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Characterization and Assessment of the Photo-catalytic Efficiency of Palladium/Silver Doped TiO_2Nanoparticles

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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 photo-catalysts 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_2formed 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_2shows 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 photocalysts 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 photo-catalysis 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) Aeroxide 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_2photocatalyst 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

nanoparticles. 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-TiO_2 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-TiO_2 increases the photo catalytic efficiency (Yu *et al.,* 2007).

Shon *et al.* (2007) reported that doping of Ag with TiO_2 (600ºC) led to decreased photocatalytic size from 37nm to 19nm, while the specific surface area increased from $45m^2/g$ to $63m^2/g$ and the photocatalytic activity increased by 18%. In addition, optical characterization of Au doped TiO_2using 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 TiO_2 structure (Shon *et al.,* 2007). The kinetic study indicated that the rate of decomposition of phenol by Au/TiO_2 photocatalyst was improved by 2-2.3 times compared to the undoped TiO_2.

Au doped TiO_2 showed higher activity for the removal of dibenzothiophene (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 TiO_2, and to compare the effects of mono- and bi-metal dopant on the photocatalytic efficiency of TiO_2 P25 Degussa.

MATERIALS AND METHOD

Preparation of Ag/TiO_2 and Pd/TiO_2catalyst: 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 TiO_2.The supported silver and silver-palladium colloids were prepared by using Poly vinyl alcohol(PVA) as protective ligand, aqueous solutions of 0.005mol/dm^3$PdCl_2$ and 0.006mol/dm^3 $AgNO_3$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 $TiO_2$was carried out as follows: To an aqueous 0.005mol/dm^3$PdCl_2$ and 0.006mol/dm^3$AgNO_3$ solution, 100 cm^3 of PVA solution (1 wt %) was added (PVA/ (Ag and Pd)(w/w) = 1.2); a freshly prepared solution of $NaBH_4$ (0.1 M, $NaBH_4$/ (Ag andPd)(mol/mol) = 5) was then added to form a dark brown sol.

After 30 min of sol generation, the colloid was immobilized by adding TiO_2 (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 120ºC 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/TiO_2, Pd/TiO_2 and Ag/Pd-TiO_2 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 40kn and 44 MA, scanned with a step size of 0.02º and a count time of 1º/min in the range of 2θ from 10º to 80º.

The textural properties such as surface area pore size distribution of Ag/TiO_2, Pd/TiO_2 and Ag/Pd-TiO_2 were analyzed by using N_2physisorption using a NOVA 2200e (Quantachrome instrument, England) surface area and pore size analyzer. After the Ag/TiO_2, Pd/TiO_2 and Ag/Pd-TiO_2 were dried, they were degassed extensively at 100ºC prior to the adsorption measurements, then the N_2 isotherm were obtained at 196ºC.

The surface area of the synthesized materials was calculated by using the Brunaer-Emmett-Teller (BET) equation with a relative pressure $^P/_{P^o}$ range of 0.05-0.30. The pore volume was determined from the amount of N_2 adsorbed at the highest relative pressure $^P/_{P^o}$ = 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/TiO_2 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 TiO_2 indicated that Pd loaded on TiO_2 surface almost has no influence on the crystalline structure of $TiO_2$when compared to the P25 Degussa TiO_2. Pd phase was not detected in the XRD pattern of Pd/TiO_2 powders, possibly because the Pd content in the TiO_2 surface is not enough to form clearly crystalline structure. The peak distribution of P25 Degussa TiO_2 standard and doped Pd/TiO_2 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/TiO_2, the peak obtained for the two sample is similar to that of predominant formation of anatase reflex at $2\theta=25.3^o$ 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/TiO_2 had sharp peak at $2\theta = 25.3^0$ and P25 degussa has sharp peak at $2\theta = 25.3^0$ for anatase and the sharp peaks formation for P25 degussa and Pd/TiO_2 is $2\theta = 27.4^0$ for rutile indicating that there is uniform distribution of Pd ion on the catalyst (TiO_2). Amano *et al.* (2009) used pt deposited on p25 TiO_2 they found out that the peak formation of the anatase and rutile was the same with sharp peak formation of $2\theta = 25.3^0$ and 27.4^0 for anatase and rutile respectively.

