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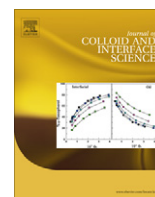
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Liquid–gas boundary catalysis by using gold/polystyrene-coated hollow titania

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ABSTRACT

A microparticle material of gold/polystyrene-coated hollow titania was successfully synthesized. The synthesis steps involved hydrothermal synthesis of a carbon sphere from sucrose as a template, coating of the carbon sphere with titania, removal of the carbon sphere to produce hollow titania, followed by coating of polystyrene on the surface of hollow titania and then attachment of gold nanoparticles. It has been demonstrated that this material can float on water due to its low density and it is a potential catalyst for liquid–gas boundary catalysis in oxidation of benzyl alcohol by using molecular oxygen.

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1. Introduction

Synthesis of a solid catalyst which can be located in the boundary of immiscible liquid–liquid and liquid–gas systems remains a big challenge today. Previously, the preparation of heterogeneous catalysts in the liquid–liquid phase boundary has been reported in scientific journals [1–6]. In this catalytic reaction system, the catalyst was placed at the liquid–liquid phase boundary between aqueous hydrogen peroxide and water-immiscible organic phase and act as an efficient catalyst for epoxidation reaction. In this paper, the study is extended to liquid–gas catalytic system. Solid–gas catalyzed-liquid reactions are often encountered in the chemical process industry, most frequently in hydroprocessing operations and in the oxidation of organic liquid phase [7–10].

The fast-growing insight into the functional materials has led the research more focused on the synthesis of materials for the specific properties. The preparation of hollow materials with low density is one of the targets [11–17]. Along this line, we have attempted to make an effective heterogeneous catalytic system for this application by using gold/polystyrene-coated hollow titania as a catalyst. Fig. 1 shows a schematic illustration of the procedure implemented for the synthesis of floating gold/polystyrene-coated hollow titania. The catalyst was prepared in several stages: (1) preparation of the template hydrothermally by using sucrose as a

precursor, (2) synthesis of hollow titania by sol–gel method and the removal the carbon template by calcination, (3) polystyrene coating of hollow titania particles, and (4) gold sputtering of polystyrene-coated hollow titania.

Reaction between two immiscible liquids requires stirring to maximize the contact area of the reactants. Nevertheless, the reaction between gas and liquid phases also need stirring to increase the solubility of the gas into the liquid. From an industrial point of view, continuous processes carried out in a gas phase are preferred; where large production is concerned, they offer advantages in the field of economy of process, plant security, process control, and heat recovery [18]. In liquid–gas reactions, a gas phase and a liquid phase are brought into contact with each other to form chemical reactions. Gas and liquid phases have various mixing patterns (plug flow, well stirred, and plug flow with axial dispersion). Often, these processes are conducted in stirred tank batch reactors; hence, the catalysts must finely divided solids to ensure easy suspension in the reaction medium.

In phase-boundary catalysis, the stirring process is not required because the mass transfer is not rate determining step in this system. Hence, this research will be great if it can contribute knowledge in floating gold/polystyrene-coated hollow titania catalysts with floating properties. Besides, efficient control of the structural properties of hollow titania and fabrication of gold/polystyrene composites are the other important subject for their application, especially in the field of catalysis. For floating purpose, it is necessary to fabricate polystyrene-coated hollow titania with low density.

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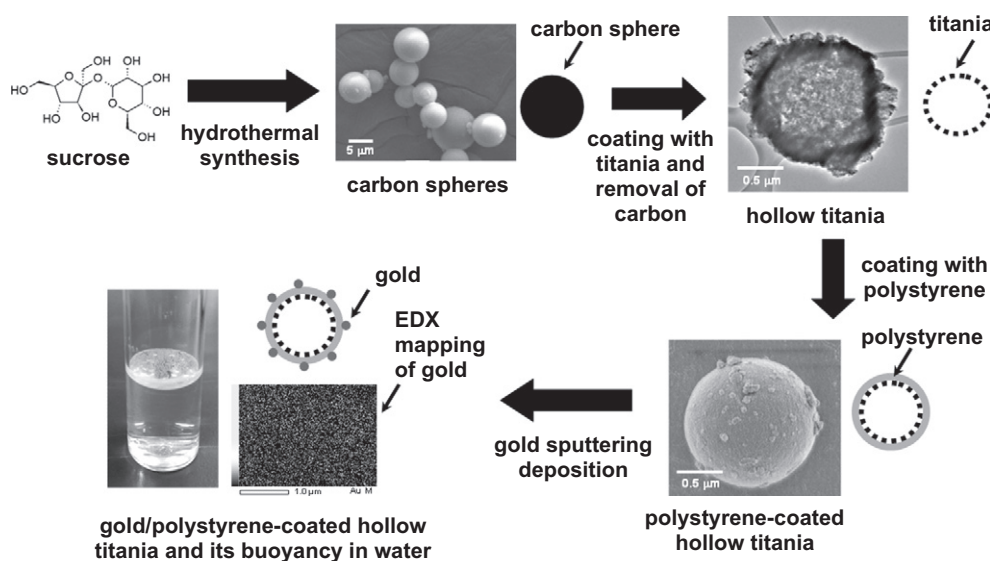


Fig. 1. Schematic illustration of floating gold/PS-HT synthesis procedure with TEM micrograph of hollow titania and FESEM micrographs of CS and PS-HT.

Gold has a rich coordination and equally effective as a heterogeneous or a homogeneous catalyst [19]. Gold nanoparticle has remarkable properties compared to gold in bulk species has been well nurtured till few decades [20]. Nano-sized metal on a support has attracted a great deal of interest owing to its novel properties as a catalyst [21]. The catalytic activity of supported metal catalyst is greatly influenced by the size of metal particles and the interaction between gold and the support. The interaction between the gold and the support is a prerequisite to increase catalytic activity because gold shows poor catalytic activity. Supported gold has been shown to be active catalyst to oxidize alcohols and polyols with O_2 and display higher resistance to intoxication than the Pt or Pd.

