

Electronic Supporting Information

Supported Bimetallic Nano-alloys as Highly Active Catalysts for the One-Pot Tandem Synthesis of Imines and Secondary Amines from Nitrobenzene and Alcohols

Meenakshisundaram Sankar ^{a,b*}, Qian He ^c, Simon Dawson ^b, Ewa Nowicka ^b, Li Lu ^c, Pieter C. A. Bruijninx ^a, Andrew M. Beale ^{a,d,e}, Christopher J. Kiely ^c, and Bert M. Weckhuysen ^{a,*}

^a *Inorganic Chemistry and Catalysis group, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands.*

^b *Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK.*

^c *Department of Material Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015-3195, USA.*

^d *UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, Oxfordshire OX11 0QX, UK.*

^e *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK.*

Corresponding authors: Dr. Meenakshisundaram Sankar, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK. Ph: +44(0)-29-2087 5748, Email: Sankar@cardiff.ac.uk

and

Prof dr. ir. Bert M. Weckhuysen, Inorganic Chemistry and Catalysis group, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands. Email: B.M.Weckhuysen@uu.nl

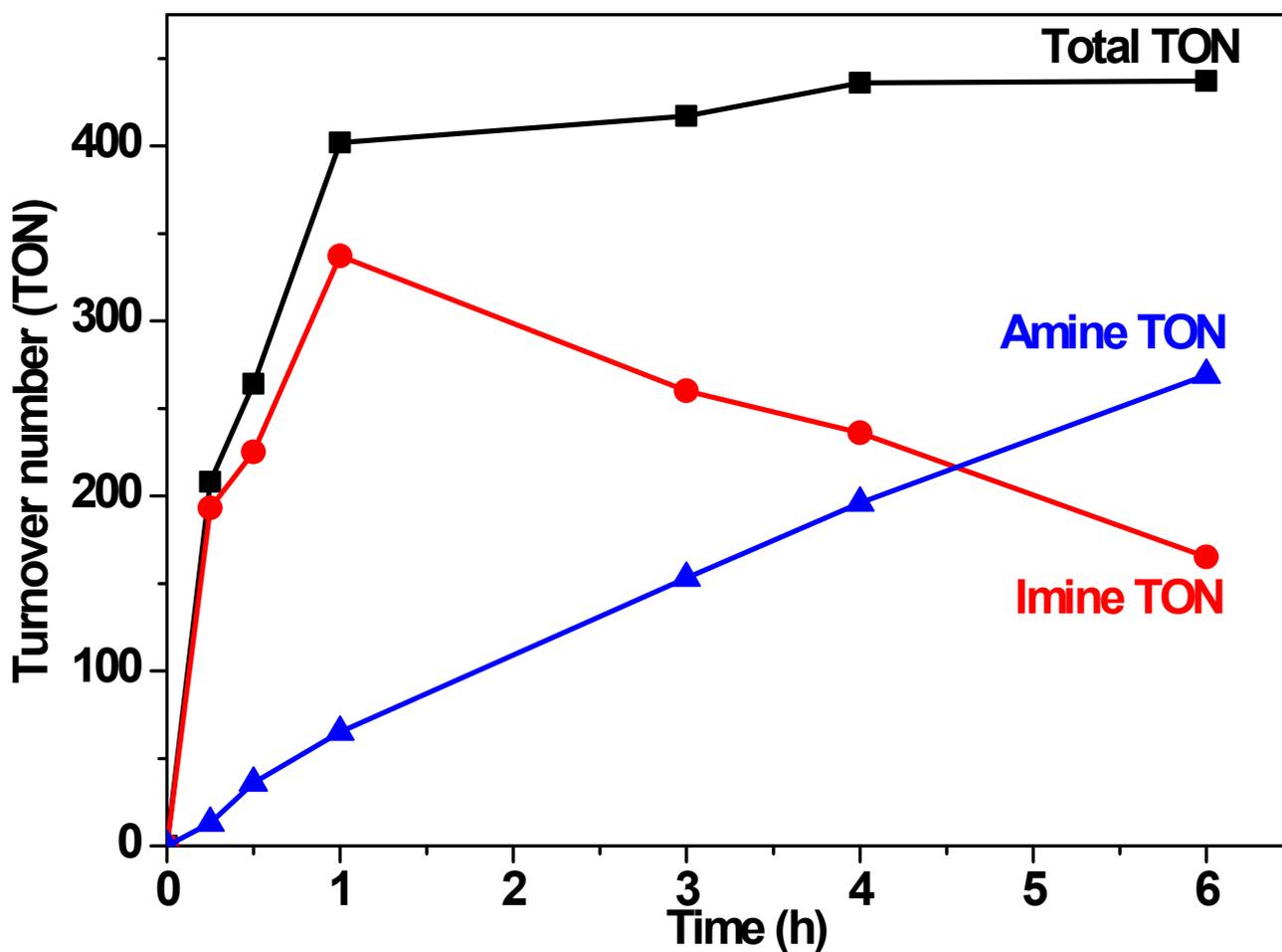


Figure S1. Time-on-line profile of the total TON and individual product TONs for the tandem synthesis of *N*-benzylideneaniline (**5**) and *N*-benzylaniline (**6**) using the 1%Ru-Pd/TiO₂ (M_{Im}) catalyst. *Reaction conditions:* catalyst: 0.1 g; nitrobenzene: 4.5 mmol; benzyl alcohol: 45 mmol; mesitylene (solvent): 5 mL; catalyst: 100 mg; Ar: 20 bar; T: 433 K. The TONs are calculated using the nominal molar metal loading, the moles of substrate (**3**) consumed and the moles of product (**6**) formed.