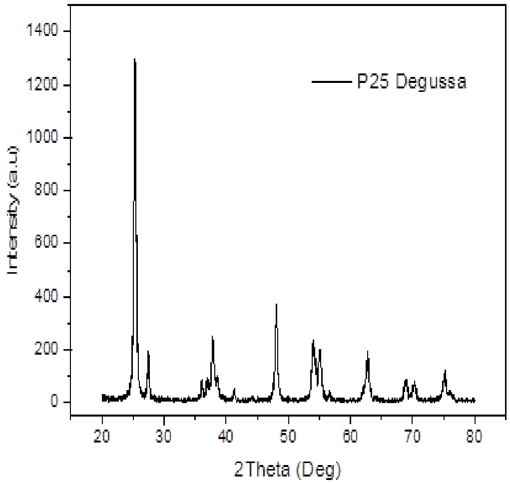

Fig 1: The XRD pattern of P25 degussa standard

Ahmed *et al.* (2013) prepared 0.05%, 0.1% and 0.3% of doped Pd on TiO_2 and compared it with the undopedTiO_2. He found out that XRD pattern of 0.05% and 0.1% palladium doped TiO_2 did not show any Pd phase even for 0.3% Pd doped TiO_2. This may reveal that Pd ions are uniformly dispersed in TiO_2 matrix. In the region of $2\theta^0 = 10^0$-80^0 the shape of diffraction peaks of the crystal planes of pure TiO_2 is quite similar to those of Pd/TiO_2 of different Pd concentration. The anatase and rutile formation was at $2\theta = 25.3^0$ and 27.4^0respecively.

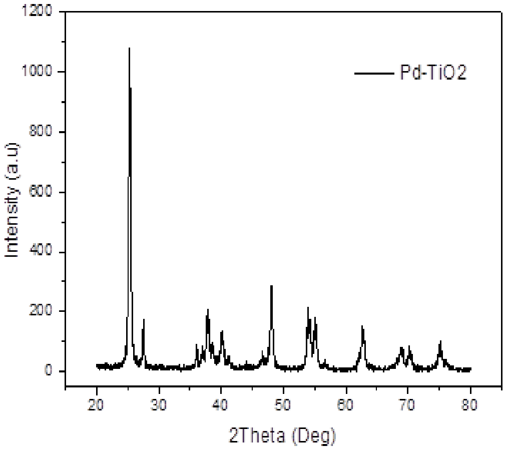

Fig 2: XRD pattern of 0.5% Pd-TiO_2

X-Ray Diffractometer (XRD) spectra of 0.5%Ag/TiO_2 catalyst: From the result of the XRD spectra of catalyst prepared using micro-emulsion, shown in Figure 3, the XRD spectra of Ag/TiO_2 was accompanied with some foreign peaks that can be ascribed to the impure nature of the $AgNO_3$ precursor used for Ag. For Ag/TiO_2, the peak formation is $2\theta = 25.3^0$ and 27.4^0respecively 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 TiO_2. The obtained peak is similar result of predominantly formation of anatase reflex at $2\theta=25.3^o$ with uniform distribution of anatase and rutile 27.4^0 with more of sharp peak of anatase reported by Ohtani *et al.* (2010).This study supports the report that P25 Degussa TiO_2 is composed of anatase and rutile crystallites, the ratio being typically 70:30 or 80:20 (Ohtani *et al.,* 2010).

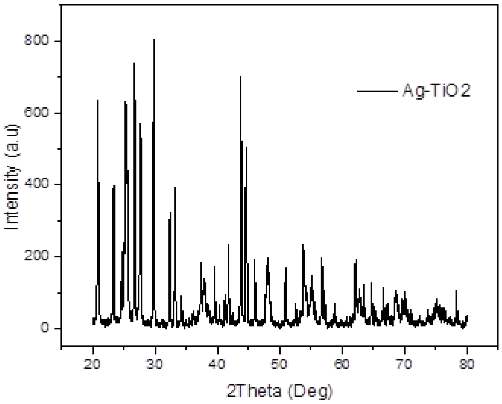

Fig 3: XRD pattern of 0.5% Ag-TiO_2

X-Ray diffractometer (XRD) spectra of 0.5%Pd/Ag-TiO_2 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 $20=25.3^o$ 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 photo- catalytic 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.

