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Thermo-photocatalytic oxidation of benzene under visible light over nitrogen-doped titania grafted with Cu and Pt

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1 Photocatalyst synthesis

The modified nitrogen-doped TiO_2 photocatalyst was synthesized via the impregnation of basic photocatalyst with an aqueous solution of precursor $Cu(CH_3COO)_2$ or H_2PtCl_6 followed by chemical reduction with a 3-fold excess of $NaBH_4$, washing in a centrifuge for 5 times, and drying at 110 °C. The amount of precursor was determined by the required metal content (wt.%) in the catalyst. The details of synthesis can be found elsewhere [1,2].

2 Catalyst characterization

The textural properties were investigated by N_2 adsorption at 77 K using an 3P sync 220A (3P Instruments GmbH & Co, Germany). A specific surface area values were calculated by BET analysis.

The UV-Vis diffuse reflectance spectra were recorded in the range of 250–850 nm with 1 nm of resolution using a Cary 300 UV-Vis spectrophotometer from Agilent (USA) equipped with a DRA-30I diffuse reflectance accessory at room temperature. A pre-packed PTFE from Agilent (USA) was used.

The X-ray photoelectron spectra were measured on a SPECS spectrometer with a PHOIBOS-150-MCD-9 analyzer (AlK_α radiation, hv = 1486.6 eV, 150 W). The binding energy (BE) scale was pre-calibrated using the positions of the peaks of $Au4f_{7/2}$ (BE = 84.0 eV) and $Cu2p_{3/2}$ (BE = 932.67 eV) core levels. The samples were loaded onto a conducting double-sided copper scotch (3M). The $Ti2p_{3/2}$ peak at 458.8 eV of the titanium oxide support was used as an internal standard [3]. The survey spectrum and the narrow spectra were registered at the analyzer pass energy 20 eV.

3 Photocatalytic experiments

The photocatalytic experiments were performed in a continuous-flow set-up using the volume flow rate 0.1 ± 0.02 L min^{-1}, the inlet concentration of acetone 38 – 42 µmol L^{-1}, the inlet concentration of benzene 10 µmol L^{-1} the relative humidity of pre-cleaned inlet air 20±2% at 25 °C. The set-up was connected to Bruker Vector 22 FTIR spectrometer (USA) to monitor periodically the changes in the gas phase. CO_2 generation rate was selected for the measure of activity [4]. The temperature of the reactor was controlled via a PC-connected thermostatic unit so that the temperature was adjusted in the range of 40-140 °C. Typical methodology of photocatalysts' pretreatment and sampling: catalyst was deposited onto a glass plate (ca. 9.1 cm^2) at a surface density of 25-30 mg cm^{-2}, for obtaining the complete light absorbance. The light source was turned on at 40-min point to ensure the absence of activity without irradiation of the sample. LED used was adjusted to the photon flux of 4.5 µE s^{-1}, or 270 µE min^{-1}). A set of light-emitting diode plates (LEDs) with a special collimating lens were employed for the photocatalyst irradiation during the experiments on action spectra obtaining following the methodology presented [4]. All LEDs were used as adjusted to the photon flux of 1.5 10^{17}photons s^{-1} (i.e., 0.25 µE s^{-1}, or 15 µE min^{-1}). The photonic efficiency during acetone photocatalytic oxidation is calculated as the activity value (CO_2 generation rate, µmol min^{-1}) divided by the total flux of photons incident onto the surface of catalyst per time interval (µE min^{-1}).

4 Stability of activity

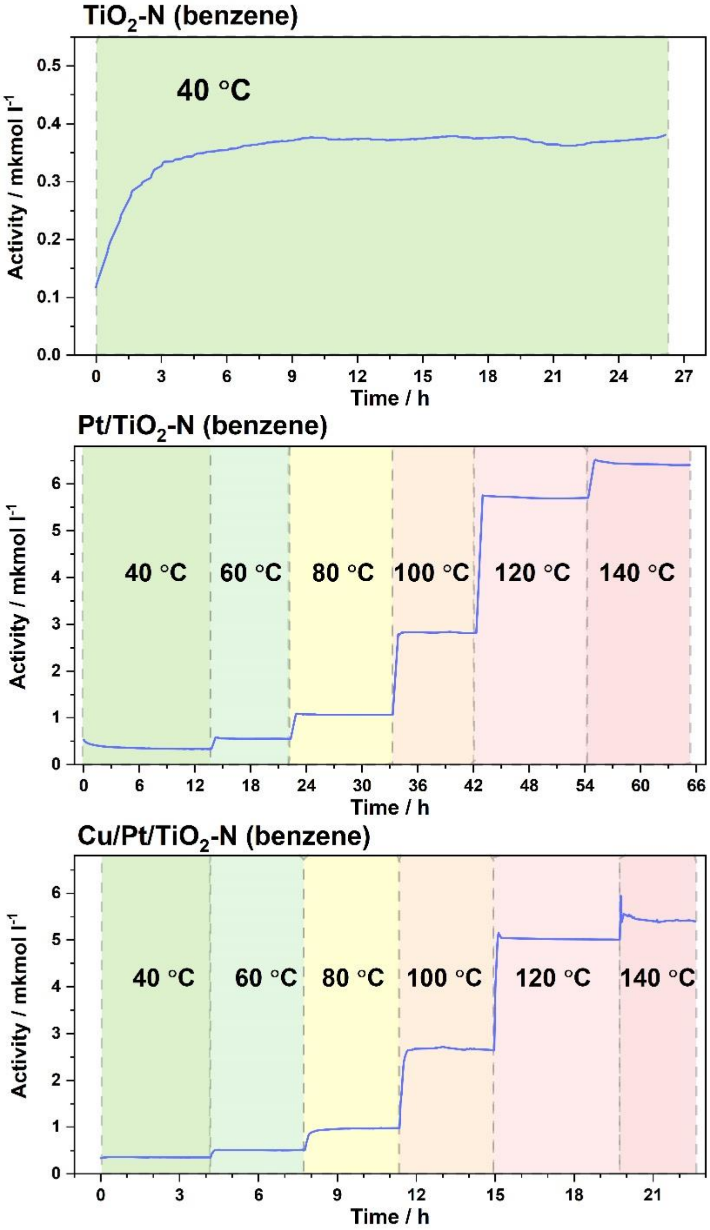

Figure S1. Activity of samples versus time

The stability of the catalyst is an important factor in describing its activity. For this reason, the activity values that are observed after at least 6 hours of exposure to lighting were taken as characteristics for the activity. To confirm the stability of activity under constant conditions, we provide activity versus time for key samples of this study in Figure S1. Data for initial TiO2-N sample presented for 40 C point as enlarged picture of activity within the single temperature step.

References

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