Supporting Information

Synergetic Catalysis of Palladium Nanoparticles Encaged within Amine-functionalized UiO-66 in Hydrodeoxygenation of Vanillin in Water

Fumin Zhang,*[ab] Shuang Zheng,[a] Qiang Xiao,[a] Yijun Zhong,[a] Weidong Zhu,[a] Andrew Lin,[b] and M. Samy El-Shall*[b]

[a]Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, 321004 Jinhua, People's Republic of China
[b]Department of Chemistry, Virginia Commonwealth University, 23284 Richmond, VA, USA

Corresponding Authors:

E-mail: zhangfumin@zjnu.edu.cn, fzhang5@vcu.edu (F. Zhang),

E-mail: mselshal@vcu.edu (M. Samy El-Shall).

Table S1. Textural properties of various catalysts.

Catalyst	S_{BET} m^2/g	V_{micro} cm^3/g
UiO-66	999.4	0.41
0.4 wt.% Pd@UiO-66	947.3	0.40
NH_2-UiO-66	931.5	0.38
2.0 wt.% Pd@NH_2-UiO-66	769.2	0.35
2.0 wt.% Pd/NH_2-UiO-66	711.5	0.30
spent catalyst 2.0 wt.% Pd@NH_2-UiO-66	734.7	0.34

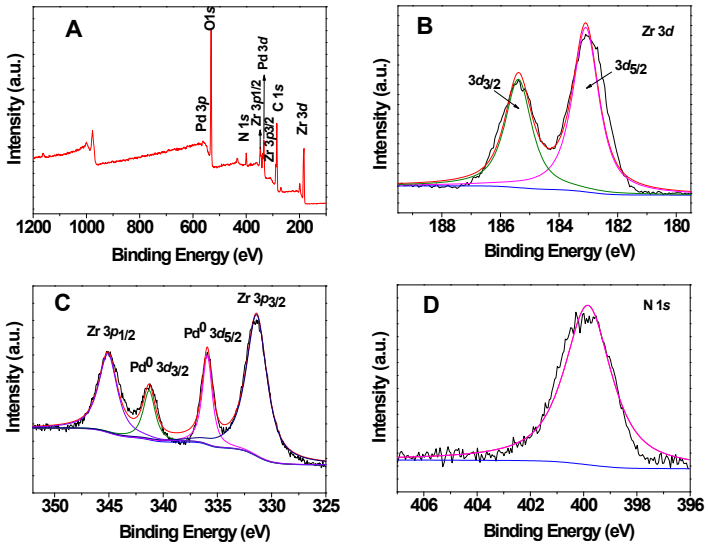

Fig. S1 XPS spectra of 2.0 wt.% Pd@NH_2-UiO-66: survey spectrum (A), high resolution of Zr spectrum (B), high resolution of Zr and Pd spectrum (C), and high resolution of Pd spectrum (D).

