Impact of Oxygen Vacancy on the Photocatalytic Selective Hydrogenation of 3-Nitrostyrene via Calcination of TiO₂

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Abstract. In this work, P25-TiO₂ was treated by calcination in air at difference temperature (600-900°C) for 5h. Treated catalysts were tested in photocatalytic selective hydrogenation of 3-nitrostyrene (3-NS) to 3-vinylaniline (3-VA). The properties of treated catalysts were characterized by using XRD, XPS, and UV-Vis spectroscopy. 3-vinylaniline and acetone were produced from photocatalytic (λ > 300nm) selective hydrogenation reaction of 3-nitrostyrene in 2-propanol and suspension with P25-TiO₂. The Ti³⁺ at locate with oxygen defect, which at below conduction band were acted as active site for trapped electron to conduction band. These effects leading to excess oxygen defect caused low activity due to recombination center. An optimal calcination temperature was 700°C ascribed to the enhancement of high conversion (71%) with 100% 3-VA selectivity due to optimal oxygen vacancies.

1. Introduction

Aniline is organic molecules and fine chemical, in which important intermediate for the synthesis of pharmaceutical, polymers, and herbicides. Functionalized aniline is generally produced by hydrogenation of nitroaromatic [1, 2]. The most catalyst hydrogenation for nitroaromatic compounds of the other reducible group (e.g. vinyl group and carbonyl group) in active with oxides catalyst or noble metal oxides catalyst and presence with molecular hydrogen (H₂) [1]. For the alternative produce to aniline from transformation of nitroaromatic is photocatalytic process include photooxidation and photoreduction without hydrogen gas. This process produces 3-vinylaniline from 3-nitrostyrene by photoreduction [1, 2]. Photocatalytic hydrogenation on semiconductor particles has several unique comparing with catalytic hydrogenation on metals or homogeneous catalysis using metal complexes. It can be defined as a light-driven reaction at solid/liquid or solid/gas interface [3]. Titanium dioxide (TiO₂) has three common polymorphic forms such as anatase, rutile, brookite [4]. TiO₂ was activated by irradiation by ultraviolet (UV) light, in which leads to enhance for selective hydrogenation of 3-NS. TiO₂ photocatalytic has widely been used in many applications such as degradation of pollutants, water splitting, and selective transformation of reactant to targeted products [5]. Shiraishi et al. [1] studied the photocatalytic selective hydrogenation of nitroaromatics on TiO₂ at room temperature and atmospheric pressure leads to the high yield of 3-VA, furthermore, noble metal dopants (Pt, Pd, Ag,
Au) showed much lower yield due to coverage of active site and suppression of nitroaromatic adsorption. Imamura et al. [2] studied the selective photocatalytic hydrogenation of 3-NS and found that the other sites products including 3-nitroethybenzene (3-ENB) and 3-aminoethylbenzene (3-EA) were not formed. The high yield of 3-VA demonstrated that neither reaction benzene ring reduction of vinyl group nor re-oxidation of the amino group of 3-VA occurred in the system, however, stoichiometry generate electron and hole were selectively used for only reduction 3-NS to 3-VA and oxidation was produced ketone group from alcohol [2].

In this work, the catalytic performance of P25-TiO₂ calcination at difference temperature in photocatalytic selective hydrogenation of 3-NS were investigated. The physiochemical properties of treated catalysts were also determined by XRD, XPS, UV-Vis.

For mechanism photocatalytic hydrogenation selective 3-NS, when TiO₂ was irradiated by UV light, charge separation occurs formed positive hole in the valence band and formed electrons in conduction band [6]. This reactions P25-TiO₂ suspended in alcohol solvents as a hydrogen source containing with nitroaromatic under inert gas atmosphere and P25-TiO₂ (anatase 83% rutile 17%) used for semiconductor and non-metal dopant. The positive hole oxidize with alcohol and formed oxidation produce ketone and protons and nitroaromatic reduced with electrons and protons formed reduction produce aniline [1, 2].

2. Experimental

2.1. Catalyst preparation
Commercial Degussa P25-TiO₂ was used as the catalyst 2g then P25-TiO₂ was transferred into the crucible and followed by the calcination at various temperatures (600, 700, 800, 900°C) in a muffle furnace for 5h.

2.2. Photocatalytic test
The mixture 200micromoles of 3-nitrostyrene, 20ml of isopropanol and 0.2g of catalyst was transferred into 75ml pyrex glass tube reactor. The mixture was sonicated for 5min then the solution was purged with N₂ for 5min. The pyrex glass tube containing substrate, solvent and catalyst were photoirradiated under mercury lamp Philip 500w (λ > 300nm) for 6h with magnetic stirrer. After that the reaction catalyst was removed by filtration and the resulting products was analyzed by GC-FID (Shimadzu with Rtx®5 columns and Shimadzu DB1-wax columns).

