Supporting Information

Enhanced Photocatalytic Efficiency of A Least Active Ag–TiO$_2$ by Amine Adsorption

Sajid Ismailkhan Mogal, Dinesh Ochhavlal Shah, Tulsi Mukherjee, Thoudinja Shripathi, and Manish Kumar Mishra

$^1$Shah-Schulman Center for Surface Science and Nanotechnology, Dharmsinh Desai University, Nadiad 387 001, Gujarat, India

$^2$UGC-DAE Consortium for Scientific Research (CSR), University Campus, Khandwa Road, Indore 452 001 (MP), India

$^3$Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat, India

E-mail: manishorgch@gmail.com
XRD patterns of TiO$_2$ and Ag-TiO$_2$ catalysts and measurement of crystallite size

All the catalysts were having purely anatase phase showing the characteristic peaks at 25.5, 37.5, 47.8, 53.8 and 54.9° 2θ for (1 0 1), (1 1 2), (2 0 0), (1 0 5), and (2 1 1) reflections of anatase phase, respectively, in XRD patterns (Figure S1). However, the XRD patterns of Ag–TiO$_2$ do not show any diffraction peaks corresponding to silver species (oxide/ silver metal) in the samples as they may be too less as well as small in size to be detected.

\section*{Figure S1.} XRD patterns of bare TiO$_2$ and Ag–TiO$_2$ catalysts.

The crystallite size of anatase phase was determined from the peak of maximum intensity of the phase using the Scherrer formula with a shape factor (K) of 0.9 as given below,

\[
\text{Crystallite size} = \frac{K\lambda}{W\cos \theta},
\]

where \( W = W_b - W_s \); \( W_b \) is the broadened profile width of experimental sample, and \( W_s \) is the standard profile width of the reference silicon sample.
Thermal analysis of spent catalysts

Figure S2. DTG profiles of spent catalysts.

Thermal analysis of benzyl amine (BA) adsorbed catalysts

Figure S3. TGA profiles of (i) BA–adsorbed TiO₂ and (ii) BA–adsorbed Ag(3.5)T.
Table S1. Ti 2p and O 1s XPS peaks for bare TiO$_2$ and Ag(3.5)T.

| Catalyst   | Ti 2p peak(s) | O 1s peak(s) |
|------------|---------------|--------------|
|            | Position (eV) | Assignments  | Position (eV) | Assignments                             |
| Bare TiO$_2$ | 458.60        | Ti$^{IV}$    | 529.37        | O atoms of Ti-O-Ti$^a$                   |
|            |               |              | 530.24        | O atoms of titanols$^a$                  |
| Ag(3.5)T   | 459.30        | Ti$^{IV}$    | 529.74        | O atoms of Ti-O-Ti                       |
|            |               |              | 531.28        | O atoms of titanols complexing AgNPs     |

$^a$The oxygen atoms (Ti-O-Ti) in TiO$_2$ has lower binding energy than surface hydroxyl/ titanols. $^2$
Characterization of surface adsorbed BA species in BA-Ag(3.5)T catalyst by XPS analysis

**Table S2.** N 1s XPS peak details for BA-Ag(3.5)T and BA-TiO₂.

| Catalyst | N 1s peak(s) | Position (eV) | Assignments |
|----------|--------------|---------------|--------------|
| BA-Ag(3.5)T | 400.1 | N atoms of quaternary ammonium group present in adsorbed BA species (denoted as Nᵢ in species i, ii and iii) |
|          | 399.2 | N atoms of adsorbed BA species having hydrogen bonding between –NH₂ group and titanols (denoted as Nᵢ in species iv) |
|          | 397.9 | N atoms of adsorbed BA species as an imine species (denoted as Nᵢ in species v) |
| BA-TiO₂  | 400.9 | N atoms of quaternary ammonium group present in adsorbed BA species (denoted as Nᵢ in species ii and iii) |
|          | 398.9 | N atoms of adsorbed BA species having hydrogen bonding between –NH₂ group and titanols (denoted as Nᵢ in species iv) |
Figure S4. N 1s XPS spectra of BA-TiO$_2$ and BA-Ag(3.5)T.

The three peaks in N 1s XPS of BA-Ag(3.5)T (Table S2 and Figure S4) reveals the presence of three types of adsorbed BA species:

