

## Electronic supplementary information (ESI)

# Superior activity of rutile-supported ruthenium nanoparticles for HCl oxidation

Evgenii V. Kondratenko,<sup>a</sup> Amol P. Amrute,<sup>b</sup> Marga-Martina Pohl,<sup>a</sup> Norbert Steinfeldt,<sup>a</sup> Cecilia Mondelli,<sup>b</sup> Javier Pérez-Ramírez\*<sup>b</sup>

<sup>a</sup> Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29 A, D-18059 Rostock, Germany

<sup>b</sup> Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland. E-mail: jpr@chem.ethz.ch; Fax: +41 44 6331405; Tel: +41 44 6337120.

## Materials

Supported RuO<sub>2</sub> catalysts were prepared according to the ethylene glycol (EG) method described in ref. 21, using TiO<sub>2</sub>-rutile (Aldrich, nanopowder, 99.5%), TiO<sub>2</sub>-anatase (Aldrich, nanopowder, 99.7%), and γ-Al<sub>2</sub>O<sub>3</sub> (Sasol, Puralux NWA155) as carriers. The two TiO<sub>2</sub> polymorphs are distinguished by the suffixes 'r' and 'a' for rutile and anatase, respectively. Ru(III)-chloride hydrate (RuCl<sub>3</sub>·nH<sub>2</sub>O, 38.30% Ru basis, Alfa Aesar) was used as the ruthenium source. This precursor was initially dissolved in ethylene glycol (EG). Then, a solution of NaOH in EG was added under stirring to adjust the pH to 12. In order to obtain the supported catalysts, the carriers were suspended in ethanol under stirring. Thereafter, the Ru/EG solution was dissolved in ethanol and added to the suspensions. The resulting mixtures were stirred overnight at room temperature. Finally, the solids were separated from the supernatant solution by centrifugation and dried. The as-prepared catalysts were used without further calcination for catalytic testing and characterisation. For comparison purpose, supported catalysts were also prepared by dry impregnation (I) of the carriers with an aqueous solution of RuCl<sub>3</sub> (0.16 and 2 wt.% Ru), followed by drying at 338 K for 12 h and calcination at 623 K (10 K min<sup>-1</sup>) in static air for 5 h.

## Characterisation

The Ru content in the samples was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Varian 715-ES setup after dissolution of the samples in an acid solution. N<sub>2</sub> sorption at 77 K was performed using a Quantachrome Quadrasorb-SI gas adsorption analyser. Prior to the measurement, the samples were evacuated at 423 K for 12 h. Temperature-programmed reduction with hydrogen (H<sub>2</sub>-TPR) was carried out using a set-up containing 8 individually heated plug-flow fixed-bed quartz tube (i.d. 6 mm) reactors (pm engineering, Germany). 40-80 mg of the catalysts (particle size = 250-500 μm) were analysed sequentially, heating the individual reactors at 10 K min<sup>-1</sup> to 873 K in a mixture of H<sub>2</sub>/Ar = 5/95 flowing at 7 cm<sup>3</sup> STP min<sup>-1</sup> through each reactor. Hydrogen consumption and water formation were monitored by a quadrupole mass spectrometer (Pfeiffer Vacuum OmniStar 200). The following atomic mass units (AMUs) were analysed: 40 (Ar), 18 (H<sub>2</sub>O), and 2 (H<sub>2</sub>). The concentration of H<sub>2</sub> was determined from the respective AMU using the sensitivity factor determined by analysing a calibration gas mixture. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) investigations were performed using an aberration-corrected JEM-ARM200F microscope, operated at 200 kV and equipped with a JED-2300 energy-dispersive X-ray spectrometer (EDXS, JEOL) for elemental analysis. Samples were deposited on a holey carbon supported copper grid (mesh 300). Small angle X-ray scattering (SAXS) measurements were carried out in a Kratky-type instrument (SAXSess, Anton Paar, Austria) operated at 40 kV and 50 mA in slit collimation using a two-dimensional CCD detector. For determining the size of the Ru NPs in solution, SAXS data were analyzed using the total scattering intensity  $I(q)$  from a polydisperse system (eq. 1) as suggested in [O. Glatter, O. Kratky (Eds.) *Small angle X-ray scattering*, Academic Press, London, 1982]:

$$I(q) = \int D_n(R) m^2(R) P(q, R) dR \quad (1)$$

where  $R$  is the particle radius,  $D_n(R)$  is the particle size distribution function,  $m(R)$  is the integral over the excess scattering length density over the surrounding medium of a particle of size  $R$  (eq. 2),  $\Delta\rho$  is the particle contrast (difference between the scattering length of a particle and that of the matrix),  $P(q, R)$  is the normalized scattered intensity of a single, spherical particle of size  $R$  and is also called the shape factor (eq. 3). The scattering vector  $q$  is defined in terms of the scattering angle  $\theta$  and the wavelength  $\lambda$  of the irradiation (eq. 4).