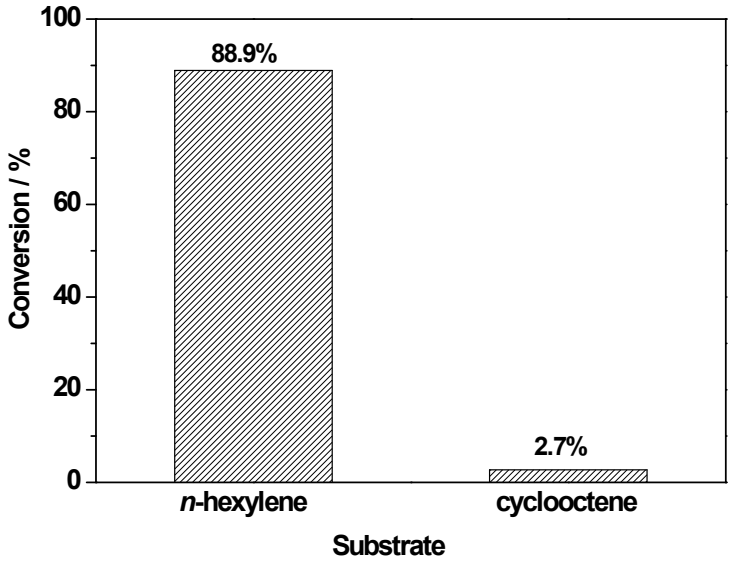

Fig. S2 Catalytic activity of 2.0 wt.% Pd@NH_2-UiO-66 in the heterogeneous hydrogenation of olefins. (Reaction conditions: substrate, 2 mmol; ethanol, 20 ml; amount of catalyst, 0.03 g; hydrogen pressure, 2.0 MPa; reaction temperature, 80 °C; reaction time, 120 min).

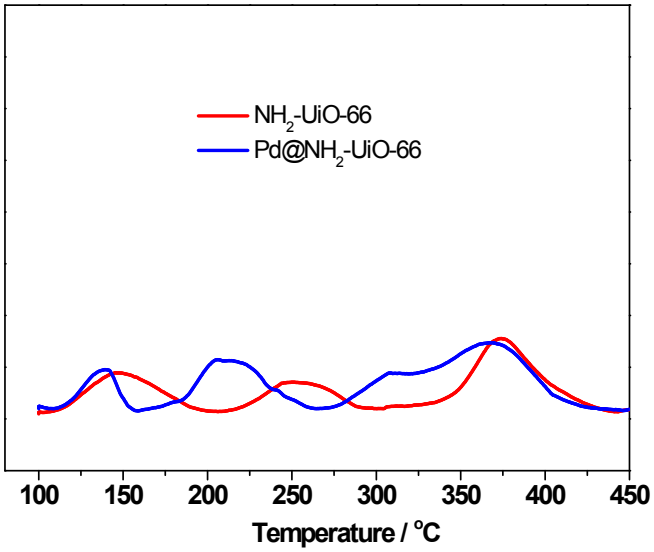

Fig. S3 NH_3-TPD profiles of NH_2-UiO-66 and 2.0 wt.% Pd@NH_2-UiO-66.

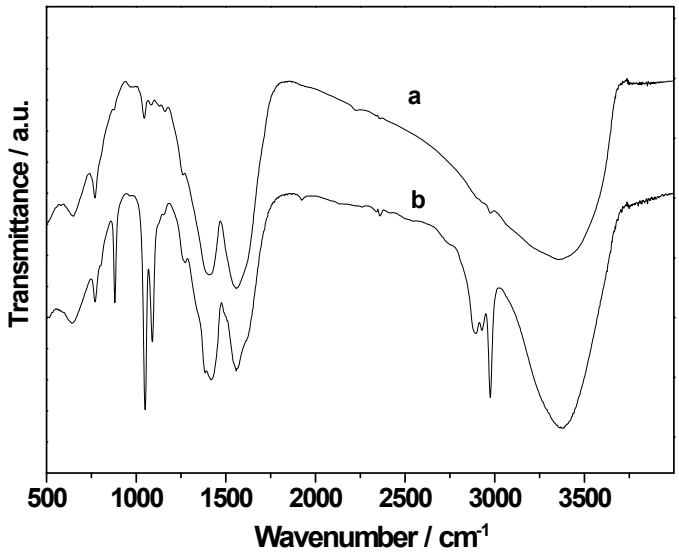

Fig. S4 FTIR spectra of (a) the fresh 2.0 wt.% Pd@NH_2-UiO-66 and (b) the sample after desorption of NH_3 at 400 °C.

