Supplementary Materials

The Effect of Aniline Pretreatment on Pt/CeO_2 Nanocatalysts for Boosting Toluene Oxidation

1 Preparation of CeO_2 with Well-Defined Facets

In a typically preparation, 5 mmol Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) was added to 20 mL of deionized water. After completely dissolving, 55 mL of 15 mol L^{-1} sodium hydroxide (NaOH) solution were slowly added dropwise. After stirring constantly for 30 min, this mixed solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave wand then kept at 150 °C in an electric oven for 48 h. After cooling to room temperature naturally, the precipitates were washed with deionized water and absolute ethanol repeatedly until pH is 7, and then dried at 80 °C overnight.

2 Catalysts Characterizations

Powder X-ray diffraction (XRD) was performed on an X-ray diffractometer (Panalytical X'pert, Netherlands) using Cu Kα radiation (λ = 1.5406 Å). The nitrogen adsorption and desorption isotherms were measured at 77 K on an ASAP 2020 system (Micromeritics, USA). in static measured mode, and the SSA was calculated using the Brunauer-Emmett-Teller (BET) model. Detailed microstructural analyses were conducted using SEM (Zeiss Ultra, Germany) at an accelerating voltage of 3 kV and TEM (JEM-2100HR, JEOL, Japan) technology. The mean size of Pt nanoparticles was determined from HRTEM images. The atomic absorption spectroscopy (AAS) (Hitachi Z-2000, Japan) was utilized to determine the Pt loading of the catalysts. The dispersion of Pt in catalysts was determined by a static CO chemisorption. X-ray photoelectron spectroscopy (XPS) was carried out using an Al Kα(hv=1486.8 eV) source on K-Alpha (ESCALAB 250, Thermo Fisher Scientifc, USA) to detect surface elements and chemical states. The powder samples were pressed into the tablet prior to the XPS detections. H_2-TPR analysis was operated in a U-shaped quartz reactor under a gas flow with a Micromeritics Autochem 2720. The sample with 100 mg was pre-treated in Ar at 300 °C for 1 h before measurement. Then the samples were measured continuously by a thermal conductivity detector (TCD) from 50 to 800 °C with 10 °C min^{-1} under 10% H_2/Ar flow. Raman spectra were obtained using a LabRAM HR Evolution Laser Raman Spectrometer (HYJ, France) with a CCD detector and a spectral resolution of 1 cm^{-1}. The laser spot size on the sample was less than 0.5 nm with the exciting lines at 325 nm for UV Raman and 532 nm for Visible Raman.

3 Catalytic Activity Evaluation

In a typical reaction, toluene catalytic oxidation was carried out in a continuous flow quartz tube micro-reactor (length = 450 mm, radius =3 mm) with 100 mg catalyst (40 -60 mesh and mixed with 400 mg quartz sand of 20 – 40 mesh) at room temperature and pressure. The composition of reactant mixture was 1000 ppm toluene (dry air as a balance gas), and the total flow was 100 mL min^{-1}, corresponding to the weight hourly space velocity (WHSV) of 48 000 mL g^{-1} h^{-1}. The toluene content in tail gas was detected by on-line gas chromatograph (GC-2014C, Shimadzu, Japan) equipped with FID and TCD detectors at a certain temperature after stabilized for 30 min.

The conversion rate (X, %) of toluene was obtained based on toluene consumption, which calculated by the intake and exhaust toluene concentration. The catalytic activities were evaluated by the 50% and 90% toluene conversion temperature, which were defined as T_{50} and T_{90}, respectively.

$$X = \frac{[Toluene]OUT}{[Toluene]IN} * 100\% \tag{1}$$

The activation energies were obtained at certain temperatures for toluene conversion lower than 20%, which is calculated using the following Arrhenius relationship.

$$ln\, r = -\frac{Ea}{RT} + ln\, A \tag{2}$$

where r, A and E_a are the reaction rate (mol s^{-1}), pre-exponential factor, and apparent activation energy (kJ mol^{-1}), respectively.

The turnover frequencies (TOFs) were the number of reactant molecules converted per unit time on the active center, and were calculated based on the following equation:

$$TOF_{Pt}(S^{-1}) = X_{toluene}F_{toluene}\,\frac{M_{Pt}}{m_{cat}X_{Pt}D_{Pt}} \tag{3}$$

$$TOF_{OV}(S^{-1}) = X_{toluene}F_{toluene}\frac{1}{\frac{m_{cat}}{MCeO_2}*I_{OV}} \quad (4)$$

where $X_{toluene}$ is the toluene conversion at certain temperature; $F_{toluene}$ denotes the toluene flow rate (mol s^{-1}); m_{cat} is the weight of catalyst; M_{Pt} is the molecular weight of platinum; M_{CeO2} is the molecular weight of CeO_2; I_{OV} is the concentration of oxygen vacancies.

4 Durability and H_2O Resistance Test

The durability test included long-term stability and high concentration stability tests. In the long-term stability, the best sample was tested at 180 °C in 1000 ppm toluene (100 mg catalyst, WHSV = 48000 ml g^{-1} h^{-1}) for 100 h. In the high concentration stability, the best sample was tested at 180 °C in 1000 ppm toluene (100 mg catalyst, WHSV = 48000 ml g^{-1} h^{-1}) for 40 h, 2000 ppm toluene for 30 h, 4000 ppm toluene for 30 h.

The H_2O resistance test was performed under the water vapor of various volume concentration of water at 180 °C in 1000 ppm toluene (100 mg catalyst, WHSV = 48000 ml g^{-1} h^{-1}) for 40 h.