Enhancement of Photocatalytic Oxidation of Glucose to Value-Added Chemicals on TiO$_2$ Photocatalysts by A Zeolite (Type Y) Support and Metal Loading

Kamonchanok Roongraung 1,2, Surawut Chuangchote 3,4,*, and Navadol Laosiripojana 1,2

1 The Joint Graduate School of Energy and Environment, King Mongkut’s University of Technology Thonburi (KMUTT), 126 Prachauthit Rd., Bangmod, Thungkru, Bangkok 10140, Thailand; r.kamonchanok@gmail.com (K.R.); navadol@igsee.kmutt.ac.th (N.L.)
2 Center for Energy Technology and Environment, Ministry of Education, Bangkok 10140, Thailand
3 Department of Tool and Materials Engineering, Faculty of Engineering, King Mongkut’s University of Technology Thonburi (KMUTT), 126 Prachauthit Rd., Bangmod, Thungkru, Bangkok 10140, Thailand
4 Research Center of Advanced Materials for Energy and Environmental Technology (MEET), King Mongkut’s University of Technology Thonburi (KMUTT), 126 Prachauthit Rd., Bangmod, Thungkru, Bangkok 10140, Thailand
* Correspondence: surawut.chu@kmutt.ac.th; Tel.: +66-2-470-9216

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Abstract: TiO$_2$-based photocatalysts synthesized by the microwave-assisted sol-gel method was tested in the photocatalytic glucose conversion. Modifications of TiO$_2$ with type-Y zeolite (ZeY) and metals (Ag, Cu, and Ag-Cu) were developed for increasing the dispersion of TiO$_2$ nanoparticles and increasing the photocatalytic activity. Effects of the TiO$_2$ dosage to zeolite ratio (i.e., TiO$_2$/ZeY of 10, 20, 40, and 50 mol %) and the silica to alumina ratio in ZeY (i.e., SiO$_2$:Al$_2$O$_3$ of 10, 100, and 500) were firstly studied. It was found that the specific surface area of TiO$_2$/ZeY was 400–590 m$^2$g$^{-1}$, which was higher than that of pristine TiO$_2$ (34.38 m$^2$g$^{-1}$). The good properties of 20%TiO$_2$/ZeY photocatalyst, including smaller particles (13.27 nm) and high surface area, could achieve the highest photocatalytic glucose conversion (75%). Yields of gluconic acid, arabinose, xylitol, and formic acid obtained from 20%TiO$_2$/ZeY were 9%, 26%, 4%, and 35%, respectively. For the effect of the silica to alumina ratio, the highest glucose conversion was obtained from SiO$_2$:Al$_2$O$_3$ ratio of 100. Interestingly, it was found that the SiO$_2$:Al$_2$O$_3$ ratio affected the selectivity of carboxylic products (gluconic acid and formic acid). At a low ratio of silica to alumina (SiO$_2$:Al$_2$O$_3$ = 10), higher selectivity of the carboxylic products (gluconic acid = 29% and formic acid = 32%) was obtained (compared with other higher ratios). TiO$_2$/ZeY was further loaded by metals using the microwave-assisted incipient wetness impregnation technique. The highest glucose conversion of 96.9 % was obtained from 1 wt. % Ag-TiO$_2$ (40 %)/ZeY. Furthermore, the bimetallic Ag-Cu-loaded TiO$_2$/ZeY presented the highest xylitol yield of 12.93%.

Keywords: glucose; photocatalysis; TiO$_2$; zeolite; value-added chemicals; biomass conversion

1. Introduction

Nowadays, biomass is an important feedstock that can be used for chemical production. The main advantage of biomass is zero CO$_2$ emission [1]. The biomass has three main components, which are cellulose, hemicellulose, and lignin. Glucose is a sugar monomer in the structure of cellulose that is one of biomass derivatives. Recently, many researches into glucose conversion are extensively studied in oxidation reactions to obtain high value products (e.g., gluconic acid, arabinose, xylitol, etc.). The synthesis of high value products from biomass can be performed via platform molecules, which can be used as building blocks for biorefinery. From a previous study of platform molecules,
gluconic acid was found to be the one of important building blocks for the medical, foodstuff, and fuel industries, which can be produced via oxidation of glucose \[2\]. Chemicals can be generally produced from many technologies, such as fermentation \[3\] and the Fischer-Tropsch process \[4\]. Conversely, they required high-energy consumption, operated under high-pressure-temperature condition, and there are many steps to produce chemicals. Photocatalysis is one of green synthesis can produce chemicals in one step at mild conditions. It can be described as the acceleration of a chemical reaction by light with a semiconductor catalyst to oxidize or reduce substances into photocatalytic-derived products. In addition, this process can be considered as an environmentally friendly method \[5\]. From many different photocatalysts, titanium dioxide (TiO\(_2\)) is a promising photocatalyst for several applications, such as organic pollutants degradation \[6\], production of hydrogen \[7\], and dye sensitized solar cells \[8\]. Its advantages are highly oxidative, chemically stable, inexpensive, and nontoxic \[9\]. However, there are some disadvantages of bare TiO\(_2\), such as high agglomeration, difficulty to separate or recycle from the solution, and a high energy band gap. This disadvantage results in a smaller effective surface area, and subsequently causes lower photocatalytic activity. Low selectivity is another limitation in TiO\(_2\) photocatalysts. Among several researches, the addition of supports such as silica (SiO\(_2\)), alumina (Al\(_2\)O\(_3\)), or zeolite for TiO\(_2\) dispersion has been studied, due to it is an interesting method for increasing photocatalytic activity \[10–13\]. Among them, zeolite is a suitable support, because it has unique structure, uniform pores, and a high surface area. Colmenares J.C., et al. \[14\] synthesized TiO\(_2\) supported on zeolite that can increase the selectivity of photocatalysts in glucose conversion for producing gluconic acid and glucaric acid compared with pristine TiO\(_2\) and commercial Evonik P-25. To our knowledge, no prior study has examined the optimal dosage of TiO\(_2\) on zeolite and the effect of the ratio of SiO\(_2\) to Al\(_2\)O\(_3\) in zeolite structure for increasing photocatalytic activity. In addition, the loading of metals into TiO\(_2\) nanoparticles is one of techniques to improve TiO\(_2\) properties, such as reducing the energy band gap. Metal ion-loading into TiO\(_2\) has been widely studied. Inexpensive metals, e.g. Ag, are ones of the interesting metals. It was reported that Ag dopant effectively increases the photocatalytic activity of TiO\(_2\) photocatalysts \[15\]. In this work, TiO\(_2\) was synthesized by the microwave-assisted sol-gel method and modified with zeolite supports for improving the dispersion and selectivity of the photocatalyst in photocatalytic glucose conversion. The effects of TiO\(_2\) dosages on zeolite and ratios of SiO\(_2\) to Al\(_2\)O\(_3\) on photocatalytic activities were studied. Moreover, TiO\(_2\)/ZeY was modified by metal loading using microwave-assisted incipient wetness impregnation for reducing the energy band gap. The effect of metal (Ag) contents were studied for optimizing the suitable conditions to get the highest photocatalytic glucose conversion.

