

CATALYTIC OXIDATION OF CINNAMYL ALCOHOL TO CINNAMALDEHYDE USING HYDROGEN PEROXIDE

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Abstract—Platinum-bismuth bimetallic catalysts supported on activated carbon powder were prepared using a colloidal method. The catalysts and their support were characterized by physisorption, Brunauer Emmet Teller (BET), high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD). The selectivity and activity of the catalysts were tested for the oxidation of cinnamyl alcohol using H_2O_2 as an oxidant. The effects of concentration, solution medium and modifier on catalysts selectivity and activity were investigated. The results showed that hydrogen peroxide could be used as an effective oxidant for the catalytic oxidation of cinnamyl alcohol. Selectivity of cinnamaldehyde (84%) was attained at 34% conversion of the cinnamyl alcohol. The catalysts were more active in water than in toluene.

Keywords- hydrogen peroxide; platinum-bismuth; selective oxidation; cinnamyl alcohol; cinnamaldehyde

1. INTRODUCTION

Cinnamaldehyde is an important organic compound that is used in making agriculture chemicals such as fungicides and insecticides [1-3]. Traditional methods for synthesizing cinnamaldehyde have been employed using dichromate and manganate ions [4, 5]. These oxidants are harmful to the environment. To replace them, researchers have also focused on using environmental friendly oxidants such as air or oxygen [6, 7].

The use of heterogeneous catalysts has dominated liquid phase oxidation reactions. Oxidation of alcohols, aldehydes and carbohydrates [8-11] has mainly focused on the use of supported Pd and Pt catalysts. The catalytic reactions occur under mild conditions in the range 293-353 K and at 1 atmospheric pressure. Carbon supported platinum and palladium catalysts are highly selective in the oxidation of carbohydrates to their corresponding organic acids [8]. Various research groups have reported the oxidation of cinnamyl alcohol to cinnamyl alcohol over Pt and Pd catalysts [12-15]. Mallat and Baiker [12] reported the selective aerial oxidation of cinnamyl alcohol to cinnamaldehyde over platinum supported on alumina. The oxidation reaction gave 88.5% selectivity to cinnamaldehyde formation.

The use of supported Pd or Pt catalysts for liquid phase selective oxidation reactions has been found to have some drawbacks, such as loss in sensitivity due to deactivation caused by poisoning from by-products, poor catalytic activity and low selectivity of the platinum group metals [16]. Given these disadvantages, efforts have now been geared towards introducing another metal to form a bimetallic catalyst that can serve as alternatives for the oxidation of the aldehydes/alcohols in the fine chemical industry hence reducing the deactivation of catalyst. Recently, researchers have shown that using a second metal component, such as Bi or Pb or Sn, is advantageous in

terms of improving the catalytic selectivity and activity and prolonging catalyst lifetime [17-25].

Hydrogen peroxide is a clear liquid, slightly more viscous than water. It is the simplest peroxide (a compound with an oxygen-oxygen single bond). The compound possesses advantages over air and oxygen such as easier control of its concentration and storage. The oxidizing capacity of hydrogen peroxide is so strong that it is considered a highly reactive oxygen species.

In this study, we investigate the effectiveness of using hydrogen peroxide as an oxidant for the selective oxidation of cinnamyl alcohol over carbon supported laboratory synthesized platinum-bismuth catalysts. The catalysts and their support are characterized by (BET), (HRTEM), (SEM) and (XRD). The selectivity and activity of the synthesized catalysts were tested through analysis of the oxidized products using gas chromatography (GC). To the best of our knowledge, application of hydrogen peroxide as an oxidant for the oxidation of cinnamyl alcohol over Pt-Bi/C catalysts has not been hitherto reported. The obtained information will aid in coming up with potential applications of carbon supported bimetallic catalysts thus enabling cheaper and efficient oxidation of alcohols in the fine chemical industrial.

2. METHODOLOGY

2.1 Chemicals

Trans-cinnamaldehyde (>98.5% purity), cinnamyl alcohol (>98.0%) and *trans*-cinnamic acid (>99.5%) were purchased from Alfa Aesar. $H_2PtCl_6 \cdot 6H_2O$ (>99.9%), $Bi(NO_3)_3 \cdot 5H_2O$ (>98.0%), hydrazine monohydrate (64-65% hydrazine in water) and activated carbon (Darco KB-G) were purchased from Sigma-Aldrich. Triton X-100 [4-(1,1,3,3-tetramethylbutyl) phenyl-polyethylene glycol] (>98.0%) was purchased from BDH-Merck. methanol (>99.5%) and biphenyl (>98.0%) were purchased from SMM instruments.

