

COMMUNICATION

Supplementary Information

## A sintering-resistance Pd/SiO<sub>2</sub> catalyst by reverse-loading nano iron oxide for aerobic oxidation of benzyl alcohol

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### Experimental

#### Catalyst preparation

Pd/SiO<sub>2</sub> was prepared via an incipient wetness impregnation method with SiO<sub>2</sub> and aqueous solution of PdCl<sub>2</sub>. The sample was dried overnight at 60 °C in vacuum oven and calcined at 400 °C for 3h in air.

Pd/bulk-FeO<sub>x</sub> was prepared via an incipient wetness impregnation method with iron oxide and aqueous solution of PdCl<sub>2</sub>. The sample was dried overnight at 60 °C in vacuum oven and calcined at 300 °C for 3h in air.

FeO<sub>x</sub>/Pd/SiO<sub>2</sub> was prepared via an incipient wetness impregnation method with the as synthesized Pd/SiO<sub>2</sub> and the aqueous solution contained certain amount of Fe(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O. The sample was dried overnight at 60 °C in vacuum oven and calcined at 400 °C for 3h in air.

FeO<sub>x</sub>/SiO<sub>2</sub> was prepared by incipient wetness impregnation method with SiO<sub>2</sub> and the aqueous solution contained certain amount of Fe(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O. The sample was dried overnight at 60 °C in vacuum oven and calcined at 400 °C for 3h in air.

#### Catalyst characterization

Transmission electron microscopy (TEM) images were obtained with a JEM-2100 transmission electron microscope operating at 200kV. Samples for TEM were prepared by supersonically dispersing them in ethanol and depositing onto a holy carbon support film. Size distributions of the particles were obtained by counting more than 200 particles in TEM images.

The binding energy of the surface Pd species was determined by X-ray photoelectron spectra (XPS) on an UIVAC-PHI 5000 Versa Probe X-ray photoelectron spectrometer with contaminated C as internal standard (C1s=284.6 eV).

Diffuse Reflectance FTIR Spectroscopy (DRIFTS) were collected on a Bruker TENSOR 27 FTIR spectrometer, using a Harrick HVC-DRP cell that allows in situ treatment with different gases at temperature up to 1183K. After activated in He the spectrum was recorded as background. Then the CO adsorption of the samples were performed at room temperature by switching gas flow into CO and then He in order to acquire the spectrum of chemisorbed CO on the catalyst.

#### Benzyl alcohol oxidation

The catalytic oxidation of benzyl alcohol by molecular O<sub>2</sub> was performed in a three-necked flask fitted with a reflux condenser under atmospheric conditions. A mixture of 0.106g catalyst(0.01mmol Pd) and 10mL o-xylene was charged into the flask under vigorous magnetic stirring and heated to 100 °C in oil bath. Oxygen was bubbled into the mixture at a constant flow of 50mL/min. Then 1.0 mmol benzyl alcohol was added into the mixture to initiate the reaction. An appropriate amount of reaction mixture (0.2 mL) was sampled at fixed intervals and analyzed by gas chromatography with a flame ionization detector and a HP-5 column.

Table S1. Information of catalysts with different composition

Catalyst	FeO <sub>x</sub> (wt%)*	Pd(wt%)	FeO <sub>x</sub> /Pd(mol) *	Fe/Pd(mol)
Pd/SiO <sub>2</sub>	-	1	-	-
FeO <sub>x</sub> /Pd/SiO <sub>2</sub> -0.25	0.25	1	0.16875	0.3375
FeO <sub>x</sub> /Pd/SiO <sub>2</sub> -0.5	0.5	1	0.3375	0.675
FeO <sub>x</sub> /Pd/SiO <sub>2</sub> -1	1	1	0.675	1.35
FeO <sub>x</sub> /Pd/SiO <sub>2</sub> -2	2	1	1.35	2.7
FeO <sub>x</sub> /Pd/SiO <sub>2</sub> -10	10	1	6.75	13.5
FeO <sub>x</sub> /SiO <sub>2</sub>	0.5	-	-	-

\*The content of iron oxide was calculated by the amounts of Fe<sub>2</sub>O<sub>3</sub>.

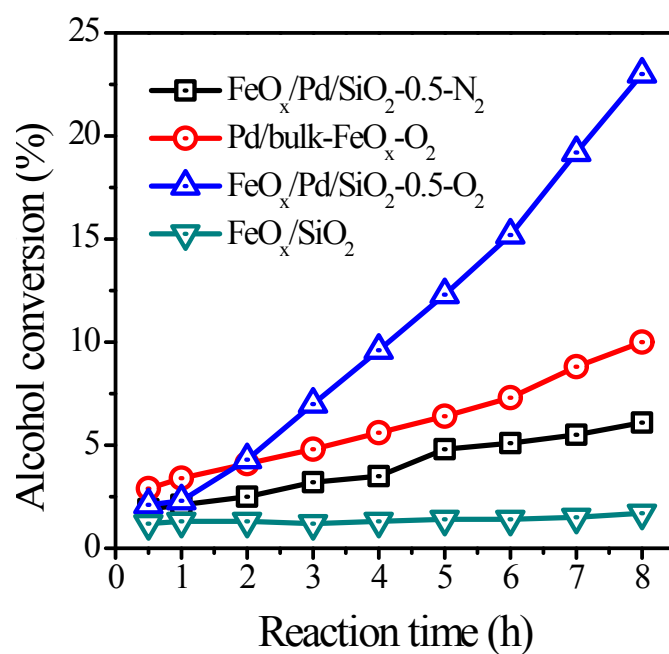


Figure S1. Benzyl alcohol oxidation in various conditions: catalyzed by FeO<sub>x</sub>-Pd-SiO<sub>2</sub>-0.5 in N<sub>2</sub> atmosphere and O<sub>2</sub> atmosphere separately; catalyzed by Pd/bulk-FeO<sub>x</sub> and FeO<sub>x</sub>/SiO<sub>2</sub> in O<sub>2</sub> atmosphere.