2. Results and Discussion

2.1. Effect of Ratio of TiO\(_2\) to ZeY

2.1.1. Characterizations

The effect of TiO\(_2\) dosages on ZeY (TiO\(_2\)/ZeY) (varying as 10, 20, 40, and 50 mol \%) on the physical and chemical properties of the samples was studied via a number of characterizations. Figure 1 shows the SEM images of surface morphology of ZeY, TiO\(_2\), and TiO\(_2\)/ZeY photocatalysts. It was found that the characteristic morphology of ZeY changed with increasing TiO\(_2\) content, because TiO\(_2\) was dispersed on the ZeY surface \[16,17\]. The particle size of TiO\(_2\)/ZeY was found to increase with increasing TiO\(_2\) content (see Table 1). At low TiO\(_2\) contents, a small particle size was found, due to TiO\(_2\) being well dispersed on the ZeY surface, while the accumulation of TiO\(_2\) nanoparticles on the ZeY surface was found at high TiO\(_2\) contents (see Figure 1b–e) compared with pristine TiO\(_2\) (Figure 1f).
Figure 1. SEM images of (a) ZeY, (b) 10%TiO$_2$/ZeY, (c) 20%TiO$_2$/ZeY, (d) 40%TiO$_2$/ZeY, (e) 50%TiO$_2$/ZeY, and (f) TiO$_2$.

Table 1. Summary of crystal phases, crystallite sizes, particle sizes, specific surface areas (S$_{BET}$), and pore diameters of TiO$_2$, TiO$_2$/ZeY (10, 20, 40 and 50 mol % of TiO$_2$ compared with ZeY), and ZeY.

| Photocatalyst | Crystal Phase (%) | Crystallite Size (nm) | Particle Size (μm) | S$_{BET}$ (m$^2$g$^{-1}$) | Pore Diameter (nm) |
|---------------|------------------|-----------------------|-------------------|--------------------------|-------------------|
| TiO$_2$       | A(95)/R(5)       | A(30.3)               | 0.56 ± 0.10       | 34.38                    | 10.40             |
| 50%TiO$_2$/ZeY| A(67)/R(33)      | A(23.57)              | 1.65 ± 0.22       | 419.44                   | 3.68              |
| 40%TiO$_2$/ZeY| A(38)/R(62)      | A(15.14)              | 1.18 ± 0.27       | 494.57                   | 3.68              |
| 20%TiO$_2$/ZeY| A(19)/R(81)      | A(13.27)              | 1.07 ± 0.20       | 524.41                   | 3.69              |
| 10%TiO$_2$/ZeY| A(0)/R(0)        | A(0)                  | 0.99 ± 0.23       | 588.36                   | 3.70              |
| ZeY           | A(0)/R(0)        | A(0)                  | 1.01 ± 0.18       | 590.76                   | 3.90              |

A = anatase, R = rutile.

Figure 2 shows XRD patterns of TiO$_2$, TiO$_2$/ZeY (with different TiO$_2$ to ZeY ratios) and ZeY (SiO$_2$:Al$_2$O$_3$ = 100). For the TiO$_2$ sample, the diffraction peaks of anatase were observed at 20 of 25.4°, 37.5°, 48.2°, 54.0°, 55.0°, and 62.7°, and the diffraction peak of rutile appeared at 27.5°. For ZeY, the samples with different ratios of SiO$_2$:Al$_2$O$_3$ (10, 100 and 500) have similar patterns, where a main peak of ZeY appeared at 27.5°, as shown in Figure S1 [18]. This peak of ZeY overlaps with that of rutile TiO$_2$ (i.e., (110) rutile). For TiO$_2$/ZeY, the characteristic peaks of TiO$_2$ were clearly observed and the intensity of the peaks was found to increase, whereas ZeY peaks intensity decreased, with increasing amount of TiO$_2$. 
Photocatalytic glucose conversions and product yields over TiO$_2$ could imply that surface area is one of the important properties for increasing the photocatalytic activity. So ZeY-supported TiO$_2$ with high surface area obtained in this state was hypothesized to enhance the photocatalytic performance for conversion of glucose.