2.2 Synthesis and characterization of the carbon-supported catalysts

2.2.1 Synthesis of carbon-supported Pt-Bi catalysts

The synthesis of carbon-supported Pt-Bi catalysts was done according to a reported procedure [26]. Activated carbon-supported 5%Pt-5%Bi catalyst was prepared by dissolving 0.105 g of $H_2PtCl_6 \cdot 6H_2O$ and 0.116 g $Bi(NO_3)_3 \cdot 5H_2O$ in a mixture of methanol and water (1:1 v/v) to which 6 ml of Triton X-100 and 0.9 g of activated carbon were added. Under vigorous stirring, an excess of a solution of 3 ml hydrazine monohydrate was added. The mixture was stirred for 6 h, filtered and washed several times with 100 ml de-ionized

water to give metal nanoparticles supported on activated carbon, which were then dried. Catalysts with varying bismuth loadings were prepared by adjusting stoichiometry of the ingredients.

2.3 Oxidation reactions

Cinnamyl alcohol (0.013 mol), 20 ml of de-ionized water and 0.2 g of the platinum-bismuth, platinum-antimony or platinum catalyst were added to a 3-necked flask equipped with a condenser and a dropping funnel. The reaction mixture was refluxed and continuously stirred in an oil bath at 60°C. An aqueous solution of H₂O₂ (0.015 moles, 30%) was added drop wise for a period of 2 h. During the course of the reaction, samples were withdrawn from the reaction mixture at regular time intervals and then stored at ambient condition before GC analysis. For comparison, the procedure was also repeated using 20 ml of toluene instead of de-ionized water as the solvent.

2.4 Chemical Analysis

Chromatographic measurements were performed on a Varian Chromapack CP-3800 gas chromatograph, equipped with a Hewlett Packard Phenomenex column Zebron ZB-5 (30 m × 0.25 mm i.d. × 0.25 µm stationary phase thickness) and a flame ionization detector (FID). The oven temperature was

programmed as follows: 80°C held for 2 min, then increased to 150°C at a rate of 25°C/min, held for 0.5 min, and increased to 190°C at a rate of 50°C/min. The injector temperature was set at 260°C in the split injection mode (ratio 10:1). The detector temperature was 300°C. For qualitative and quantitative analysis, peaks were identified using pure cinnamyl alcohol, cinnamaldehyde and cinnamic acid standards. Biphenyl was used as an internal standard.

3. RESULTS AND DISCUSSION

3.1 Characterization of the catalyst

3.1.1 Physicochemical properties:

The chemical compositions and some physical properties of the carbon-supported platinum catalysts are illustrated in Table 1. The metal loadings determined using ICP-OES were generally close to the values targeted during catalyst preparation. The surface areas of the carbon supported catalysts were always lower than that of the activated carbon as shown in Table 1. The crystallite sizes were found to be between 3.2-3.9 nm and 4.4-5.8 nm for bismuth and platinum respectively.

Table 1. Chemical composition and physical properties of carbon supported Pt-Sb catalysts

Catalyst	Metal content (mass%)		Crystallite size (nm)		BET surface area (m ² g ⁻¹)
	Pt	Bi	*Pt	*Bi	
Activated C	-	-	-	-	864
5%Pt/C	4.8	-	5.0	-	698
5%Pt-5%Bi/C	4.9	4.8	5.8	3.9	728
5%Pt-3%Bi/C	4.8	2.8	4.4	3.6	731
5%Pt-1%Bi/C	4.9	0.9	4.5	3.3	746

*Particle size as determined by XRD

3.1.2 Chemical composition

Figure 1 shows a wide angle XRD pattern of the carbon-supported platinum catalyst. The broad peaks indicate that small nanometer-size particles are present. The diffraction peaks indicated as (111), (200) and (220) 2θ values of 39.6°, 46.3° and 67.4° respectively are attributed to platinum. The peaks indicate that platinum is present in the face-centered cubic structure [27]. A broad feature in the region of 20-22° is commonly attributed to amorphous carbon phases [28-29]. The XRD pattern of the 5%Pt-5%Bi/C catalyst is illustrated in Figure 2. Bismuth is present as bismuth (III) oxide. The (111), (200) and (220) reflections at 2θ values of 39.8°, 46.2° and 67.5° respectively are attributed to face-centered cubic platinum structure [27].