3. Results and discussion

3.1. Characterization of P25-TiO₂ catalysts after calcination at difference temperature

3.1.1. X-ray diffraction (XRD)
The XRD patterns of P25-TiO₂ were treated with difference calcination temperature are shown in Figure 1. The P25-TiO₂ catalyst exhibited the characteristic peaks for anatase (101) phase at 2θ degrees = 25.3° and rutile (110) phase at 2θ degrees = 27.4° [7]. In this work, P25-TiO₂ was treated at calcination temperature range of 600-900°C for 5h. P25-TiO₂ including both anatase and rutile phases. Calcination at 600°C the peaks of anatase decreased slightly along with increased rutile. Moreover, higher temperature calcination leads to the rapid increased rutile phase and crystallite size [8, 9]. P25-TiO₂ calcination at 700°C, peaks of anatase phase component decreased rapidly and 77% of rutile phase was formed. Anatase phase was decreased and lastly disappeared after calcination at 800 and 900°C. The calcination temperature clearly influenced the phase composition and crystallization. It is reasonable to suggest that high temperature calcination leads to phase transformation anatase to rutile [8, 9]. Therefore, phase transformation is associated with crystal growth. Table 1 shows the phase composition and crystallite size of P25-TiO₂ calcination at temperature range of 600-900°C.
Figure 1. XRD patterns of P25-TiO₂ samples treated with difference calcination temperature.

Table 1. Phase composition and crystallite size of P25-TiO₂ calcination difference temperature.

| Sample            | %Anatase | %Rutile | Crystallite size Anatase (101) (nm) |
|-------------------|----------|---------|------------------------------------|
| P25   | 83       | 17      | 23                                 |
| P25-600-air       | 73       | 27      | 29                                 |
| P25-700-air       | 23       | 77      | 43                                 |
| P25-800-air       | -        | 100     | n/a                                |
| P25-900-air       | -        | 100     | n/a                                |

3.1.2. X-ray photoelectron (XPS)

XPS was used for determine and analyze the surface chemistry elemental composition, chemical state of the TiO₂ [10]. The deconvolution peaks of Ti 2p core levels of pure TiO₂ was fitted with four peaks consistent with titanium dioxide (Ti⁴⁺) and titanium sub oxide (Ti³⁺) are shown in Figure 2 [10].
However, TiO$_2$ having typical Ti 2p binding energies both Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$. At peak 458.5 eV and 464.5eV are associated with the Ti$^{4+}$ of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ valence state respectively [10-12]. Titanium sub oxide has two peaks at 457.7 and 463.0eV are associated Ti$^{3+}$ of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ valence state respectively, which corresponding with oxygen vacancies (O$_V$) defect in the system [11, 14]. For deconvolution peaks of Ti 2p core levels with Gaussian fitting are shown in Figure 2 including both Ti 2p$_{3/2}$ and Ti2p$_{1/2}$.

![Figure 3. XPS Ti 2p region spectra with difference temperature calcination of P25-TiO$_2$ samples.](image)

The relative concentration Ti$^{3+}$ of P25-TiO$_2$ was increased when the high calcination temperature, the concentration of surface Ti$^{4+}$ was reduced along with a loss of oxygen from the surface TiO$_2$, Ti$^{4+}$ ions receive electrons from lattice oxygen, which are removed from stoichiometric TiO$_2$ are shown in Figure 3 [13]. Meanwhile, the concentration Ti$^{3+}$ was decreased after calcination at 900°C due to more energy was supplied electron became very weak due to the phase transition reaction from anatase to rutile [13].

![Figure 4. XPS O1s region spectra with deconvolution peaks with Gaussian fitting curve of P25-TiO$_2$ samples.](image)
The deconvolution peaks of O1s core levels of P25-TiO₂ are shown in Figure 4. It showed two main peaks centered at 529.80 and 531.30 eV, which are assigned to Ti⁴⁺ and Ti³⁺ - oxygen vacancies sites, respectively [11-12, 14]. In addition P25-TiO₂ was calcination at high temperature, the peak at 529.80 was reduced due to broken Ti-O-Ti, then oxygen vacancies was formed and corresponding with the calcination in oxygen deficient environmental are shown in Figure 5 [12].

![Figure 5. XPS O1s region spectra with difference temperature calcination of P25-TiO₂ samples.](image)

3.1.3. UV-Visible spectroscopy (UV-Vis)
The influences of calcination temperature on the light absorption were investigated by UV-Vis spectroscopy. The UV-Vis spectra of P25-TiO₂ calcination at difference temperatures are shown in Figure 6. Increasing of calcination temperature leads to the adsorption of visible wavelength, which could be ascribed to the absorption of light caused by excitation of electrons from valence band to conduction band. The difference of adsorption wavelength was changed due to change of crystallite size and phase structure [8].

