Palladium Nanoparticles Incorporated within Sulfonic Acid-Functionalized

MIL-101(Cr) for Efficient Catalytic Conversion of Vanillin

Fumin Zhang,*^{ab} Yan Jin,^a Yanghe Fu,^a Yijun Zhong,^a Weidong Zhu,^a Amr Awad Ibrahim,^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, United States

Supporting Information

Corresponding Authors: Tel.: +86 579 82288919; Fax: +86 579 82282234; E-mail: zhangfumin@zjnu.edu.cn, fzhang5@vcu.edu (F. Zhang), mselshal@vcu.edu (M. Samy El-Shall).



Fig. S1. Wide-angle XRD patterns of SO_3H -MIL–101(Cr) (a), and 2.0 wt.% Pd/SO₃H-MIL–101(Cr) (b).

Catalyst	$S_{\rm BET}$	V _{total}
	$m^2 g^{-1}$	$\mathrm{cm}^3~\mathrm{g}^{-1}$
SO ₃ H-MIL–101(Cr)	1754	0.91
2.0 wt.% Pd/SO ₃ H-MIL–101(Cr)	820.3	0.60
2.0 wt.% Pd/MIL-101(Cr)	2596	1.35
2.0 wt.% Pd/C	1245	0.81
Spent Catalyst	798.7	0.59
2.0 wt.% Pd/SO ₃ H-MIL–101(Cr)		

Table S1 Textural properties of various catalysts



Fig. S2. FT-IR spectra of the synthesized MIL-101(Cr) (a), SO₃H-MIL-101(Cr) (b), and 2.0 wt.% Pd/SO₃H-MIL-101(Cr) (c)



Fig. S3. Hydrogenolysis of vanillin alcohol over 2.0 wt.% Pd/SO₃H-MIL-101(Cr) in the absence (a) and in the presence of pyridine (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 pyridine was 0.02 g when used).



Fig. S4. Effect of hydrogen pressure on the conversion of vanillin over 2.0 wt.% Pd/SO₃H-MIL-101(Cr) (Reaction conditions: vanillin, 2 mmol; water, 20 ml; amount of catalyst, 50 mg; S/C = 200; reaction temperature, 100 °C; reaction time, 60 min).



Fig. S5. Effect of reaction time on the conversion of vanillin over 2.0 wt.% Pd/SO₃H-MIL-101(Cr) (Reaction conditions: vanillin, 2 mmol; water, 20 ml; amount of catalyst, 50 mg; S/C = 200; hydrogen pressure, 0.5 MPa; reaction time, 60 min).



Fig. S6. TEM image of the used 2.0 wt.% Pd/SO₃H-MIL-101(Cr)