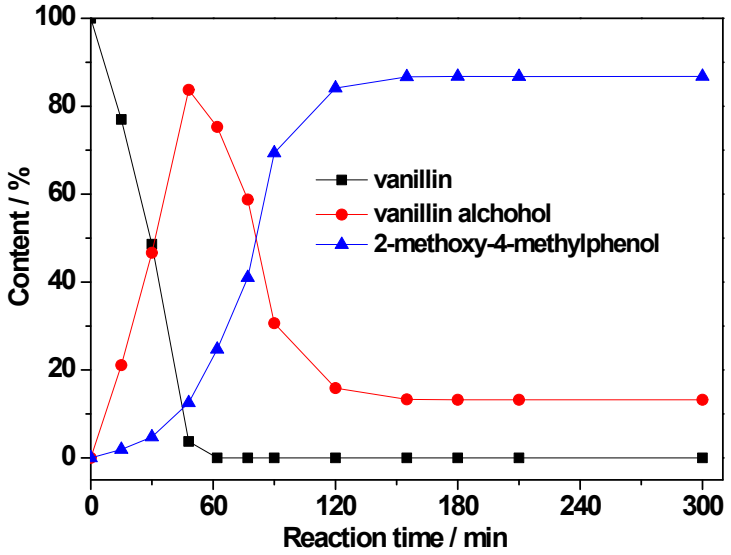

Fig. S5 Changes of reactant and product distributions as a function of reaction time over 2.0 wt.% Pd@NH_2-UiO-66 (Reaction conditions: vanillin, 2 mmol; water, 20 ml; amount of catalyst, 29 mg; S/C = 350; hydrogen pressure, 0.5 MPa; reaction temperature, 60 °C).

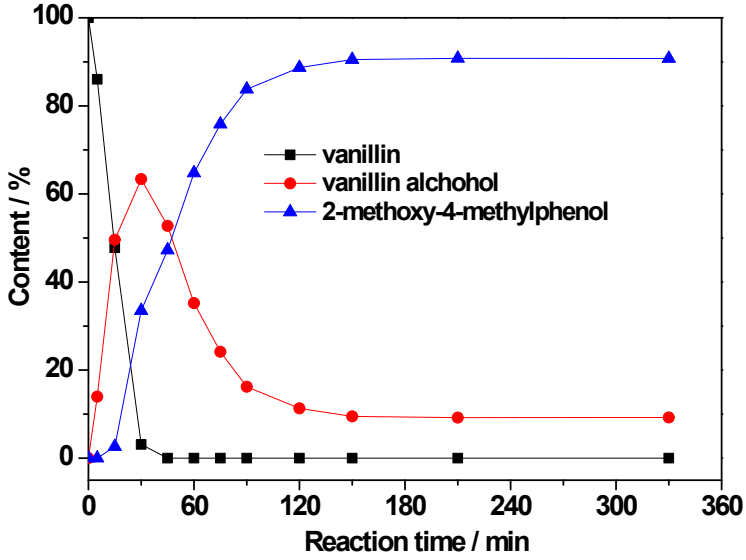

Fig. S6 Changes in the reactant and product distributions as a function of reaction time over 2.0 wt.% Pd@NH_2-UiO-66 catalyst. (Reaction conditions: vanillin, 2 mmol; water, 20 ml; amount of catalyst, 50 mg; S/C = 200; hydrogen pressure, 0.5 MPa; reaction temperature, 60 °C).

