

Supporting Information

Covalent triazine framework as support for liquid phase reaction

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Materials. 1,4-Dicyanobenzene (DCB) was purchased from Alfa Aesar and was used as received. Zinc chloride (Alfa Aesar, anhydrous, 98%) was stored in a glove box and used as received. Na_2PdCl_4 , was from Aldrich (99.99% purity) and activated carbon from Camel (X40S; SA = 900–1100 m^2/g ; PV = 1.5 ml/g; pH 9–10). Before use the carbon was suspended in HCl 6 M and left under stirring for 12 h, then washed several times with distilled water by decantation until the pH of the solution reached values of 6–6.5. At the end the carbon was filtered off and dried for 5–6 h at 150 °C in air. The final water content was evaluated to be < 3%. NaBH_4 of purity > 96% from Fluka, polyvinylalcohol (PVA) (Mw = 13000–23000 87–89% hydrolysed,) from Aldrich were used. Gaseous oxygen from SIAD was 99.99% pure.

Synthesis. 1,4-Dicyanobenzene, the monomer and ZnCl_2 , in a ratio 1:5 molar were transferred into a quartz ampoule (3 × 12 cm) under an inert atmosphere. The ampoule was then evacuated, sealed and heated within 30 minutes to 400°C. After 20 hours at 400°C the ampoule was further heated within one hour to 600 °C where it was held for 20 more hours. The ampoule was then cooled to room temperature and opened. The resulting reaction mixture was washed several times, with diluted HCl followed by distilled water, under stirring to remove most (only 0.3 wt.% of Zn remains) of the ZnCl_2 . The resulting

black powder, after filtration, was dried at 150°C and finely grinded to give CTF. A yield of 98% was obtained. In addition a second sample was prepared with a higher amount of Zn (1.3 wt.% checked by ICP), by impregnation with ZnCl₂.

Metal sol immobilization. Pd sol: Solid Na₂PdCl₄ (0.043 mmol) and 880 µl PVA solution (2% w/w) (Pd/PVA 1:1 wt/wt) were added to 130 ml of H₂O. After 3 min, 860 µl of 0.1M NaBH₄ solution was added to the yellow-brown solution under vigorous magnetic stirring. The brown Pd(0) sol was immediately formed. An UV-visible spectrum of the palladium sol was recorded for ensuring the complete reduction of Pd (II).

Within few minutes from their generation, the colloids (acidified at pH 2, by sulfuric acid) were immobilized by adding carbon under vigorous stirring. The amount of support was calculated in order to obtain a final metal loading of 1wt.% (on the basis of quantitative loading of the metal on the support).

Catalyst characterization. Morphology and microstructures of the catalysts are characterised by TEM and SEM. The powder samples of the catalysts were ultrasonically dispersed in ethanol and mounted onto copper grids covered with holey carbon film. A Philips CM200 LaB₆ electron microscope, operating at 200 kV and equipped with a Gatan CCD camera, was used for TEM observation. A Hitachi S-5200 in lens UHR FE-SEM was used for SEM observation.

The X-ray diffraction (XRD) measurements were performed on a Panalytical X'Pert Pro with Cu-Kα radiation (Figure 1 and 2). An outgasing procedure in vacuo at 423 K for 3 hours on Quantachrome Autosorb-1 precedes the determination of the catalysts surface areas by applying the Brunauer – Emmett – Teller (BET) equation (Figure 3).

ICP analyses were performed using a Jobin Yvon JV24 to verify the quantitative metal loading on the support. The final total metal of Pd loading was 1 wt. %.

Catalytic test. The reactions were carried out in a thermostated glass reactor (30 mL) equipped with an electronically controlled magnetic stirrer connected to a large reservoir (5000 mL) containing

oxygen at 1.5 atm. The oxygen uptake was followed by a mass flow controller connected to a PC through an A/D board, plotting flow vs time. Glycerol solution (0.3 M and NaOH/Glycerol ratio = 4 mol/mol), and the catalyst (substrate/metal) 1000 mol/mol were mixed in distilled water (total volume 10 mL). The reactor was pressurized at the desired pressure of O₂ and thermostated at 50 °C. The reaction was initiated by stirring. The identification and analysis of the products were performed on Agilent Technologies HPLC equipped with a Rezex™ RCM-Monosaccharide from Phenomenex® column. H₂SO₄ (0.005 M) was used as eluent.

