Supporting information

Catalyst Characterizations and Other Experimental Data

Surface modification by amino group inducing for highly efficient catalytic oxidation of toluene over a Pd/KIT-6 catalyst

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1. Catalyst Characterizations

X-Ray Diffraction (XRD) characterization (Bruker AXS, D2 PHASER) was performed to characterize the crystal plane structure of the supports and the phase composition of the catalysts. Test conditions: Cu target ray, λ= 0.15418 nm at 40 kV and 40 mA, with a scanning rate from 0.5~10° and from 10° to 80°.

The absorption-desorption curve and pore size distribution of samples were measured by ASAP 2460 N_2 physical desorption and desorption apparatus (Micromeritics, ASAP 2460). 150 mg samples were degassed at 300℃ to remove surface impurities and water. After cooling, N_2 desorption and desorption tests were performed by adding liquid nitrogen. The specific surface area was calculated by Brunauer-Emmett-Teller (BET) formula, and the pore size distribution was obtained by Barrett-Joyber-Halenda (BJH) model.

The morphology of samples was observed by Japanese JEM-2100 transmission electron microscope. The samples were dried at 60℃ for 3 h in a vacuum drying oven before testing. The test conditions were LaB_6 (lanthanum hexaboride) electron gun, with point resolution of 0.23 nm and line resolution of 0.14 nm, and the acceleration voltage of 200 kV.

The surface morphology of samples was observed by TEM-IT500HR scanning electron microscope. Before the test, the samples were placed in a vacuum drying oven at 60℃ for 6 h. The 0.5% IM catalyst and 0.5% GR catalyst were reduced for 2 h in H_2/Ar atmosphere at 300℃ and 500℃, respectively. The sample powder was dispersed and adhered to the conductive adhesive in advance, and the observation was performed after spraying gold for 30 seconds.

The FTIR spectra were recorded by a Thermo Scientific Nicolet iS50 FTIR spectrometer. The samples were dried in a vacuum drying oven at 60℃ for 6 h before testing, and the test wavelength ranged from 400 to 4000 cm^{-1}.

In-situ X-ray photoelectron spectrometer (ThermoFischer, ESCALAB 250Xi) was used to test the catalysts. The catalysts prepared by impregnation method and immobilization method were reduced in-situ for 2 h in H_2/Ar atmosphere at 300℃ and 500℃ respectively. Test conditions: vacuum of the analysis room was 8×10^{-10} Pa, the

excitation source was Al Ka ray (hv=1486.6 eV), the working voltage was 12.5 kV, the filament current was 16 mA, and the signal was accumulated for about 2-10 cycles, Passing-Energy was 30 eV, step length was 0.1 eV.

The O_2-TPD was performed in a Tianjin Xianquan automatic chemical adsorption instrument. Before the test, 0.5% IM or 0.5% GR catalyst (50 mg) was reduced *in-situ* for 2 h in H_2/Ar atmosphere at 300℃ and 500℃ respectively. In the test, the sample was heated from room temperature to 500℃ in a 5% O_2/He flow and maintained for 30 min. After cooling to room temperature, the sample was heated to 800℃ (10℃/min) in a He flow. The desorption amount of oxygen was detected by a TCD detector.

The amount of CO chemisorption of the catalyst was measured by a gas chromatogram (GC 920, China) equipped with a TCD detector using dynamic pulse method. Prior to the measurement, 50 mg sample was reduced by 10% H_2/Ar (40 ml min^{-1}) at 300°C or 500℃ for 2 h and then the gas was switched to Ar (40 ml min^{-1}) at the same temperature for 1 h. Pulses of 5% CO/N_2 were introduced to the sample until uptake saturation. The Pd dispersion was calculated by the following equation:

$$Dispersion = \frac{MV}{vm} \times 100\%$$

Where M is the atomic weight of Pd (106.42 g mol^{-1}), V is the amount of CO adsorbed (mol), v is the adsorption stoichiometry (1 mol CO per surface atom of Pd), and m is the amount of Pd (g).

The turnover frequency (TOF) of the catalysts for toluene oxidation was determined in separate experiments. The TOF was calculated as following:

$$TOF = \frac{Cx\%}{n}$$

Where C is the toluene passed through the catalyst per hour (mol), x% is the conversion of toluene, n is the number of surface Pd active site of the catalyst determined by ICP and CO chemisorption.