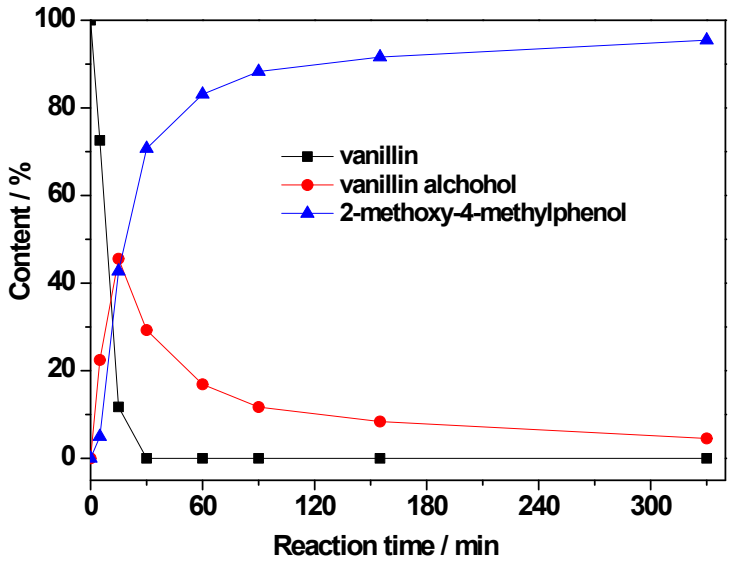

Fig. 7 Changes in the reactant and product distributions as a function of reaction time over 2.0 wt.% Pd@NH_2-UiO-66 catalyst. (Reaction conditions: vanillin, 2 mmol; water, 20 ml; amount of catalyst, 50 mg; S/C = 200; hydrogen pressure, 0.5 MPa; reaction temperature, 80 °C).

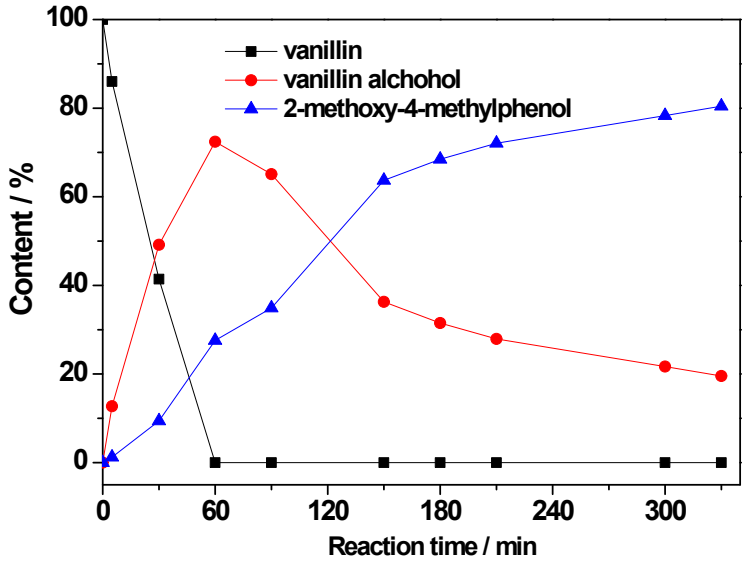

Fig. S8 Changes of reactant and product distributions as a function of reaction time over 2.0 wt.% Pd@NH_2-UiO-66 (Reaction conditions: vanillin, 2 mmol; water, 20 ml; amount of catalyst, 10.6 mg; S/C = 1000; hydrogen pressure, 0.5 MPa; reaction temperature, 80 °C).