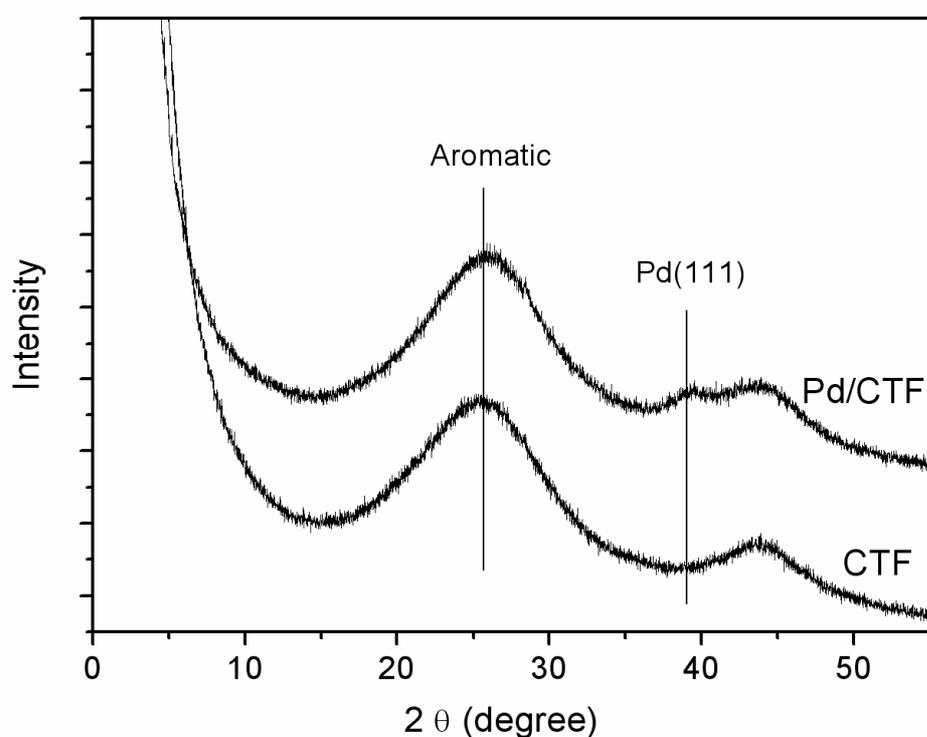


Figure S1. Diffractogram of the CTF and Pd/CTF

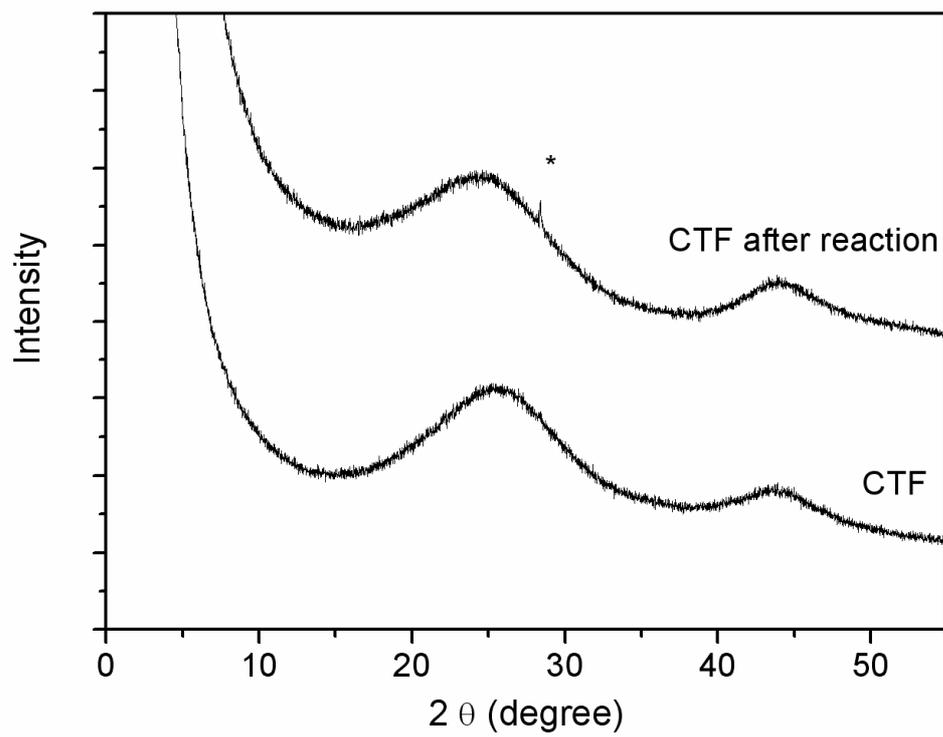


Figure S2. Diffractogram of the CTF before