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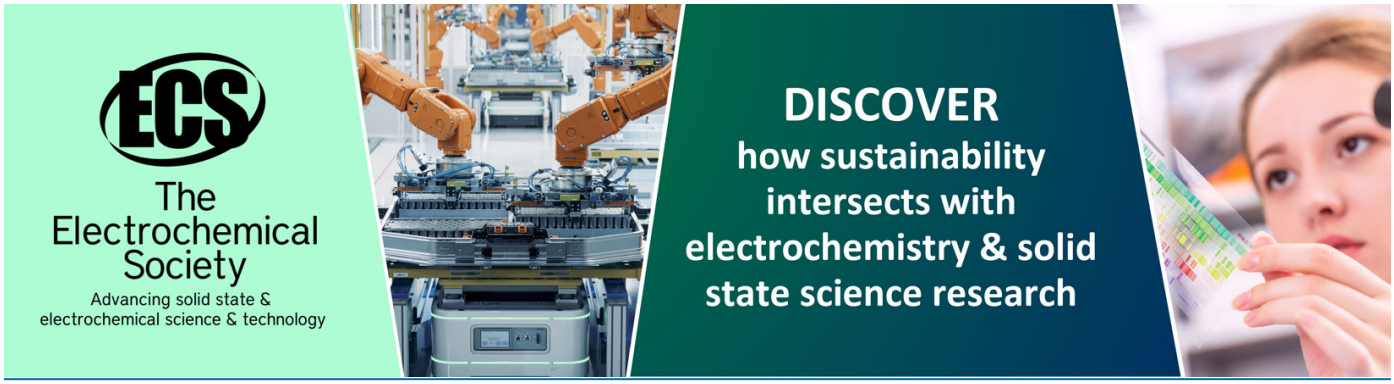

Preparation of TiO_2- SiO_2 via sol-gel method: Effect of Silica precursor on Catalytic and Photocatalytic properties

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Abstract. TiO_2- SiO_2have been synthesized by the sol-gel method from titanium isopropoxide and varied silica precursors: tetraethyl orthosilicate and tetra methyl ortho silicate. To study the effect of the precursor, prepared materials were characterized by X-ray diffraction, scanning electron microscopy, Diffuse Reflectance UV-vis optical absorption, and also gas sorption analysis. XRD patterns showed the formation of TiO_2 anatase in the TiO_2-SiO_2 composite with different crystallite size from different silica precursor as well as the different surface morphology. The DRUV-vis absorption spectra exhibit similar band gap energy correspond to 3.21eV value while the surface area, pore volume and pore radius of the materials seems to be affected by the precursor. The higher specific surface area contributes to give the enhanced activity in phenol hydroxylation and methylene blue photodegradation.

1. Introduction

Titanium dioxide is popular semiconductor material in some application including photocatalysis and dye-sensitized solar cell. To enhance its performance, some modifications have been investigated by such chemical and physical treatment[1][2]. Beside of doping and structural modification of titania nanoparticles, supporting titania has been reported to exhibit different photocatalytic performance from that titania itself. The contribution of support material has been explained to give better mechanism regarding the interaction between titanium oxide and the support[3][4]. By this scheme, titania-silica (TiO_2/SiO_2) composite is the well-known and intensively studied. Some studies revealed the relationship among surface titanium oxide structure, preparation method and loading amount, etc. with its photocatalytic activity.

As the different mechanism of preparation as well as synthesis route, TiO_2/SiO_2 material will give different performance related to its physicochemical character. Moreover, the porous structure of silica within the formation of the composite is also affected by some parameters, and one of these is the silica precursor. The composite formation between silica and titania precursors occurs between silanols or hydrolysis of titania from its hydroxides[5]. The condensation reaction between the titania precursor and the silica surface depends mostly on the hydroxyl groups of the silica since the rest of the silica is very inert and it is affected by the method used, and the amount of water and its pH used. In this present work the hydrolysis of tetra alkyl ortho silicate with two variations: tetraethyl ortho silicates (TEOS) and tetra meth kor to silicate (TMOS) is compared. Different hydrolysis rate is hypothesized to be the factor that controlling the physicochemical character and it may affect the photocatalytic properties. The physicochemical character is studied using UV/Vis diffuse reflectance, XRD, FTIR and also gas sorption analyzer; we discuss the relation between structure as a function of silica precursor and photocatalytic performance of TiO_2/SiO_2. Photocatalytic activity of the prepared

materials was studied in methylene blue (MB) photodegradation and phenol oxidation reaction using H2O2 as oxidant.