1) The XPS peak at 400.1 eV (Table S2 and Figure S4) can be ascribed to the nitrogen ($N^a$) of a quaternary ammonium group present in adsorbed BA species$^{3,4}$ such as BA adsorbed on AgNPs (species i), BA adsorbed on Ti-sites on TiO$_2$ surface (species ii) and protonated BA on titanols (species iii). However, the lower binding energy (B.E.) of $N^a$ (400.1 eV) for BA-Ag(3.5)T as compared to BA-TiO$_2$ (400.9 eV, which represents species ii and iii) indicates the predominant existence of species i, i.e., adsorbed BA on AgNPs, in BA-Ag(3.5)T. The lower B.E. of $N^a$ for BA-Ag(3.5)T is possibly because of comparatively weaker interaction of BA (through N) with Ag$^+$ sites than Ti$^{4+}$ sites. The following spectral changes occurred in 3dAg XPS of Ag(3.5)T after BA adsorption (Figure 6b in manuscript) confirms the presence of adsorbed BA on AgNPs (species i) in significant amount showing: (1) disappearance of the peak at 365.4 eV for interfacial Ag$^0$ atoms having high electron density, and (2) appearance of a new peak at 367.5 eV for Ag$^+$ species (where BA molecules get adsorbed on AgNPs). Furthermore, the increasing adsorption capacity of catalysts with silver content (Figure 5 in manuscript) also
suggests that the silver or AgNPs are the major sites for BA adsorption in Ag(3.5)T. The decrease in B.E. of Ti\textsuperscript{IV} (Table S3 and Figure S5) and the red shifted TiO\textsubscript{2} absorption edge in DRS/ reduced band gap of TiO\textsubscript{2} (see Figure 8a in manuscript) reveal the presence of adsorbed BA species on Ti\textsuperscript{IV} sites (as species ii) of TiO\textsubscript{2} surface in BA-Ag(3.5)T. Similarly, the presence of species iii and iv in BA-Ag(3.5)T is also evident from O 1s XPS results (Table S4 and Figure S6). The titanols in Ag(3.5)T are involved in complexation of AgNPs at interface, which are possibly made free due to nucleophilic attack of BA (for adsorption; Scheme S1) on AgNPs sites and thus the free titanols will be available for BA adsorption in above two modes giving two B.E.s representing O\textsuperscript{a} and O\textsuperscript{b} (for species iii and iv; Table S4).

SchemeS1. Adsorption of BA over an AgNP in Ag(3.5)T catalyst.

In Ag(3.5)T, the BA molecules can be adsorbed on AgNPs-TiO\textsubscript{2} interfacial Ag\textsuperscript{0} atoms, which are complexed with titanols. The –OH groups complexing interfacial Ag\textsuperscript{0} atoms can be replaced by amine group of BA (more nucleophilic than –OH group) by ligand substitution mechanism. In addition, the BA molecules are also adsorbed on the other parts of AgNPs by creating Ag\textsuperscript{+} sites,
which is evident from the significantly higher proportion of Ag\(^+\) as compared to Ag\(^0\) (see Figure 6b in manuscript) showing the conversion of some amount of Ag\(^0\) into Ag\(^+\).

Table S3. Ti 2p XPS peak details for different catalysts.

| Sample       | Ti 2p peak(s) | Assignments |
|--------------|---------------|--------------|
| TiO\(_2\)    | 458.60        | Ti\(^{IV}\)  |
| Ag(3.5)T     | 459.30        | Ti\(^{IV}\)  |
| BA-TiO\(_2\) | 458.08        | Ti\(^{IV}\)  |
| BA-Ag(3.5)T  | 458.35        | Ti\(^{IV}\)  |
**Figure S5.** Ti 2p XPS of fresh (i) TiO$_2$, (ii) Ag(3.5)T, (iii) BA-TiO$_2$ and (iv) BA-Ag(3.5)T.

**Table S4.** O 1s XPS peak details for different catalysts.

| Catalyst       | O 1s peak(s) | Position (eV) | Assignments                                                                 |
|----------------|--------------|---------------|-----------------------------------------------------------------------------|
| Bare TiO$_2$   |              | 529.37        | O atoms of Ti-O-Ti (denoted as O$^T$)                                       |
|                |              | 530.24        | O atoms of titanols (denoted as O$^{OH}$)                                   |
| Ag(3.5)T       |              | 529.74        | O atoms of Ti-O-Ti (denoted as O$^T$)                                       |
|                |              | 531.28        | O atoms of titanols complexing AgNPs (denoted as O$^{Ag}$)                  |
| BA-TiO$_2$     | O atoms of Ti-O-Ti (denoted as O$^T$) | 528.93        |                                                                             |
|                | O atoms of titanols protonating BA (denoted as O$^{a}$ in iii; O$^{a}$ atoms will be electron rich and have lower B.E. as compared to O$^{OH}$ of pristine TiO$_2$) | 529.68        |                                                                             |
|                | O atoms of titanols having hydrogen bonding with –NH$_2$ of BA (denoted as O$^{b}$ in iv; O$^{b}$ will be electron deficient and have higher B.E. as compared to O$^{OH}$ of pristine TiO$_2$) | 530.95        |                                                                             |
| BA-Ag(3.5)T    | O atoms of Ti-O-Ti (O$^T$) | 529.14        |                                                                             |
|                | O atoms of titanols protonating BA (O$^{a}$) | 529.99        |                                                                             |
|                | O of titanols having hydrogen bonding with –NH$_2$ of BA (O$^{b}$) | 531.64        |                                                                             |
2) **The XPS peak at 399.2 eV (Table S2 and Figure S4)** denotes the nitrogen (N⁰) of adsorbed BA species having hydrogen bonding with titanols (species iv). The B.E. values of 531.34 eV and 530.95 eV can be ascribed to O of titanols engaged in hydrogen bonding with BA molecules (iv) in BA-Ag(3.5)T and BA-TiO₂, respectively. The N 1s XPS spectrum of BA-TiO₂ (Figure S4) shows comparatively higher proportion of iv than other species revealing that the BA are adsorbed in higher proportion by hydrogen bonding over surface titanols in bare TiO₂ as compared to Ag(3.5)T.