and after glycerol reaction

* peak at 28.4 ° due to Si sample holder

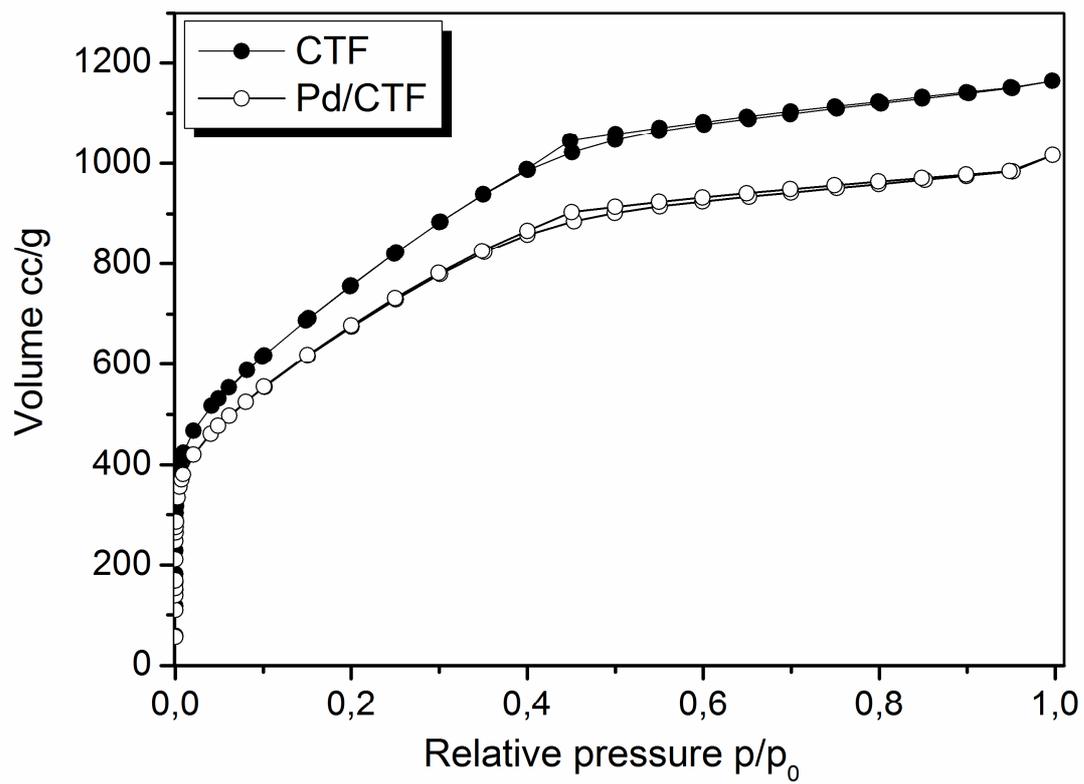


Figure S3. Nitrogen sorption isotherms of the CTF and Pd/CTF