Electronic Supplementary Information

Replacement reaction-based synthesis of supported palladium catalysts with atomic dispersion for catalytic removal of benzene

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"Center for Mesoscience, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China The total conversion of benzene ($\eta_{benzene}$) was calculated according to the following equation:

$$\eta_{benzene} = \frac{c_{benzene,in} - c_{benzene,out}}{c_{benzene,in}} \times 100$$

Where $c_{benzene,in}$ (ppm) and $c_{benzene,out}$ (ppm) are the concentration of benzene in the inlet and outlet gas, respectively.

The turnover frequency (TOF) of the reaction is calculated according to the conversion of benzene (η) , the flow rate of the reactants (V), the initial concentration of benzene (c_0) , the mass of the catalyst (m), the loading (x) and the dispersion degree (s) of Pd. The calculation formula is as follows:

$$TOF = \frac{(Vc_0\eta)/V_{mol}}{(mxs)/M_{mol}}$$

Where V_{mol} and M_{mol} are the molar volume of the gas and the molar mass of the active component, herein, they are 22.4 L mol⁻¹ and 106.4 g mol⁻¹, respectively.

Catalysts	Cu 2p	_{3/2} (eV)	- Cu ²⁺ /Cu ⁰	Pd 3d _{5/2} (eV)		D40/D42+	O 1s (eV)		0 /0
(Cu-Pd/γ-Al ₂ O ₃)	Cu ²⁺	Cu ⁰	- Cu /Cu ^o	Pd ⁰	Pd^{2+}	Pu*/Pu-*	O _{latt}	O _{ads}	O _{ads} /O _{latt}
1/1	935.10	932.60	2.24	336.11	337.61	1.70	530.76	532.28	0.55
0.5/1	934.74	932.84	1.49	336.13	337.62	1.58	530.83	532.45	0.49
0.2/1	934.74	932.94	1.02	336.13	337.67	1.53	530.84	533.47	0.42

Table S1. Binding energies and area percentage of Cu $2p_{3/2}$, Pd $3d_{5/2}$ and O 1s analyzed by the XPS spectra.

Table S2. The characteristic temperature of catalysts for the oxidation of benzene ^{a)}.

Catalysts	T ₁₀ ^{b)} (°C)	T ₅₀ ^{b)} (°C)	T ₉₀ ^{b)} (°C)
γ -Al ₂ O ₃	235	332	>350
$1Pd-1Cu/\gamma-Al_2O_3$	<100	218	248
$0.5Pd-1Cu/\gamma-Al_2O_3$	138	229	258
$0.2Pd-1Cu/\gamma-Al_2O_3$	161	239	268

^{a)} Reaction conditions: A fixed-bed reactor; catalyst weight, 100 mg; atmospheric pressure; feed stream composition, 100 ppm benzene, air balance; WHSV (weight hourly space velocity) = $60,000 \text{ mL } \text{g}_{\text{cat}^{-1}} \text{ h}^{-1}$;

^{b)} T_x , the temperature for the x% conversion of benzene.



Fig. S1 TEM image (a) and HRTEM image (b) of the as-synthesized Cu seed particles in oleylamine.



Fig. S2 XRD patterns of bimetallic Cu-Pd alloy nanoparticles with different Pd/Cu molar ratios. The references for face centered cubic (FCC) Cu and Pd phases (JCPDS Card File 851326 and 882335, respectively) are also displayed.



Fig. S3 The stability curve of the Cu-Pd/ γ -Al₂O₃ catalysts with Pd/Cu ratio of 0.2/1 after calcination for benzene oxidation. The measure temperature is 300°C.