The oxidation of benzyl alcohol to benzaldehyde by molecular oxygen was used as a model reaction to examine the performance of gold/polystyrene-coated hollow titania floating catalyst. Benzaldehyde is commercially obtained by hydrolysis of benzyl chloride and the oxidation of toluene [22,23]. However, the chlorine produced may contaminate the reaction and reduce the selectivity. Therefore, the oxidation of benzyl alcohol is preferred reaction route for the production of chlorine-free with improved selectivity. The conventional methods for the oxidation of alcohols are based on the stoichiometric amount of inorganic oxidants (such as chromate) or organic oxidants (such as DMSO) [24]. Nevertheless, these methods have led to environmentally and economically problems due to their large production of byproducts. The selection of oxidant is important in order to make a clean oxidation process. The catalytic oxidation with molecular oxygen is a crucial process for the synthesis of fine chemicals. Water formed as the sole co-product and low cost of the oxygen/air make it a suitable candidate as an oxidant.

2. Experimental

2.1. Materials

Chemicals and materials used were deionized water (Barnstead and Hamilton); ethanol (R&M Chemicals, 99.7% v/v minimum denatured); tetramethylammonium chloride, TMAC (Fisher, 98%); *n*-hexadecyltrimethylammonium bromide, HTAB (TCI); titanium(IV) isopropoxide, TIP (Merck); hydrogen peroxide, H_2O_2

(QRec, 30%); styrene (Sigma–Aldrich, 97%); acetonitrile (Merck); and benzyl alcohol (Merck).

2.2. Preparation of carbon microspheres

In typical synthesis of colloidal carbon microspheres [25], 0.04 mol of sucrose was dissolved in 50 ml (0.8 M) deionized water. Sucrose solution was sonicated for 5 min to homogenize the solution. Hydrothermal method was adopted for carbon sphere synthesis. The solution was sealed in 125 ml autoclave and maintained at 170 °C for 5 h. The products were centrifuged, washed, and redispersed in ethanol and water for five times. The carbon sphere was dried overnight in an oven at 90 °C. The same procedure was repeated for 0.4, 0.5, 0.6, 0.7, 1.0, and 2.0 M of sucrose. In order to investigate the effect on particle size, surfactant such as TMAC or HTAB was added with a different ratio to 0.5 M concentration of sucrose. Carbon sphere particle was labeled as CS.

2.3. Preparation of hollow titania

Preparation of hollow titania was described elsewhere [12] using sol–gel method. The coating was carried out at room temperature in 20 ml ethanol with 3.0 ml titanium(IV) isopropoxide (TIP) as titanium precursor and 0.3 g of prepared the CS from 0.8 M sucrose solution. The mixture was stirred for 24 h to allow completed precipitation of TIP on carbon particles. The product was separated and washed by centrifugation with ethanol three times at 3500 rpm for 5 min. The obtained titania–carbon composite (Ti/C composite) was dried at room temperature for 12 h followed by drying at 60 °C for 2 h before calcination at 500 °C for 3 h in air. Hollow titania was labeled as HT.

2.4. Synthesis of polystyrene-coated hollow titania

The prepared HT (50 mg) was wetted with aqueous H_2O_2 (5 mmol) to facilitate in situ polymerization of styrene on HT. Styrene (5 mmol) was added as polystyrene precursor and 5 ml acetonitrile as solvent. The mixture was stirred gently at 80 °C for 8 h. The product obtained was separated by centrifugation and dried overnight at 60 °C. Polystyrene-coated hollow titania was labeled as PS-HT.

Table 1

The name of samples and their preparation methods.

Sample ^a	Preparation of sample
Gold 30/PS	Polystyrene beads were coated with gold nanoparticle with deposition time 30 s
Gold 30/TiO ₂	Titanium dioxide particles were coated with gold nanoparticle with deposition time 30 s
Gold 30/PS-HT	PS-HT ^b particles were coated with gold nanoparticle with deposition time 30 s
Gold 40/PS-HT	PS-HT ^b particles were coated with gold nanoparticle with deposition time 40 s
Gold 50/PS-HT	PS-HT ^b particles were coated with gold nanoparticle with deposition time 50 s
Gold 60/PS-HT	PS-HT ^b particles were coated with gold nanoparticle with deposition time 60 s

^a Sample was deposited by gold in auto fine coater and was placed 30 mm below the gold target disk. Amount of sample before gold deposition was 10 mg.

^b Polystyrene-coated hollow titania.

2.5. Impregnation of gold onto catalyst by sputtering deposition

The PS-HT (10 mg) was placed on a glass slide before put in Auto Fine Coater JFC 1600 for gold deposition. The distance between the targeted plate disk (gold) with specimen stage was adjusted to 30 mm. Gold loading was controlled by varying times for gold deposition from 30 to 60 s for respective PS-HT. Polystyrene beads (PS) and titanium dioxide (TiO₂) also underwent the same procedure by placing the samples in the coater for 30 s. The gold/polystyrene-coated hollow titania was labeled as gold/PS-HT.

