

# SYNTHESIS OF NANO Ag CATALYST EMBEDDED VANADIUM PHOSPHORUS OXIDE FOR OXIDATION OF STYRENE TO BENZALDEHYDE BY HYDROGEN PEROXIDE

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**Abstract.** In this work, silver nanocatalyst loaded on vanadium phosphorus oxide (Ag/VPO) for oxidation of styrene to benzaldehyde was synthesized by method including impregnating of VPO substrate with colloid solution of Ag nanoparticles (NPs). VPO substrate was prepared by microwave-assisted reaction of vanadium and phosphorus precursors. Meanwhile, Ag/PVP NPs with the size of 7.5 nm and spherical shape, determined by transmission electron microscopy (TEM), were prepared in solution using NaBH<sub>4</sub> as reducing agent and polyvinylpyrrolidone (PVP) as protecting agent. The Ag/VPO catalyst with Ag loading of 10.5 % providing by atomic emission spectroscopy (AES) was gained. The immobile of Ag on VPO was evidenced by XRD, UV-VIS spectroscopy, scanning electron microscopy (SEM), and TEM imaging. SEM and TEM showed that the morphology of Ag-VPO is insignificantly different from the pristine VPO. The Ag/VPO catalyst was characterized in oxidation reaction of styrene to benzaldehyde in which the products were determined by gas chromatography (GC) coupled with flame ionization detector (FID). The results showed that the conversion of styrene reaching high value of > 97.5 % after reaction time of one hour.

**Keywords:** benzaldehyde, impregnant, nano silver particles, styrene oxidation, VPO catalyst.

**Classification numbers:** 2.4.2, 2.6.1.

## 1. INTRODUCTION

Vanadyl phosphorus oxide (VPO) have widely used as the most effective catalyst in production of maleic anhydride from oxidation of n-butane in industrial economies. VPO composed of many active phases such as VOHPO<sub>4</sub>·2H<sub>2</sub>O, VOHPO<sub>4</sub>, VO(PO<sub>3</sub>)<sub>2</sub>, vanadyl pyrophosphate (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> is active phase in oxidation of n-butane [1,2]. Previous studies have indicated that the ratio V/P and reducing agent mainly determine the phase composition of the catalyst [3].

There are many reports of doped-VPO to enhance the selectivity and conversion over substrates or products of oxidation reactions [4–8]. Doping metal to VPO could change properties of the catalyst, strengthen the structure and adjust the ratio of V<sup>5+</sup>/V<sup>4+</sup> at the surface

that effect to the catalytic ability. Gallium-doped VPO (Ga-VPO) at low doping concentration exhibited higher conversion of n-butane to maleic anhydride [4]. One of the most studied metal dopant introduced in VPO catalyst is cobalt [9] which has many constructive influence on the surface structure of the catalyst. Co-VPO showed high catalyst capability for oxidation of benzyl alcohol to benzaldehyde [9]. Besides, the combination of Au and VPO results in synergistic effect Au-VPO for significantly enhancing activity of aerobic oxidation of benzyl alcohol to benzyl benzoate [8]. So, the corporation of metal to VPO could effectively change not only the conversion but the selectivity of the catalyst as well.

Benzaldehyde is an important intermediate in the industrially synthesis for perfumes, flavorings, pharmaceuticals, etc. The conventional preparation of benzaldehyde is based on the hydrolysis of benzyl chloride that introducing uneco-friendly chlorine. Benzaldehyde can be obtained as an intermediate in direct oxidation of toluene to benzoic acid so the conversion and selectivity were low [10, 11]. The catalytic oxidation of styrene by  $H_2O_2$  to produce benzaldehyde was evidenced as high selective and feasible process. Many types of catalyst for oxidation of styrene to benzaldehyde base on metals, MOFs and oxides [12 - 15].

Noble metals such as Pt, Ag, etc. exhibited high efficiency in transformation of organic substrates [16 - 20] but the high cost of the catalyst reduces their practical applicability. Reducing metal catalysts in nano size has been well known to enhance catalytic efficiency because of extending surface area and surface to volume ratio and reducing the use of metal as well that capable to apply to noble metal catalysts. Nonetheless, using support-free nanosized catalysts have obstacles of agglomeration of particles that reduce the active surface and difficulty of recovery. Supports provide high surface area for nano particles to affix preventing them from agglomeration, high mechanical strength and thermal stability and ease of recovery the catalysts [21]. There are many choices of substrate for nano metal catalysts such as carbonaceous materials, ceramics, oxides, etc. [19, 21, 22] which are either inert supports or active supports. The adhesion between catalyst particles and the substrate influence the morphology, distribution of active particles and stability of the catalyst. With advantages of available producing chains and abundance, VPO could be used as an active support for metal catalysts in large scale industrial process.