![Figure 6. UV-Vis wavelength absorption of P25-TiO₂ samples with difference temperature calcination.](image)
The adsorption edges wavelength after calcination at 600°C indicated the decrease band gap energy as shown in Figure 7. The band gap energy can be determined from a plot of \((h\nu\alpha)^{1/2}\) versus photon energy \((h\nu)\). Calcination of P25-TiO\(_2\) at high temperature leads to decrease of band gap energy because the increase of crystallite size results in the decrease of band gap. On the other hand, after calcination at 600°C might be a result of phase transformation from anatase to rutile [8].

![Figure 7. Band gap that plot between \((h\nu\alpha)^{1/2}\) versus photon energy of P25-TiO\(_2\) with difference calcination temperature.](image)

**Table 2.** UV-Vis results and band gap energy of all catalysts.

| Sample          | Wavelength (nm) | Band gap (eV) |
|-----------------|-----------------|---------------|
| P25             | 392             | 3.18          |
| P25-600-air     | 405             | 3.14          |
| P25-700-air     | 416             | 3.05          |
| P25-800-air     | 417             | 3.01          |
| P25-900-air     | 418             | 2.98          |

The adsorption edges wavelength and band gap were shown in Table 2. The adsorption edge wavelength were increased due to phase transition anatase to rutile. Furthermore band gap were decreased due to increasing of crystallite size.

### 3.2. Photocatalytic activity

The photocatalytic activity of the P25-TiO\(_2\) after calcination at difference temperature was carried out by photocatalytic selective hydrogenation 3-NS, then photocatalytic (\(\lambda \geq 300\text{nm}\)) irradiated 6h selective hydrogenation reaction of 3-nitrostyrene 200micromoles in 2-propanol 20ml and suspension with P25-TiO\(_2\) 0.2g.

\[
\text{NO}_2\text{C}_6\text{H}_4 + 3(\text{CH}_3)_2\text{CHOH} \xrightarrow{\text{Catalyst 0.2g}} \text{NH}_2\text{C}_6\text{H}_4 + 3(\text{CH}_3)_2\text{CO} + \text{H}_2\text{O}
\]
The %conversion 3-NS and %selective 3-VA are shown in Table 3, which show the catalytic performance of P25-TiO$_2$ calcination at difference temperature. P25-TiO$_2$ calcination at 700°C shows the highest conversion 3-NS with nearly 100% 3-VA selectivity. The enhancement of photocatalytic activity can be attributed to the decreasing of band gap energy, including of oxygen vacancies contents and suitable phase components. It is well known that mixture of anatase and rutile phase have efficiency photoactivity [8]. It also reported that in photocatalytic hydrogenation selective 3-NS the surface Ti$^{3+}$ atoms of rutile TiO$_2$ behaved as the absorption site for nitroaromatic trapping for photoformed at conduction band [1, 2]. In our present work, P25-TiO$_2$ exhibit insufficient photoactivity 3-NS, so improvement photoactivity the calcination at high temperature leads to transition of morphology, band gap, oxygen vacancy and phase components of P25-TiO$_2$ results in higher photoactivity. Moreover, P25-TiO$_2$ calcination at 700°C with relative mixed phase ratio (rutile 77%, anatase 23%) exhibit highest photoactivity due to the including of oxygen vacancy. On the other hand, P25-TiO$_2$ calcination above 800°C leads to excess oxygen vacancy might be caused as the recombination center due to un-localized below at conduction band, which blocked the electron transferring to conduction band [9]. On the other hand, mixture of anatase and rutile phase, moreover increasing rutile content attributed to enhancement photoactivity due to optimal oxygen vacancies leads to inhibit recombination results in higher photoactivity due to inhibit recombination electron-hole. Thus both oxygen vacancy and interface between anatase and rutile has a positive role play photocatalytic [10].

### Table 3. Results of photocatalytic hydrogenation selective 3-NS over difference temperature calcination P25-TiO$_2$ by UV light irradiated 6h.

| Sample        | %Conversion of 3-NS | %Selectivity to 3-VA |
|--------------|---------------------|----------------------|
| P25          | 45.4                | 96.7                 |
| P25-600-air   | 43.1                | 100                  |
| P25-700-air   | 70.9                | 100                  |
| P25-800-air   | 57.8                | 100                  |
| P25-900-air   | 51.5                | 100                  |

4. Conclusion
Calcination treatment of P25-TiO$_2$ influence on microstructure such as crystallite size, wavelength absorption, rutile phase content, oxygen vacancy sites and photocatalytic activity. P25-TiO$_2$ treated at optimal calcination temperature at 700°C exhibit the highest photoactivity due to the including of oxygen vacancy, Ti$^{3+}$ sites and interface between anatase and rutile, which improve the nitroaromatic trapping and retarded electron-hole recombination process. However, excess oxygen vacancy leads to recombination center results in the decreasing of photocatalytic activity.

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