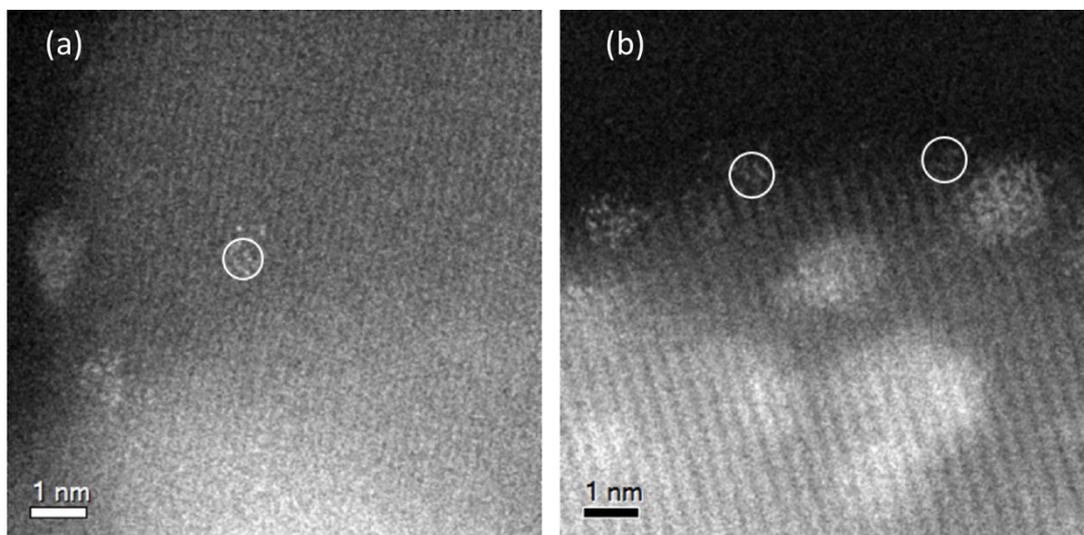


Figure S2. Representative high angle annular dark field (HAADF) images of the (a) 1%Au-Pd/TiO₂ and (b) 1%Ru-Pd/TiO₂ M_{Im} samples showing the existence of sub-nm metal clusters (white circles).

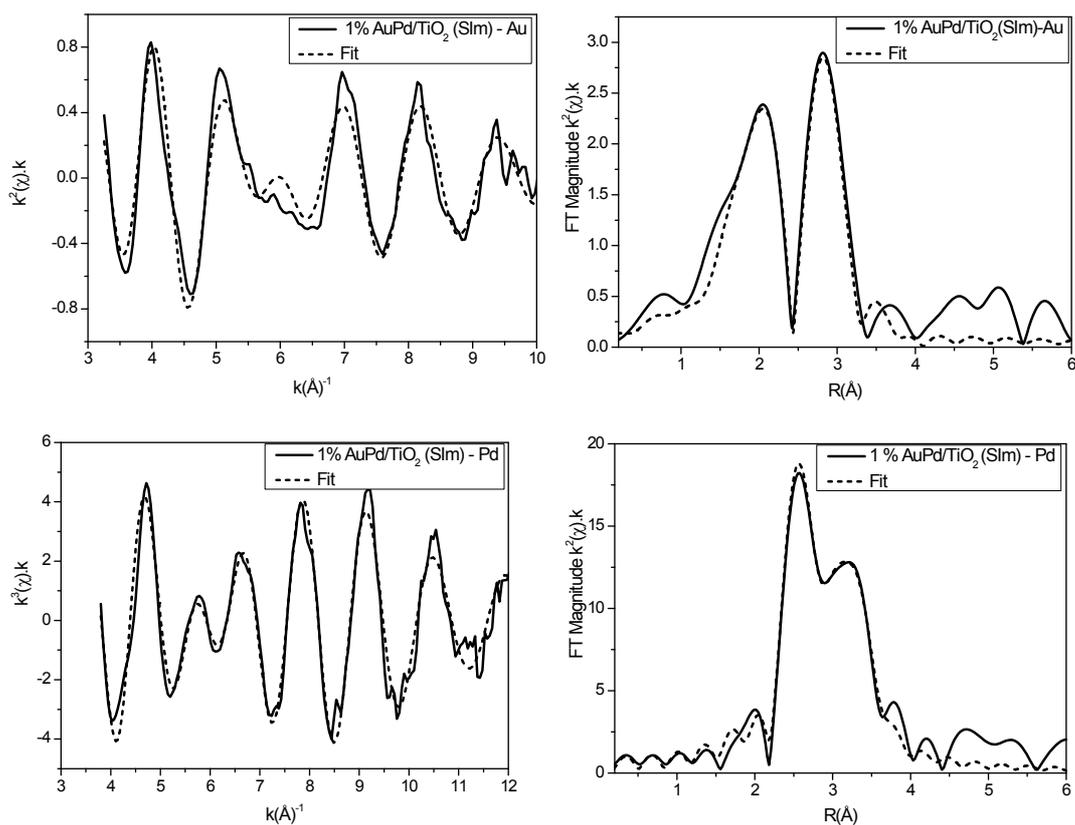


Figure S3. Isolated Au L₃-edge and Pd K-edge EXAFS and associated Fourier Transform data for the two-shell fits for 1% Au-Pd/TiO₂ (S_{1m}). Key: Solid line: experimental data, dotted line: theoretical fit; top two spectra were recorded at Au L₃ edge and bottom two spectra were recorded at Pd K-edge. EXAFS spectra were fitted in k -space.