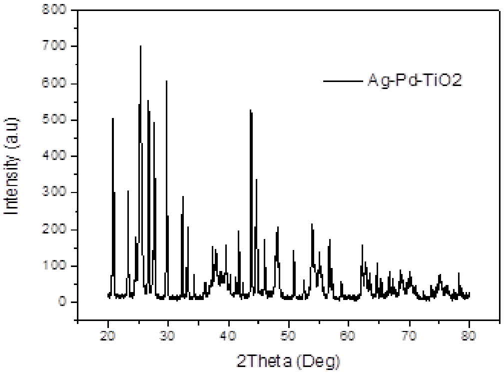

Fig 4: XRD pattern of 0.5% Pd/Ag-TiO_2

Table 1: XRD pattern of the crystalline size and full width at half maximum (FWHM) under different angles of diffraction for 0.5% Pd/TiO_2

2θ	Crystalline size	FWHM
25.40	23.50	0.362
27.46	49.39	0.173
36.12	61.49	0.142
37.84	24.93	0.352
48.06	23.19	0.392
52.92	21.76	0.428
62.70	22.04	0.441

Table 2: XRD pattern of the crystalline size and full width at half maximum (FWHM) under different angles of diffraction for 0.5% Ag/TiO_2

2θ	Crystalline size	FWHM
25.207	20.85	0.408
31.97	24.62	0.352
37.78	16.78	0.523
48.01	28.05	0.324
57.77	31.66	0.294

Table 3: XRD pattern of the crystalline size and full width at half maximum (FWHM) under different angles of diffraction for 5% Pd/Ag-TiO_2

2θ	Crystalline size	FWHM
23.23	75.13	0.113
32.357	86.43	0.100
43.77	76.46	0.117
44.60	51.27	0.175
62.16	52.68	0.184

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.

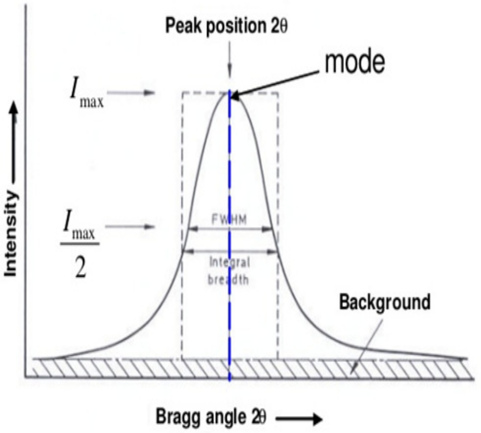

Fig 5: Full width at half maximum

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	$S_{BET}{}^a$ (m^2 g^{-1})	Pore Volume(cm^3g^{-1})	PD^b(nm)	TiO_2 size (±1nm)
0.5%Pd-TiO_2-RED	49.66	1.779	1.433	32.32
0.5%Ag-TiO_2-PD	43.73	1.509	1.380	24.39
0.5%Pd-AgTiO_2-TM	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^3g^{-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 pore volume of 17.7m^3/g 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-TiO₂ catalyst: Furthermore, Figure 8,9,10, and 11 indicated thatAg-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 photo catalytic 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 photo catalytic 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 47m^2/g and 0.5% Pd/TiO_2 has specific surface area of 51m^2/g showing that doped Pd/TiO_2 has more photocatalytic efficiency than doped Ag/TiO_2.

