

## Pd local structure and size correlations on the activity of Pd/ TiO<sub>2</sub> for photocatalytic reforming of methanol

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### Experimental procedure

To provide detailed morphological and compositional information about the studied samples at micro and nano-scale, transmission electron microscope (TEM) system JEOL 2100 (LaB6) is employed. For the analysis, the material was ground and mixed with water and 2 mL of materials in water suspension was placed on the TEM grid and dried. The instrument is equipped with a high-resolution Gatan digital camera (2k x 2k) providing maximum resolution of 0.2 Å which makes possible detailed observation of the crystal lattice, obtaining diffraction patterns and accurate measurement of the lattice d spacing with the help of Digital Micrograph software. In scanning transmission electron microscopy (STEM) mode, dark field (HAADF/Z-contrast) detector was used to provide excellent compositional contrast. An energy dispersive X-ray spectrometer (EDS) system (Oxford Instruments), was equipped with a large-area 80 mm<sup>2</sup> SDD (Silicon Drift Detector). X-MaxN 80 T was employed for the elemental analysis in line scans, and elemental mapping modes. To analyse the EDS data, the latest version of AZtecTEM software was utilized. The particle diameter of Pd was obtained based on 100 Pd particles observed in TEM images using ImageJ software.

X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis Ultra-DLD XPS spectrometer with a monochromatic Al K $\alpha$  source (75-150 W) and analyser pass energies of 160 eV (for survey scans) or 40 eV (for detailed scans). Samples were mounted using a double-sided adhesive tape and binding energies referenced to the C (1s) binding energy of adventitious carbon contamination which was taken to be 284.7 eV. Data were analyzed using Casa XPS software <sup>2</sup>.

Pd K edge X-ray absorption spectra (XAS) were obtained on the B18 beamline at Diamond Light Source, Didcot, UK. Measurements were performed using a QEXAFS set-up with a fast-scanning Si (311) double crystal monochromator. The time resolution of the spectra reported herein was 1 min/spectrum ( $k_{\max} = 16$ , step size 0.5 eV), on average six scans were acquired to improve the signal to noise level of the data for transmission measurements. All samples were diluted with cellulose and pressed into pellets to optimise the effective edge-step of the X-ray absorption fine structure (XAFS) data and measured in transmission mode using ion chamber detectors. All XAFS spectra were acquired concurrently with the appropriate foil placed between  $I_t$  and  $I_{ref}$ . XAFS data processing was performed using IFEFFIT <sup>3</sup> with the Horae package <sup>4</sup> (Athena and Artemis). The amplitude reduction factor,  $S_0^2$ , was derived from EXAFS data analysis of a known reference materials and used as a fixed input parameter.

## Characterisation results

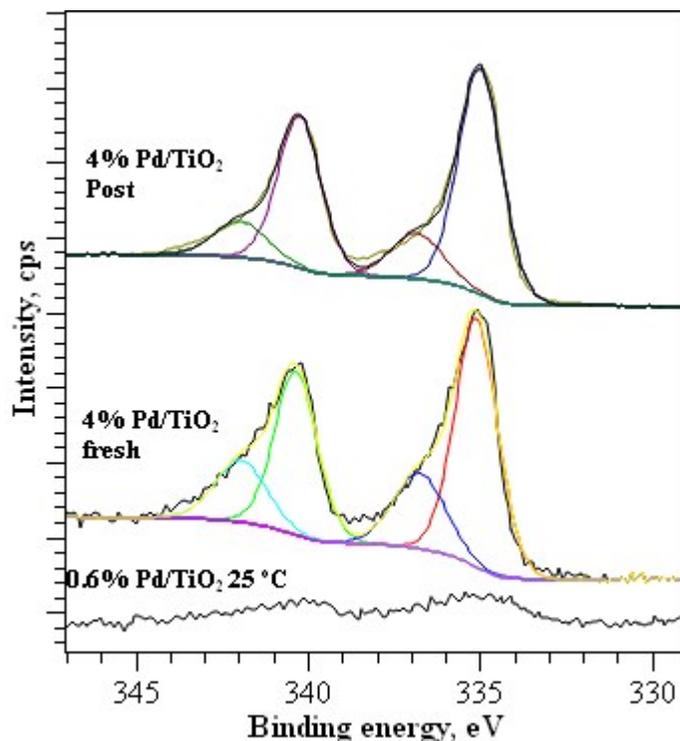


Fig S1. XPS Pd 3d analysis of Pd/TiO<sub>2</sub> catalysts.

