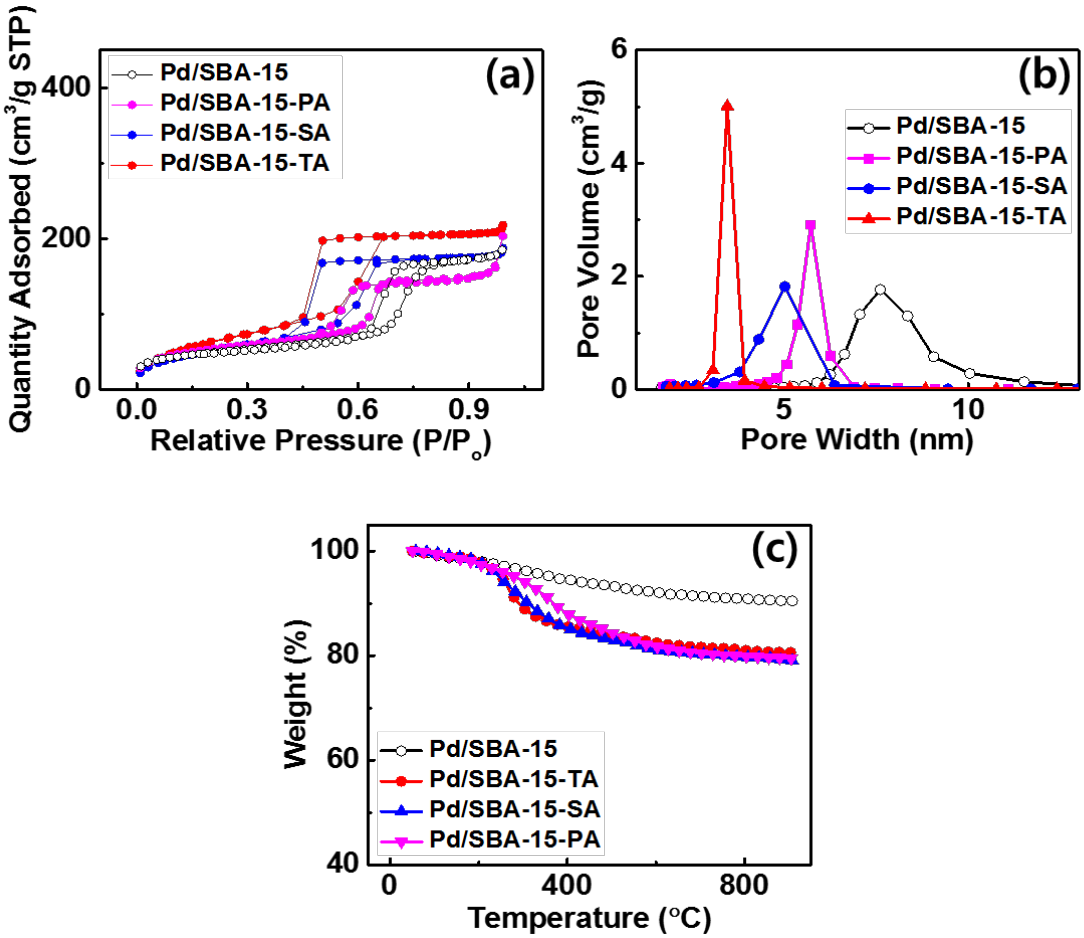

Figure S4. (a) N_2 Adsorption/desorption profiles, (b) pore size distributions, and (c) thermogravimetric analysis (TGA) traces of Pd/SBA-15-Amine materials (where Amine is PA, SA, or TA groups).