2.1.2. Photocatalytic Glucose Conversions

The photocatalytic oxidation of glucose on TiO$_2$ and TiO$_2$/ZeY (10, 20, 40 and, 50 mol %), and selectivity toward organic compounds under UV irradiation were studied. Figure 3 shows that the good dispersion of Ti$^{4+}$ precursor on high amounts of ZeY content could inhibit the anatase crystal growth by reduction of nuclei formation on the support during sol-gel synthesis [19]. In addition, the results from specific surface areas showed that TiO$_2$/ZeY had higher specific surface areas compared to pristine TiO$_2$. This could imply that ZeY helped to improve the surface area, because of the general high surface area of ZeY (590.76 m$^2$g$^{-1}$). It could indicate that the surface area of TiO$_2$/ZeY relative decreased with an increasing amount of TiO$_2$ loaded onto the support, because TiO$_2$ was dispersed on the surface of ZeY [20]. Moreover, it could confirm that TiO$_2$ particles cannot form inside the pores of ZeY, because the pore size of ZeY (3.90 nm) was smaller than the diameters of the TiO$_2$ particles (10.40 nm). Previous studies in our group have established that TiO$_2$ fabricated by a surfactant-assisted technique has high surface area, resulting in high photocatalytic oxidation of glucose and high product yields [16]. It could imply that surface area is one of the important properties for increasing the photocatalytic activity. So ZeY-supported TiO$_2$ with high surface area obtained in this state was hypothesized to enhance the photocatalytic performance for conversion of glucose.

![XRD patterns of TiO$_2$, TiO$_2$/ZeY (at different amounts of TiO$_2$), and ZeY (at different ratios of SiO$_2$:Al$_2$O$_3$).](image)

Figure 2. XRD patterns of TiO$_2$, TiO$_2$/ZeY (at different amounts of TiO$_2$), and ZeY (at different ratios of SiO$_2$:Al$_2$O$_3$).

The crystal phase and crystallite sizes of prepared photocatalysts are presented in Table 1. It was found that TiO$_2$/ZeY has smaller crystallite sizes compared with pristine TiO$_2$. The crystallite size in the samples was smaller when the percentage of ZeY increased. From Table 1, it could be explained that the good dispersion of Ti$^{4+}$ precursor on high amounts of ZeY content could inhibit the anatase crystal growth by reduction of nuclei formation on the support during sol-gel synthesis [19]. In addition, the results from specific surface areas showed that TiO$_2$/ZeY had higher specific surface areas compared to pristine TiO$_2$. This could imply that ZeY helped to improve the surface area, because of the general high surface area of ZeY (590.76 m$^2$g$^{-1}$). It could indicate that the surface area of TiO$_2$/ZeY relatively decreased with an increasing amount of TiO$_2$ loaded onto the support, because TiO$_2$ was dispersed on the surface of ZeY [20]. Moreover, it could confirm that TiO$_2$ particles cannot form inside the pores of ZeY, because the pore size of ZeY (3.90 nm) was smaller than the diameters of the TiO$_2$ particles (10.40 nm). Previous studies in our group have established that TiO$_2$ fabricated by a surfactant-assisted technique has high surface area, resulting in high photocatalytic oxidation of glucose and high product yields [16]. It could imply that surface area is one of the important properties for increasing the photocatalytic activity. So ZeY-supported TiO$_2$ with high surface area obtained in this state was hypothesized to enhance the photocatalytic performance for conversion of glucose.
TiO$_2$ synthesized by CTAB-assisted sol-microwave method) [16]. In comparison to TiO$_2$ with a support, the highest photocatalytic glucose conversion in this work is also higher than the previous work (49% from TiO$_2$ with zeolite type Y support) [14]. The good dispersion of TiO$_2$ on the ZeY support caused the result of high performance of photocatalyst. High TiO$_2$ contents on the support (40%TiO$_2$/ZeY and 50%TiO$_2$/ZeY) led to the agglomeration of TiO$_2$ on the catalyst surface, resulting in lower photocatalytic conversions of glucose (Figure 3d,e).

Figure 3. Photocatalytic glucose conversions (■) and product yields [gluconic acid (○), formic acid (●), arabinose (△), and xylitol (■)] over (a) TiO$_2$, (b) 10%TiO$_2$/ZeY, (c) 20%TiO$_2$/ZeY, (d) 40%TiO$_2$/ZeY, and (e) 50%TiO$_2$/ZeY, and (f) selectivity of gluconic acid at different ratios of SiO$_2$:Al$_2$O$_3$. 

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The organic compounds found in the converted solution were divided in two groups, i.e., (1) carboxylic (gluconic acid and formic acid,) and (2) aldehyde (arabinose and xylitol) products. The yields of the main products obtained from the use of 20%TiO$_2$/ZeY at 120 min were 9% gluconic acid, 35% formic acid, 26% arabinose, and 4% xylitol, as shown in Figure 3c. A number of researchers presented pathway conversions of glucose to these value-added chemicals. Colmenares et al. [21] and Chong et al. [22] described the steps of glucose converting to gluconic acid and arabinose, respectively, but xylitol was not found in the proposed reactions. Thus, based on the findings, the glucose conversion in this work follows the reaction pathway with xylitol [23]. The pathway can be explained using three main reactions, including (1) photocatalytic oxidation of glucose for production of gluconic acid, (2) productions of aldopentose (arabinose) and carboxylic products (i.e., formic acid) from the conversion of gluconic acid through photocatalytic decarboxylation, and (3) photocatalytic decomposition of glucose to xylitol. The amount of gluconic acid was found to slightly decrease after 60 min, which supports this proposed pathway.

2.2. Effect of Ratio of SiO$_2$:Al$_2$O$_3$ in ZeY

Glucose conversions via 20%TiO$_2$/ZeY at different ratios of SiO$_2$:Al$_2$O$_3$ in ZeY (10, 100, and 500) were carried out for 120 min under UV irradiation. The selectivity of gluconic acid over 20%TiO$_2$/ZeY at different ratios of SiO$_2$:Al$_2$O$_3$ is shown in Figure 3f. It can be seen that the ratio of SiO$_2$:Al$_2$O$_3$ in ZeY affects the photocatalytic oxidation of glucose. The highest glucose conversion over 20%TiO$_2$/ZeY was obtained at the SiO$_2$:Al$_2$O$_3$ ratio (mol:mol) of 100.