3) **The XPS peak at 397.9 eV (Table S2 and Figure S4)** shows the lower binding energy of nitrogen or electron rich nitrogen, which can be assigned to the nitrogen (N⁰) of adsorbed BA
species existing as an imine species ($\nu$), which was also evident from FTIR studies. In FTIR spectrum of BA-Ag(3.5)T sample (Figure S7), the peaks at 1644 cm$^{-1}$ and 1471 cm$^{-1}$ are C=N stretching and C-H bending frequencies, respectively, of imine group representing the presence of the imine species formed after adsorption of BA. The characteristic peaks of BA at 1603 and 1495 cm$^{-1}$ for aromatic ring, 1583 cm$^{-1}$ for N-H bending and 1452 cm$^{-1}$ for benzylic C-H bending are presented in FTIR spectrum of neat BA (Figure S7). The group of bands (which are merged together; shown in circle) in FTIR spectrum of BA-Ag(3.5)T, are shifted bands of aromatic group (1603 cm$^{-1}$ and 1495 cm$^{-1}$) and $\delta_{N-H}$ (1583 cm$^{-1}$; due to $\ddots$N(H)H….OH.Ti≡ hydrogen bonding), and the bands for $\ddots$NH$_3^+$ and $\ddots$NH$_2^+$-Ag (due to protonation and coordination of amine group). There was no evidence of surface adsorbed imine species in BA-TiO$_2$ from XPS and FTIR. The imine species formation in BA-Ag(3.5)-T sample is expected to occur at silver-titania interface due to the interaction of the hydrogen atoms of amine groups (NH$_2$) with titanols (as basic sites) and the interaction of benzylic hydrogen atoms (-CH$_2$-) with silver.

![Figure S7. FTIR spectra](image-url)
of (i) benzyl amine (neat; ATR) and (ii) pristine and benzyl amine adsorbed catalysts.

**Effect of solvent volume in photocatalytic dehydrogenation of benzyl alcohol to benzaldehyde using BA-Ag(3.5)T**

The volume of solvent (ACN) greatly influenced the photocatalytic dehydrogenation reaction of benzyl alcohol to benzaldehyde using BA-Ag(3.5)T catalyst: on increasing the solvent volume from 5 mL to 14 mL, there was gradual increase in conversion giving highest 88% conversion (in UV light), which slightly decreased at 15 mL solvent volume. The increase in conversion with increase in solvent volume can be attributed to better dispersion of catalyst particles providing better accessibility of active sites by reactant molecules and better light penetration in the reaction mass at large volume of the solvent.

**Figure S8.** Variation in conversion of benzyl alcohol in BA-Ag(3.5)T catalyzed dehydrogenation of benzyl alcohol at different acetonitrile (solvent) volumes [Reaction
condition: 93 µmol benzyl alcohol, 10 mg catalyst, N₂ atmosphere, UV light (wavelength: 365 nm), 6 h; selectivity of imine: 100%].

References

1. Mogal, S. I.; Gandhi, V. G.; Mishra, M. K.; Tripathi, S.; Shripathi, T.; Joshi, P. A.; Shah, D. O. Single-Step Synthesis of Silver-Doped Titanium Dioxide: Influence of Silver on Structural, Textural, and Photocatalytic Properties. *Ind. Eng. Chem. Res.* 2014, 53, 5749–5758.

2. Ohtsu, N.; Masahashi, N.; Mizukoshi, Y.; Wagatsuma, K. Hydrocarbon Decomposition on a Hydrophilic TiO₂ Surface by UV Irradiation: Spectral and Quantitative Analysis Using in-Situ XPS Technique. *Langmuir* 2009, 25, 11586–11591.

3. Farfan-Arribas, E.; Madix, R. J. Characterization of the Acid–Base Properties of the TiO₂(110) Surface by Adsorption of Amines. *J. Phys. Chem. B* 2003, 107, 3225–3233.

4. Nakayama, N.; Hayashi, T. Preparation of TiO₂ nanoparticles surface-modified by both carboxylic acid and amine: Dispersibility and stabilization in organic solvents. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 2008, 317, 543–550.

5. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, John Wiley & Sons Inc., Hoboken, NJ, 1991.

6. Tayade, K. N.; Mishra, M. Catalytic activity of MCM-41 and Al grafted MCM-41 for oxidative self and cross coupling of amines. *J. Mol. Catal. A: Chem.* 2014, 382, 114–125.