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Supplementary Materials

A Novel Pd-P Nano-Alloy Supported on Functionalized Silica for Catalytic Aerobic Oxidation of Benzyl Alcohol

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Abstract: Catalytic aerobic oxidation of benzyl alcohol (BnOH) to benzaldehyde (PhCHO) over supported noble metal catalysts has grabbed the attention of researchers due to the critical role of PhCHO in numerous industrial syntheses. In the present study, a novel catalyst, Pd-P alloy supported on aminopropyl-functionalized mesoporous silica (NH_2-SiO_2), was prepared through in situ reduction and characterized by BET-BJH analysis, SEM, TEM, XRD, FTIR, TG-DTA, and XPS. Chemical properties and catalytic performance of Pd-P/NH_2-SiO_2 were compared with those of Pd^0 nanoparticles (NPs) deposited on the same support. Over Pd-P/NH_2-SiO_2, the BnOH conversion to PhCHO was much higher than over Pd^0/NH_2-SiO_2, and significantly influenced by the nature of solvent, reaching 57% in toluene at 111 °C, with 63% selectivity. Using pure oxygen as an oxidant in the same conditions, the BnOH conversion increased up to 78%, with 66% selectivity. The role of phosphorous in improving the activity may consist of the strong interaction with Pd that favours metal dispersion and lowers Pd electron density.

Keywords: benzyl alcohol; functionalized silica; palladium nanoparticles; palladium-phosphorous alloy; aerobic oxidation; benzaldehyde; selectivity

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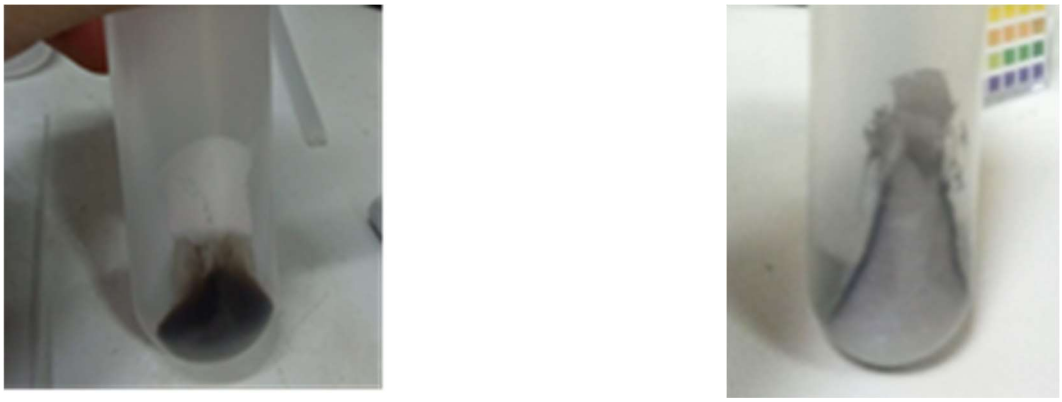

(**a**) (**b**)

Figure S1. Materials produced by loading (**a**) Pd^0, (**b**) Pd-P alloy particles on pristine silica support.

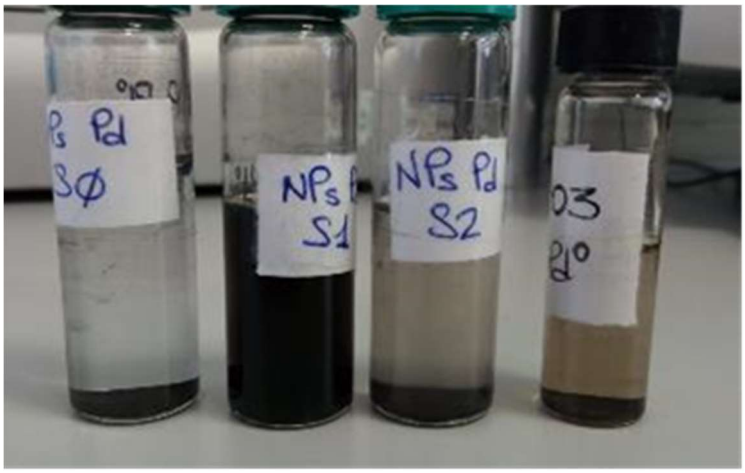

Figure S2. Products of palladium nanoparticles syntheses, varying the Oam/TOP ratio and the reaction time.