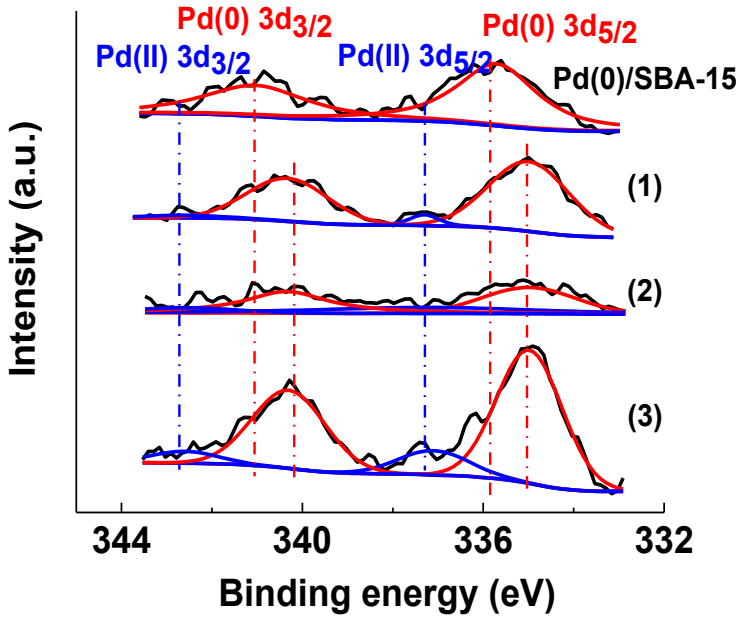

Figure S5. Comparison of Pd 3d peaks of Pd(0)/SBA-15 and different Pd(0)/SBA-15-Amine materials (where Amine is PA, SA, or TA groups).