$$m(R) = \frac{4\pi}{3} R^3 \Delta\rho \quad (2)$$

$$P(q, R) = \left( \frac{3[\sin(qR) - (qR)\cos(qR)]}{(qR)^3} \right)^2 \quad (3)$$

$$q = 4\pi\lambda^{-1} \sin \frac{\theta}{2} \quad (4)$$

The volume-weighted distribution function  $D_v(R)$  (eq. 5) was evaluated assuming a polydisperse system of spherical particles. Indirect

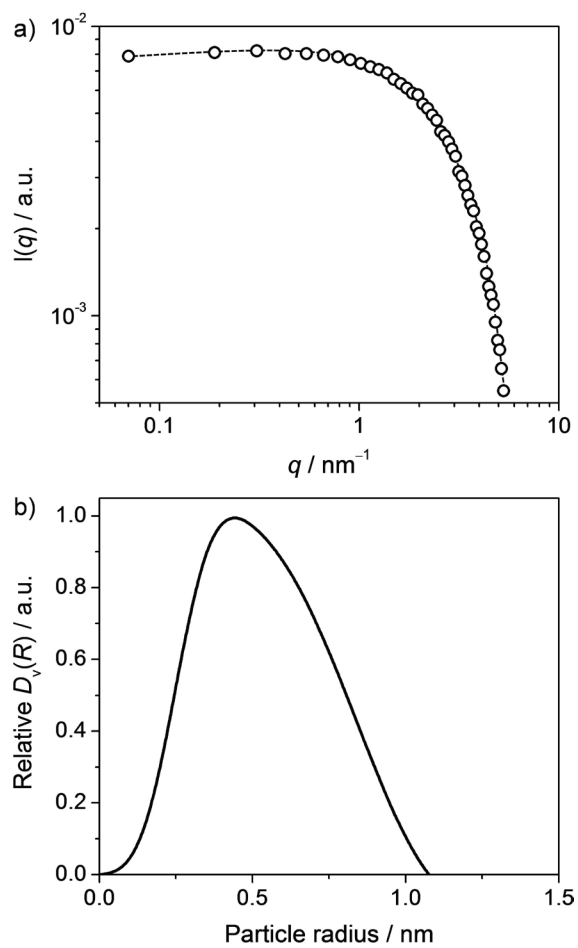
Fourier transformation (IFT) (program GIFT implemented in the PCG software package, version 2.02.05, University of Graz) was used to solve the integral eq. 1 with respect to the volume distribution function  $D_V(R)$ . The program takes into account the instrumental smearing and fits the experimental (smeared) scattering curves directly.

$$D_V(R) = D_n(R) \cdot R^3 \quad (5)$$

### 5 Catalytic testing

The gas-phase oxidation of hydrogen chloride was studied in a continuous-flow fixed-bed quartz micro-reactor (8 mm i.d.) at 1 bar. 0.25 g of catalyst (particle size = 0.4-0.6 mm) were loaded in the reactor and pre-treated in  $N_2$  at 623 K for 30 min. Thereafter, a total flow ( $F_T$ ) of  $166 \text{ cm}^3 \text{ STP min}^{-1}$  containing 10 vol.% HCl and 0-70 vol.%  $O_2$  balanced in  $N_2$  was fed to the reactor at bed temperatures ( $T_{\text{bed}}$ ) in the range of 543-653 K. The produced  $Cl_2$  was quantified by iodometric titration using a Mettler Toledo G20 Compact Titrator.

10 The percentage of HCl conversion was determined as  $X_{\text{HCl}} = (2 \times \text{mole } Cl_2 \text{ at the reactor outlet/mole HCl at the reactor inlet}) \times 100$ . The used catalysts were collected for characterisation after rapid cooling to room temperature in  $N_2$  flow.