Based on its convention, impregnant method has long time used to load active phases upon supports. The efficiency and mass loading were achieved by control the synthesized condition such as reaction time, reducing agents, chemistry of ligands and precursors, etc [21]. Cornaglia *et al.* synthesized Co/VPO by impregnating of  $VOHPO_4 \cdot 0.5H_2O$  into solution of cobalt acetyl acetate [5]. Herein, the Ag-VPO catalyst was prepared by impregnant method with synthesized VPO and colloid solution of nano Ag particles. The as-prepared Ag-VPO was employed to oxidation of styrene by  $H_2O_2$ .

## 2. EXPERIMENTAL

### 2.1. Synthesis of Ag/VPO catalyst

All the chemicals were used as purchased without further purification. The VPO was prepared via microwave-assisted reaction between vanadium and phosphate precursors. Typically, a single distillation apparatus including a 3-necked ground bottom flask placing inside a household microwave oven (Akira) connecting to distillation tube overhead.  $V_2O_5$  (2.00 g, Alpha Chemika, > 98 %) was dispersed in 20 mL of 1-butanol (Chemsol,  $\geq 99.5$  %) and 10 mL of benzyl alcohol (Xilong, 99.9 %) inside the flask under stirring at 300 rpm to make

homogenous dispersion then heated by microwave with power of 900 W for 30 min (6 times with 5 min intervals). Afterward, a mixture of H<sub>3</sub>PO<sub>4</sub>/1-butanol (4:10 v/v) (Xilong, ≥ 85 %) was added dropwise to the flask and the mixture was heated by microwave for another 30 min (6 times with 5 min intervals). After cooling to room temperature, the solid part was filtrated and washed many times with distilled water to eliminate residues to obtain a blue precipitation which was then dried at 110 °C overnight and grounded and heated at 480 °C for 4 hours to obtain VPO substrate.

Nano silvers were synthesized in solution with PVP as protecting agent. 0.852 g PVP (M<sub>w</sub> = 40,000 g/mol, Himedia) was dissolved in 50 mL distilled water under magnetic stirring and heating at 60 °C. 0.101 g AgNO<sub>3</sub> (Xilong, 98 %) was weighted and dissolved the PVP solution in concentration of 8.5 mM Ag<sup>+</sup> and stirred for another 30 min. Then 20 mL of solution of reducing agent NaBH<sub>4</sub> (Sigma-Aldrich, 90 %) was added dropwise and stirred for 60 min for completing reaction to obtain yellowish colloid solution of Ag-PVP.

Depositing nano Ag on VPO to prepare Ag/VPO catalyst was carried out using 20 mL colloid nano silver solution and 0.200 g VPO and stirred for 12 hours. The solid was obtained by filtration and washed many times by distilled water/ethanol and dried in vacuum at 60 °C for 6 hours.

## 2.2. Characterization techniques

X-ray diffraction (XRD) for phase composition analysis of the silver nano particles, VPO and Ag/VPO, was carried out on D2 Phaser (Bruker) using CuKα radiation (λ = 1.5406 Å) in the 2θ range of 15-50° with step size of 0.02°/0.25s. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) images were collected using FEI Tecnai G2 F20. UV-VIS absorption spectra were collected on Cary 100 (Agilent) at Applied Physical Chemistry Laboratory, VNUHCM-University of Science. The element analysis was conducted by Atomic Emission Spectroscopy (AES) on ICP-MS 7500 series (Agilent) at VNUHCM-University of Science.