Acidity strength and acidity (acid amount) affect catalytic properties in several catalysts. The TiO$_2$/ZeY with the ratio of SiO$_2$:Al$_2$O$_3$ higher than 10 shows a stronger acid strength property [24]. The increase in acid strength resulted in an increase in photocatalytic conversion, although the rate of reaction is known to decrease at too high an acid strength, because of the excess of H$^+$ (to SiO$_2$:Al$_2$O$_3$ ratio of 500) (result not shown here). For acidity, the temperature programmed desorption of ammonia (NH$_3$-TPD) values of ZeY with SiO$_2$:Al$_2$O$_3$ ratios of 10 and 500 are 1.1 and < 0.1 mmol g$^{-1}$, respectively (data from TOSOH Corporation, Japan). It results in the TiO$_2$/ZeY at SiO$_2$:Al$_2$O$_3$ ratio of 10 showing more yield and selectivity of functional carboxylic acid chemicals (i.e., gluconic acid, 29%) than that at SiO$_2$:Al$_2$O$_3$ ratio of 100 and 500 (11% and 10%, respectively) (Figure 3f). Moreover, it would be come from the Al$_2$O$_3$ content in the zeolite structure. TiO$_2$/ZeY with higher Al$_2$O$_3$ content contains more negative charges in the zeolite structure. Thus, TiO$_2$/ZeY with a low SiO$_2$:Al$_2$O$_3$ ratio has more framework cations in its structure.

2.3. Effect of Metal (Ag, Cu, and Bimetallic Ag-Cu) Loading on TiO$_2$ (40%)/ZeY

2.3.1. Characterizations

It was found that surface morphology of TiO$_2$ (40%)/ZeY changed after Ag loading, but the particle of Ag on the surface of TiO$_2$/ZeY could not be clearly observed (Figure S2). To confirm the Ag content contained on the catalyst surface, Ag-TiO$_2$ (40%)/ZeY were determined by EDS. The peaks of Ag were observed at 3 keV (Figure S2G), which can confirm that Ag nanoparticles had been deposited onto the surface of TiO$_2$. For 1 wt. % Cu and 1 wt. % Ag-Cu on TiO$_2$ (40%)/ZeY SEM images, the same morphology compared with Ag-TiO$_2$ (40%)/ZeY was observed. The EDS analyses of all catalysts are presented in Table 2. From these data the amount of metal is not directly equal to actual loading, because EDS analysis represents only surface concentration. This is because many parameters, such as layer thickness, metal cluster size, and surface coverage, also strongly influence EDS analysis. The Ag content relatively increased with increasing Ag loading in catalyst preparations. The appearance of Ag in TiO$_2$ can be confirmed by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD). The binding energies of Ag 3d at a binding energy of 367.7 eV assigned to Ag$_2$O was observed (result not shown here). Based on previous works, Ag$_2$O was used as a co-catalyst for increasing photocatalytic activity, because it can reduce charge recombination. The electrons can be excited to a conduction
band of TiO$_2$, and the hole can be left at the valence band of Ag$_2$O, leading it to promote an interfacial electron transfer [25–27]. XRD patterns of TiO$_2$ (40%)/ZeY (unloaded); and 0.5, 1, 3, and 5 wt. % Ag loading on TiO$_2$ (40%)/ZeY are illustrated in Figure 4. All photocatalysts presented the strong diffraction peaks of anatase at 25.4°. The characteristic peaks of Ag and Cu are not obviously observed on the XRD patterns. This phenomenon may be ascribed to the Ag, Cu, and Ag-Cu, which were loaded at a content below the detection limitation of instrument or high dispersion of metals on the surface of TiO$_2$/ZeY [28]. It was observed that the crystallite size of anatase decreased after the loading of Ag on TiO$_2$ (40%)/ZeY (Table S1). It indicates that loaded Ag affected in increase of anatase phase in TiO$_2$, due to the rearrangement of titanium and oxygen ions in anatase grain boundaries, which would be greatly disturbed by the silver ions. The transferring of materials in anatase grains increased energy for the movement of anatase grain boundary, resulting in slower grain growth [29]. But at a 5 wt. % Ag loaded sample, the crystallite size was larger than unloaded ones. It could be explained that the greater Ag content over TiO$_2$/ZeY surface enhanced the growth of the crystallite size. So the crystallite size increased with higher Ag content [30]. In addition, both of Cu-loaded TiO$_2$/ZeY and Ag-Cu-loaded TiO$_2$/ZeY increased anatase crystal phase. It indicated that Cu and bimetallic Ag-Cu inhibited phase transformation from anatase to rutile. The phenomena occurred due to the incorporation of Cu and bimetallic Ag-Cu into the TiO$_2$ lattice. Cu$^{2+}$ (0.73 Å) and Ti$^{4+}$ (0.64 Å) have a similarity in the ionic radius, so the Cu ions can substitutionally replace Ti ions in the TiO$_2$ lattice, and might exist in the form of Ti-O-Cu: three elements around the anatase crystallites, which possibly inhibited the transformation to the rutile phase [31].