2. Material and Method

2.1 Materials

Titanium (IV) isopropoxide, methylene blue, phenol, tetra ethyl ortho silicate (TEOS), tetra methylortho silicate (TMOS), and H_2O_2 were purchased from Merck.

2.2 Preparation of TiO_2-SiO_2

The materials were prepared with a sol-gel mechanism by mixing titania and silica precursors for two h under reflux condition. The molar ratio of Ti: Si is 4:9. The filtrate of each reflux mixture was evaporated and followed by calcination for four h at 773K. By varied precursor, the obtained material is encoded as TS-M and TS-E respect to the use of tetra methyl orthosilicate and tetra etylortho silicate.

The specific surface area (SSA) of the samples was determined using Quantachrome NOVA 1200e equipment. SSA analysis was based on Bruner-Emmet-Teller (BET) model of N2 low-temperature adsorption while the pore volume and pore radius were calculated using Barret-Jonna-Halenda (BJH) equation. Powder X-ray diffraction (XRD) patterns were collected using Shimadzu X6000 instrument. Ni-filtered CuKα radiation was used for collecting reflections in the 2θ range 15–80° with a step of 0.02°. Crystalline phases were identified by comparison with the JCPDS data files. Crystallites size of materials was estimated according to the Scherrer equation. FTIR spectra of prepared materials were obtained using Perkin-Elmer instrument.

2.3 Catalytic activity of TiO_2-SiO_2

For catalytic activity study of the prepared materials, phenol hydroxylation and methylene blue photodegradation were conducted. The hydroxylation reactor and photocatalytic reactor were set up as the scheme in Figure 1 and Figure 2. UV Lamp used in the reactor is Philips UVB Lamp with the power of 40W.

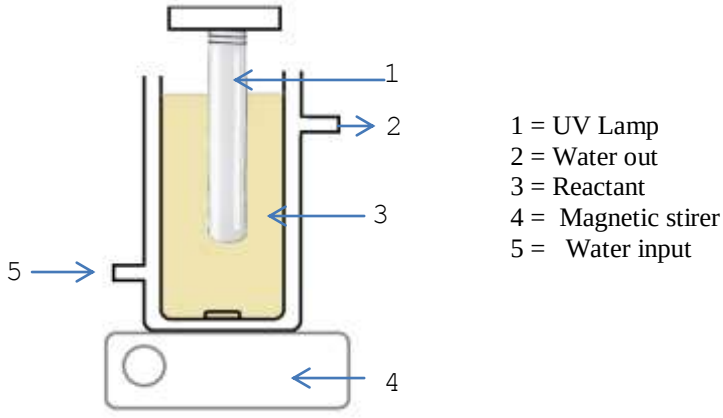
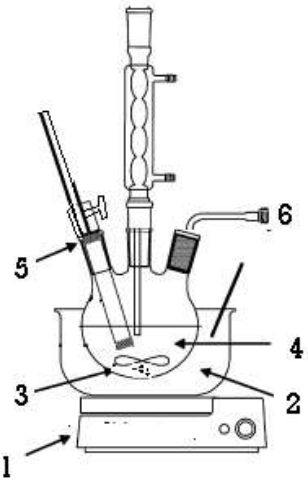


Figure 1. Scheme of photocatalytic reactor



1 = Magnetic stirrer-heater
2 = Water bath
3 = Stirer
4 = Reactants
5 = H_2O_2 input
6 = Sampler

Figure 2. Scheme of phenol hydroxylation reactor

3. Results and Discussion

X-ray diffraction technique was performed to analyze and identify phase formation and crystallographic information of the samples. The XRD pattern of TiO_2/SiO_2 powder prepared from both precursors is given in **Figure 3**. The diffraction patterns indicate the formation of TiO_2 match very well with those of tetragonal TiO_2 anatase for both samples (JCPDS-21-1272). The presence of silica is not clearly indicated from patterns probably due to the high crystalline TiO_2 formed to cover amorphous silica which is also act as TiO_2 support. The patterns are similar with what obtained from the utilization of surfactant in sol-gel synthesis by using titanium isopropoxide precursor[6,7].