## 2.3. Catalyst activity measurement

The as-prepared Ag-VPO were evaluated for styrene oxidation reaction in round bottom flask equipped with a reflux condenser. Ag-VPO (0.100 g, 0.5 mmol Ag) was added in solution of styrene (1.15 mL, 10 mmol) and acetonitrile (ACN, 5 mL, Xilong, 99.9 %) with nitrogen bubbling for 10 min then vigorously stirred under inert nitrogen atmosphere for 30 min. H<sub>2</sub>O<sub>2</sub> (Xilong, 30 %, 3.1 mL, 30 mmol) was supplied and the dark-green suspension turned brown. The flask was heated in oil bath at 60 °C for reaction times of 1, 2 and 3 hours under inert nitrogen atmosphere. The liquid part of reaction solution was diluted by methanol and was analyzed by Gas Chromatography-Mass Spectroscopy (GC-MS). The conversion (%) was calculated by equation (1):

$$100 - \frac{z}{y} \frac{100x}{100 - x} \quad (1)$$

where, x: % peak area of ST50 in the substrate (contained ST50 and styrene); y: % peak area of ST50 in the sample; z: % peak area of the remaining styrene in the sample.

### 3. RESULTS AND DISCUSSION

Figure 1 shows XRD pattern of the parent VPO and the synthesized Ag/VPO. The XRD pattern of VPO displays peaks revealing the presence of at least two phases named  $(VO)_2P_2O_7$  (PDF No. 041-0696) and hydrate phase (PDF No. 084-0761) and the latter is prominent phase according to estimated peak ratio between the two phases. The hydrate phase is mingled phase including complex co-crystalline of hydrophosphate and pyrophosphate phases with VO and  $VO_2$  as cations. It is noticed that peaks of the hydrate phase disappeared while peaks of  $(VO)_2P_2O_7$  remained in the XRD pattern of Ag-VPO sample, revealing that the hydrate phase could be dissolved in the immersed solution or transferred to other phase(s) after drying the Ag-VPO, as previous studies indicated [1]. The crystallinity of  $(VO)_2P_2O_7$  increase as the diffraction peaks intensity increase. There are also many phases that could be formed from the condensation of  $Ag/Ag^+$  on VPO such as  $Ag_2(VO)_2(PO_4)$ ,  $AgV_2P_2O_{10}$ , etc. [6, 23] but could not be detected due to low crystallinity of the Ag-VPO. Instead of the above compounds, Ag could be detected with diffraction peaks (marked as \*) located at  $2\theta^\circ = 38.1^\circ$  and  $44.3^\circ$  in the XRD pattern of Ag-VPO sample, which reveal a deposition of Ag on the surface of VPO as substrate has taken place.

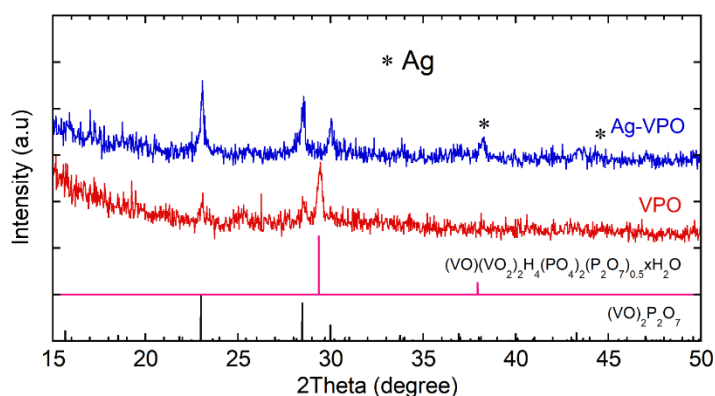


Figure 1. XRD patterns of the synthesized samples of VPO and Ag-VPO and the reference diffraction positions given in the bottom.

UV-VIS spectroscopy was used to trace the silver nano particle formation and transformation after immerse process. UV-VIS spectra of the silver solution during immerse process have been recorded and shown in Figure 2. It could be noticed that  $NaBH_4$  and PVP do not show observable absorption band in the wavelength range. Meanwhile, the solution of  $AgNO_3$  and  $AgNO_3/PVP$  displayed absorption band of  $Ag^+$  at about 305 nm. The spectrum of the solution after reduced by  $NaBH_4$  displays clearly absorption band of nano Ag particles at 398 nm and low absorption band at below 305 nm could be indexed as  $Ag^+$  remaining [24,25]. So, Ag nano particles have been prepared by  $NaBH_4$  reduction and could be used in the impregnated step. UV-VIS spectra of the solution after the impregnated step exhibit two absorption bands locating at above 300 nm and 600 nm. The shifting and absence of absorption band at 398 nm and the low intensity of band above 300 nm indicate a decreasing of Ag concentration in the solution which could be contributed to the deposition of nano particles on the surface of VPO. The presence of absorption band above 600 nm could be resulted from agglutination of nano particles as pointed out elsewhere [25].