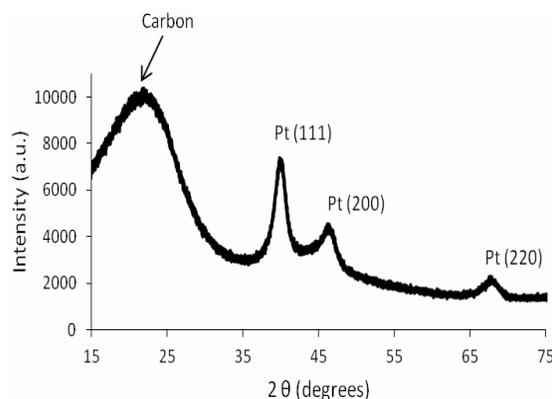


Figure 1. XRD diffraction pattern of 5%Pt/C catalyst

spots (confirmed by EDX analysis) in Figure 4b show evenly dispersed Pt-Bi particles.

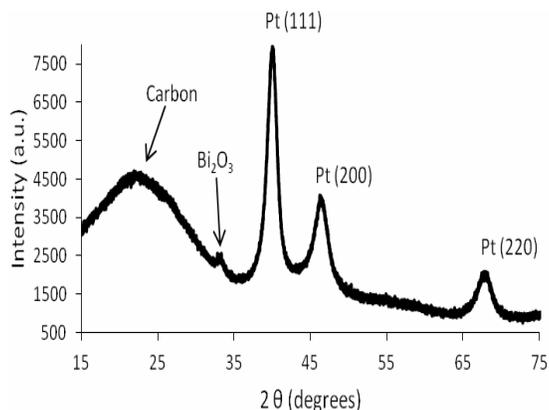


Figure 2. XRD diffraction pattern of 5%Pt-5%Bi/C catalyst

3.1.3 HRTEM analysis

High Resolution Transmission Electron Microscopy was used to characterize the extent of dispersion of the 5%Pt-5%Bi catalyst on the carbon surface (Figure 3). As can be seen from the image, the black dots which represent the metals in this case are supported as discrete particles. The corresponding histograms of the particle size distributions indicate that the average particle size on the Pt-Bi/C catalyst is between 10-11 nm. The average particle sizes were larger than the crystallite sizes determined by XRD indicating that the particles determined by HRTEM could possibly have been clusters formed by more than one crystal.

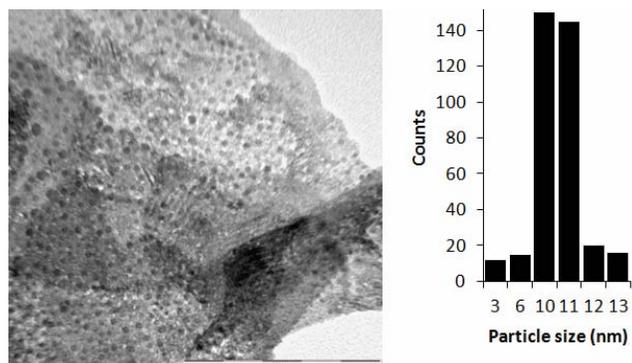


Figure 3. HRTEM images and particle distribution histogram of 5%Pt-5%Bi/C catalyst

3.1.4 SEM analysis

Scanning electron microscopy was used to characterize and compare the surface morphology of the activated carbon and the 5%Pt-5%Bi catalyst. Figure 4 represents micrographs of the activated carbon and 5%Pt-5%Bi catalysts. As can be seen and compared with activated carbon (Figure 4a), the white

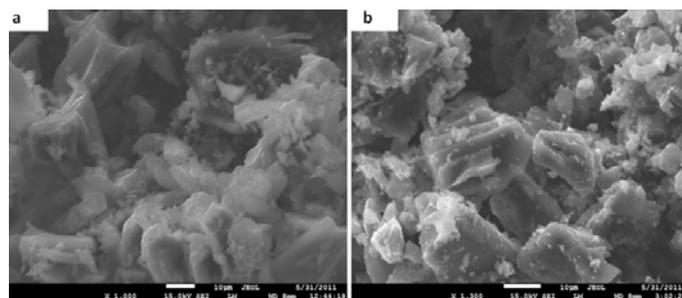
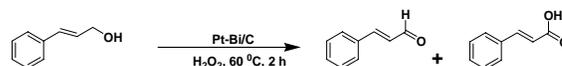