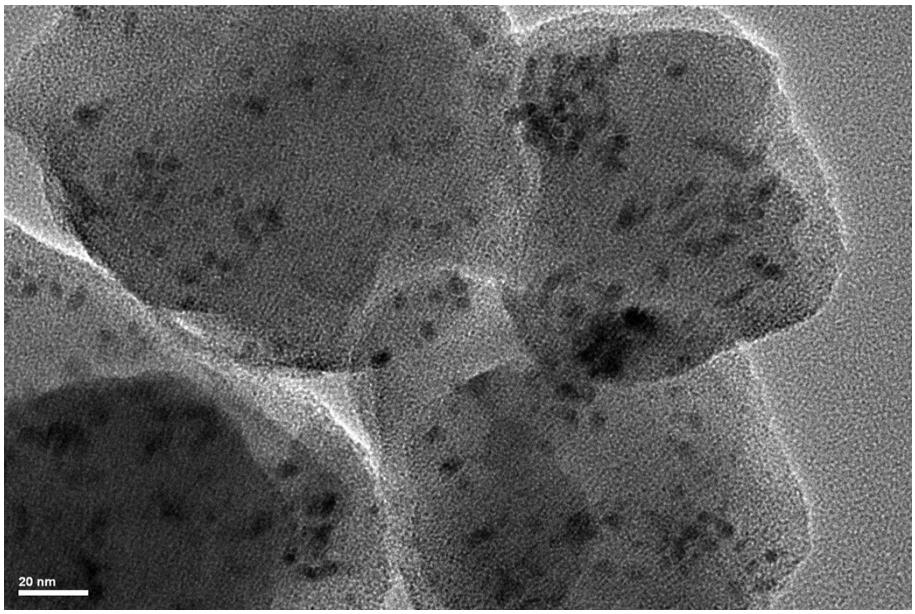

Fig. S9 TEM image of 2.0 wt.% Pd/NH_2-UiO-66

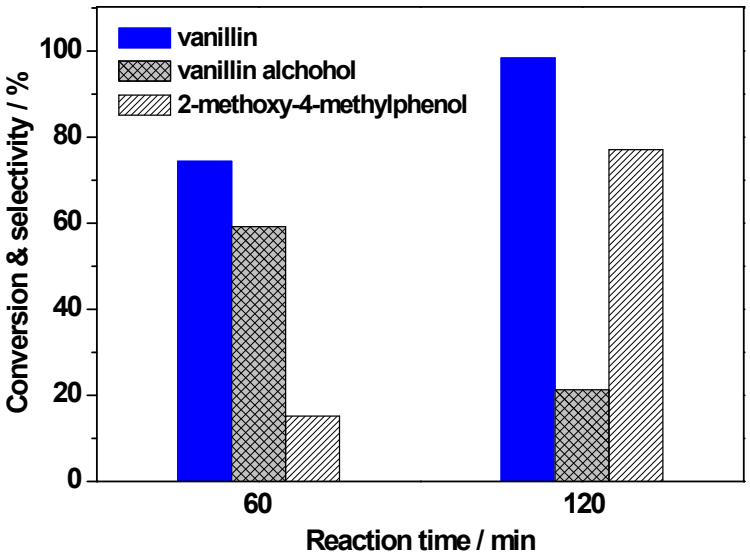

Fig. S10 Activity and selectivity for 2.0 wt.% Pd/NH_2-UiO-66 in the hydrodeoxygenation of vanillin at 60 min and 120 min. (Reaction conditions: vanillin, 2 mmol; water, 20 ml; amount of catalyst, 50 mg; S/C = 200; hydrogen pressure, 0.5 MPa; reaction temperature, 90 °C).

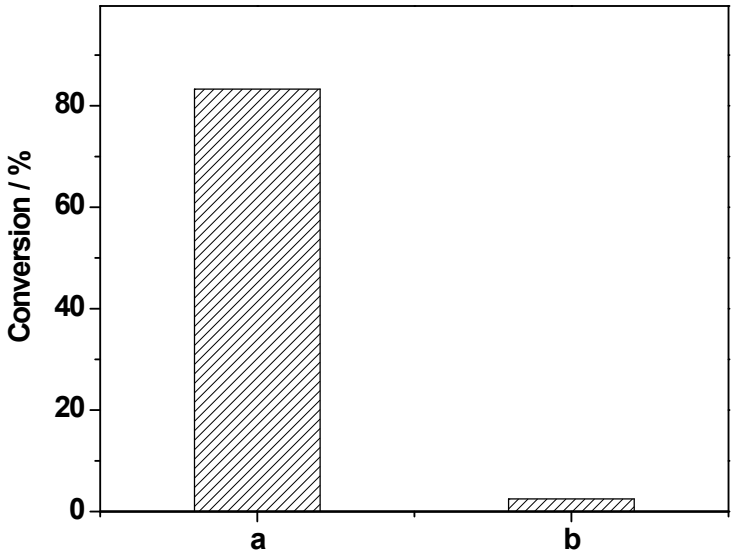

Fig. S11 Hydrogenolysis of vanillin alcohol over 2.0 wt.% Pd@NH_2-UiO-66 in the absence (a) and in the presence of NaOH (b). (Reaction conditions: vanillin alcohol, 2 mmol; water, 20 ml; amount of catalyst, 50 mg; S/C = 200; reaction temperature, 80 °C; reaction time, 180 min; the amount of NaOH was 0.15 mmol when used).