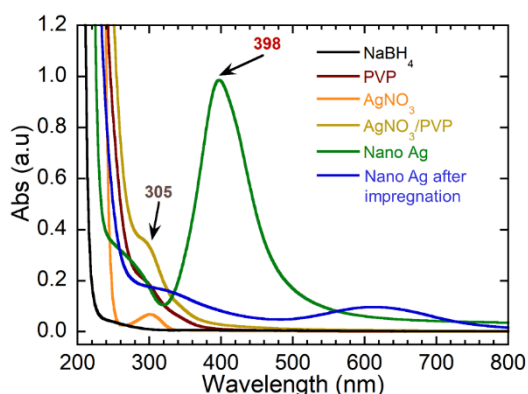


Figure 2. UV-VIS spectra for analyzing the reaction mixture during impregnation process.

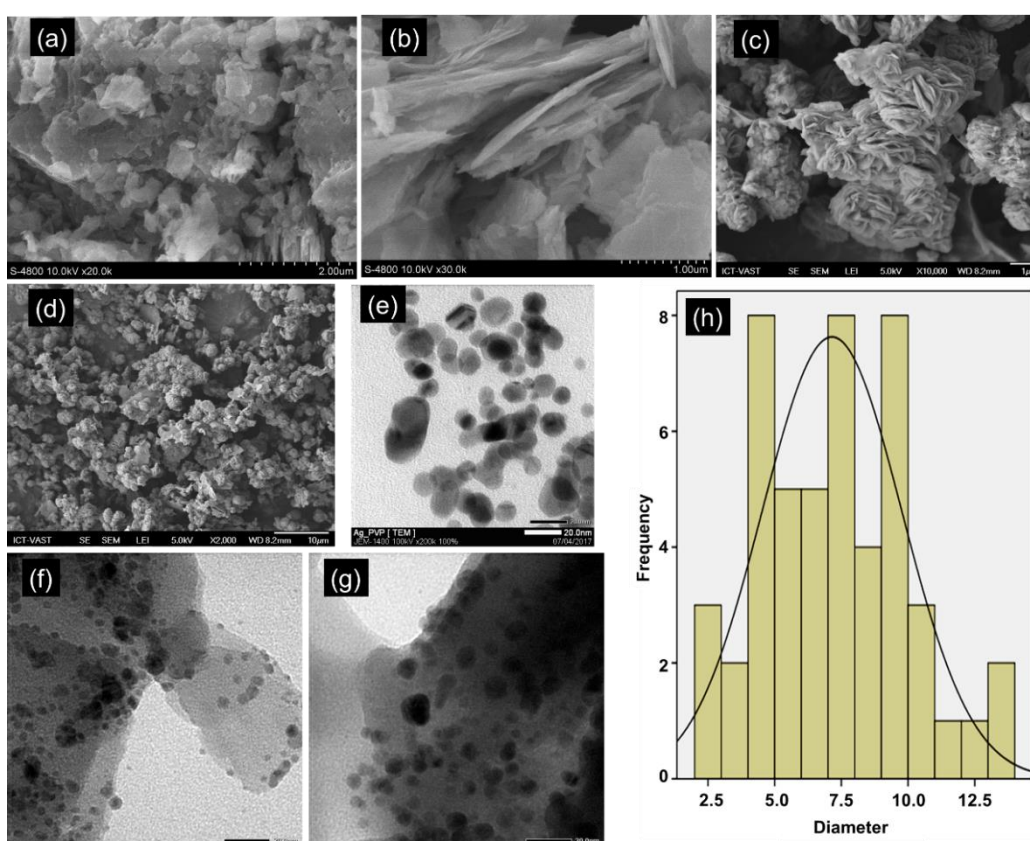


Figure 3. SEM images of the samples VPO (a-b) and Ag-VPO (c-d). TEM images of the Ag NPs (e) and Ag-VPO (f-g). Histogram of particle size distribution of Ag nanoparticles in colloid solution (h).