2.6. Oxidation of benzyl alcohol

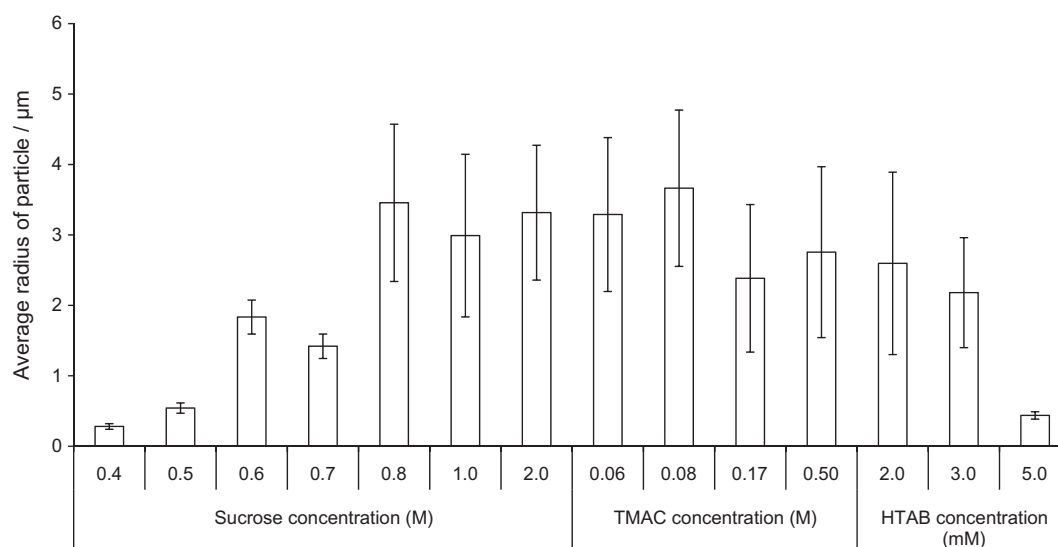
The gold/PS-HT catalyst (10 mg) was weighed and let to be floating in Schlenk tube (25 ml) containing 0.3 M NaOH (5 ml) and 0.3 M benzyl alcohol (5 ml) solution. 3-way stopcock was fitted to Schlenk tube before connected with a balloon containing excess gas oxygen (3 l). The oxygen gas was allowed to flow in the system for 5 s before the reaction to make sure that the air in the system was replaced with oxygen gas. The reaction was conducted for 22 h. The reaction with agitation was compared with static condition. After the reaction end, the catalyst was filtered off and the mixture was extracted using toluene. Recovery was always $98 \pm 3\%$ with this procedure. The product of the reaction, benzaldehyde, was analyzed by Shimadzu 2014 equipped with a capillary BPX5 column and a Flame Ionization Detector (FID). Comparison with authentic samples was done. For the quantification of the reactant products, the calibration method using an external standard was

employed. The sample names for benzyl alcohol oxidation were recorded according to the time taken during gold deposition (Table 1). The turn over number (TON) was measured using the following equation:

$$\text{Turn over number (TON)} = \frac{\text{Yield of product (mole)}}{\text{Amount of gold (mole)}} \quad (1)$$

2.7. Characterizations

The FTIR spectrum was prepared according the following procedure. A CS pallet was prepared by grinding the CS powder with dry KBr as a binder (1:100 ratio) and hold for 8 tons for 3 min. The measurement was done at ambient condition at range 400–4000 cm⁻¹ using Perkin-Elmer Spectrum spectrometer. Field emission scanning electron microscopy (FESEM) study was carried out on JEOL JSM-670 IF operated at 2.0 kV. The samples used for FESEM analysis were prepared by separating floating PS-HT from the non-floating ones in water. Transmission electron microscopy (TEM) study was conducted with JEOL JEM-2100 at 200 kV. The TEM samples were prepared by drying drops of dispersing samples in ethanol on copper grids coated with formvar/carbon. X-ray diffraction (XRD) spectroscopy was conducted with Bruker AXS D8 in ranges $2\theta = 10\text{--}90^\circ$ using Cu K α radiation with $\lambda = 1.5418 \text{ \AA}$ at 40 kV and 40 mA, step 0.030 and step time 1 s (1.2° min scanning speed). The samples were also characterized using diffuse reflectance ultra-violet spectrometer (DR-UV) (Lambda 900 Perkin Elmer) from 200 to 900 nm wavelength, and weight loss study was carried out using TGA-SDTA of TGA/SDTS851 Mettler Toledo in the range

**Fig. 2.** Distribution of particles average radius of carbon spheres with/without surfactant.

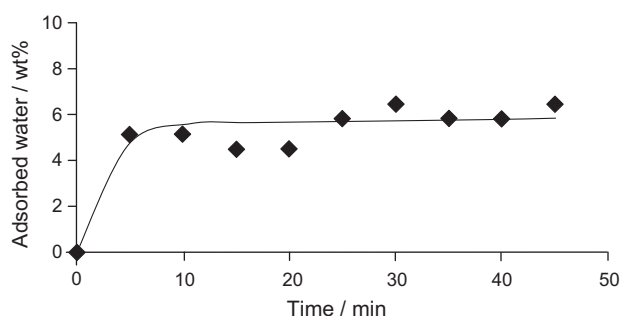


Fig. 3. Percentage of adsorbed water on the surface of 0.8 M CS.

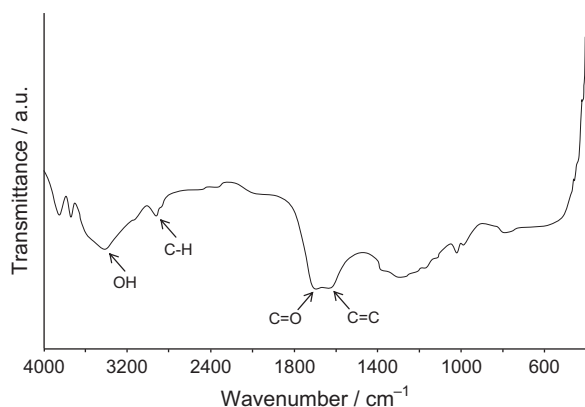


Fig. 4. IR spectrum of CS from 0.8 M of sucrose.

of 25–900 °C. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Axis Ultra DLD Shimadzu electron spectrometer equipped with monochromated Al K α , Dual (Al and Mg) X-ray sources. The binding energy (BE) of the C 1s peak at 284.5 eV was taken as an internal standard.

Hydrophilicity of carbon sphere from 0.8 M sucrose solution was analyzed using water adsorption technique. The sample was dried in an oven at 110 °C for 12 h to remove all the physically adsorbed water. After dehydration, the sample was exposed to water vapor at room temperature, followed by the determination of the percentage of adsorbed water per gram solid as a function of time.