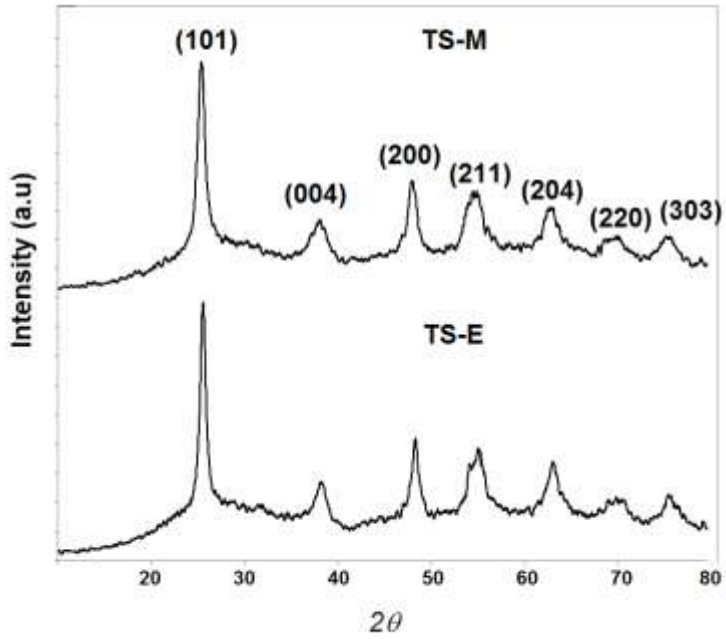
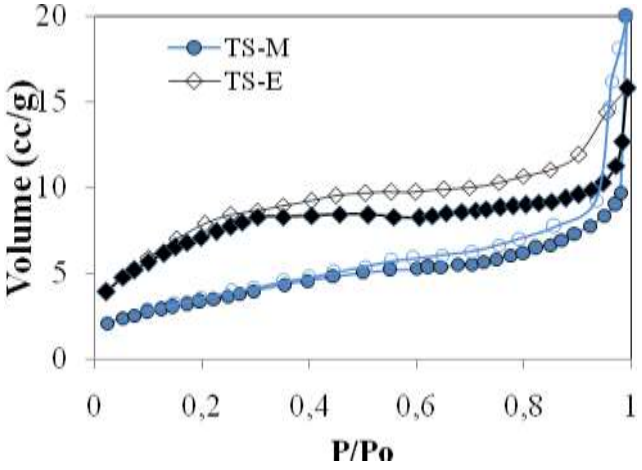


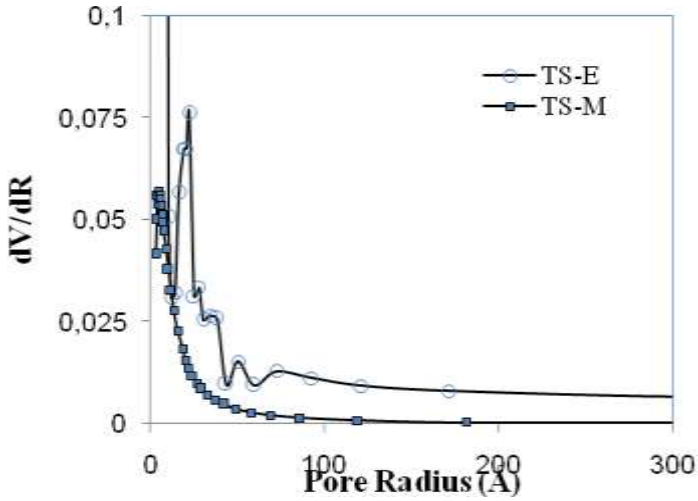
Figure 3. XRD pattern of prepared materials

The typical plot of N_2 adsorption-desorption isotherm and pore size distribution curves of the prepared TS samples are in Figure 4. Both samples exhibited type IV (BDDT classification) of isotherm with

hysteresis loops of type H3 at relative pressure range of 0.65–1.0, representing the mesoporous structure. The pore size distributions indicated that TiO_2 presented a relatively narrow distribution ranging from 5 nm to 60Å. From the calculation it is found that the specific surface area of TS-E is higher compared to TS-M. It is also indicated from the pore distribution that TS-E gives the higher pore volume in all pore region. However the properties are not significantly appeared from the SEM profile analysis (Figure 5) in that both precursors give flaky morphology. The band gap energy values of TS-M and TS-E are also similar.