The electronic microscopy images of VPO and Ag-VPO samples are presented in Figure 3. The VPO samples show a platelet morphology with very thin and uneven fairly rounded shaped crystals with diameter of about 1  $\mu\text{m}$ . The Ag-VOP sample displays similar morphology to that of VPO indicating that the morphology of crystals of the VPO is almost unchanged after impregnation, coinciding with previous studies [4, 26]. The platelet crystals randomly agglomerate in clusters with diameter about 2 - 3 times larger than that of single platelets. In

high magnification TEM images, Ag/PVP NPs show almost spherical shape with wide range of size distribution from a few nm to about 20 nm (Figure 3(e)), and a high population of the Ag NPs on VPO catalyst's surface could be clearly observed (Figure 3(f-g)), indicating high mass loading of Ag on VPO substrate. Indeed, Ag nano particles seem to fill the spaces between the platelet crystals of VPO. The PVP protecting agent could not be observed in the microcopy images. In Figure 3(h), the size distribution of nano particles exhibits three local maximums at about 4, 7.5 and 10 nm due to conglomeration of the particles. The mean diameter of about 7.5 nm was obtained according to peak of the distribution curve but the value seems lower because there are high population of particle with diameter below 7.5 nm presenting in SEM images of Ag-VPO (Figure 3(f-g)).

To this point, it is evidenced that nano Ag could be mounted on surface structure of VPO substrate by impregnating method. XRD pattern shows characteristic peaks of Ag, and the UV-VIS spectra also display the disappearance of absorption band of nano Ag at 400 nm. SEM and TEM images clearly show well distribution of nano particles on the surface of VPO. Loading number of Ag on VPO was determined by AAS. It is found that the obtained loading number is 10.5% compared to the theoretical value of 20% based on amount of Ag on nano Ag solution, and the efficiency of impregnant is 52.6%. Because of relative high mass loading, the nano particles tend to agglomerate as could be seen in TEM images.

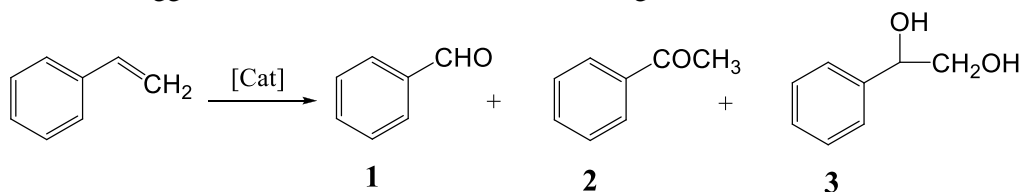


Figure 4. Oxidation of styrene over Ag-VPO catalysts.

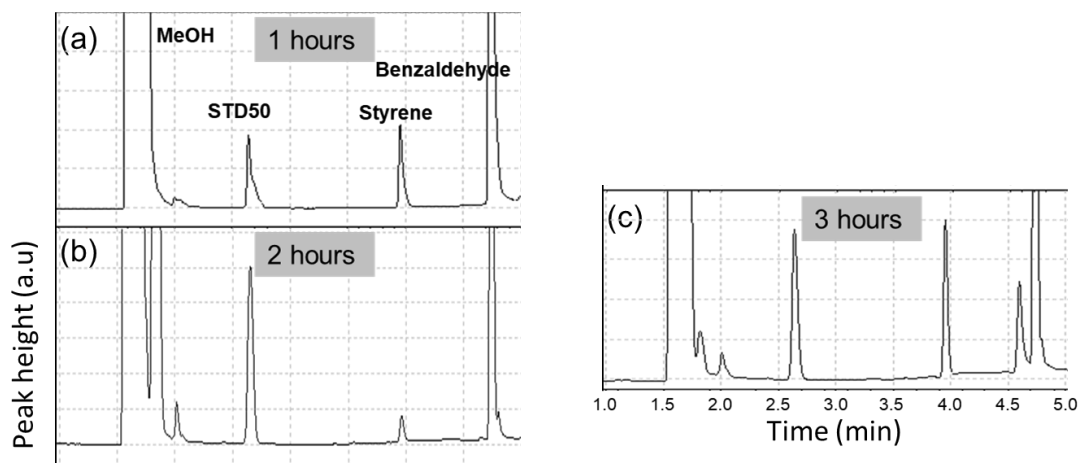


Figure 5. GC-MS results of the liquid after testing of catalytic activity for 1 hour (a), 2 hours (b) and 3 hours (c).