![Figure 4](image)

**Figure 4.** XRD patterns of TiO$_2$, TiO$_2$ (40%)/ZeY, Ag-TiO$_2$ (40%)/ZeY (at different wt. %), 1 wt. % Cu-TiO$_2$ (40%)/ZeY, and 1 wt. % Ag-Cu-TiO$_2$ (40%)/ZeY.
Table 2. Results from elemental analysis (from EDS) of photocatalysts.

| Photocatalyst                  | Nominal Metal Loading (wt. %) | EDS Analysis (wt. %) |
|--------------------------------|-------------------------------|----------------------|
| 0.5 wt. % Ag-TiO$_2$/ZeY      | 0.5                           | 0.75 - 4.02 2.15 31.67 61.41 |
| 1 wt. % Ag-TiO$_2$/ZeY        | 1                             | 0.81 - 10.99 0.58 29.05 58.57 |
| 3 wt. % Ag-TiO$_2$/ZeY        | 3                             | 1.76 - 9.21 0.54 26.74 61.75 |
| 1 wt. % Cu-TiO$_2$/ZeY        | 1                             | - 0.87 10.06 0.46 30.68 57.93 |
| 1 wt. % Ag-Cu-TiO$_2$/ZeY     | 1                             | 0.28 0.08 10.35 0.36 27.62 61.12 |

The specific surface area and pore volumes of TiO$_2$/ZeY, 1 wt. % Ag-TiO$_2$/ZeY, and 3 wt. % Ag-TiO$_2$/ZeY are tabulated in Table S2. The specific surface area was slightly decreased (from 494.57 to 480.41 m$^2$ g$^{-1}$) after the loading of the Ag ion. It could be explained that the successful loading of the Ag could be achieved through the incipient wetness impregnation method on the surface of TiO$_2$/ZeY. The pore volume of samples increased with increasing Ag content, due to the high dispersion of Ag on surface of TiO$_2$/ZeY. The effect of Ag loading content on the absorption threshold and the band gap energy of TiO$_2$ were also examined by UV-visible diffuse reflectance spectroscopy.

The optical absorbance spectra of pure TiO$_2$ (40%)/ZeY, 0.5 wt. % Ag-TiO$_2$ (40%)/ZeY, 1 wt. % Ag-TiO$_2$ (40%)/ZeY, and 3 wt. % Ag-TiO$_2$ (40%)/ZeY are shown in Figure 5. The absorption edge of 0.5 wt. % Ag-TiO$_2$ (40%)/ZeY, 1 wt. % Ag-TiO$_2$ (40%)/ZeY, and 3 wt. % Ag-TiO$_2$ (40%)/ZeY shifted to a longer wavelength in the UV-vis region, indicating that Ag loaded TiO$_2$/ZeY broadened the absorption edge of TiO$_2$. The band gap energy of TiO$_2$ (40%)/ZeY, 0.5 wt. % Ag-TiO$_2$ (40%)/ZeY, 1 wt. % Ag-TiO$_2$ (40%)/ZeY, 3 wt. % Ag-TiO$_2$ (40%)/ZeY, and 5 wt. % Ag-TiO$_2$ (40%)/ZeY were 3.00, 2.89, 2.82, 2.74, and 2.68 eV, respectively, as shown in Table 3. It implied that when the Ag loading content increased, the absorption edge shifted towards a longer wavelength, which affected the decrease of the band gap. The shortening of the band gap may induce TiO$_2$/ZeY more photocatalytic activity, due to the decrease of the yield of photogenerated electron-hole pairs [14]. The UV-visible diffuse reflectance spectra of 1 wt. % Cu-TiO$_2$/ZeY and 1 wt. % Ag-Cu-TiO$_2$/ZeY are shown in Figure S3. The absorption spectra of Cu and Ag-Cu loaded TiO$_2$/ZeY show the same results as Ag-TiO$_2$/ZeY. The values of Eg for 1 wt. % Cu-TiO$_2$/ZeY and 1 wt. % Ag-Cu-TiO$_2$/ZeY were 2.78 and 2.91 eV, respectively, as shown in Table 3. In addition, the inducing impurity energy level by loading metal (Cu and Ag) affects the separation of electron-hole pairs. As the valence band of Cu$^{2+}$ based metal oxide is lower than that of Ti$^{4+}$ based TiO$_2$, so Cu loaded TiO$_2$ will induce oxygen vacancies, which act as the active sites, and can also capture the holes to restrain the recombination of hole-electron pairs [32].
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the band gap. The shortening of the band gap may induce TiO2/ZeY more photocatalytic activity, due to the decrease of the yield of photogenerated electron-hole pairs [14]. The UV-visible diffuse reflectance spectra of 1 wt. % Cu-TiO2/ZeY and 1 wt. % Ag-Cu-TiO2/ZeY are shown in Figure S3. The absorption spectra of Cu and Ag-Cu loaded TiO2/ZeY show the same results as Ag-TiO2/ZeY. The values of Eg for 1 wt. % Cu-TiO2/ZeY and 1 wt. % Ag-Cu-TiO2/ZeY were 2.78 and 2.91 eV, respectively, as shown in Table 3. In addition, the inducing impurity energy level by loading metal (Cu and Ag) affects the separation of electron-hole pairs. As the valence band of Cu2+ based metal oxide is lower than that of Ti4+ based TiO2, so Cu loaded TiO2 will induce oxygen vacancies, which act as the active sites, and can also capture the holes to restrain the recombination of hole-electron pairs [32].

Figure 5. UV–vis diffuse reflectance spectra of Ag-loaded TiO2 (40%)/ZeY (100%). The inset shows plots of (F(R) * \(h\nu\))^{0.5} versus \(h\nu\) of the catalysts.

Table 3. Summary of characteristics of Ag-loaded TiO2 (40%)/ZeY (70%) catalysts prepared by microwave-assisted incipient wetness impregnation obtained from UV-vis diffuse reflectance spectra.

| Photocatalyst | Wavelength (nm) | Eg (eV) |
|---------------|----------------|---------|
| Unloaded      | 386            | 3.00    |
| 0.5 wt. % Ag  | 389            | 2.89    |
| 1 wt. % Ag    | 392            | 2.82    |
| 3 wt. % Ag    | 394            | 2.74    |
| 5 wt. % Ag    | 395            | 2.68    |
| 1 wt. % Cu    | 389            | 2.78    |
| 1 wt. % Ag-Cu | 390            | 2.91    |

