Spectroscopic Analysis of Proton Exchange during the Photocatalytic Decomposition of Aqueous Acetic Acid: An Isotopic Study on Product Distribution and Reaction Rate

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SI-1. Material Characterization

SI-1.1 XPS Spectrum

X-ray photoelectron spectroscopy (XPS) measurements were conducted in a PHI Versaprobe II Scanning ESCA Microprobe (Physical Electronics) equipped with a monochromatized Al Kα X-ray source (100 W) and an Ar ion gun. Data was evaluated with CasaXPS software.

![XPS Spectrum](image)

**Figure S1.** XPS spectrum recorded for Pt/TiO₂ prepared by an impregnation method.

XPS spectrum recorded for the Pt/TiO₂ particles exhibited a doublet signal at binding energy 4f \(7/2 = 70.1\) eV and \(5/2 = 73.2\) eV corresponding to the metallic Pt (i.e., Pt⁰) (Figure S1). This means that Pt NPs exist on the surface of TiO₂ in their Pt⁰ oxidation state\(^1\).
SI-1.2 TEM Micrographs

The TEM micrographs were taken by Transmission electron microscopy, model: Tecnai G2 F20 TMP (FEI) with acceleration voltage 200 kV.

Figure S2. TEM images of Pt/TiO$_2$ prepared by an impregnation method.

Figure S2 depicts the TEM micrographs obtained for Pt/TiO$_2$ photocatalyst. Here, brighter spherical structures represent the TiO$_2$ particles whereas darker spots correspond to the Pt nanoparticles (NPs) deposited on the surface of TiO$_2$. The particle size for TiO$_2$ was found to be 15 – 25 nm, while Pt NPs were observed in between 15 – 20 nm. It can also be seen in the TEM images, that the dispersion of Pt NPs is very uniform over the whole TiO$_2$ matrix (Figure S2). In high-resolution TEM micrographs, the crystal lattice is also quite visible for both Pt NPs and TiO$_2$ particles. Also, the interface between Pt NPs and TiO$_2$ particles is very obvious (marked with red circles) in the high-resolution TEM images.
SI-2. Photocatalytic Set-up

![Photocatalytic Set-up Diagram]

Figure S3: Schematic illustration of Photocatalytic Set-up.

SI-3. pH Adjustments of Suspension

The same Hg pH electrode was used for the adjustment of pH and pD for both water and deuterated solutions, according to the Gross-Butler-Purlee-theory expressed by the following relation (Eq. S1). The pH value of the suspension was found to play an important role in the overall reaction mechanism. So, pH 2 was found to be the best in a series of experiments for the determination of acetic acid reaction mechanism.

\[ pD = pH + 0.44 \]  

Eq. S1
Figure S4. $^1$H NMR spectra for reaction system (ii) CD$_3$COOD-H$_2$O, employing 1 wt% Pt TiO$_2$, photocatalyst concentration = 0.5 g L$^{-1}$, acetic acid concentration = 0.5 M, before illumination.
Figure S5. $^1$H NMR spectra for reaction system (v) CH$_3$COOH-D$_2$O, employing 1 wt% Pt TiO$_2$, photocatalyst concentration = 0.5 g L$^{-1}$, acetic acid concentration = 0.5 M, before illumination (a) Full spectrum, (b) Zoom image representing methyl group.
Figure S6. $^1$H NMR spectra for reaction system (vii) CD$_3$COOD-H$_2$O, employing bare TiO$_2$, photocatalyst concentration = 0.5 g L$^{-1}$, acetic acid concentration = 0.5 M, after 15 h illumination.

It can be seen in Figure S6 that NMR spectrum depicted only a peak corresponding to the H$_2$O signal. No other peak can be seen in the spectrum recorded from NMR spectroscopy for reaction system (vii) TiO$_2$-CD$_3$COOD-H$_2$O.
Figure S7. $^1$H NMR spectra for reaction system (viii) CH$_3$COOH-D$_2$O, employing bare TiO$_2$, photocatalyst concentration = 0.5 g L$^{-1}$, acetic acid concentration = 0.5 M, after 15 h illumination.

Figure S7 demonstrates the NMR spectrum obtained for reaction system (viii) TiO$_2$-CH$_3$COOH-D$_2$O. Here, a peak corresponding to the methyl (CH$_3$) group of acetic acid at the chemical shift 2 p.p.m is obvious. Other than this, a peak related to water (H$_2$O) signals can also be seen at about chemical shift 5 p.p.m. This peak might come from the residual protons of D$_2$O.
Figure S8. Absorption spectrum of suspended TiO$_2$ particles in water and irradiance of 30 mWcm$^2$ Xenon lamp in the range of 295-450 nm.
References