(**a**) (**b**)

Figure S3. (**a**) Pd^0/NH_2-SiO_2, (**b**) Pd-P/NH_2-SiO_2 before final drying.

Table S1. Effect of 3-APTES concentration on surface area of SiO_2 nanoparticles. (T=110 °C, time of reflux 48 h).

Scheme 2. APTES.	BET S.A. m^2g^{-1}
no APTES	564
3,10	173
1,55	88

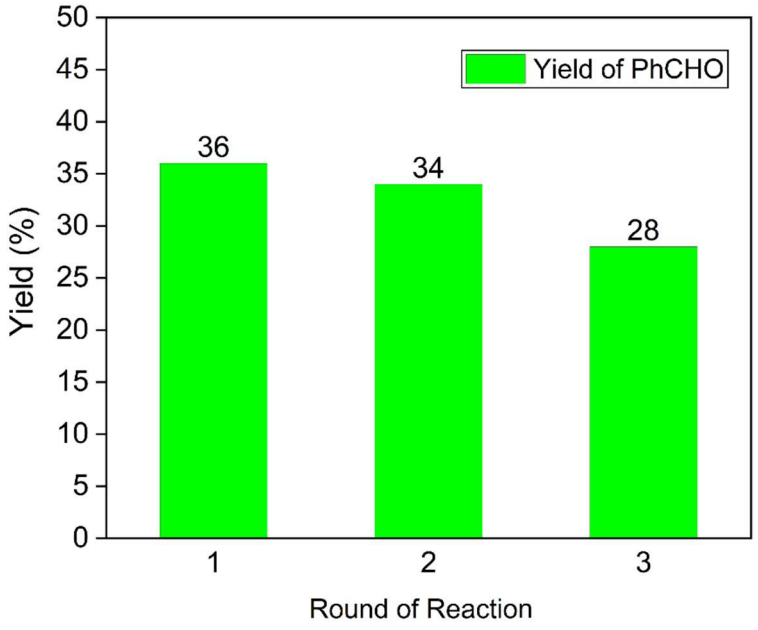

Figure S4. Recyclability of Pd-P/NH2-SiO2 in terms of PhCHO yield. Reaction was performed using 10 mL BnOH 0.1 M solution in toluene, 53 mg catalyst, and 20 mL min-1 air flow at 111 °C for 5 h. After each round of the reaction, the catalyst was recovered by centrifugation and washing with cyclohexane three times, following by drying in room temperature over the night.

Table S2. Details of calculation of TOF and TOFbulk of Pd-P/NH2-SiO2.

Entry	T (°C)	Oxidant (20 ml min^{-1})	TOF (h^{-1})[a]	t (min)[b]	X (%)[c]	TOF_{bulk} (h^{-1})[d]	X_{1h} (%)[e]
1	50	Air	55	300	11	29	4
2	80	Air	255	60	10	90	10
3	111	Air	4999	5	16	1134	37
4	111	O_2	5982	5	19	1431	57

a Calculated using "equation 10" for the conversions (X) of at least 10 %, considering Pd dispersion (D) = 32 % (based on TEM analysis) and Pd content = 0.91 ± 0.23 %w/w (by SEM-EDS)

b Time at which the TOF is calculated (values converted to "hour" before being used in the equation 10)

c Conversion at the time "t"

d Calculated using "equation 11" for t = 1 h

e Conversion at 1 h, used for the calculation of TOFbulk

Reaction Conditions: 10 mL BnOH 0.1M solution in toluene, 53 mg Pd-P/NH2-SiO2.