The electrochemical impedance spectra (EIS) of TiO2/ZeY and Ag-TiO2/ZeY are shown in Figure 6. It was found that the Ag-TiO2/ZeY displays a smaller semicircular diameter compared with unloaded (TiO2/ZeY). It can be concluded that Ag can improve the electronic conductivity and increase the charge separation, leading to improvement in photocatalytic activity [33].
The photocatalytic activity of TiO$_2$ facilitated the increase of photogenerated electron-hole pairs produced: xylitol, gluconic acid, arabinose, and formic acid. The highest glucose conversion of 96.90% and the yield of gluconic acid, arabinose, xylitol, and formic acid of 3.43%, 9.97%, 11.87%, and 57.79, respectively, were obtained from 1 wt. % Ag-TiO$_2$ (40%)/ZeY. It indicated that a high surface area (487.53 m$^2$g$^{-1}$), mixed phase of anatase and rutile (anatase:rutile = 42% to 58%), small crystallite size (11.81 nm), and small band gap (3.08 eV) of 1 wt. % Ag-TiO$_2$ (40%)/ZeY could promote high photocatalytic activity. The small band gap facilitated the increase of photogenerated electron-hole pairs and easier electron transfer. It was reported that an Ag dopant could be inserted into the TiO$_2$ lattice as an impurity state, over the valance band and below the conduction band of TiO$_2$. For a photocatalytic reaction of glucose under mercury lamp irradiation, electrons in the valence band were excited to Ag impurity state, left holes in the valence band, and after that these electrons transferred from impurity state to conduction band. Ag impurity state like intermediate band that electrons stay there for a short time, and then transferred again facilitated the photoactivity in the visible light region [34]. On the other hand, 5 wt. % TiO$_2$ (40%)/ZeY enhanced the lowest glucose conversion, because high Ag loading might close some active sites of catalysts, resulting in low photocatalytic activity. This result can confirm by turnover number (TON) and turnover frequency (TOF) of Ag-TiO$_2$/ZeY. Higher Ag contents, lower TONs and TOFs were obtained (e.g., TOFs of 50.40 h$^{-1}$ and 3.57 h$^{-1}$ for 0.5%Ag-TiO$_2$/ZeY and 5%Ag-TiO$_2$/ZeY, respectively, as shown in Table S3). Furthermore, Ag might defect into the TiO$_2$ lattice, resulting in too many oxygen vacancies in the lattice [33]. Oxygen vacancies act as recombination centers of generated electron-hole pairs, resulting in decreased photocatalytic activity [35].

![Graph](image_url)

**Figure 6.** Electrochemical impedance spectra (EIS) of TiO$_2$/ZeY and 1 wt. % Ag-TiO$_2$/ZeY measured at −0.20 V forward bias.

2.3.2. Photocatalytic Conversion of Glucose

Glucose conversions on Ag-TiO$_2$/ZeY based catalysts were carried out for 120 min. The photocatalytic activity of TiO$_2$/ZeY and Ag-TiO$_2$/ZeY catalysts with an Ag loading content of 0.5, 1, 3, and 5 wt. % are shown in Figure 7a, and the maximum yields of products are shown in Figure 7b. The result indicated that after 120 min irradiation time, four organic compounds were produced: xylitol, gluconic acid, arabinose, and formic acid. The highest glucose conversion of 96.90% and the yield of gluconic acid, arabinose, xylitol, and formic acid of 3.43%, 9.97%, 11.87%, and 57.79, respectively, were obtained from 1 wt. % Ag-TiO$_2$ (40%)/ZeY. It indicated that a high surface area (487.53 m$^2$g$^{-1}$), mixed phase of anatase and rutile (anatase:rutile = 42% to 58%), small crystallite size (11.81 nm), and small band gap (3.08 eV) of 1 wt. % Ag-TiO$_2$ (40%)/ZeY could promote high photocatalytic activity. The small band gap facilitated the increase of photogenerated electron-hole pairs and easier electron transfer. It was reported that an Ag dopant could be inserted into the TiO$_2$ lattice as an impurity state, over the valance band and below the conduction band of TiO$_2$. For a photocatalytic reaction of glucose under mercury lamp irradiation, electrons in the valence band were excited to Ag impurity state, left holes in the valence band, and after that these electrons transferred from impurity state to conduction band. Ag impurity state like intermediate band that electrons stay there for a short time, and then transferred again facilitated the photoactivity in the visible light region [34]. On the other hand, 5 wt. % TiO$_2$ (40%)/ZeY enhanced the lowest glucose conversion, because high Ag loading might close some active sites of catalysts, resulting in low photocatalytic activity. This result can confirm by turnover number (TON) and turnover frequency (TOF) of Ag-TiO$_2$/ZeY. Higher Ag contents, lower TONs and TOFs were obtained (e.g., TOFs of 50.40 h$^{-1}$ and 3.57 h$^{-1}$ for 0.5%Ag-TiO$_2$/ZeY and 5%Ag-TiO$_2$/ZeY, respectively, as shown in Table S3). Furthermore, Ag might defect into the TiO$_2$ lattice, resulting in too many oxygen vacancies in the lattice [33]. Oxygen vacancies act as recombination centers of generated electron-hole pairs, resulting in decreased photocatalytic activity [35].
The photocatalytic activity of Ag-Cu-TiO$_2$ compared with Ag-TiO$_2$ and Cu-TiO$_2$ catalysts are shown in Figure 7c. It was found that glucose conversions on 1 wt. % Cu-TiO$_2$/ZeY and 1 wt. % Ag-Cu-TiO$_2$/ZeY were achieved at 82.23% and 94.71%, respectively. Among them, 1 wt. % Cu-TiO$_2$/ZeY showed the lowest glucose conversion. The maximum yields of products: xylitol, gluconic acid, arabinose, and formic acid were 12.93%, 5.92%, 20.49%, and 59.73%, respectively. When compared with the unloaded sample (TiO$_2$ (40%)/ZeY), 1 wt. % Cu-TiO$_2$ still presented a higher glucose conversion, because Cu-loaded samples have a smaller band gap than TiO$_2$/ZeY, so the electron can transfer from the conduction band of TiO$_2$/ZeY to metallic copper ion. This result facilitates the charge separation, and hence enhances the photocatalytic performance of TiO$_2$/ZeY. In a previous work, Jin et al. [36] used a precious bimetallic catalyst (Pt/Pd) to modify TiO$_2$ for increasing the selectivity of glucaric acid (S = 44%) compared with Ag-TiO$_2$ (40%)/ZeY, Cu-TiO$_2$ (40%)/ZeY, and Ag-Cu-TiO$_2$ (40%)/ZeY under UV irradiation for 120 min [(a) and (c)]. Product yield of main products under UV irradiation at 120 min [(b) and (d)].