3. Results and discussion

Fig. 2 shows particle size distribution of carbon particles at different concentration of sucrose with/without surfactant. The size of CS increased as the concentration of sucrose solution increased. This verified that the concentration of sucrose aqueous plays an important role for nucleation during hydrothermal reaction. Average radius of the CS which produced from 0.4 to 0.7 M of sucrose

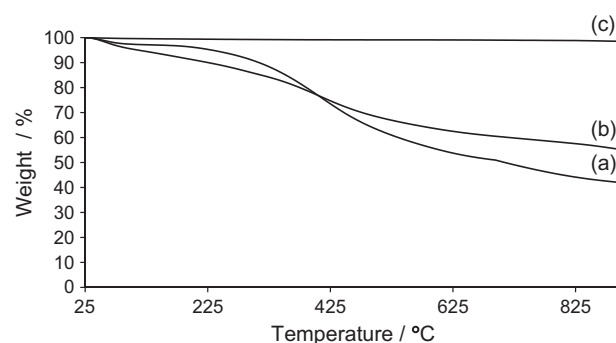


Fig. 6. TGA curves of the: (a) CS, (b) Ti/C composite and (c) HT.

solution showed a narrow distribution compared to 0.8–2.0 M sucrose solution. The size deviation is higher at concentration more than 0.8 M indicated that the carbon particle size has poor distribution might due to the particles collide or stick together to form larger particles. The deviation of particle size can be explained by Ostwald ripening whereby non-uniform size distribution is driven by solid particles dispersed in saturated or supersaturated solution to achieve a minimum total surface free energy. Therefore, smaller particle reduced its size while the bigger particle kept on growing [26]. The CS synthesized by using 0.8 M sucrose was selected as the template for synthesis of HT because its particle size was relatively big. In addition, particle size of CS from 1.0 M and 2.0 M concentration of sucrose not differ much from 0.8 M. As shown in Fig. 1, carbon particle obtained was then coated by titania. One expects that the bigger the size of CS, the lower the density of HT produced.

Addition of TMAC with a different ratio on 0.5 M sucrose solution gives no significance changes on particle size, plus the dispersion was also poor. Nevertheless, it was found that addition of TMAC into sucrose solution led to substantial increase in particle size. The diameter of TMAC carbon particle was from 2 μm up to 12 μm . On the other hand, it is reversely observed in the addition of HTAB in sucrose solution. The size of carbon particle was decreased as the concentration of HTAB increased. As the concentration was further increased, the nucleation was fully inhibited with no longer the formation of solid particles was observed. The surfactant not only can boost up the size of the CS, but it is also can reduce the size of carbon particle.

The mechanism of carbon spheres formation was described elsewhere [27,28] according to following steps: (1) sucrose undergoes hydrolysis to produce corresponding monosaccharide; glucose and fructose, (2) these monomers are then dehydrated and condensed/polymerized generating aromatized molecules and (3) appearance of a short burst of nucleation when the concentration of aromatic clusters in the aqueous solution reaches the critical supersaturation point to form microspheres. The graph in Fig. 3 shows the adsorption of water by carbon sphere. The water vapor

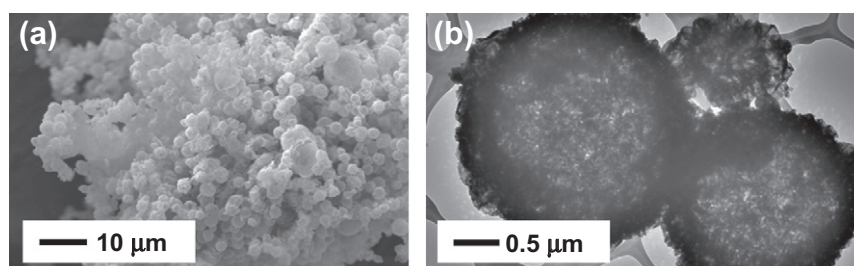


Fig. 5. Hollow titania images under (a) FESEM and (b) TEM.

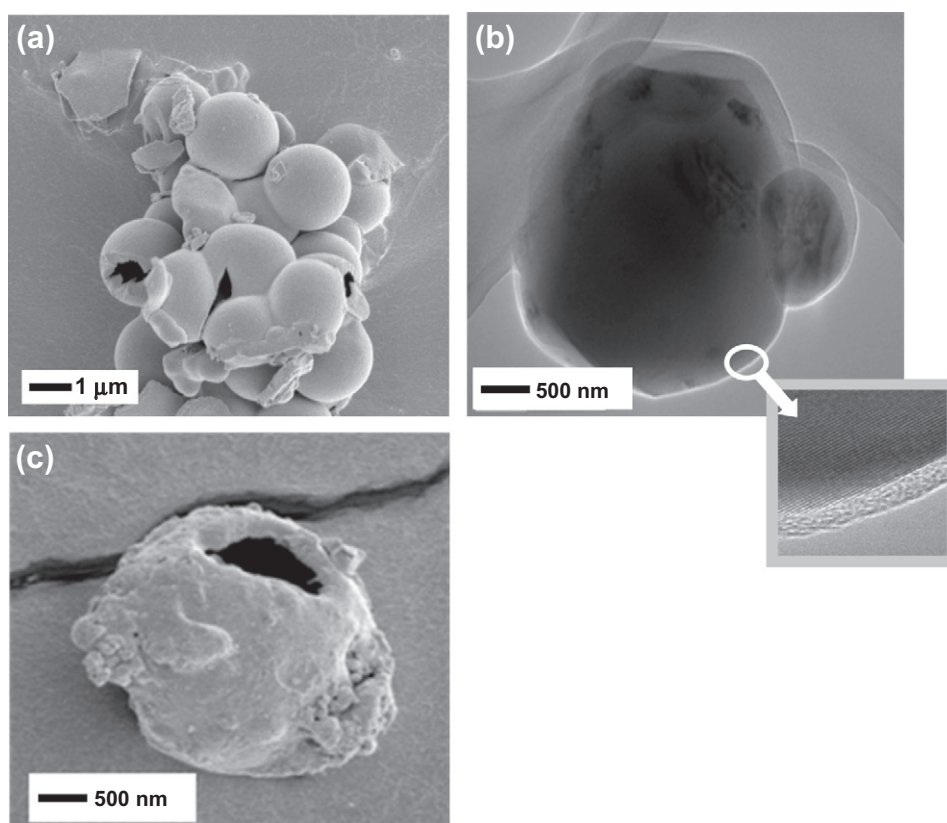


Fig. 7. (a) FESEM micrograph of PS-HT and (b) TEM micrograph of PS-HT and (c) PS-HT perforated structure.

