Characterization and Assessment of the Photo-catalytic Efficiency of Palladium/Silver Doped TiO$_2$Nanoparticles

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ABSTRACT: The effect of modified TiO$_2$ with palladium, silver and co-dopant of palladium and silver on TiO$_2$ with its photocatalytic efficiency were studied using X-ray diffraction (XRD) and Brunauer-Emmet–Teller (BET). The photocatalysts were prepared by sol immobilization method and characterized using XRD and BET techniques. The X-ray diffraction patterns of the dopants were found to be uniform with the standard P25 degussa TiO$_2$. From the peak formation of anatase and rutile phases, it was found that the Pd/TiO$_2$ formed uniform matrix of anatase and rutile indicating that palladium ion disperses evenly on P25 degussa TiO$_2$. The peak formation on Ag/TiO$_2$ and Pd/AgTiO$_2$ shows the same uniform distribution of silver and palladium ion, only that foreign peak were observed on the formation of anatase and rutile because of impurity on silver. The crystalline size of the catalyst and full width at half maximum (FWHM) were also calculated at different angles of diffraction. The BET shows that the photocatalysts were mesoporous and is type IV isotherm. The high mesopore of the catalyst increases its photocatalytic activity, so also type IV isotherm. The BET analysis shows that the pore size distribution of the catalyst is between 2nm and 50nm which shows that the catalyst is mesoporous. It also gives high surface area with high volume and low pore size (crystalline size) which increases the photocatalytic efficiency. So co-doping of palladium and silver on TiO$_2$ can serve as a strategy for design of high performance photocatalysts for environmental benefits.

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A photo-catalyst is defined as a substance that is activated by the absorption of photon and helps to accelerate a reaction without being consumed (Abhang et al., 2011). Titanium (IV) oxide photo-catalyst is one of the revolutionized technologies in the field of environmental purification and energy generation, and has found extensive application in heterogeneous photocatalysis for removing organic pollutants from air, water, soil and also in hydrogen production from photocatalytic water-splitting. Its use is popular because of its low cost, low toxicity, high chemical and thermal stability (Shon et al., 2007). The standard P25 degussa (Evonik) Aerioxide is a widely used titaniaphotocatalyst because of its relatively high levels of activity in many photo-catalytic reaction systems. It is not easy to find a photocatalyst showing activity higher than that of P25degusaTiO$_2$(Ohtani et al., 2010).

In recent years, photocatalytic degradation of organic compounds has been widely studied. One of the most important photocatalyst being frequently employed in this process is titania. TiO$_2$ occurs in three polymorphous states: anatase, rutile and brookite (Jakub et al., 2012). Unfortunately, only the anatase and to a lesser extent, rutile TiO$_2$ exhibit noticeable photo-activity under UV light. Anatase-titania is usually considered to be more active that rutile. Though, the latter is a thermodynamically stable phase, and reveals a lower band gap than the anatase (Silva et al., 2009).

In addition, research on TiO$_2$ has attracted extensive interest because of its potential applications to photocatalysis, chemical sensors, solar cell electrodes and hydrogen storage materials (Kunst et al., 2006). Notwithstanding, TiO$_2$ photocatalyst is known to have some shortcomings in practical applications. One of these is that TiO$_2$ has activity when it is only under light of wavelength shorter than 388nm, because of its wide band gap (3.2eV) (Ge and Xu, 2006). The wide band gap limits the use of sunlight as excitation energy and the high rate of recombination of photo-generated electron hole pairs inTiO$_2$ results in low photocatalytic efficiency (Ahmed et al., 2013).

Therefore, in order to surmount these two problems, many efforts have been made to modify TiO$_2$
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nанопarticles. One of the promising approaches is based on the metal loading. Various metals such as Pt, Au, Pd, Rb and Ag have been used as electron acceptors to separate the photo-induced hole/electron pair and promote interfacial charge-transfer process (Wu and Chen, 2004).

Moreover, to achieve high photocatalytic degradation efficiency, nano-TiO₂ should be mesoporous and should exhibit high crystallinity and high specific area (Young et al., 2018). The formation of a high percentage of the anatase phase, small crystallite size and high specific surface area of nano-doped-TiO₂ increases the photocatalytic efficiency (Yu et al., 2007).

