Supporting information

Evidence of rutile-to-anatase photo-induced electron transfer in mixed-phase TiO₂ by solid-state NMR spectroscopy

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Experiments and Methods

Preparation of the TiO₂ samples

The anatase phase TiO_2 Hombikat UV-100 was provided by Sachtleben Chemie GmbH and the mixed-phase TiO_2 Degussa P25 (TiO_2 -P25) was provided by Evonik Degussa GmbH. The rutile phase was obtained through calcination of TiO_2 -P25 at 1023 K for 12 hours. All the samples were calcined in flowing air at 673 K for 6 h before use.

TiO₂-P25 was used as support and Me/TiO₂ (Me = Pd, Pt, Ir, Ag) materials with metal mass loadings of *ca*. 2% were prepared by so-called photo-deposition method. In a typical procedure for the preparation of Pd/TiO₂, a certain amount of PdCl₂ solution, 500 mg of TiO₂-P25 and 10 mL of methanol were added into a round-bottom quartz flask under vigorous stirring to form a slurry. The pH value of the slurry was adjusted to 11.0±0.2 using either 1M HCl or 1M NaOH aqueous solution and the slurry was then irradiated by 250 W high-pressure mercury light with the main wavelength of 365 nm for 6 h under the protection of flowing nitrogen. After irradiation, the solid particles were filtered, thoroughly washed, dried and reduced in hydrogen at 473 K for 2 h.

For comparison, Pd/TiO₂ with similiar mass loading of *ca*. 2 % was also prepared via wet impregnation method. A certain amount of PdCl₂ solution was added to 500 mg of TiO₂-P25 to get a 50 mL suspension, then the mixture was evaporated under stiring at constant temperature of 353 K. The as-obtained particles were carefully washed with deionized water, dried at ambient conditions. Afterwards, the sample

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was reduce in hydrogen at 473K for 2 h.

Characterization of TiO₂ samples

The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE powder diffractometer using Cu-K α radiation (λ = 0.1542 nm) at a scanning rate of 4°/min in the region of 2 θ = 10-80°.

Transmission electron microscopy (TEM) images were taken on a Philips Tecnai G^2 20 S-TWIN electron microscope at an acceleration voltage of 200 kV. A few drops of alcohol suspension containing the sample were placed on a carbon-coated copper grid, followed by evaporation at ambient temperature.

¹³C CP/MAS NMR investigations were carried out on a Bruker Avance III 400 WB spectrometer at resonance frequencies of 100.6 MHz, and with the sample spinning rate of 8 kHz using 4 mm MAS rotors. Cross-polarization (CP) MAS NMR spectra were recorded with the contact time of varying from 0.05 ms to 4 ms and the repetition time of 8 s. Before the measurements, the samples were first dehydrated at 673 K for 10 h under a pressure of less than10⁻² mbar to remove the surface physisorbed and hydrogen-bonded water and other impurities. ¹³C-enriched ethanol (CH₃¹³CH₂OH) was used as a probe molecule to investigated the chemisorption of ethanol at the surface sites of the different TiO₂ and Pd/TiO₂ materials. After dehydration, the samples were loaded with a certain amount of ¹³C-enriched ethanol on a vacuum line. Subsequently, the samples were transferred into the MAS NMR rotors inside a glove box under the protection of dry nitrogen.

Figures and Tables



Figure S1. XRD patterns of the pure anatase, rutile and mixed-

phase TiO₂-P25.



Figure S2. ¹³C CP/MAS NMR spectra of ethanol loaded on

dehydrated TiO₂-P25 and recorded with contact pulses varying





Figure S3. Surface modes of anatase and rutile.

Figure S4. Scheme for the preparation of TiO₂-supported metal nano-clusters by photo-

deposition.

The scheme for the preparation of TiO₂-supported metal nano-clusters prepared by photo-deposition processes is described in **Figure S4**.

$$TiO_{2} + hv \rightarrow TiO_{2} + h^{+} + e$$
$$Me^{n+}_{aq} \rightarrow Me^{n+}_{ads}$$
$$Me^{n+}_{ads} + n e^{-} \rightarrow Me^{-0}_{ads}$$
$$m Me^{-0}_{ads} \rightarrow Me_{m}$$

Under ultraviolet irradiation ($hv \ge Eg = 3.02 \text{ eV}$), electron-hole pairs are created on the surface of TiO₂. The metal ions with positive charges preferentially adsorb at electron rich areas of the TiO₂ surface via electrostatic interactions and are subsequently reduced by the photo-induced electrons to metal atoms. Meanwhile, the photo-induced holes are eliminated by reacting with the scavenger methanol. For metal modified TiO₂, the photo-induced electrons tend to accumulate on metal surface under irradiation, due to the higher work function of the metal (Pd, Pt, Ir and Ag) compared with TiO₂. Therefore, subsequent metal atoms targetedly deposit on the already-existing metal atoms and metal clusters are formed on the surface of TiO₂.



photo-deposition

wet-impregnation

Figure S5. TEM images of the 2%Pd/TiO₂-P25 samples prepared via photo-

deposition and wet-impregnation.







Chemical shift	Conten
	t
58 ppm	21.8 %
62 ppm	16.6 %
67 ppm	39.9 %
70 ppm	21.7 %
Chemical shift	Conten
	t
58 ppm	21.5 %
63 ppm	7.6 %
67 ppm	48.8 %
70 ppm	22.1 %
Chemical shift	Conten
	t
58 ppm	20.0 %
63 ppm	8.4 %
67 ppm	50.8 %
70 ppm	20.8 %

loaded on 2%Pt/TiO₂-P25, 2%Ir/TiO₂-P25, and 2%Ag/TiO₂-P25 samples prepared via photo-deposition. From top to bottom: experimental spectrum, simulated spectrum and deconvoluted components.