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Electronic Supplementary Information (ESI) for

Reductive cyclization of 2-nitro-2'-hydroxy-5'-methylazobenzene to benzotriazole over K-doped Pd/γ-Al_2O_3

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Catalyst preparation

Pd/γ-Al_2O_3 was prepared as follows: Initially, 50.00 g pseudo boehmite was kneaded vigorously with 60 mL water and molded into bars with a diameter of 3 mm by an extruder, dried at 120 °C for 6 h and then calcined at 500 °C for another 4 h to yield supports. Furthermore, 0.26 g palladium (II) chloride was dissolved into 21 mL 8 wt% hydrochloric acid solution. The above obtained supports (15.55 g) were impregnated into this solution. After 12 h, the bars were successively dried in air at 120 °C for 6h and then calcined at 500 °C for 4 h. [1] The experimental details of Pd/γ-Al_2O_3-X preparation were described as follows: the obtained Pd/γ-Al_2O_3 catalyst was impregnated into the solution of the corresponding potassium salt (KNO_3, K_2CO_3, or KOH), and the mass ratio of potassium and Pd/γ-Al_2O_3 was 1:10. After 12 h, the catalysts were successively dried in air at 120 °C for 6 h and calcined at 500 °C for another 4 h. All catalysts were reduced at 300 °C in a hydrogen stream (1.0 MPa) for 3 h before use.

Catalyst characterization.

FT-IR spectra were recorded on a Nicolet 22 AVATAR 370 FT-IR spectrometer (Thermo Nicolet Corporation, US). XRD patterns were collected on a Rigaku D/max 2500 (Rigaku Corporation, Japan) using a Cu-Kα X-ray source (40 kV, 100 mA) in the range of 5–80°. TEM micrographs were obtained with a JEM-2100F multipurpose, high resolution transmission electron microscope (JEOL, Japan) operating at an electron beam voltage of 200 kV. STEM-elemental mapping analyses were performed on a FEI Tecnai G2 F20 S-TWIN microscope at an extraction voltage of 3950 V. Powder samples were dispersed onto a carbon-coated copper grid for TEM/EDX and STEM-elemental mapping analyses. The specific surface areas were determined by Brunauer–Emmer–Teller (BET) method with N_2 adsorption-desorption measurements

at liquid nitrogen temperature using a NOVA 2000e analyzer (Quantachrome, US). The pore size distributions were obtained using the method of Barret–Joyner–Halenda (BJH). CO_2-TPD was performed on a Thermo-Finnigan TPDRO 1100 equipment. The sample was firstly calcined at 500 ^oC for 0.5 h and subsequently cooled to ambient temperature under a helium flow (30 mL/min), saturated with dry gaseous carbon dioxide (30 mL/min) for 30 min. CO_2-TPD was performed at a rate of 10 ^oC/min to 900 ^oC. H_2-temperature programmed reduction (H_2-TPR) was measured using Thermo-Finnigan TPDRO 1100 with a temperature range from ambient temperature to 800 ^oC at a rate of 10 ^oC/min, and a gas flow of 5% H_2 in nitrogen (20 mL/min).

Catalytic Performance

The reductive cyclization of 2-nitro-2'-hydroxy-5'-methylazobenzene (NAB) was carried out in a tubular, fixed-bed reactor with an inner diameter of 15 mm and a length of 650 mm, which was charged with 40 mL catalysts. A solution of NAB (5 wt%) in toluene was dosed into the reactor by a syringe pump. The temperature in the reaction zone was measured with a thermocouple placed in the center of the tube and regulated by use of a proportion integration differentiation (PID) cascade controller. The hydrogen pressure in the reaction system was set by use of a hydrogen regulator. The reaction mixture was analyzed by a high performance liquid chromatography (HPLC) with a column of Extend C18 (250 mm × 4.6 mm, 10 μm, Agilent technologies, USA). [1]

BET surface area measurement.

The specific surface areas and pore structural parameters of all the three catalysts are summarized in Table 1. Compared with Pd/γ-Al_2O_3, [1] the BET surface area and pore volume of these three catalysts decreased sharply, and the average pore radius increased accordingly. It might be mainly due to the blockage of some micro pores. [2, 3] The modification of Pd/γ-Al_2O_3 with potassium salts presented a marked effect on their physical and textural properties.

Table S1. Surface areas, pore volume, and average pore radius of Pd/γ-Al_2O_3-KNO_3, Pd/γ-Al_2O_3-K_2CO_3, and Pd/γ-Al_2O_3-KOH, Pd/γ-Al_2O_3 and γ-Al_2O_3.

Sample	S_{BET} (m^2/g)	V_{total} (cm^3/g)	$R_{average}$ (nm)
Pd/γ-Al_2O_3-KNO_3	157	0.38	4.84
Pd/γ-Al_2O_3-K_2CO_3	170	0.58	6.83
Pd/γ-Al_2O_3-KOH	159	0.55	6.87
Pd/γ-Al_2O_3 [1]	1130	1.87	3.30
γ-Al_2O_3 [1]	252	0.70	5.59

CO_2-TPD

Table S2. Surface basicity of catalysts by CO_2-TPD.

Catalyst	Basicity amount (mmol/g)				Ratio basicity of W/M/S
	Weak (W)	Medium (M)	Strong (S)	Total	
Pd/ γ -Al_2O_3- KNO_3	11.08	6.02	8.94	26.04	1/0.54/0.81
Pd/γ-Al_2O_3-K_2CO_3	11.84	1.67	7.14	20.65	1/0.14/0.60
Pd/γ-Al_2O_3-KOH	10.05	4.91	9.13	24.09	1/0.49/0.91
Pd/γ-Al_2O_3	0.64	0.68	0.67	1.99	1/1.07/1.04
Al_2O_3	0.64	0.69	0.70	2.03	1/1.08/1.09

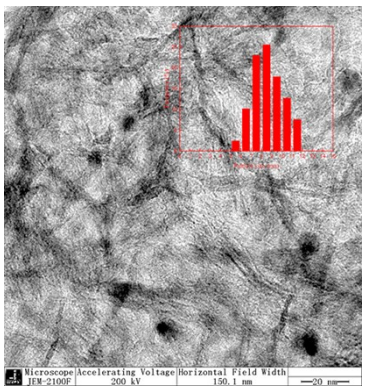

Fig. S1. TEM images and Pd particle size distributions of Pd/γ-Al_2O_3.

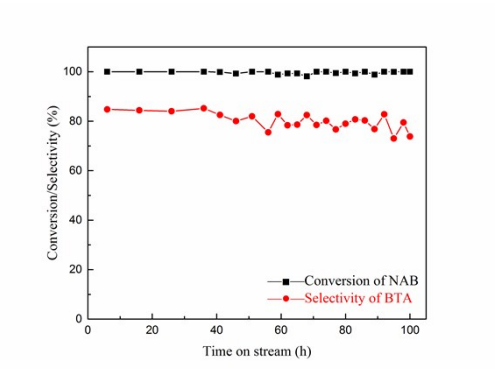

Fig. S2. Time on stream performance of Pd/γ-Al_2O_3-KNO_3.

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