Shon et al. (2007) reported that doping of Ag with TiO₂ (600°C) led to decreased photocatalytic size from 37nm to 19nm, while the specific surface area increased from 45m²/g to 63m²/g and the photocatalytic activity increased by 18%. In addition, optical characterization of Au doped TiO₂ using UV-visible spectrophotometry showed a shift in optical absorption wavelength to visible region which may be attributed to the incorporation of gold nanoparticles (1-2%) into TiO₂ structure (Shon et al., 2007). The kinetic study indicated that the rate of decomposition of phenol by Au/TiO₂ photocatalyst was improved by 2-2.3 times compared to the undoped TiO₂.

Au doped TiO₂ showed higher activity for the removal of dibenzo thiophene (DBT) compared to pure titania, with the optimum Au loading being 1.5 wt% Au. The Au nanoparticles act as electron sink to enhance e/h⁺ charge separation and produce number of oxidizing species, thereby increasing the reaction rate (Suzan and Selva, 2008).

Therefore, the aim of this work is to assess the effect of palladium and silver dopants on TiO₂, and to compare the effects of mono- and bi-metal dopant on the photocatalytic efficiency of TiO₂ P25 Degussa.

MATERIALS AND METHOD
Preparation of Ag/TiO₂ and Pd/TiO₂ catalyst: The catalysts used were prepared using sol immobilization method as reported by Moses (2014), with a few modifications. Standard sol-immobilization method was utilized to prepare the Ag, Pd, Ag-Pd nano particles supported on TiO₂. The supported silver and silver-palladium colloids were prepared by using Poly vinyl alcohol(PVA) as protective ligand, aqueous solutions of 0.005mol/dm³PdCl₂ and 0.006mol/dm³AgNO₃ were prepared. A 1wt % aqueous PVA, (Aldrich, MW = 10000, 80% hydrolyzed) solution was freshly prepared just prior to synthesis of the metal colloid. A representative protocol for preparing a catalyst comprising Ag-Pd nano-particles with 1 wt% total metal loading on a TiO₂ was carried out as follows: To an aqueous 0.005mol/dm³PdCl₂ and 0.006mol/dm³AgNO₃ solution, 100 cm³ of PVA solution (1 wt %) was added (PVA/A (Ag and Pd)(w/w) = 1.2); a freshly prepared solution of NaBH₄ (0.1 M, NaBH₄/ (Ag and Pd)(mol/mol) = 5) was then added to form a dark brown sol.

After 30 min of sol generation, the colloid was immobilized by adding TiO₂ (acidified to pH 1-2 by using tetraoxosulphate (VI) acid with vigorous stirring with a glass rod. The amount of support material required was calculated to have a total final metal loading of 1 wt %. After 2 h, the slurry was filtered and the catalyst washed thoroughly with distilled water (neutral mother liquors) and dried at 120°C overnight in an oven. Sol immobilized mono-metallic silver and palladium catalysts were prepared using similar procedure.

Characterization of Catalyst(Ge and Xu (2006): X-ray diffraction measurement of Ag/TiO₂, Pd/TiO₂ and Ag/Pd-TiO₂ was performed at room temperature using a Rigakuutima IV X-ray diffraction meter with CU-Kα & radiation (Philips) in England. The diffraction meter was operated at 40kW and 44 MA, scanned with a step size of 0.02° and a count time of 1°/min in the range of 2θ from 10° to 80°.

The textural properties such as surface area pore size distribution of Ag/TiO₂, Pd/TiO₂ and Ag/Pd-TiO₂ were analyzed by using N₂ physisorption using a NOVA 2200e (Quantachrome instrument, England) surface area and pore size analyzer. After the Ag/TiO₂, Pd/TiO₂ and Ag/Pd-TiO₂ were dried, they were degassed extensively at 100°C prior to the adsorption measurements, then the N₂ isotherm were obtained at 196°C.

The surface area of the synthesized materials was calculated by using the Brunauer-Emmett-Teller (BET) equation with a relative pressure $p/p₀$ range of 0.05-0.30. The pore volume was determined from the amount of N₂ adsorbed at the highest relative pressure $p/p₀ = 0.99$, then the diameter and pore size distribution plots were designed by applying the Barrett-Joyner Halenda (BJH) model.