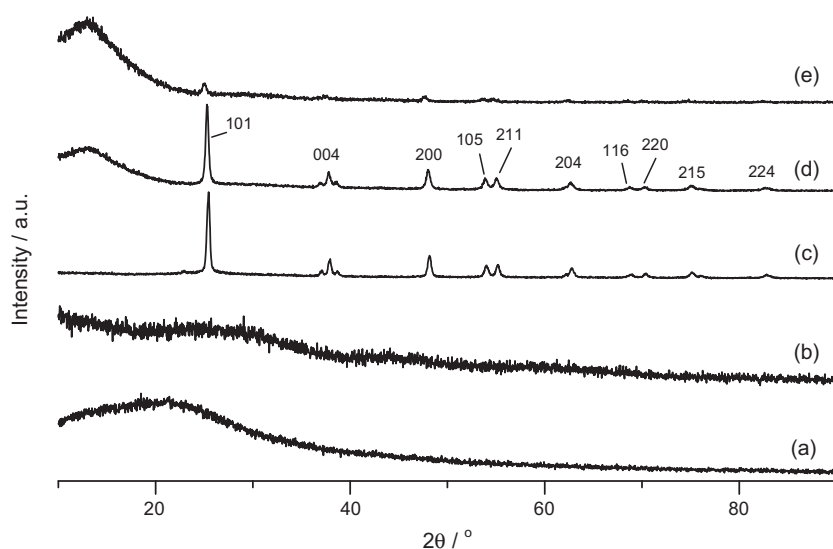


Fig. 8. XRD pattern of (a) CS, (b) Ti/C composite, (c) HT, (d) PS-HT, and (e) gold/PS-HT.

was attracted to carbon sphere via the available OH group on the carbon surface. Hence, this indicates that the carbon sphere is hydrophilic enough to trap moisture in air. The FTIR spectrum in Fig. 4 endorsed that the CS contains OH group and acquires hydrocarbon characteristic. There is strong characteristic peak stretching vibration of O–H bond at 3444 cm^{-1} . The peaks at 2924 cm^{-1} originated from the stretching vibration of C–H bond. The peak of stretching vibration of carboxyl groups C=O can be observed at 1688 cm^{-1} . The peak at 1620 cm^{-1} indicated that the presence of C=C group.

The peak at 1285 cm^{-1} is due to the stretching vibration of C–O bond. Since the carbon particles have dangling OH group on its surface, no functionalization needed for carbon to react with the desired metal oxide precursor.

In the next stage to produce gold/PS-HT, the obtained CS particles were then coated with titanium precursor, TIP. After calcination to remove the carbon template, the diameter of HT was reduced to *ca.* $2.0\text{ }\mu\text{m}$ (Fig. 5) with wall thickness *ca.* 140 nm . The shrinkage probably caused by further dehydration of the loosely

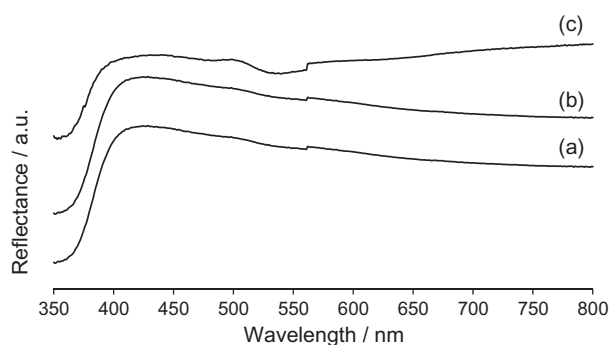


Fig. 9. DR UV-Vis spectra of (a) HT, (b) PS-HT, and (c) gold/PS-HT.

cross-linked structure of the carbon spheres [29] which lead to densification of HT. The thermogravimetric curves of the carbon sphere (CS), titania–carbon composite (Ti/C composite) and hollow titania (HT) are shown in Fig. 6. For CS and Ti/C composite, the weight loss region below 100 °C could be attributed to physically adsorbed water and residual of solvent in the sample and the weight loss at 350 °C could be resulted from decomposition of organic compound. For HT, the straight line indicated that carbon particle was completely removed by calcination.

As shown in Fig. 7a, it has been clearly observed that pore of HT was fully covered by polystyrene as a ball-like material which appeared in smooth surface. The size of PS-HT is ca. 2.0 μm is not much different from HT. Wall thickness of polystyrene is ca. 50–200 nm (see Fig. 7b). A void inside the sphere cannot be observed under TEM due to the thick wall of PS-HT. Fortunately, the layer of polystyrene and titania can be distinguished by differences in the color contrast. The crystalline phase of titania was clearly observed by the emerging of titania lattice under high-resolution TEM image. The outer layer indicates the amorphous phase of polystyrene. The particles of PS-HT which did not float on the surface of water were also analyzed using FESEM. Since it is difficult to determine the density of PS-HT, the presence of perforated polystyrene-coated hollow titania (Fig. 7c) proved that the material contained an empty space within its sphere.

The crystallinity of CS, Ti/C composite, HT, PS-HT, and gold/PS-HT was confirmed by using XRD. Fig. 8a shows that CS produced by hydrothermal method displayed an amorphous phase since there is no peak appears in the XRD pattern. Only a hump at $2\theta = 20^\circ$ was observed. Amorphous titania was also obtained after the carbon sphere was coated with titanium precursor to form titanium–carbon composite (see Fig. 8b). During the hydrothermal reaction, the pressure is created in an autoclave (autogeneous pressure) thus gives impact on the product. The hydrothermal reaction which takes place at moderate temperature in the 170–350 °C range from sucrose produced amorphous carbon [28]. However, if the hydrothermal reaction takes place at elevated temperature,

