

SUPPORTING INFORMATION

Selective Nitrate-to-Ammonia Transformation on Surface Defects of Titanium Dioxide Photocatalysts

Hiroaki Hirakawa,[†] Masaki Hashimoto,[†] Yasuhiro Shiraishi,^{*,†,‡} and Takayuki Hirai[†]

[†] Research Center for Solar Energy Chemistry, and Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka 560-8531, Japan

[‡] PRESTO, JST, Saitama 332-0012, Japan

E-mail: shiraish@cheng.es.osaka-u.ac.jp

CONTENTS

	page
Figure S1. XRD patterns of the catalysts.....	2
Figure S2. DRIFT spectra of nitrobenzene adsorbed onto TiO ₂	3
Figure S3. DRIFT spectra of pyridine adsorbed onto TiO ₂	3
Figure S4. ESR spectra of the reaction solutions with a Fe-DTCS probe.....	4
Table S1. Results for photocatalytic NO ₃ ⁻ reduction on metal-loaded catalysts.....	4

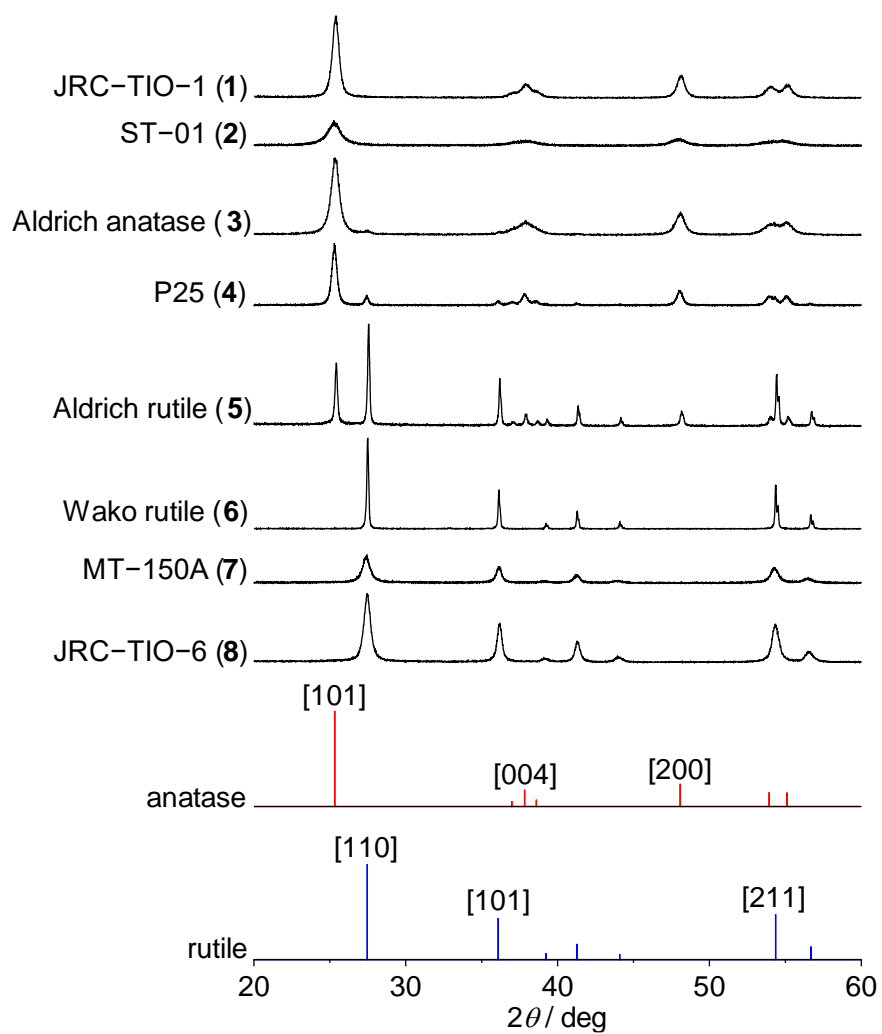


Figure S1. XRD patterns for respective TiO_2 particles, and standard patterns for anatase (JCPDS 21-1272) and rutile TiO_2 (JCPDS 21-1276). The number in parentheses denotes the sample number listed in Table 1 (manuscript).