The XPS Pd 3d analysis of 0.6% Pd TiO<sub>2</sub> catalysts prepared at 1 °C showed a broad feature with significantly low intensity of the peak due to the low amount of Pd loading on TiO<sub>2</sub>. Increasing the Pd loading significantly enhanced the Pd signal as shown in 4% Pd loading. The XPS 3d peaks appeared at 335.0 eV corresponded to Pd<sup>0</sup>. Peak corresponded to PdO was also observed at 336.7 eV that corresponded to oxide surface. The XPS analysis of the post-reaction 4% Pd/TiO<sub>2</sub> catalyst revealed no significant changes on the peak position which centred at 355.0 eV corresponded to the presence of Pd<sup>0</sup> and also PdO at 336.7 eV.

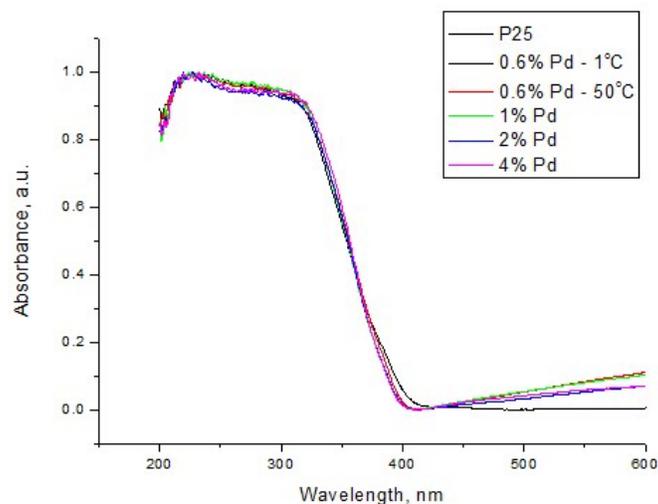


Fig S2. UV-visible spectroscopy of P25, 0.6 % Pd/TiO<sub>2</sub> synthesised at 1 °C and 50 °C, 1% Pd/TiO<sub>2</sub> synthesised at 1 °C, 2% Pd/TiO<sub>2</sub> synthesised at 1 °C and 4 % Pd/TiO<sub>2</sub> synthesised at 1 °C.

The UV-visible spectroscopy analysis of the catalysts show no significant differences on the light adsorption properties of the catalysts at different Pd loading. There is no changes in the band gap of TiO<sub>2</sub> upon deposition of Pd with its corresponding TiO<sub>2</sub> P25 support

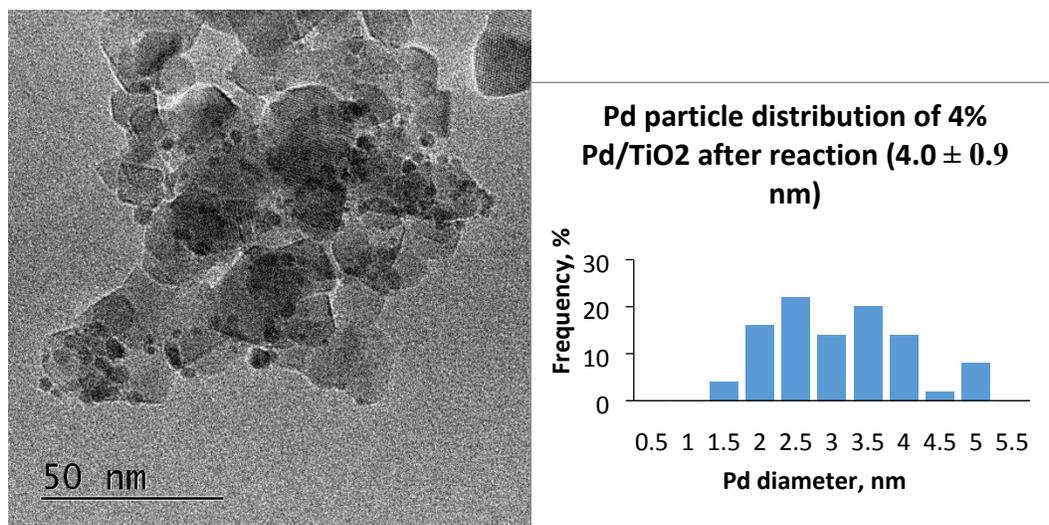


Fig S3. TEM analysis of 4% Pd/TiO<sub>2</sub> after photocatalytic reaction.