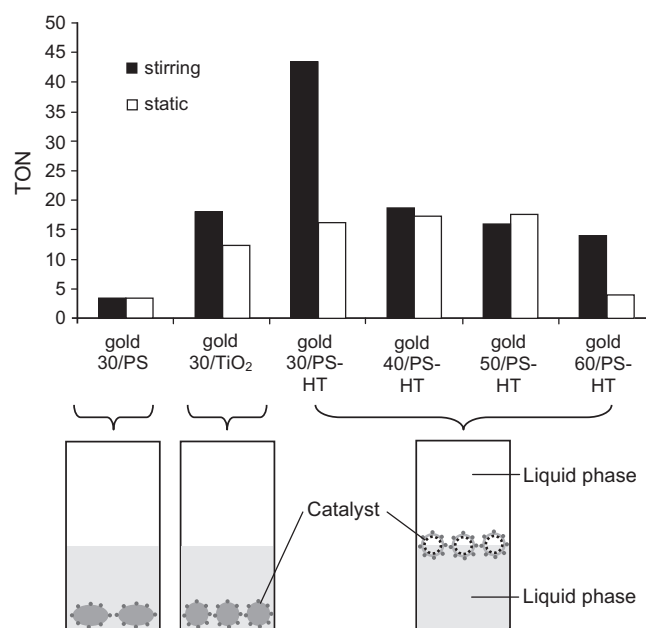


Fig. 11. The TON of liquid–gas boundary catalysis in oxidation of benzyl alcohol by using molecular oxygen over gold/PS-HT, gold/PS beads and gold/TiO₂ under static and stirring conditions.

saccharide-type of monomer will yield graphite-type of the carbon [30,31]. After calcination at high temperature, HT was transformed to anatase phase (see Fig. 8c). Since HT was covered with polystyrene, the intensity of HT anatase peaks was reduced (see Fig. 8d and e).

Fig. 9 shows HT and PS-HT have the same reflectance in the visible region which is 420 nm. On contrary, the gold/PS-HT showed a hypsochromic shift 390 nm and showed a marked decrease at 540 nm which indicated the characteristic of gold nanoparticles [32]. Images of Au sputtered on the surface of the support and size distribution were presented in Fig. 10. Measurement of size distribution based on the images showed has mean particle size of ca. 11.0 nm with broad distribution range 5–17 nm. High-resolution imaging was performed on the gold particle and exhibited lattice fringes 2.53 Å. There is no change in the size of gold particles as the sputtering time increasing. The different is only the amount of gold deposited on the PS-HT. This observation is similar to the previous report [33].

Fig. 11 shows the turnover number (TON) of the catalytic reaction of the oxidation of benzaldehyde by molecular oxygen under stirring and static conditions. The TON was determined based on the amount of gold nanoparticles deposited on PS-HT. The reaction of gold/PS-HT was also compared with gold 30/PS and gold 30/TiO₂. The gold 30/PS showed a relatively low production of

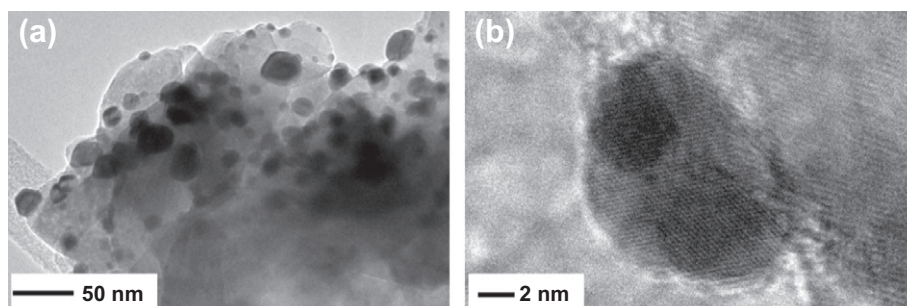


Fig. 10. Representative TEM images of (a) gold distribution and (b) lattice fringes appearance of 1% Au loading on gold/PS-HT.

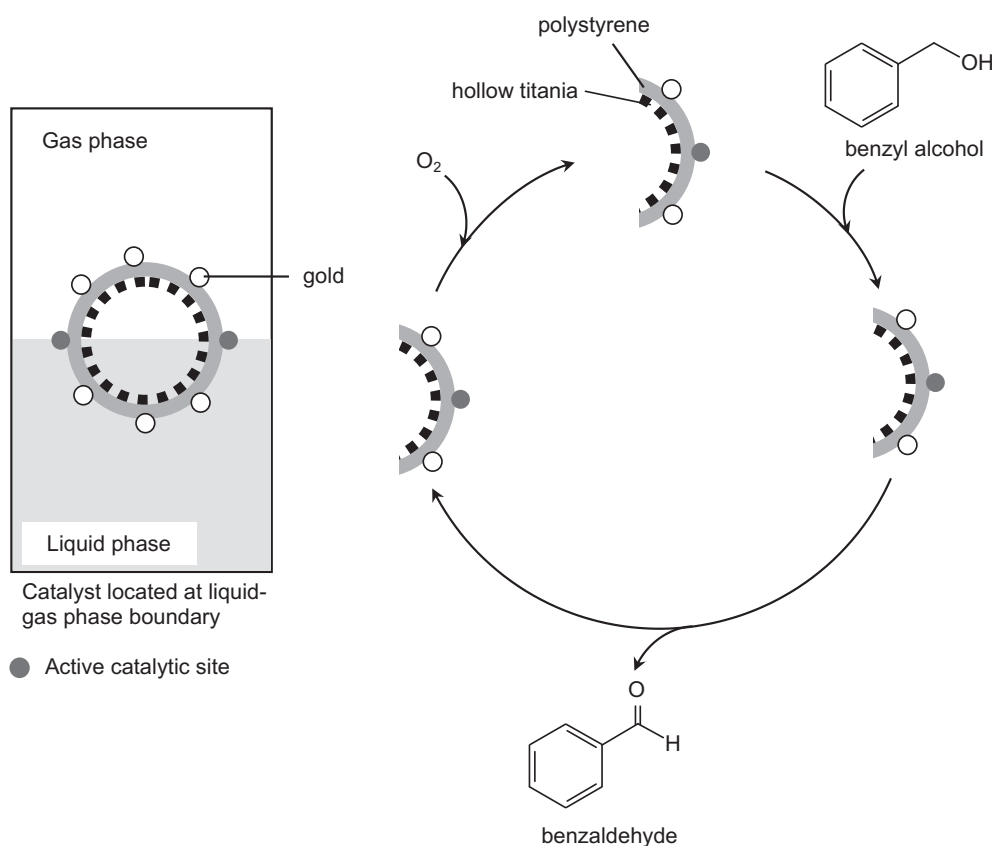


Fig. 12. Proposed model of the gold/PS-HT phase-boundary catalyst and the catalytic pathway of benzaldehyde formation over active Au-site.