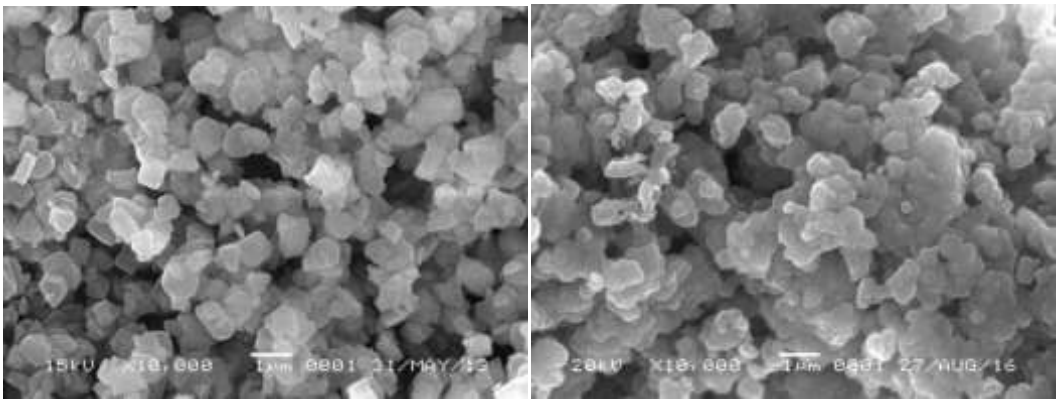


(a)



(b)

Figure 4. (a) Adsorption-desorption profile of materials (b) pore distribution curve of materials



(a) (b)

Figure 5. SEM profile of (a) TS-E (b) TS-M

The band gap energy of the materials are related to the photoactivity of materials and for anaysis DRUV-Vis was employed. The band gap energy is calculated as function of the edge wavelength (λ_{edge}) by following equation:

$$E_g = \frac{1240}{\lambda_{edge}} \quad (1)$$

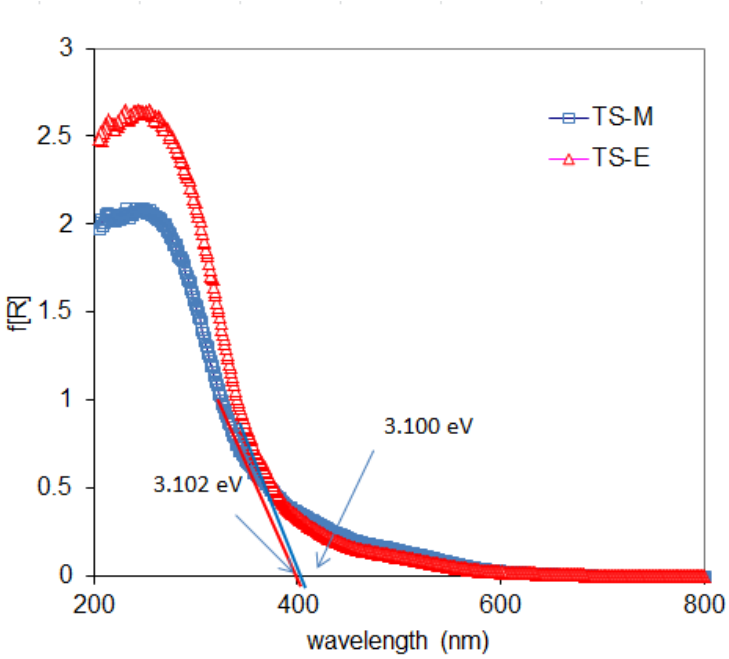


Figure 6.DRUV-Vis spectra of materials

Table 1: Surface profile data of prepared materials

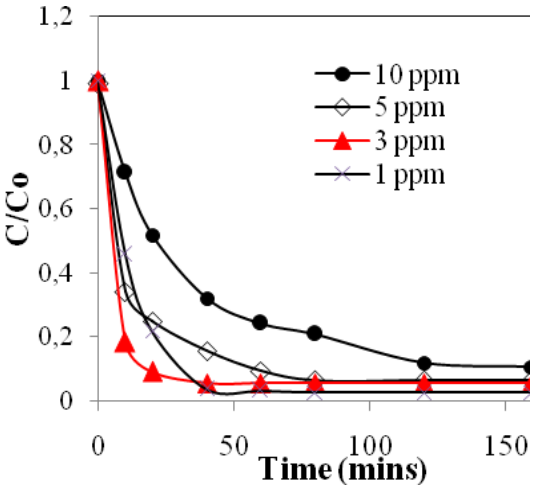
Sample	**Specific surface area (m^2/g)**	**Pore Volume (cc/g)**	**Pore radius (Å)**
TS-E	235.71	0.2786	13.4
TS-M	128.22	0.1208	10.1

Photocatalytic activity of the materials is expressed from the kinetics of MB photooxidation in varied MB concentration presented in Figure 7. From the kinetics constant values (k) it is confirmed that TS-E gives higher rate respect to the faster MB degradation in the same pattern from varied time and concentration. The same pattern found that the higher MB concentration, the higher kinetic constant obtained. The data is fit with the theoretic concept in which the higher MB concentration creates more interaction from the more collision between catalyst surface and the reactants. Furthermore, related to the physicochemical properties of the materials the photocatalytic activity suggests that the specific surface area plays important role in the photodegradation mechanism. TS-E with the higher specific surface area provides more active sites to be effectively adsorb the MB molecules before oxidation with the presence of H2O2 as the oxidant in the system.