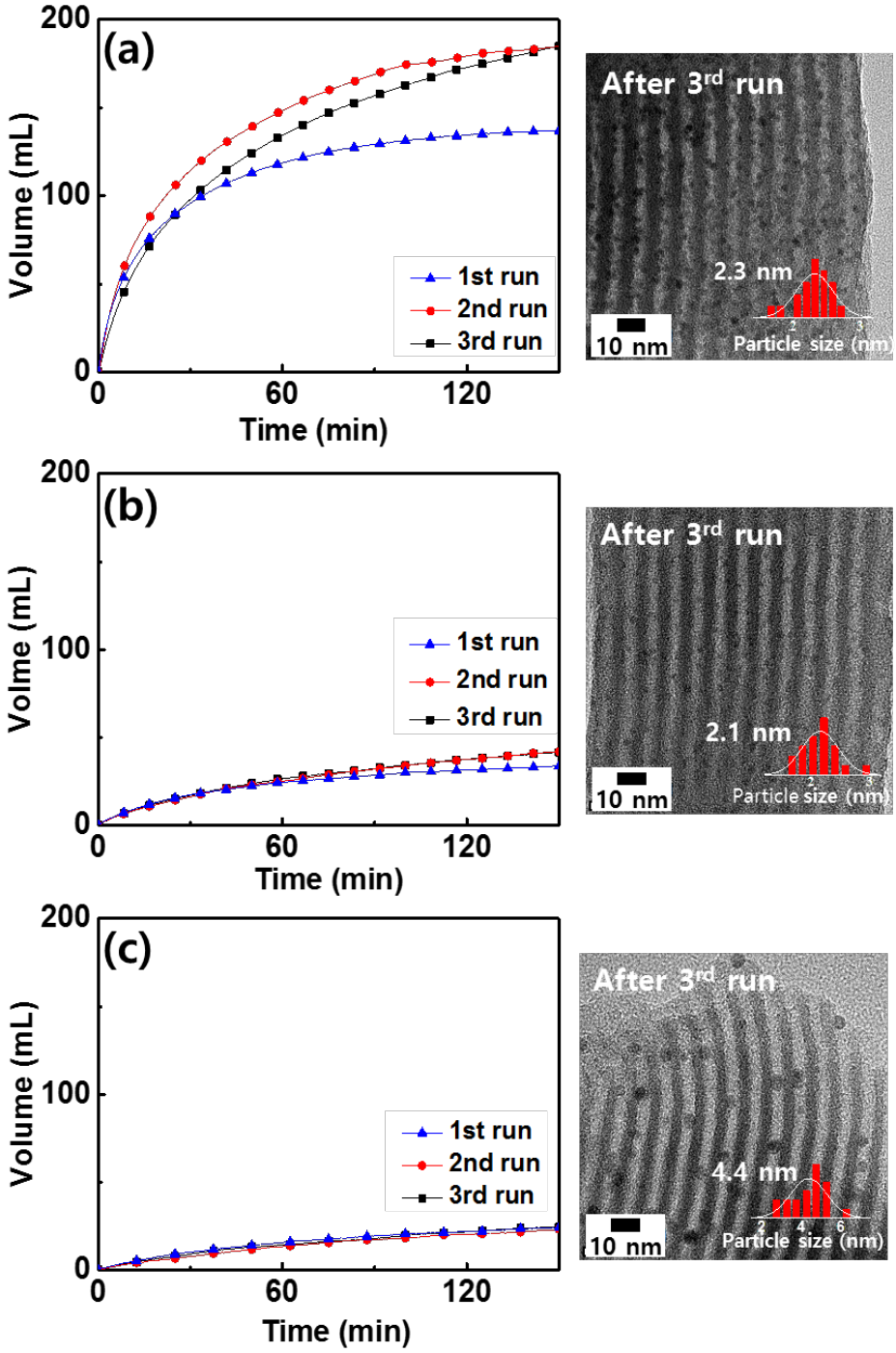

Figure S6. Recyclability test results for three Pd/SBA-15-Amine catalysts in formic acid dehydrogenation reaction: (a) Pd/SBA-15-PA (**1**), (b) Pd/SBA-15-SA (**2**), and (c) Pd/SBA-15-TA (**3**). The size distribution of the Pd NPs in the catalysts after 3rd reaction cycle is presented inside each TEM image.

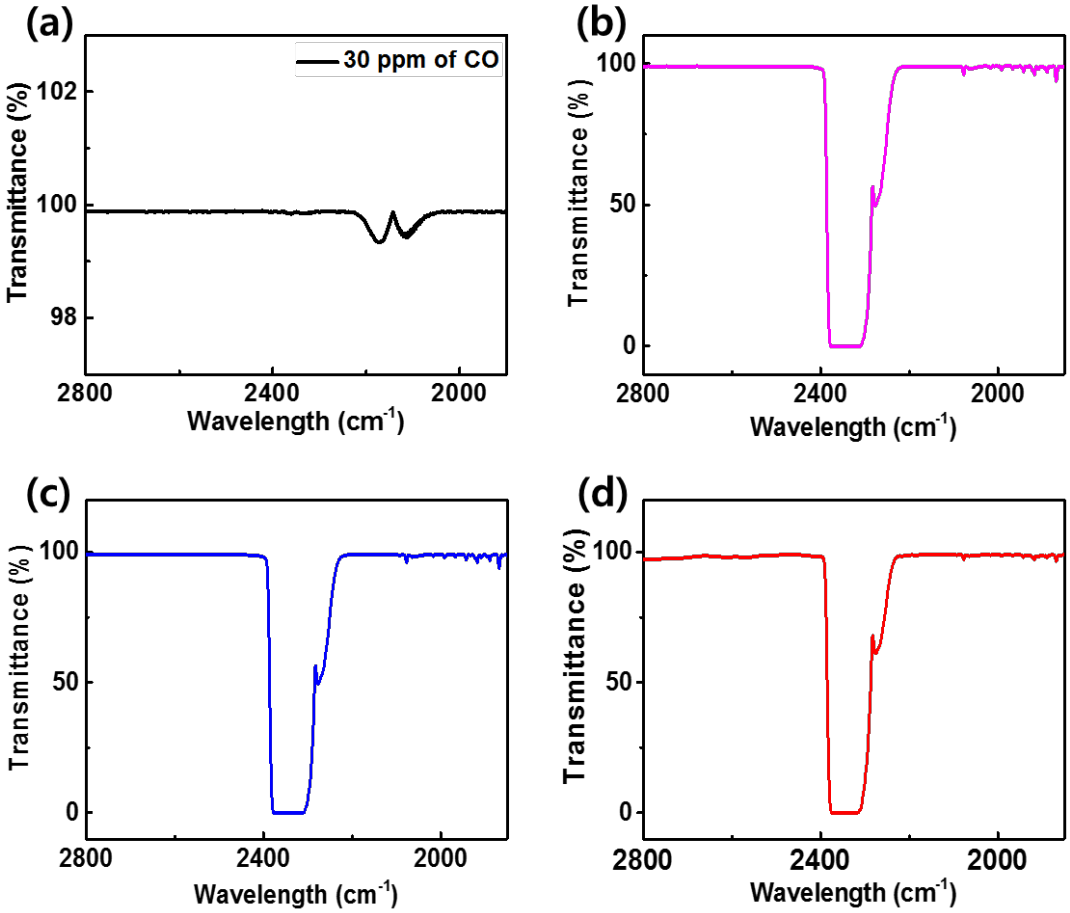

Figure S7. FT-IR spectra of 30 ppm of CO gas (a control experiment) (a), and the gaseous products of the reaction during reaction (at 50 min) over (b) Pd/SBA-15-PA, (c) Pd/SBA-15-SA, and (d) Pd/SBA-15-TA catalysts. The latter three spectra show the absence of a peak corresponding to C=O stretching or the absence of CO in the reaction products.