The oxidation of styrene to benzaldehyde on Ag-VPO catalyst was investigated elsewhere, phenylacetaldehyde, styrene oxide, benzoic acid are main by-products [6,10], beyond the expected benzaldehyde (Figure 4). In the activity test, the reaction was lasting for 1 hour, 2 hours and 3 hours and the liquid phase was diluted by methanol and was analyzed by GC-MS, the results shown in Figure 5. In the chromatogram, the highest peak belongs to solvent MeOH

appearing at 1.5 - 2 min, before the peaks belonging to reactants and products. Peak of standard STD50 could be seen to locate at 2.6 min. According to standard of styrene and benzaldehyde, peak of styrene appears at 3.9 min while peak of product appears at higher retention time of 4.7 min, as shown in Figure 5(a). The GC-MS results were recorded in range of 5 min, therefore any peak(s) appearing at higher retention time would be excluded.

The ratio between peaks of styrene and benzaldehyde depends on reaction time while the ratio between peaks of STD50 and styrene was used to calculate the conversion efficiency. It could be seen that peaks of benzaldehyde appears with high intensity within 1 hours of reaction. After 2 hours, peaks of styrene reduce to the minimum. As depicted, benzaldehyde was formed as the major product implying high selectivity of benzaldehyde during reaction time of 2 hours. It could be noticed that another peak appears at 4.6 min when further increase reaction time of 3 hours. The present of this peak could be explained by other product(s) previously mentioning formed after long reaction time. As result, the selectivity of benzaldehyde reduces as well. Because the peak of benzaldehyde is overloaded, the peaks area could not be depicted and therefore the selectivity could not be determined.

The conversion was plotted with respect to time of reaction in Figure 6. The conversion of styrene is always higher 97.5 % after just one hours of reaction. The conversion slightly increased with the increase of reaction time and reaches 99.6 % at three hours. The GC results demonstrated that the reaction time last a few hours to obtain high conversion efficiency of styrene and high selectivity of benzaldehyde. It is noticed that Ag nanoparticles have higher catalytic activity in oxidation of styrene to benzaldehyde compared to some oxide-based catalysts [12 - 15]. With a low concentration of Ag on VPO, high conversion and selectivity of above 90 % could be obtained in short reaction time. The activity could be enhanced by using nano-size Ag particles and high mass loading catalyst, compared to previous studies [10,23], so that the method used in this research demonstrated to be efficient.

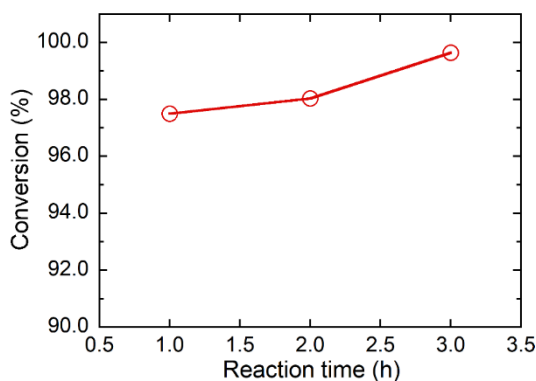


Figure 6. Plot of conversion of styrene to benzaldehyde versus reaction time.

#### 4. CONCLUSIONS

Ag-VPO catalyst has been synthesized by impregnating VPO on colloid solution of Ag/PVP. The as-prepared catalyst exhibited  $(VO)_2P_2O_7$  and pure Ag as main and active phase, respectively. Loading of Ag did not have affect to morphology of the Ag-VPO compared to the pristine VPO. Spherical shape nano Ag particles with mean diameter of about 7.5 nm well distribute on the gap between plated crystals of VPO with some amount of agglomeration, which might be due to high loading amount of 10.5 %. The Ag-VPO catalyst exhibited high activity on



oxidation reaction of styrene to benzaldehyde. The conversion of styrene reaches high value of 97.5 % and high selectivity for benzaldehyde after reaction time of one hours and gains the peak of 99.6 % at two hours then the conversion declines to 98.0 % along with reducing in selectivity for benzaldehyde at 3 hours. Further studies are conducting to find the optimal conditions of impregnant process to reduce agglomeration of Ag nano particles and to evaluate the role of Ag and VPO on oxidation of styrene as well as determine byproduct and selectivity of the reaction.

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