Figure 7. Photocatalytic conversion of glucose of Ag-TiO$_2$ (40%)/ZeY, Cu-TiO$_2$ (40%)/ZeY, and Ag-Cu-TiO$_2$ (40%)/ZeY under UV irradiation for 120 min [(a) and (c)]. Product yield of main products under UV irradiation at 120 min [(b) and (d)].
3. Materials and Methods

3.1. Photocatalyst Preparation

3.1.1. TiO₂/ZeY Photocatalyst

Zeolite type Y (ZeY) (SiO₂:Al₂O₃ = 10, 100, and 500) provided by the Tosoh Corporation (Tokyo, Japan) was used as a support. TiO₂ particles were prepared with the microwave-assisted sol-gel technique. Titanium (IV) butoxide (Sigma-Aldrich, Queenstown, Singapore) and acetylacetone (Sigma-Aldrich, Queenstown, Singapore) were mixed by stirring for 3 min. Then, isopropyl alcohol (80 ml) was dropped in the mixture solution with constant stirring [37]. After that, ZeY was added in the prepared mixture under constant stirring for 10 min. The TiO₂ hydrosol was heated for 4 min by microwave irradiation (Whirlpool, 970W, 2.45 GHz, Michigan, MI, USA) to accelerate the TiO₂ gel formation, followed by drying in a hot-air oven at 80 °C for 24 h. Finally, TiO₂/ZeY powder was calcined at 500 °C for 2 h.

3.1.2. Metal-TiO₂/ZeY Photocatalyst

The metal-loaded TiO₂ catalysts were prepared by aqueous incipient wetness impregnation of TiO₂ using metal ion salts, Ag(NO₃) and Cu(NO₃)₂·3H₂O, as the precursors for Ag and Ag-Cu loading, respectively. Accordingly, a solution of metal ion salts in distilled water was stirred, and then added into TiO₂ (40%)/ZeY. The solvent was treated with microwave irradiation (40% power) for 4 min (Whirlpool, 2.45 GHz, 970W, Michigan, MI, USA). The 0.5, 1, 3, and 5 wt. % of metal ions were introduced as the dopant. The samples were then dried in an oven at 80 °C overnight and then calcined at 400 °C for 4 h.

3.2. Photocatalyst Characterizations

The crystal phases and crystallite sizes of the synthesized TiO₂ photocatalyst ware determined by the X-ray powder diffraction (XRD) technique using an XRD spectrometer (Rigaku RINT 2100, Tokyo, Japan) with Cu Kα radiation (λ = 0.15418 nm, 40 kV). The scanning angle of 2θ was from 10 to 80°, with a scanning speed of 0.05° s⁻¹. The XRD results were used to identify the crystal phases of prepared catalysts. The crystallite size of catalysts was calculated using the Scherrer equation (Equation (1)) [38].

\[
D = \frac{K\lambda}{\beta\cos\theta}
\]

where \(D\) is crystallite size, \(K\) is a coefficient (0.94), \(\lambda\) is X-ray wavelength, \(\beta\) is intensity of the full width at half maximum of the peak, and \(\theta\) is diffraction angle [39]. The percentage of anatase (A) was calculated using Equation (2).

\[
A(\%) = \frac{100}{1 + 1.265(I_R + I_A)}
\]

where \(I_R\) is intensity of the rutile (110) peak and \(I_A\) is intensity of the reflection of the anatase (101) phase.

A scanning electron microscopy (SEM) (Hitachi SU-6600, Tokyo, Japan) was employed to observe the surface morphologies and determine particle sizes of photocatalysts. The average particle sizes of synthesized catalysts were calculated with 50 measurements from SEM images.

Specific surface area, pore size, and pore volume were obtained by the measurement of N₂ physisorption analysis (BEL, Osaka, Japan, BELSORP 18) via Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods.

To estimate the band gap energies (\(E_g\)), the Kubelka–Munk function (\(F(R)\)) was considered (Equation (3)).

\[
F(R) = \frac{\alpha}{s} = \frac{(1 - R)^2}{2R}
\]
where $R$ is reflectance from diffuse reflectance spectrum, $\alpha$ is absorption coefficient, and $s$ is scattering factor. The scattering factor is wavelength independent, while $(R)$ is proportional to the absorption coefficient. The optical band gaps ($E_g$) were determined according to Equation (4).

\[
(F(R)h\nu)^{\frac{2}{n}} = k(h\nu - E_g)
\]

where $h\nu$ is photon energy ($h$ is Planck constant and $\nu$ is frequency of electromagnetic waves), $k$ is energy-independent constant, and the exponent $n$ is determined by the type of transition. In this work, the optical band gap is best described by an indirect allowed transition ($n = 2$). Thus, the optical band gap can be determined by plot $(F(R)h\nu)^{0.5}$ versus $h\nu$, and extrapolating the linear regression into the $h\nu$ axis [40,41].

Electrochemical impedance spectra (EIS) were performed by a Versa STAT4 potentiostat instrument (Tennessee, TN, USA). Potassium chloride (KCl) solution with the concentration of 0.1 M was used as an electrolyte. A bias voltage of −0.20 V was used to drive the photogenerated electron transfers from a working electrode to a platinum electrode.