Figure 4. SEM images, (a) activated carbon (b) 5%Pt-5%Bi

3.2 Catalyst testing

The selective oxidation of cinnamyl alcohol to cinnamaldehyde is used as the test reaction:



3.2.1 Activity of modified and unmodified catalyst

3.2.1.1 Effects of hydrogen peroxide concentration

The effects of different hydrogen peroxide concentrations are illustrated in Figure 5. The catalytic activity increased with increasing hydrogen peroxide concentration up to 70 min. After 70 min, the activity levels off possibly due to catalyst deactivation by strong adsorption of (by)products [30]. The 30% hydrogen peroxide concentration was observed to have the fastest and highest conversion. A similar trend was observed using toluene as solvent (Figure not shown).

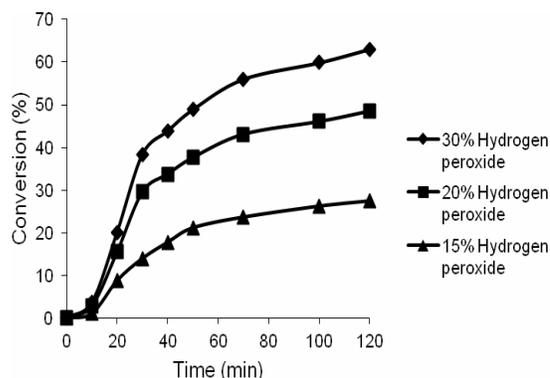


Figure 5. Conversion as a function of time for the oxidation of cinnamyl alcohol over carbon supported 5%Pt-5%Bi catalyst in water (60°C, 2 h)

3.2.1.2 Effects of modifier

The activities of platinum catalysts in water are illustrated in Figure 6. The activity of bismuth promoted catalyst decreases with an increase in bismuth loading possibly due to blockage of active sites on the platinum surface. Unmodified platinum catalyst exhibited the least activity (36% in 2 h) due to over oxidation of the platinum surface. These results clearly show that bismuth has a modification role on

platinum catalysts. To illustrate the effect of using platinum catalyst of different metal loadings an F-test was used. The data in Table 2 indicates that there is a significant difference in the mean conversion of cinnamyl alcohol over these catalysts signifying that the presence of the modifier has got an effect on conversion.

Table 2 Comparison of means of conversion of cinnamyl alcohol in water after 2 h over carbon-supported, Pt-Bi catalysts at $p \leq 0.01$

Replicate	Conversion (%)			
	5%Pt	5%Pt-1%Bi	5%Pt-3%Bi	5%Pt-5%Bi
1	36.1	88.4	78.4	61.3
2	35.4	83.7	83.7	65.4
3	36.5	85.6	79.4	62.4
mean	36.0	85.9	80.5	63.1
F _{critical}	4.1	4.1	4.1	4.1

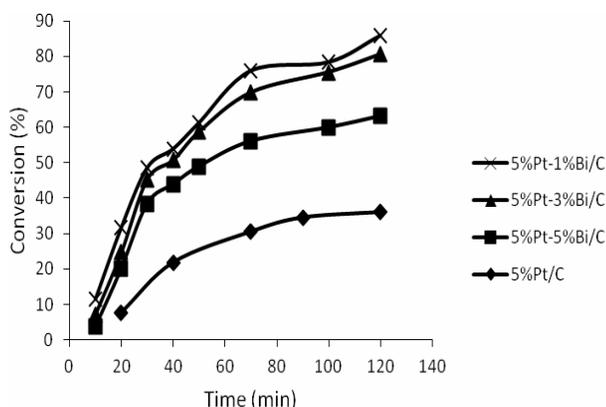


Figure 6. Conversion as a function of time for the oxidation of cinnamyl alcohol over carbon supported catalysts in water (60°C, 2 h)

3.2.1.3 Effects of aqueous and non-aqueous medium

The behavior of the as prepared catalysts in different media is illustrated in Figure 7. As can be seen, the platinum catalysts have higher conversion in water than in toluene, at any given time interval. A dehydrogenation mechanism [31] for oxidation of alcohols proposes that hydrogen is initially abstracted from the -OH bond to form an alkoxide ion. Based on this dehydrogenation mechanism, water is a weak base that possibly facilitates hydrogen abstraction from alcohol, thus enhancing catalytic activity.