2. Other Figures

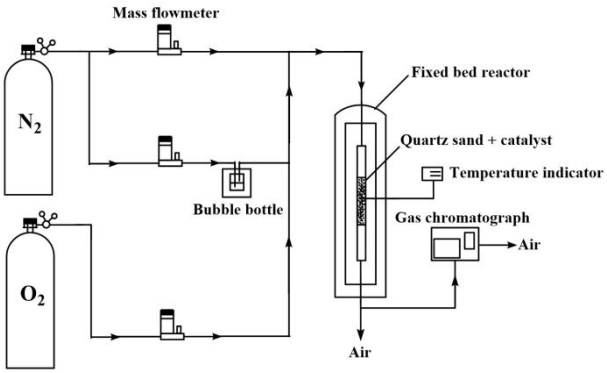


Figure S1 Diagram of catalyst activity evaluation device

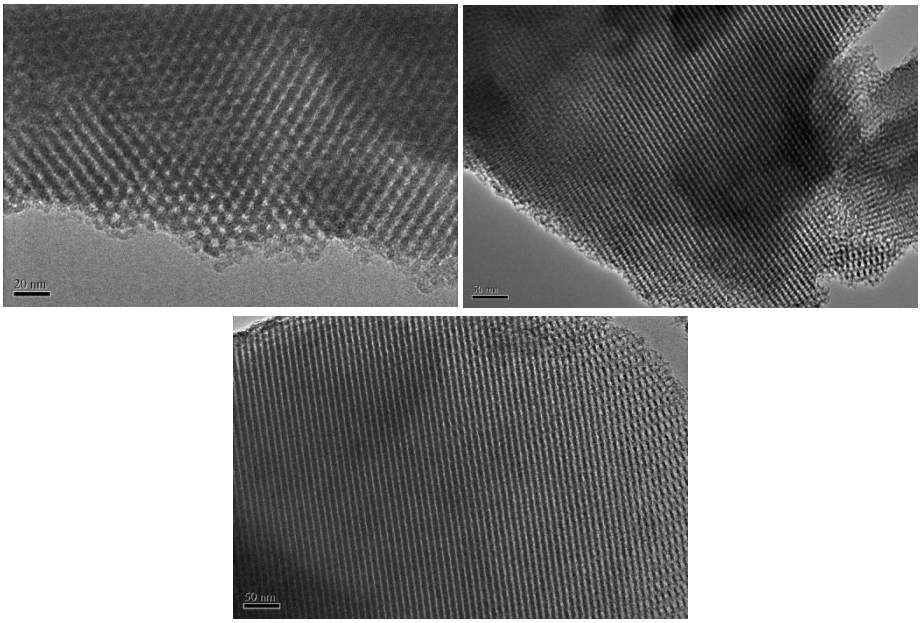


Figure S2 TEM images of KIT-6

2. Other Figures

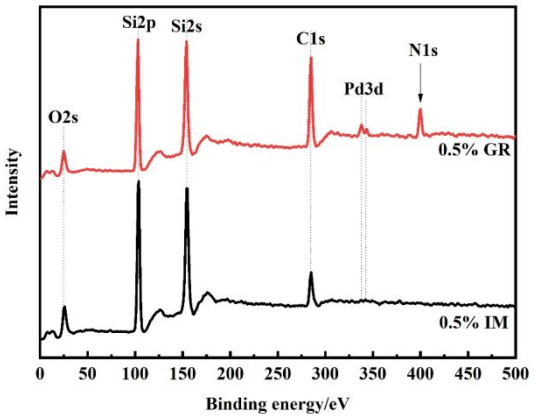


Figure S3 XPS spectra of 0.5% IM catalyst and 0.5% GR catalyst

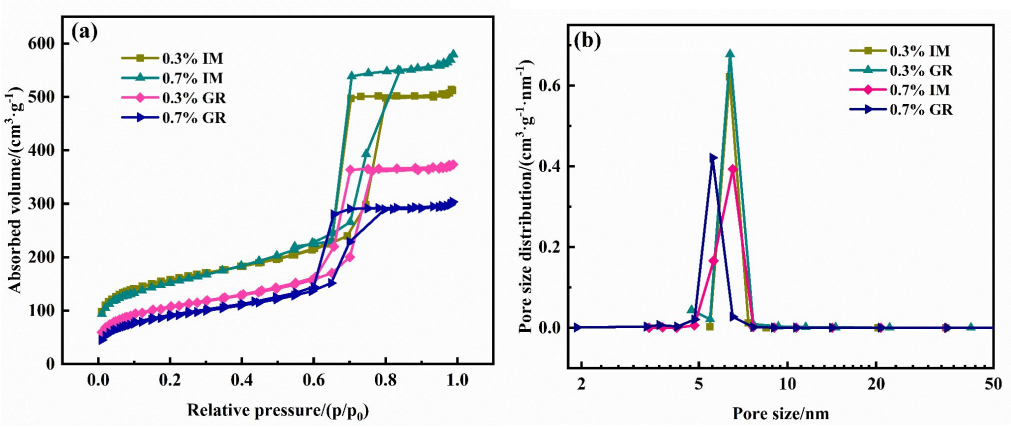


Figure S4 N_2 adsorption/desorption isotherms (a) and pore size distributions (b) of the catalysts

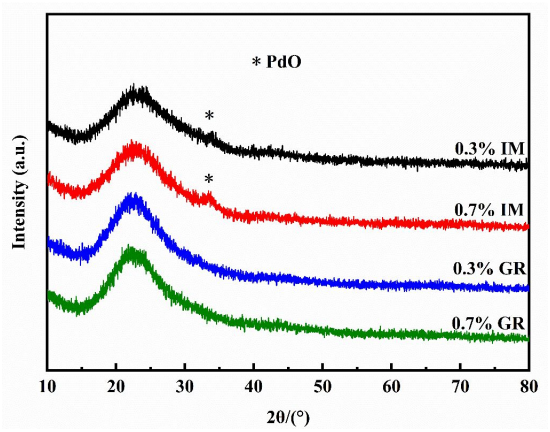
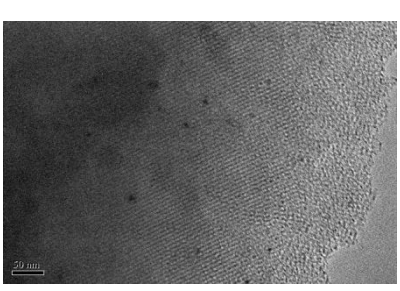
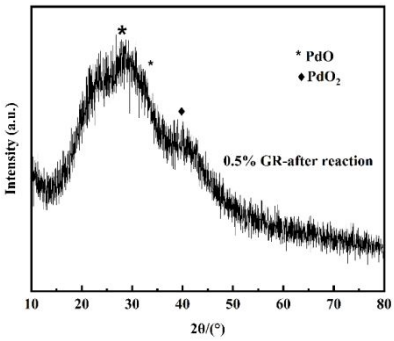


Figure S5 XRD pattern of catalysts





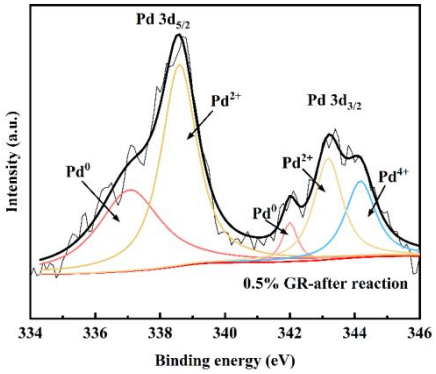


Figure S6 TEM image, XRD pattern and XPS spectrum of 0.5% GR catalyst after reaction

3. Other Tables

Table S1 O_2-TPD and TOF data of the catalysts

catalyst	Total amount of adsorbed oxygen (μmol g^{-1})	$O_2^-{}_{ad}$ (μmol g^{-1})	$O^-{}_{ad}$ (μmol g^{-1})	$O^{2-}{}_{lat}$ (μmol g^{-1})	TOF (h^{-1})
0.5% IM	50.5	14.6	26.9	9.0	4.6
0.5% GR	62.6	21.0	37.4	4.2	9.7

Table S2 Catalytic oxidation performance of toluene with different catalysts

Samples	T_{10}(℃)	T_{50}(℃)	T_{75}(℃)	T_{90}(℃)
0.3% IM	155	180	183	185
0.3% GR	150	175	178	182
0.5% IM	159	175	179	182
0.5% GR	145	162	166	171
0.7% IM	159	168	170	171
0.7% GR	147	158	162	165

Table S3 Catalytic performance of 0.5% GR at different WHSV

Catalyst	WHSV (mL·g^{-1}·h^{-1})	T_{50}(℃)	T_{90}(℃)
0.5% GR	10800	156	168
	24000	162	171
	32100	181	200