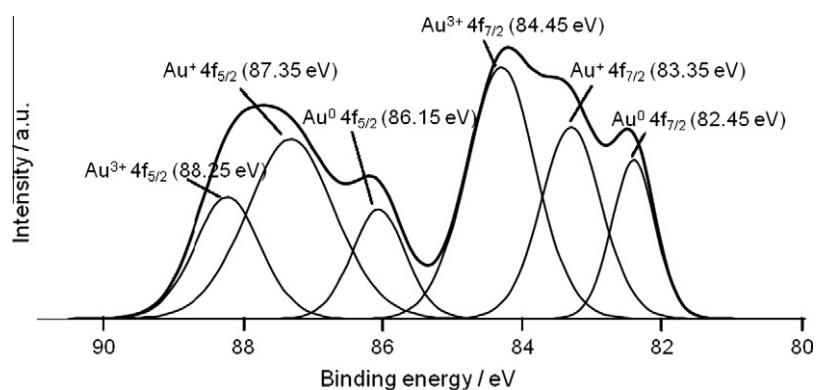


Fig. 13. XPS spectrum of gold nanoparticles deposited on PS-HT.

benzaldehyde in both stirring and static condition. This presumably due to the location of polystyrene beads is at the bottom of the mixture which makes it hard to be accessed by oxygen gas. Gold 30/PS was proven to be less active for this catalysis. The gold 30/TiO₂ showed better production of benzaldehyde, yet the PS-HT with gold catalysts still performed better. As can be seen, stirring condition contributes higher yield of benzaldehyde than static condition. The stirring circumstance could enhance the reaction by allowing more gaseous reactants to reach the catalyst surface because it has overcome the gas-liquid and liquid-solid mass transfer resistance. Thus, the interfacial interaction increases between the catalyst and the reactant since the gas can diffuse to the liquid to increase the contact area for oxidation. On the other hand, under static condition, the degree of interaction between the gold and substrates is constrained, though it showed good catalytic activity

under static condition in gold 40/PS-HT and gold 50/PS-HT. According to production of benzaldehyde, the TON decreased as the gold loading increased. An increase in the loading of gold nanoparticles could result in a low yield of product due to the gold existed as a bulk [34]. It can be proposed that the higher TON of gold 30/PS-HT under stirring condition among the others is due to the high availability of effective active sites to catalyze the oxidation reaction. By the increase in sputtering time, the gold particles tend to agglomerate to form large clusters hence reduced the activity of the catalyst. Besides, the oxidation state of gold is believed has contributed to the enhancement of the TON which will be explained in the next paragraph.

Proposed model of phase-boundary catalyst and its catalytic pathway is depicted in Fig. 12. The active Au-site is located at the interphase of organic and gas phases. During the reaction,

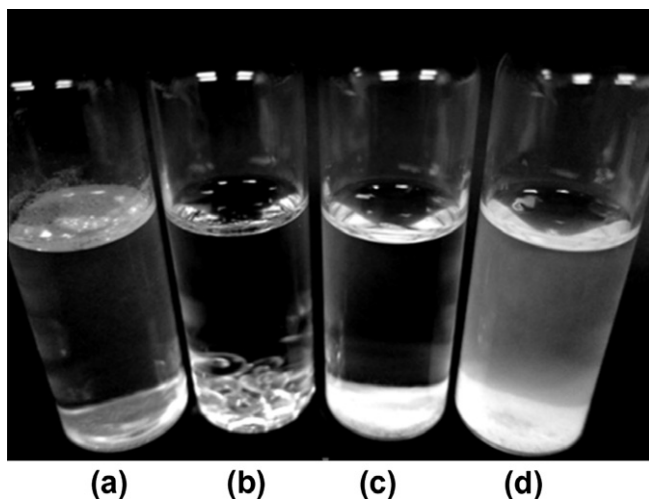


Fig. 14. Dispersion comparison of (a) gold/PS-HT, (b) PS beads, (c) HT, and (d) TiO_2 in water.

the substrate and O_2 that are in contact with Au will be consumed thus created the concentration gradient. The continuous supplies of the substrates from its bulk act as a driving force which enables the reaction to proceed without enforcing the mass transfer to occur [2]. Oxygen can dissolve in water allowing the active site in the liquid phase to carry out the reaction but not active as the active site located at the boundary.

The oxidation state of gold in gold 30/PS-HT was analyzed by XPS technique [24], and the spectrum of Au 4f region is presented in Fig. 13. It revealed that the traces of Au^0 , Au^+ , and Au^{3+} contents in the sample. The peaks at 82.45 and 86.15 eV correspond to Au $4f_{7/2}$ and $4f_{5/2}$ species. Peaks at 84.45 and 88.25 eV correspond to Au^{3+} $4f_{7/2}$ and $4f_{5/2}$, and those at 83.35 and 87.35 eV correspond to Au^+ $4f_{7/2}$ and $4f_{5/2}$. Au^{3+} was observed to have the largest peak area at $4f_{7/2}$ and Au^+ has the largest peak area at $4f_{5/2}$, while the peaks of Au^0 in $4f_{7/2}$ and $4f_{5/2}$ show the smallest peak area. Since the gold was sputtered from a gold target disk, the transition of the gold should be Au^0 . It has been reported that Au^0 is the most active species in the catalytic activity of benzyl alcohol compared to oxidized gold [35]. This might be the reason of low catalytic activity of gold/polystyrene-coated hollow titania.