3.3. Photocatalytic Conversion

Photocatalytic conversion was performed in a double-walled glass reactor (Pyrex) under irradiation of UV (mercury lamp, 400 W, $\lambda_{\text{max}} = 365$ nm). A cooling water system was used for controlling the temperature in this reaction. The initial glucose concentration was set as 1 g/L in a 10:90 v/v of distilled water and acetonitrile mixture [15]. Prior to staring the photocatalytic experiment, the system was constantly stirred under dark conditions for 30 min to make a homogenous dispersion of the photocatalyst in the solution. The reaction time for photocatalytic glucose conversion was 120 min. Since the reactions were performed under the open system, the gas-phase products were not detected. The liquid products from glucose conversion were analyzed by high-performance liquid chromatography (HPLC) technique (Shimadzu LC-20AD, (Kyoto, Japan), equipped with an Aminex HPX-87H column (Bio-Rad, 300 × 7.8 mm), and a refractive index detector (RID-10A)). The separation was operated under a temperature of 60 °C at a constant flow rate of 0.5 mL/min, using a sulfuric acid solution (5 mM) as a mobile phase [16]. Glucose conversion, product yield, product selectivity, turnover number, and turnover frequency were calculated according to Equations (5)–(9), respectively.

\[
\text{Glucose conversion (\%)} = \frac{\text{The initial concentration of glucose} - \text{The concentration of glucose at } t \text{ time}}{\text{The initial concentration of glucose}} \times 100
\] (5)

\[
\text{Product yield (\%)} = \frac{\text{The concentration of product at } t \text{ time}}{\text{The initial concentration of glucose}} \times 100
\] (6)

\[
\text{Product selectivity (\%)} = \frac{\text{The amount of product } i}{\text{The total amount of products}} \times 100
\] (7)

\[
\text{Turnover number (TON)} = \frac{\text{Mole of glucose consumed}}{\text{Mole of Ag–TiO}_2/\text{ZeY catalyst}}
\] (8)

\[
\text{Turnover frequency (TOF) } (h^{-1}) = \frac{\text{TON}}{\text{Time of reaction}}
\] (9)

4. Conclusions

TiO$_2$ particles were prepared by microwave assisted sol-gel technique and mixed with ZeY support for dispersion of the particles. TiO$_2$/ZeY photocatalysts were successfully used as photocatalysts for producing value-added chemicals via the photocatalytic conversion of glucose. Well dispersed TiO$_2$ particles on surface of the support can be observed in 20%TiO$_2$/ZeY at the SiO$_2$:Al$_2$O$_3$ ratio of 100. This catalyst was found to be the best photocatalyst to achieve the highest glucose conversion of 75%.
Unique properties of photocatalysts, i.e., a high specific surface area (524.41 m$^2$/g), small anatase crystallite size (13.27 nm), and small particle size (1 μm) cause high photocatalytic activity, resulting in greater glucose conversion. Four organic compounds, i.e., gluconic acid, formic acid, arabinose, and xylitol, were found as the main products from photocatalytic glucose conversion. The yields of products were 9%, 35%, 26%, and 4%, respectively. Moreover, the low ratio of SiO$_2$/Al$_2$O$_3$ was significantly affected by the selectivity of the carboxylic products. At the ratio of SiO$_2$/Al$_2$O$_3$ of 10, the highest selectivity of gluconic acid (29%) and formic acid (32%) were achieved. The modification of TiO$_2$/ZeY by metal loading were carried out by microwave-assisted incipient wetness impregnation method. The highest glucose conversion of 96.9% were obtained from 1 wt. % Ag-TiO$_2$ (40%)/ZeY, which was the sample that provided the smallest anatase crystallite size (11.81 nm), the highest S$_{BET}$ (487.5 m$^2$/g), low band gap (2.82 eV), and mixed anatase-rutile phase (42:58). The 1 wt. % Cu-TiO$_2$/ZeY and bimetallic loaded samples, i.e., 1 wt. % Ag-Cu-TiO$_2$/ZeY, were synthesized for comparison with 1 wt. % Ag-TiO$_2$/ZeY. Among them, the bimetallic 1 wt. % Ag-Cu-TiO$_2$/ZeY presented a higher glucose conversion (94.71%) than 1 wt. % Cu loaded TO$_2$/ZeY (82.23%). In addition, the bimetallic Ag-Cu-TiO$_2$/ZeY presented the highest of xylitol yield (12.93%), compared with the other samples.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/10/4/423/s1, Figure S1: XRD patterns of TiO$_2$ (20%)/ZeY and ZeY with different SiO$_2$/Al$_2$O$_3$ ratios; Figure S2: SEM images (30000×) of (A) TiO$_2$ (20%)/ZeY, (B) 0.5 wt. % Ag, (C) 1 wt. % Ag, (D) 3 wt. % Ag, (E) 1 wt. % Cu, and (F) 1 wt. % Ag-Cu on TiO$_2$ (40%)/ZeY; and (G) EDS spectrum of 1 wt. % Ag TiO$_2$ (40%)/ZeY; Figure S3: UV-vis diffuse reflectance spectra of 1% Ag-, 1% Cu-, and 1% Ag-Cu-loaded TiO$_2$ (30%)/ZeY (70%), the inset shows plots of ($f(R(\text{in})$) versus $\text{hv}$ of the catalysts; Table S1: Summary of crystal phases and crystallite sizes of Ag-loaded TiO$_2$ (40%)/ZeY prepared by incipient wetness impregnation with microwave assistance ($A =$ anatase, $R =$ rutile); Table S2: Specific surface areas ($S_{\text{BET}}$), pore volumes ($V_p$), and pore diameters of TiO$_2$/ZeY and (1% and 3%) Ag-loaded TiO$_2$ (40%)/ZeY; Table S3: Turnover number (TON) and turnover frequency (TOF) of Ag-TiO$_2$/ZeY (with different Ag contents) and Ag-Cu-TiO$_2$/ZeY.

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