**Fig. S1** (a) Scattering profile of Ru NPs in ethylene glycol solution as a function of the scattering vector  $q$ . Measured data points and curve simulation are represented by symbols and dashed line, respectively. (b) Corresponding volume-weighted particle size distribution ( $D_v(R)$ ).

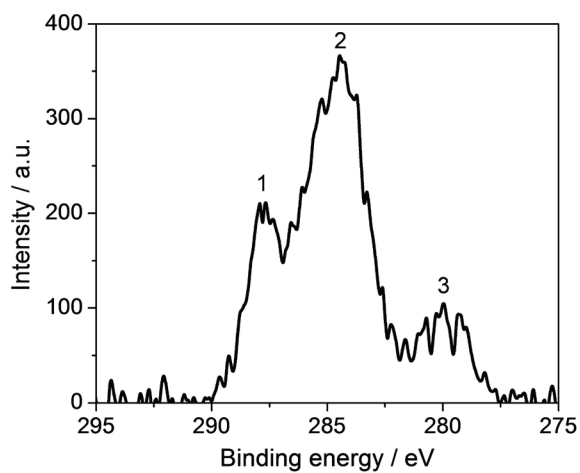
5

10

15

20

25

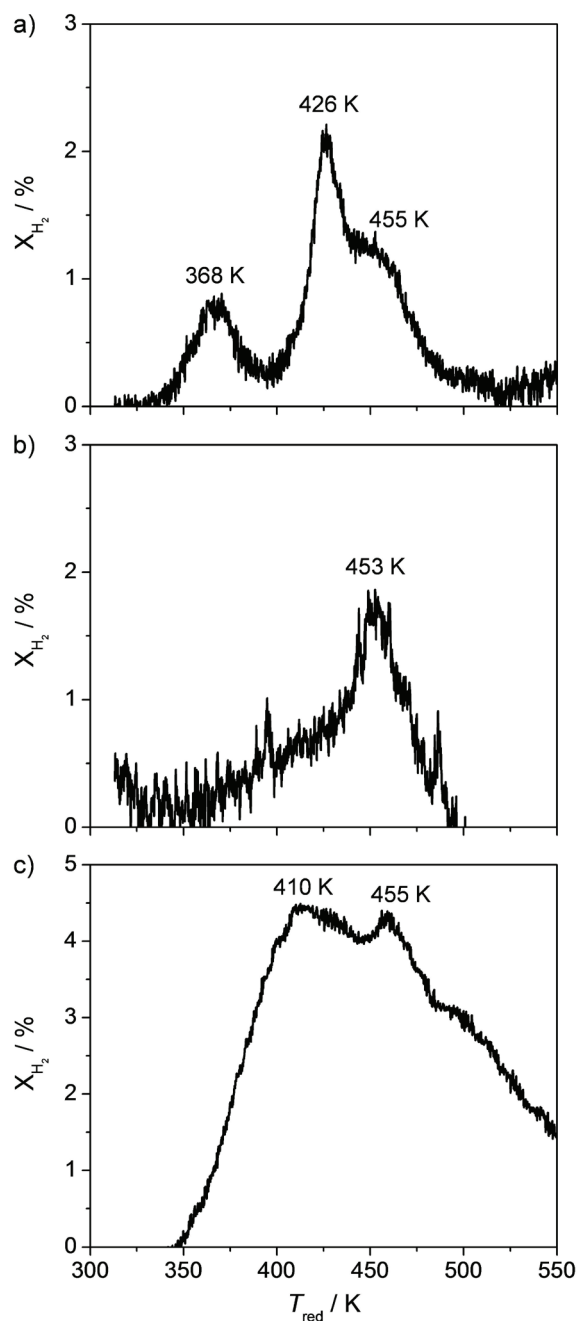


**Fig. S2** XPS spectrum of the as-prepared RuO<sub>2</sub>/TiO<sub>2</sub>-r-EG catalyst. Three main signals are present: (1) C 1s due to the presence of EG on the catalyst surface, (2) C 1s due to surface contamination upon exposure of the catalyst to air, and (3) Ru 3d indicating the presence of metallic ruthenium (279.8 eV is the binding energy value for metallic ruthenium according to the NIST database).

5

10

15



**Fig. S3** Hydrogen conversion during H<sub>2</sub>-TPR of selected catalysts used in HCl oxidation for 2 h at 623 K: RuO<sub>2</sub>/TiO<sub>2</sub>-r-EG (a), RuO<sub>2</sub>/TiO<sub>2</sub>-a-EG (b), and RuO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-EG (c).