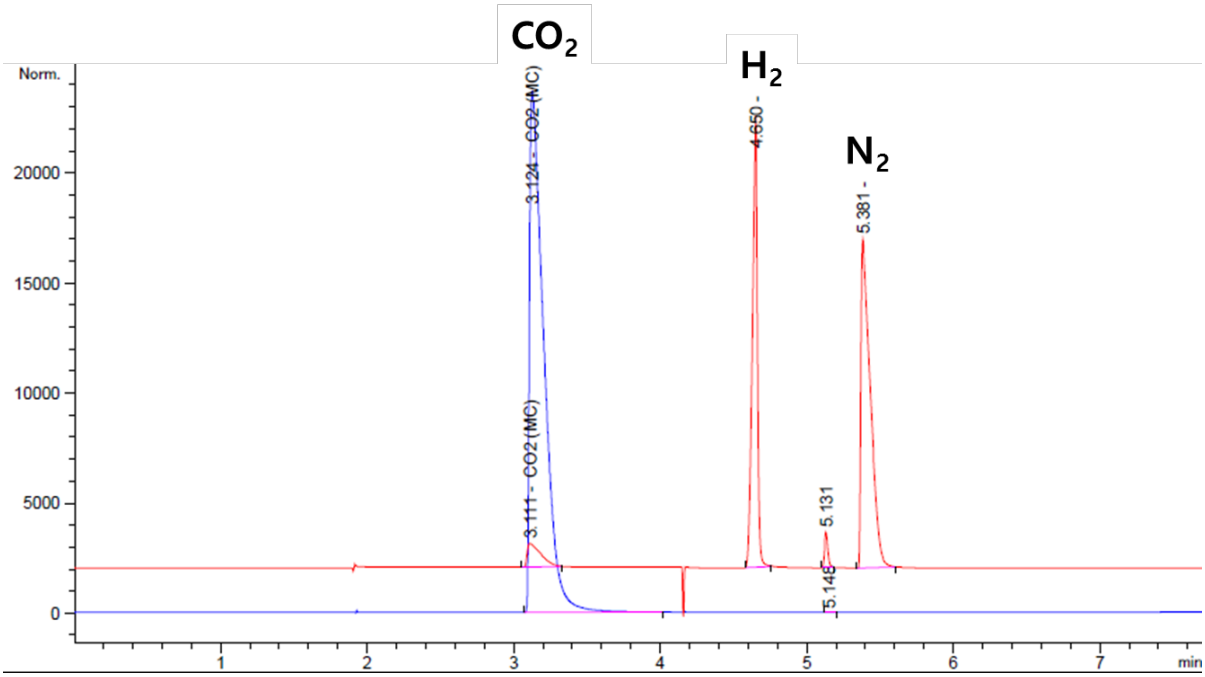

Figure S8. GC result after FA dehydrogenation reaction for 3 h over Pd/SBA-15-PA (catalyst **1**). Blue line is peak of CO_2 and red line is peak of H_2. The result shows peaks corresponding only to CO_2 and H_2 (and no CO).

Table 1. Comparison of the catalytic TOFs at 10 min of Pd/SBA-15-Amine catalysts with respect to those of other recently reported catalysts without additives.[a]

Entry	Catalyst	Temperature [K] [b]	TOF [h^{-1}]	Additives	Reference
1a	Pd/SBA-15-PA	299	355	None	This work
1b	Pd/SBA-15-SA	299	190	None	This work
1c	Pd/SBA-15-TA	299	70	None	This work
2	AgPd/C	298	309	None	[1]
3	Pd/mpg-C_3N_4	298	144	None	[2]
4	PdAu/C	298	63	None	[3]
5	Pd/C_3N_4 (+ hv)	288	68	None	[4]
6	CoAuPd/C	298	61	None	[5]
7	Pd/CN	298	286	None	[6]
8	$Pd_{0.5}Au_{0.3}Mn_{0.2}$/N-SiO_2	298	172	None	[7]
9	Ag_1Pd_4/UiO-66	298	107	None	[8]
10	AuPd-CeO_2/N-rGO	298	98	None	[9]

11	Au/SiO_2-Amine	323	806	SF[c], 25 %	[10]
12	Pd/PDA-rGO	323	385	SF[c], 50 %	[11]
13	AuPd/SBA-15-Amine	323	160	SF[c], 50 %	[12]

[a] The TOFs of some of the catalysts were calculated based on information provided in the research results reported in the literature; [b] Please note that the temperature is different in different cases; [c] SF represents sodium formate that was used as additive in the reaction, and its percentage is calculated based on the total volume of formic acid/formate in the solution.

Reference for Table 1:

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