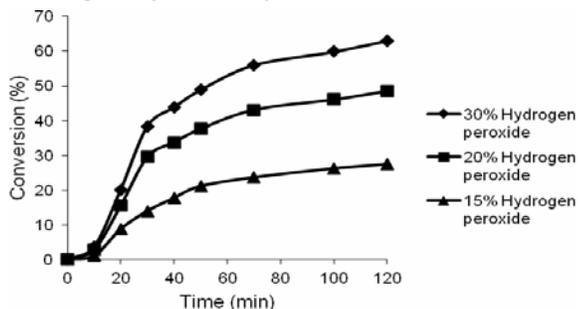


Figure 7. Conversion as a function of time for the oxidation of cinnamyl alcohol over 5%Pt-5%Bi/C (60°C, 2 h)

3.2.2 Selectivity

3.2.2.1 Effect of different modifiers

Addition of bismuth modifier to Pt affects catalytic selectivity. Figure 8 shows that the selectivity of bismuth modified catalysts to cinnamaldehyde decreases with increase in time. However, the rate of decrease follow the order 5%Pt-5%Bi/C > 5%Pt-3%Bi/C > 5%Pt-1%Bi/C > 5%Pt /C. The observation can be attributed to adsorption of oxidized (by)products. Selectivity was lowest over the unmodified Pt/C catalyst (57% after 2 h). The corresponding percentages for the bismuth-modified catalyst were 73, 69 and 61% for 5%Pt-5%Bi/C, 5%Pt-3%Bi/C and 5%Pt-1%Bi/C catalysts respectively. The significant difference in selectivity of the data is illustrated by use of an F-test. The data in Table 3 indicates that there is a significant difference in the mean selectivity of cinnamyl alcohol over bismuth modified catalysts signifying that the presence of the modifier has got an effect on selectivity.

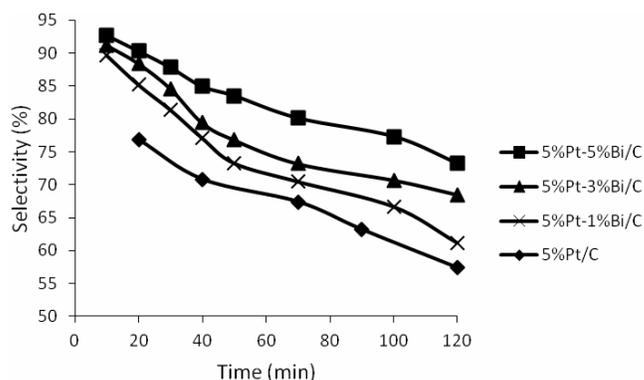


Figure 8. Selectivity as a function of time for the oxidation of cinnamyl alcohol over carbon supported catalysts in water (60°C, 2 h)

Table 3. Comparison of means of selectivity of cinnamyl alcohol in water after 2 h over carbon-supported, Pt-Bi catalysts at $p \leq 0.01$

Replicate	Selectivity (%)			
	5%Pt	5%Pt-1%Bi	5%Pt-3%Bi	5%Pt-5%Bi
1	57.0	61.1	68.1	76.0
2	57.3	61.4	68.8	70.9
3	57.9	61.1	68.6	72.8
mean	57.4	61.2	68.5	73.2
F _{critical}	4.1	4.1	4.1	4.1

3.2.2.2 Effect of aqueous and non-aqueous medium

The medium in which an unmodified and modified catalyst works is important since it affects its degree of selectivity. Figure 9 shows that the 5%Pt-5%Bi/C catalyst was more selective towards the formation of cinnamaldehyde in toluene than in water (84.3% and 73% after 2 h respectively). Water reacts with the cinnamaldehyde to form an aldehyde hydrate that further oxidizes to form cinnamic acid [32] according to the following equation:

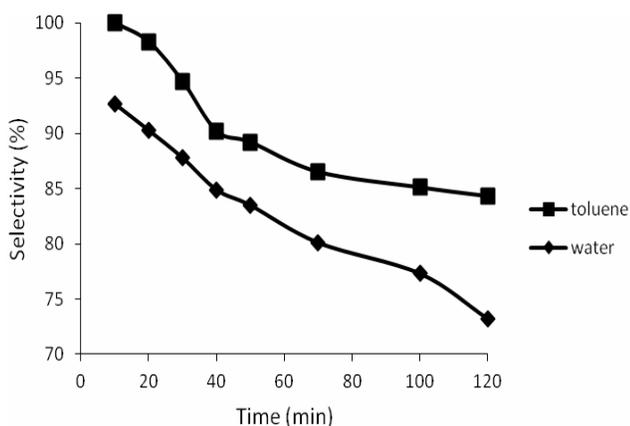


Figure 9. Selectivity as a function of time for the oxidation of cinnamyl alcohol over 5%Pt-5%Bi catalysts in water and toluene (60°C, 2 h)

3.2.2.3 Effect of hydrogen peroxide concentration

The selectivity of 5%Pt-5%Bi catalyst using different concentrations of hydrogen peroxide is illustrated in Figure 10. With increase in time, the selectivity decreases using different concentrations. The change in selectivity follows the order 15% > 20% > 30% hydrogen peroxide concentration. The change is selective during the course of reaction can be explained by adsorption of reaction species that block some of the active sites.

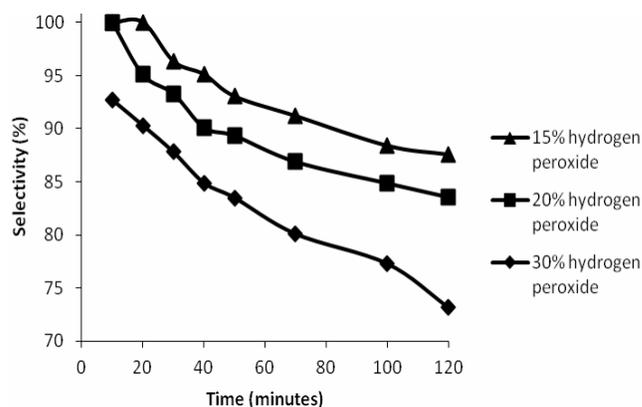


Figure 10. Selectivity as a function of time for the oxidation of cinnamyl alcohol over 5%Pt-5%Bi/C catalysts in water (60°C, 2 h)

3.2.3 Overview summary of activity (conversion) and selectivity of supported platinum catalysts

Table 4 gives a summary of selectivity and activity of platinum catalysts. The results obtained from the prepared Pt-Bi/C show good selectivity and conversion in different media when compared to other studies reported in literature as shown in Table 4. Although values for selectivities and conversions from the current study are lower than previous reported results they show great potential of using hydrogen peroxide as a complementary oxidant to oxygen.

4. CONCLUSION

In this study the carbon-supported platinum catalysts were successfully synthesized and characterized using BET, XRD, HRTEM and SEM. The oxidation of cinnamyl alcohol to cinnamaldehyde was investigated over carbon-supported platinum catalysts. The results have shown a great potential of using hydrogen peroxide as an environmentally friendly and cost-effective oxidant. The selectivity to cinnamaldehyde formation over 5%Pt-5%Bi/C was high ($\geq 84\%$) in toluene. However, under the reaction conditions used, Pt-Bi/C catalysts are less active than previously reported results. That is, after a reaction time of 2 h, conversions of 34% and 63% were recorded for 5%Pt-5%Bi/C, in water and toluene respectively. Catalyst activities were higher in water than in toluene, but toluene has a positive influence on the cinnamaldehyde selectivity. The aldehyde selectivity improves with increasing base metal loading of the catalyst (Bi), while the catalyst activity concurrently decreases. Future perspectives related to the kinetics on the addition of oxidant and change of the

catalyst support would possibly bring significant changes in the catalyst selectivity and activity.

Table 4 Comparative results for catalytic oxidation of cinnamyl alcohol

Catalyst	Selectivity (%)	Conversion (%)	Conditions	Reference
5%Pt-5%Bi/Al ₂ O ₃	96-98	96	Air, 40-80°C,	13
5%Pt-5%Pd-5%Bi/C	97	97	detergent	
5%Pt/Al ₂ O ₃	88	10		
5%Pd/Al ₂ O ₃	90	21	Air, 65°C, toluene	14
5%Pd/Al ₂ O ₃	89	50	Air, 80°C, toluene	15
5%Pt-5%Bi/C	73	63	Air, 60°C, water	Current study
5%Pt-5%Bi/C	84	34	Air, 60°C, toluene	

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