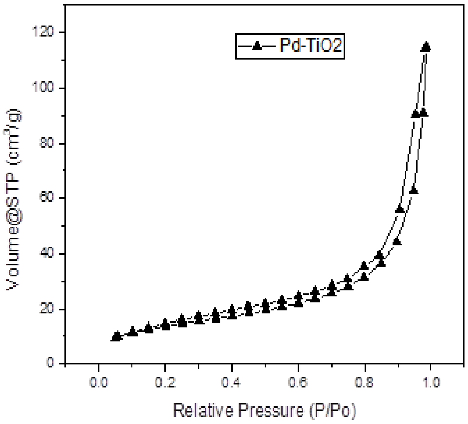

Fig 6: The Nitrogen adsorption-desorption Isotherm for 0.5% Pd/TiO_2

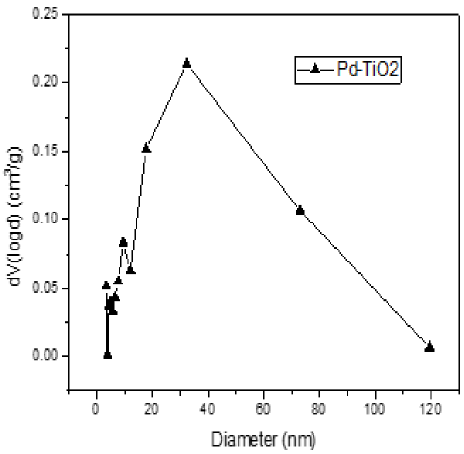

Fig 7: Pore size distribution for 0.5% Pd/TiO_2

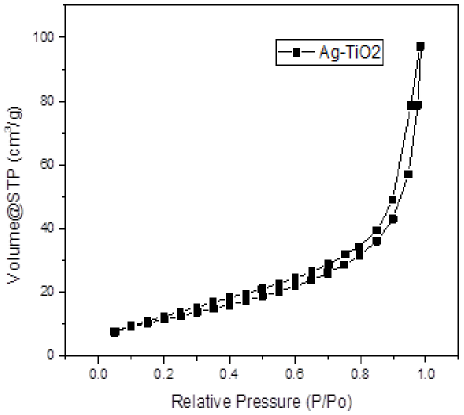

Fig 8: The Nitrogen adsorption-desorption Isotherm for 0.5% Ag/TiO_2

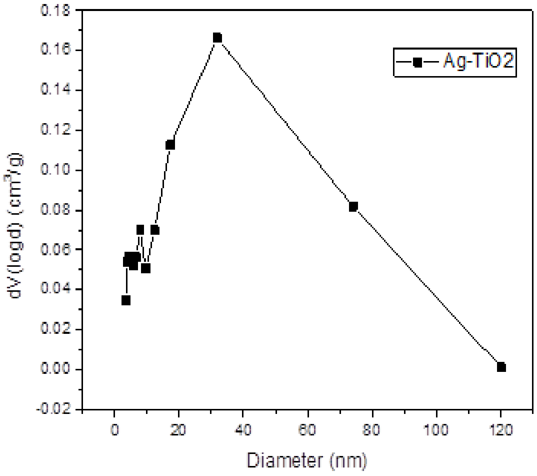

Fig 9: Pore size distribution for 0.5% Ag/TiO_2

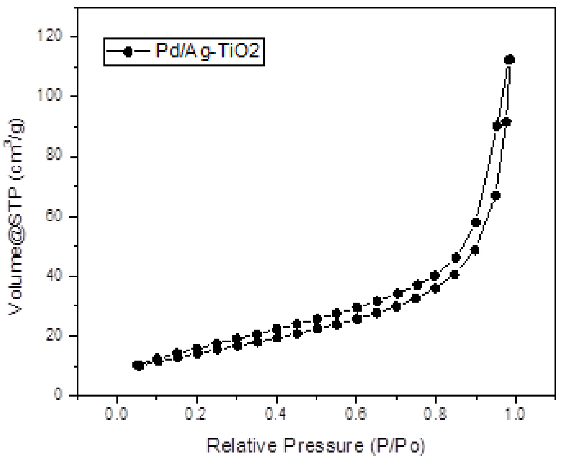

Fig 10: The Nitrogen adsorption-desorption Isotherm for 0.5% Pd/Ag-TiO_2

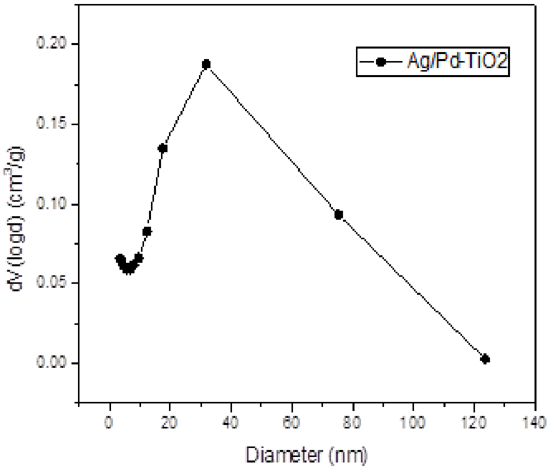

Fig 11: Pore size distribution for 0.5% Pd/Ag-TiO_2

Conclusion: The doping and codoping of Pd/TiO_2, Ag/TiO_2 and Ag/Pd/TiO_2 improve the photocatalytic activity of P25 degusa TiO_2 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 photo catalytic activity. The XRD of Pd/TiO_2, Ag/TiO_2 and Ag/Pd/TiO_2 shows uniform dispersion of the transition metal dopants on TiO_2 matrix. There was high reactive phase of anatase and improvement in surface area, pore volume and crystalline size of doped TiO_2 for enhanced photocatalytic.

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