RESULTS AND DISCUSSION
X-Ray Diffractometer (XRD) spectra of P25 Degussa and 0.5%Pd/TiO₂ catalyst: From the result of the XRD spectra of the catalyst prepared using micro-emulsion (Figure 1 and 2). The XRD pattern of P25 degussa TiO₂ indicated that Pd loaded on TiO₂ surface almost

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has no influence on the crystalline structure of TiO₂ when compared to the P25 Degussa TiO₂. Pd phase was not detected in the XRD pattern of Pd/TiO₂ powders, possibly because the Pd content in the TiO₂ surface is not enough to form clearly crystalline structure. The peak distribution of P25 Degussa TiO₂ standard and doped Pd/TiO₂ showed the same peak formation. The shape of diffraction peaks of the crystal plane of P25 Degussa standard is quiet similar to those of Pd/TiO₂, the peak obtained for the two sample is similar to that of predominant formation of anatase reflex at 2θ=25.3° with uniform distribution of anatase and rutile with more of sharp peak of anatase reported by Ohtani et al. (2010) [3]. Also, 0.5% Pd/TiO₂ had sharp peak at 2θ = 25.3° and P25 degussa has sharp peak at 2θ = 25.30° for anatase and the sharp peaks formation for P25 degussa and Pd/TiO₂ is 2θ = 27.40° for rutile indicating that there is uniform distribution of Pd ion on the catalyst (TiO₂). Amano et al. (2009) used pt deposited on p25 TiO₂ they found out that the peak formation of the anatase and rutile was the same with sharp peak formation of 2θ = 25.30° and 27.40° for anatase and rutile respectively.

Fig 1: The XRD pattern of P25 degussa standard

Ahmed et al. (2013) prepared 0.05%, 0.1% and 0.3% of doped Pd on TiO₂ and compared it with the undoped TiO₂. He found out that XRD pattern of 0.05% and 0.1% palladium doped TiO₂ did not show any Pd phase even for 0.3% Pd doped TiO₂. This may reveal that Pd ions are uniformly dispersed in TiO₂ matrix. In the region of 2θ = 10°-80° the shape of diffraction peaks of the crystal planes of pure TiO₂ is quite similar to those of Pd/TiO₂ of different Pd concentration. The anatase and rutile formation was at 2θ = 25.30° and 27.40° respectively.

Fig 2: XRD pattern of 0.5% Pd-TiO₂

X-Ray Diffractometer (XRD) spectra of 0.5% Ag/TiO₂ catalyst: From the result of the XRD spectra of catalyst prepared using micro-emulsion, shown in Figure 3, the XRD spectra of Ag/TiO₂ was accompanied with some foreign peaks that can be ascribed to the impure nature of the AgNO₃ precursor used for Ag. For Ag/TiO₂, the peak formation is 2θ = 25.30° and 27.40° respectively for anatase and rutile phase only that you have to look very closely in order to read out the peak because of the foreign peak formed. The result also reveals that Ag ions are uniformly dispersed in TiO₂. The obtained peak is similar result of predominantly formation of anatase reflex at 2θ=25.3° with uniform distribution of anatase and rutile 27.4° with more of sharp peak of anatase reported by Ohtani et al. (2010). This study supports the report that P25 Degussa TiO₂ is composed of anatase and rutile crystallites, the ratio being typically 70:30 or 80:20 (Ohtani et al., 2010).

Fig 3: XRD pattern of 0.5% Ag-TiO₂

X-Ray diffractometer (XRD) spectra of 0.5% Pd/Ag-TiO₂ catalyst: The XRD spectra of the photocatalyst prepared using micro-emulsion (Figure 4), has peak
similar to that of the mono metal Ag/TiO$_2$ with 2$\theta$ = 25.3$^0$ and 27.4$^0$ for anatase and rutile respectively. Contamination found in Ag/TiO$_2$ affects the peak formation of Pd/Ag-TiO$_2$, making it to give more foreign peaks. The result obtained is similar to that of predominant formation of anatase reflex at 2$\theta$=25.3$^0$ with uniform distribution of anatase and rutile, though with more sharp peak of anatase. XRD pattern of Pd/TiO$_2$, Ag/TiO$_2$ and Ag/Pd-TiO$_2$ compared to P25 degussa TiO$_2$ standard indicated that the peak formation of the anatase and rutile were uniformly distributed. Peak formation of the anatase and rutile phase increases the photocatalytic efficiency of doped Pd/TiO$_2$, Ag/TiO$_2$ and Ag/Pd-TiO$_2$ as more of anatase is formed, which is the reactive phase.

From Tables 1, 2 and 3, the full width at half maximum (FWHM) was calculated using the formula shown in Figure 5. From the calculation, Pd/Ag-TiO$_2$ gives smaller crystalline size, so this supports its high photocatalytic activity.

