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Table S1. Element content of the unreduced catalysts, fresh catalysts and used catalysts.									
sample	Pd wt% (XPS)	Pd wt% (ICP)	P wt% (XPS)	P wt% (ICP)					
Pd/C-b	2.19	1.89	-	-					
Pd/C	2.26	2.01	-	-					
Pd/C-EG-b	2.17	1.85	-	-					
Pd/C-EG	2.21	1.96	-	-					
Pd/C-P-EG-b	2.13	1.94	0.57	0.55					
Pd/C-P-EG	2.18	2.03	0.58	0.52					
Pd/C-P-EG-used	2.14	1.98	0.54	0.49					

## Supporting Information

Table S2. Percentage of different forms of phosphorus for Pd/C-P-EG obtained by XPS.

sample	P-C /total ratio	phosphate/total ratio	phosphide/total ratio
Pd/C-P-EG	74%	14%	12%

Supplementary experiment: Effect of Phosphate on Selectivity

## **Catalyst Preparation**

In order to investigate the effect of phosphate on the selectivity of the catalytic reaction for the hydrogenation of p-CNB, the following experiment was carried out. According to the proportion of phosphorus in Pd/C-P-EG catalyst obtained by XPS, sodium phosphate dibasic dodecahydrate (0.0469g) was dissolved into deionized water (15 mL) and then was added to the fresh Pd/C-EG catalyst (5.0001g) which had been previously prepared. After being dried at room temperature for 2 days, the sample was dried at 110°C in a vacuum oven for 8 h and cooled to room temperature. The catalyst was labelled as Pd/C-EG-PO.

Table S3. Catalytic performance of Pd/C-EG-PO for the hydrogenation of p-CNB<sup>a</sup>.

Catalyst	Temperature (K)	H <sub>2</sub> pressure (MPa)	Reaction time (min)	$\begin{array}{l} Reaction \ rate \\ (mol_{sub}h^{-1}g_{Pd}^{-1}) \end{array}$	p-CNB conversion(%)	Selectivity of products(%)	
						p-CAN	aniline
Pd/C-EG-PO	363	1.0	226	12.6	100	84.76	15.24

<sup>a</sup> Reaction conditions: p-CNB, 15.0 g; catalyst, 0.1g; solvent-free.