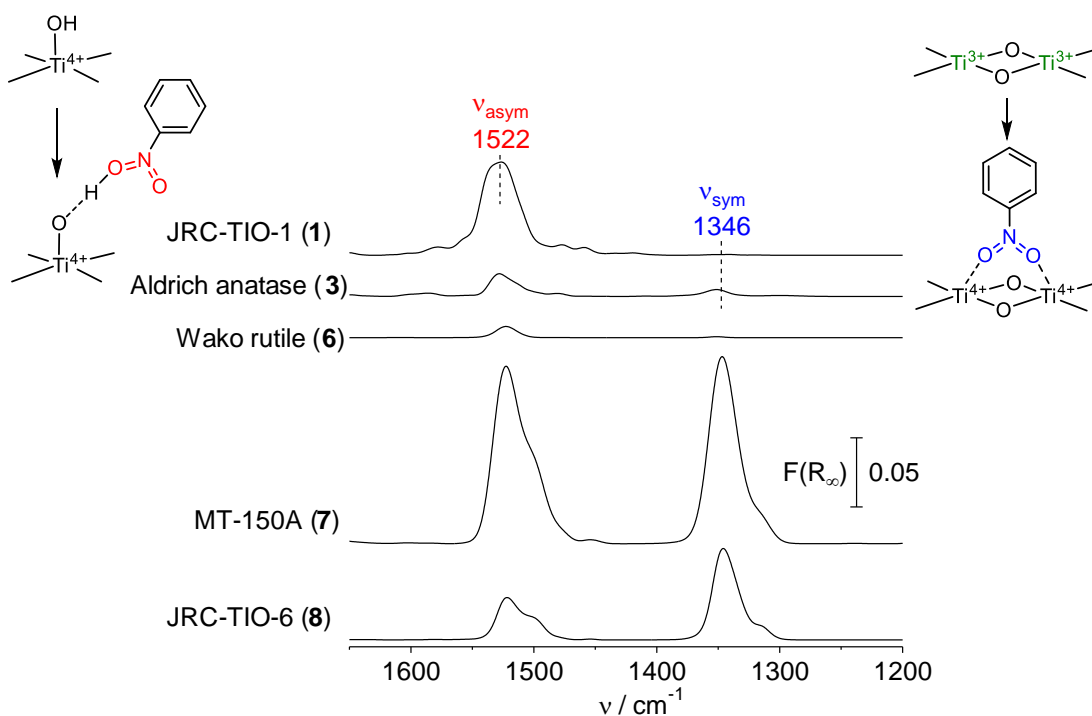


Figure S2. DRIFT spectra of nitrobenzene adsorbed onto the respective TiO_2 particles in the gas phase at 303 K. The spectra were measured as follows: TiO_2 (50 mg) were placed in a DR cell and evacuated (0.9 Pa) at 423 K for 3 h. Nitrobenzene (17 μmol) was introduced to the cell at 303 K and left for 1 h. The cell was then evacuated (0.9 Pa) for 1 h to remove the physically adsorbed nitrobenzene.