**BET Analysis Result:** $S_{BET}$$^a$-surface area determined by applying Brunauer-Emmett-Teller (BET) equation to a relative pressure ($P/P_0$) range of 0.05 – 0.35 of the adsorption isotherm. PD$^b$-pore diameter was calculated from the Barrett-Joyner-Halenda (BJH) equation using the desorption isotherm.

### Table 4: Textural properties of Ag-Pd-TiO$_2$ composite materials

| Materials       | $S_{BET}$' (m$^2$g$^{-1}$) | Pore Volume (cm$^3$g$^{-1}$) | PD (nm) | TiO$_2$ size (±1nm) |
|-----------------|-----------------------------|-----------------------------|---------|---------------------|
| 0.5%Pd-TiO$_2$  | 49.66                       | 1.779                       | 1.433   | 32.32               |
| 0.5%Ag-TiO$_2$  | 43.73                       | 1.509                       | 1.380   | 24.39               |
| 0.5%Pd-AgTiO$_2$| 52.85                       | 1.749                       | 1.322   | 68.39               |

Brunauer-Emmett-Teller (BET) of 5% Pd-TiO$_2$ catalyst: Table 4 shows that Pd/Ag-TiO$_2$ has the highest surface area (52.85 m$^2$g$^{-1}$), higher pore volume (1.749 cm$^3$g$^{-1}$) and smallest pore diameter (1.322 nm) which favours high photocatalytic activities. From Figure 6 and 7, the pore size distribution of Pd/TiO$_2$ has the width to be between 2 nm and 50 nm. Therefore, this implies that Pd/TiO$_2$ is mesoporous, so the physisorption isotherm is type IV isotherm which favours high photocatalytic activity (Sing et al., 1984). Pd/TiO$_2$ has surface area of 49.66 m$^2$g$^{-1}$, higher pore volume of 17.7m$^3$g$^{-1}$ and pore size of 13.8 nm signifying high surface area, high pore volume and small pore size implies high photocatalytic efficiency. In conformity with some other work, doping techniques promote the production of smaller crystallite nano-doped TiO$_2$.
with resultant larger surface area, so as to prevent the problem of particle agglomeration (Asilturk et al., 2009).

**Brunauer-Emmett-Teller (BET)** of 5% Pd/Ag-TiO$_2$ catalyst: Furthermore, Figure 8, 9, 10, and 11 indicated that Ag-TiO$_2$ and Pd/Ag-TiO$_2$ are mesoporous and is type IV isotherm. According to Sing et al. (1984), the pore widths of between 2 nm and 50 nm is called mesopores. From the plot of pore size distribution, the pore size declined between the ranges of 2 nm to 50 nm, whereas cluster in the plot indicated the pore size. According to Wu et al. (2004), transition metals dopants such as palladium, chromium and silver enhance the photocatalytic performance of nano-doped TiO$_2$. Among the transition metals used as dopants, Pd ion showed the strongest interaction with nano-TiO$_2$ and improved its morphology most effectively.

From this study, when Ag is co-doped to form Pd/Ag TiO$_2$, this better improved the photocatalytic property to give larger surface area, high pore volume and small pore size which favours photolytic efficiency of the prepared catalyst Pd/Ag-TiO$_2$. Shon et al. (2007) reported that doping silver on TiO$_2$ decreases its crystalline size from 37 nm to 19 nm and specify surface area increased from 45 m$^2$/g to 63 m$^2$/g, thereby increasing its photocatalytic efficiency. The report of this study is similar to that of Kirilov et al. (2006) in which 0.5% Ag/TiO$_2$ has specific surface area of 47 m$^2$/g and 0.5% Pd/TiO$_2$ has specific surface area of 51 m$^2$/g showing that doped Pd/TiO$_2$ has more photocatalytic efficiency than doped Ag/TiO$_2$.
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Conclusion: The doping and codoping of Pd/TiO₂, Ag/TiO₂ and Ag/Pd/TiO₂ improve the photocatalytic activity of P25 degusa TiO₂ by production of more active phase (anatase) which favours photocatalysis. The BET analysis indicates that doping also helps to increase surface area of the catalyst, the pore volume and reduces the pore size thereby increasing photocatalytic activity. The XRD of Pd/TiO₂, Ag/TiO₂ and Ag/Pd/TiO₂ shows uniform dispersion of the transition metal dopants on TiO₂ matrix. There was high reactive phase of anatase and improvement in surface area, pore volume and crystalline size of doped TiO₂ for enhanced photocatalytic.

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