TEM analysis of 4% Pd TiO<sub>2</sub> following photocatalytic reaction shows the average diameter of Pd of 4.0±0.9 nm.

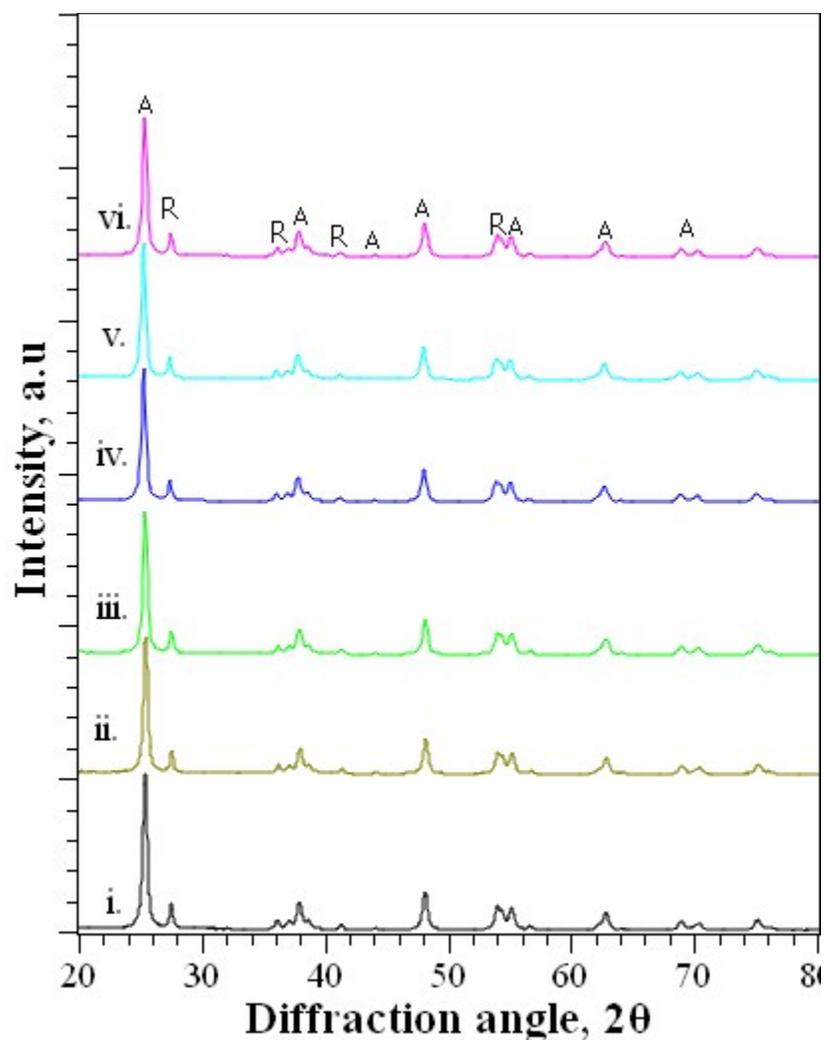


Fig S4. XRD analysis of i. P25 TiO<sub>2</sub>, ii. 0.6% Pd/TiO<sub>2</sub> catalyst produce at 1 °C, iii. 25 °C, iv. 50 °C, v. 75 °C and vi. 4% Pd/TiO<sub>2</sub>.

XRD analysis shows the presence of peaks at 25.3°, 36.1°, 37.8°, 39.2°, 41.2°, 44.0°, 48.1°, 54.2°, 62.5°, 69.0°, 70.0° and 75.1° associated with the anatase crystal plane (JCPDS card No 21-1272). Peaks associated with rutile crystal plane at 27.4°, 38.6° and 47.9° indicating the presence of anatase and rutile mixture in P25 (JCPDS card no. 21-1276). The presence of Pd supposedly occurred at 41° is not detected presumably due to highly dispersed Pd nanoparticles with small particle on TiO<sub>2</sub>.