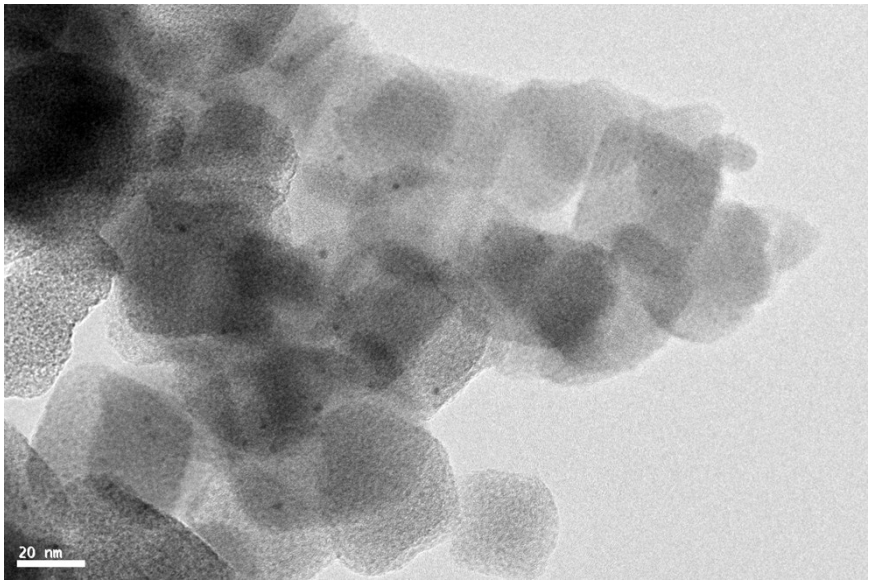

Fig. S12 TEM image of the spent 2.0 wt.% Pd@NH_2-UiO-66 catalyst.

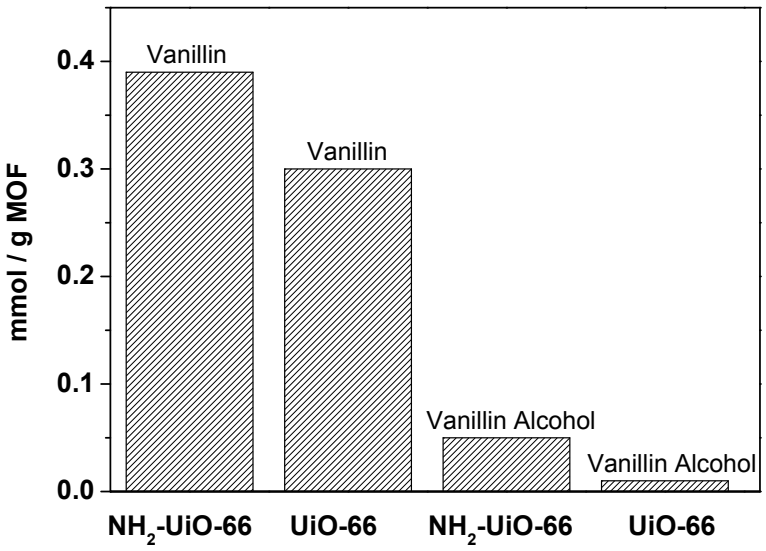

Fig. S13 Adsorption of vanillin and vanillin alcohol by NH_2-UiO-66 and UiO-66.