Fig. 14 shows the apparent distribution of gold/PS-HT, gold/PS beads, HT, and TiO_2 in water. It was observed that the gold/PS-HT was effectively floated on the surface of water, TiO_2 was well-dispersed in water, and gold/PS and HT settle down to the bottom of the bottle. The higher density of the polystyrene beads (1.05 g cm^{-3}) than water (1.00 g cm^{-3}) could be the reason why the particles of polystyrene settle down to the bottom of the bottle. It was also observed that HT sinks faster than the TiO_2 due to its perforated structure. In gold/PS-HT case, only ca. 30% of it can be floated on water. The powder of gold/PS-HT was immediately spread on water after being added and later formed a tiny layer of particles which remains floating until now.

4. Conclusion

In conclusion, gold/polystyrene-coated hollow titania can be made by using sucrose, titanium(IV) isopropoxide, and styrene as

precursors. Hollow titania was simply synthesized by using carbon spheres as a template. Polystyrene was coated onto hollow titania to prevent water from penetrating into the system and making it float on the water. It is observed that, after polystyrene-coated hollow titania was sputtered with gold nanoparticles, this material was active in liquid–gas boundary catalysis in oxidation of benzyl alcohol by using molecular oxygen.

Acknowledgments

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References

- [1] H. Nur, S. Ikeda, B. Ohtani, *Chem. Commun.* 22 (2000) 2235–2236.
- [2] H. Nur, S. Ikeda, B. Ohtani, *J. Catal.* 204 (2001) 402–408.
- [3] H. Nur, S. Ikeda, B. Ohtani, *React. Kinet. Catal. L* 82 (2004) 255–261.
- [4] H. Nur, S. Ikeda, B. Ohtani, *J. Braz. Chem. Soc.* 15 (2004) 719–724.
- [5] H. Nur, N.Y. Hau, I.I. Mison, H. Hamdan, M.N.M. Muhid, *Mater. Lett.* 60 (2006) 2274–2277.
- [6] S. Ikeda, H. Nur, T. Sawadaishi, K. Ijiri, M. Shimomura, B. Ohtani, *Langmuir* 17 (2001) 7976–7979.
- [7] G.J. Brink, I.W.C.E. Arends, R.A. Sheldon, *Science* 287 (2000) 1636–1639.
- [8] I.E. Markó, P.R. Giles, M. Tsukazaki, S.M. Brown, C.J. Urch, *Science* 274 (1996) 2044–2046.
- [9] S.R. Cicco, M. Latronico, P. Mastrorilli, G.P. Suranna, C.F. Nobile, *J. Mol. Catal. A: Chem.* 165 (2001) 135–140.
- [10] A.F. Lee, J.J. Gee, H.J. Theyers, *Green Chem.* 2 (2000) 279–282.
- [11] S. Yu, H. Liu, J. Yu, *J. Catal.* 249 (2007) 59–66.
- [12] Y. Ao, J. Xu, D. Fu, C. Yuan, *Catal. Commun.* 9 (2008) 2574–2577.
- [13] J. Yu, W. Liu, H. Yu, *Cryst. Growth Des.* 8 (2008) 930–934.
- [14] F. Magalhães, R.M. Lago, *Sol. Energy* 83 (2009) 1521–1526.
- [15] L.C.R. Machado, C.B. Torchia, R.M. Lago, *Catal. Commun.* 7 (2006) 538–541.
- [16] H. Han, R. Bai, *Ind. Eng. Chem. Res.* 48 (2009) 2891–2898.
- [17] H. Bala, Y. Yu, Y. Zhang, *Mater. Lett.* 62 (2008) 2070–2073.
- [18] W. Liu, S. Roy, X. Fu, *AIChE J.* 51 (2005) 2285–2297.
- [19] A.S.K. Hashmi, G.J. Hutchings, *Angew. Chem. Int. Ed.* 45 (2006) 7896–7936.
- [20] M. Haruta, *Catal. Today* 36 (1997) 153–166.
- [21] K. Sayo, S. Deki, S. Hayashi, *J. Mater. Chem.* 9 (1999) 937–942.
- [22] A. Martin, U. Bentrup, A. Brückner, B. Lücke, *Catal. Lett.* 59 (1999) 61–65.
- [23] V.R. Choudhary, P.A. Chaudhari, V.S. Narkhede, *Catal. Commun.* 4 (2003) 171–175.
- [24] N. Dimitratos, A. Villa, D. Wang, F. Porta, D. Su, L. Prati, *J. Catal.* 244 (2006) 113–121.
- [25] M. Zheng, J. Cao, X. Chang, J. Wang, J. Liu, X. Ma, *Mater. Lett.* 60 (2006) 2991–2993.
- [26] C.S. Cundy, P.A. Cox, *Micropor. Mesopor. Mater.* 82 (2006) 1–78.
- [27] M. Zheng, Y. Liu, Y. Xiao, Y. Zhu, Q. Guan, D. Yuan, J. Zhang, *J. Phys. Chem. C* 113 (2009) 8455–8459.
- [28] M. Sevilla, A.B. Fuertes, *Chem. Eur. J.* 15 (2009) 4195–4203.
- [29] X. Sun, Y. Li, *Angew. Chem. Int. Ed.* 43 (2004) 3827–3831.
- [30] Y. Mi, W. Hu, Y. Dan, Y. Liu, *Mater. Lett.* 62 (2008) 1194–1196.
- [31] D. Zhang, Y. Hao, Y. Ma, H. Feng, *Appl. Surf. Sci.* 258 (2012) 2510–2514.
- [32] N.L. Lala, T.C. Deivaraj, J.Y. Lee, *Colloid Surf. A* 269 (2005) 119–124.
- [33] X. Zhou, Q. Wei, K. Sun, L. Wang, *Appl. Phys. Lett.* 94 (2009) 133107–133107-3.
- [34] M. Comotti, C.D. Pina, R. Matarrese, M. Rossi, *Angew. Chem.* 116 (2004) 5936–5939.
- [35] G. Zhan, J. Huang, M. Du, D. Sun, I. Abdul-Rauf, W. Lin, Y. Hong, Q. Li, *Chem. Eng. J.* 187 (2012) 232–238.