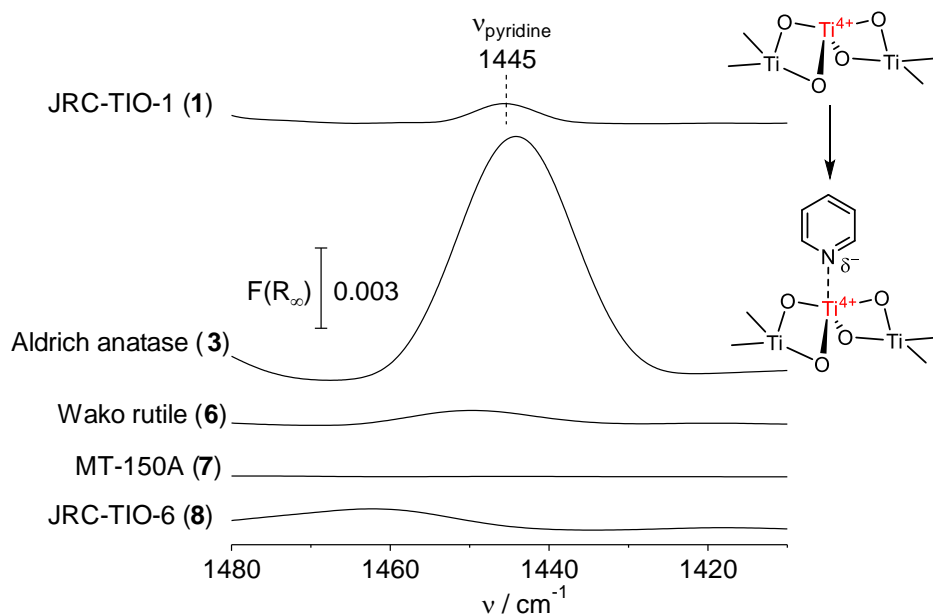


Figure S3. DRIFT spectra of pyridine adsorbed onto the respective TiO_2 particles in the gas phase at 303 K. The spectra were measured as follows: a mixture of TiO_2 (5 mg) and KBr (45 mg) were placed in a DR cell and evacuated (0.9 Pa) at 423 K for 3 h. Pyridine (21 μmol) was introduced to the cell at 303 K and left for 1 h. The cell was then evacuated (0.9 Pa) for 1 h to remove the physically adsorbed pyridine.

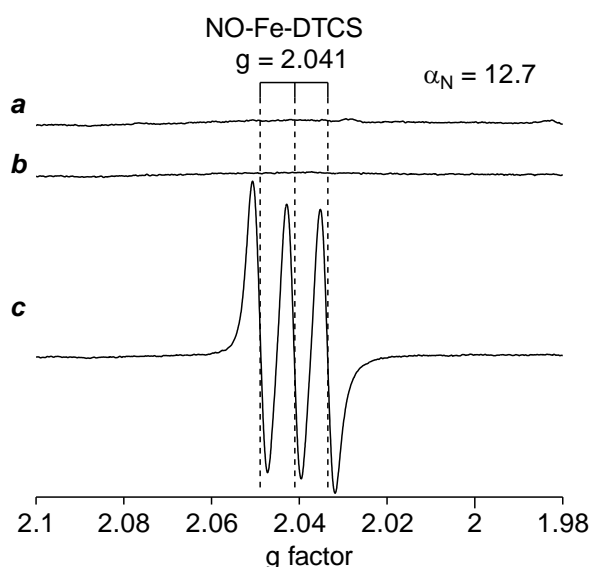


Figure S4. ESR spectra measured at 298 K for the solutions obtained by $\lambda > 300$ nm light irradiation of (a) JRC-TIO-1 (**1**) and (b) JRC-TIO-6 TiO₂ (**8**) (10 mg) in a 2-PrOH/water mixture (5 wt % 2-PrOH, 2 mL) with Fe-DTCS (20 μ mol) for 3 min. (c) ESR spectrum measured at 298 K for the solution obtained under NO gas bubbling through a 2-PrOH/water mixture (5 wt % 2-PrOH, 2 mL) with Fe-DTCS (20 μ mol) for 3 min.

Table S1. Results for photocatalytic NO₃[−] reduction on JRC-TIO-6 (**8**) loaded with various metal particles.^a

entry	catalyst	NO ₃ [−] conv. / %	amount / μ mol			NH ₃ (NH ₄ ⁺) select. / %
			N ₂	NH ₃ (NH ₄ ⁺)	H ₂	
1	JRC-TIO-6 (8)	79	<0.1	38.4	<0.1	97
2	Pt/JRC-TIO-6 (8) ^b	3	<0.1	1.3	150.1	96
3	Au/JRC-TIO-6 (8) ^b	66	3.8	25.3	62.6	76
4	Ag/JRC-TIO-6 (8) ^b	89	4.5	25.5	2.3	57
5	Cu/JRC-TIO-6 (8) ^b	74	1.6	34.1	5.3	92
6	CuPd/JRC-TIO-6 (8) ^c	44	1.7	18.6	255.9	85

^a Reaction conditions: KNO₃ (50 μ mol), water (50 mL), HCOOH (0.5 wt %, 5.4 mmol), catalyst (100 mg), Ar (1 atm), temperature (303 K), $\lambda > 300$ nm irradiation by a 2 kW Xe lamp (light intensity at 300–450 nm, 30 W m^{−2}), time (24 h). ^b Prepared by impregnation of metal precursors followed by H₂ reduction, where the metal loading [= M/TiO₂ × 100] is 0.37 wt %. ^c Prepared with a polyvinylpyrrolidone (PVP) template using NaBH₄ as a reductant, where the alloy particles consist of 0.14 wt % Cu and 0.23 wt % Pd.