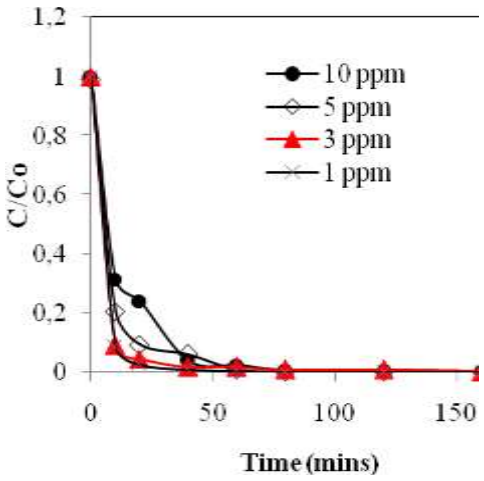
The similar reasons may apply for the kinetic of phenol hydroxylation data as presented in Figure 8. The trend of phenol conversion (Conv.(%)) as function of time of reaction represents that TS-E has higher activity than TS-M. Conv.is calculated with following equation:

$$Conv.(\%) = 100\left(\frac{[phenol]o-[phenol]t}{[phenol]o}\right) \quad (2)$$

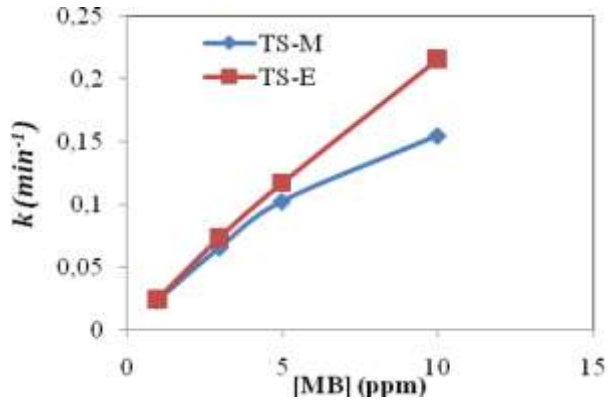
With [phenol]o and [phenol]t are initial phenol concentration and phenol concentration in time t of sampling.



(a)



(b)



(c)

Figure 7. (a) Kinetic of MB photodegradation over TS-M (b) Kinetic of MB photodegradation over TS-E (c) Effect of MB concentration on kinetic constant

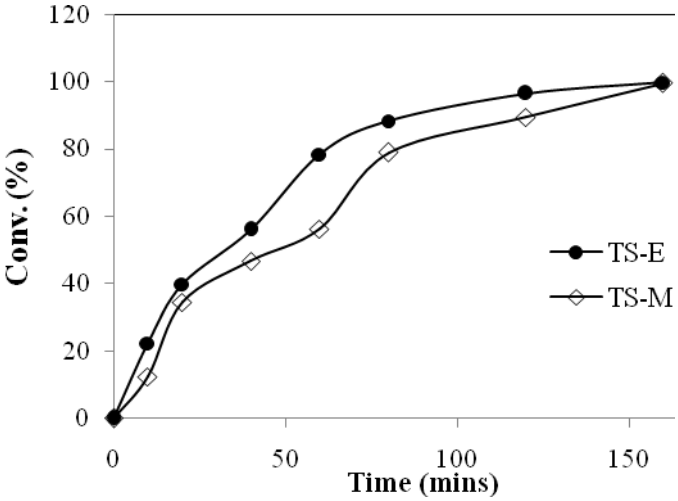


Figure 7. Kinetic of phenol hydroxylation by varied catalyst

4. Conclusion

In summary, the preparation of TiO_2/ SiO_2 composites with varied silica precursor has been successfully investigated. The physicochemical character of the materials reveals that the use of tetraethyl orthosilicate gives higher specific surface area and pore volume while the band gap energy and XRD analysis give similar pattern and the values of band gap energy as well as crystallite size. The parameter of specific surface area and pore volume of material facilitate the photocatalytic and catalytic activities resulting from the higher activity of TS-E compared to TS-M.

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