Research Article

Efficient Oxidation of Benzyl Alcohol to Benzaldehyde with Hydrogen Peroxide Mediated by Palladium Chloride Impregnated on Aluminium Oxide-Pillared Clay

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Abstract

Aldehydes, such as benzaldehyde, are very important in many industries and can be prepared from alcohols. In this research, aluminium oxide-pillared bentonite (Al-PILC) was prepared by inserting aluminium (III) chloride into the interlayers and calcination. Then $PdCl_2$ was impregnated into Al-PILC and calcined to produce Pd/Al-PILC. The synthesized clay and raw clay were characterized by X-ray diffraction (XRD) and N_2 adsorption-desorption (Brunauer-Emmett-Teller; BET) techniques. From the characterization, XRD pattern exhibited the characteristic peaks of montmorillonite at 2θ of 7° and 22°. Additionally, the N_2 adsorption-desorption isotherm of Pd/Al-PILC indicated mesoporous structure and BET specific surface area was 102 m^2/g. The catalytic activity of Pd/Al-PILC was investigated for the oxidation of benzyl alcohol with H_2O_2 furnishing benzaldehyde. In the optimum condition, 82% of benzaldehyde was produced *via* the reaction of benzyl alcohol and H_2O_2 in the presence of a catalytic amount of Pd/Al-PILC in refluxing acetonitrile for 3 h under mild reaction conditions.

Keywords: Aluminium oxide-pillared clay, Palladium chloride, Benzyl alcohol, Benzaldehyde

1 Introduction

Benzaldehyde is an important precursor to be used in industrial applications as a chemical intermediate for the synthesis of pharmaceuticals, agricultural chemical and it has been widely used in the manufacture of perfumes [1]. In addition, it has been used as an important starting material for the manufacture of odorants, flavors, and triphenylmethane dyes [2]. Benzaldehyde can be synthesized using various methods, such as Friedel-Crafts alkylation [3], direct carbonylation of benzene in ionic liquids [4], aerobic oxidation in water catalyzed by aqua-soluble multicopper(II) triethanolaminate compounds [5], oxidation catalyzed by a pentamethylcyclopentadienyl iridium complex [6], oxidation with hydrogen peroxide promoted by TPAP-doped ormosils [7], oxidation over silver-containing hexagonal mesoporous silica [8], and oxidation catalyzed by vanadium phosphorus oxide with cobalt doping [9]. However, some methods have complications for catalyst preparation. For both environmental and economic reasons, oxidation of organic molecules with H_2O_2 as the oxidant is important in synthetic organic chemistry. Preparation of benzaldehyde has been reported using homogeneous catalysts, mainly mineral acids as catalysts, as well as Brønsted acid, such as CH_3COOH [10], and Lewis acid, such as iron (III) tosylate [11], rhodium (I) complex [12], cobalt complex [13], vanadium phosphorus oxide [9], $FeSO_4$ [14], and $Fe(NO_3)_3 \cdot 9H_2O$ [15]. However, homogeneous catalysts have many disadvantages, for example, difficult separation of the catalyst from the product, requiring expensive and toxic catalysts, longer reaction time, and high reaction temperature. The use of modified clay as a heterogenous catalyst is aimed to study and develop. Bentonite clay is a solid phase found in natural materials. There is no effect on the health and environment. When modified bentonite clay was used in the reactions, such as the transformation of epoxide to aldehyde and acetonide [16], Ullmann coupling reaction [17], reduction and formation of benzimidazoles [18], reduction of nitrobenzene [19], reduction of nitroarenes and Biginelli reactions [20], acylation reaction [21], Friedel-Crafts alkylation [22], hydrogenation [23], the outstanding features were the high percentage yield and selectivity. Moreover, it can be easily separated from the catalyst. The catalyst is also reusable.

Modified clay catalysts are of great interest because of their potential application as catalysts in the oxidation of benzyl alcohol [24]–[26]. While, palladium has long been used for the oxidation of various compounds [27], [28]. However, there has been no report on the utilization of $PdCl_2$ impregnated into Al-PILC (Pd/Al-PILC) as a catalyst. In this research, Pd/Al-PILC was synthesized, characterized and used as an efficient catalyst in the synthesis of benzaldehyde under mild reaction conditions. Various reaction factors, such as amount of Pd/Al-PILC, reaction temperature, reaction time, and type of solvent, were varied in order to optimize the reaction conditions to produce the highest yields.

2 Materials and Methods

2.1 *Materials*

Bentonite clay (commercial grade, Cernic International), with these typical percentages by weight of chemical analysis: SiO_2 (63.60), Al_2O_3 (17.60), Na_2O (3.40), Fe_2O_3 (3.10), CaO (3.00), and K_2O (0.50), used in the fabrication the catalyst, was purified by fractionated centrifugation for the removal of quartz and other dense impurities. In addition, reagent grades of NaOH (Merck), $AlCl_3 \cdot 6H_2O$ (Fluka) and $PdCl_2$ (Fluka) were also used without prior purification.

2.2 *Preparation of Al-PILC*

The raw clay mineral used in this work was bentonite clay. First, it was decontaminated by dispersion in distilled water and subsequent fractionated centrifugation to eliminate quartz and other dense contaminants. This purified bentonite clay was used to prepare Na-clay by a cationic exchange. In brief, the purified clay was suspended in 5 M NaOH for 24 h at room temperature. Then, hydroxide ions were removed from Na-clay using a dialysis membrane until neutral pH. Later, the product was dehydrated at 100 °C for 24 h.

The prepared Na-clay was then intercalated with aluminium polyoxocations, which act as a pillaring reagent [19]. The aluminium polyoxocations were prepared by combining 0.2 M NaOH and 0.2 M $AlCl_3$ that had the molar ratio of OH^-/Al^{3+} at 1.9 under vigorous stirring for 24 h. This Al pillaring solution was then slowly added to the Na-clay suspension at

Al^{3+}/clay of 3.8 mol/kg. The slurry was aged under stirring for 24 h, and then washed by centrifugation with deionized water until the absence of chloride by dropping silver nitrate solution into the supernatant. The intercalated solid was separated by filtration, dried at 100 °C for 24 h, and calcined at 500 °C by increasing the temperature at the rate of 5 °C/min and then hold at 500 °C for 1 h.

2.3 *Preparation of Pd/Al-PILC*

Pd/Al-PILC was fabricated by impregnation of the Al-PILC with 2 wt% of $PdCl_2$ in methanol. After the impregnation, the resulting wet solid was dried at 80 °C for 2 h and finally calcined for 4 h at 450 °C.

2.4 *Characterization of the prepared catalyst*

The fabricated catalysts were characterized by X-ray diffraction (XRD) and surface area analyzer. The XRD patterns of raw clays and synthesized clay catalysts between 2° and 30° of 2θ [29] were measured by a Rigaku D/Max 2200/Ultima+ X-ray powder diffractometer (40 kV, 30 mA) (Tokyo, Japan) with a monochromator and Cu K_α radiation. The BET specific surface areas were acquired using the Quantachrome Autosorb-1 nitrogen adsorptometer (Boynton Beach, Florida, USA). The adsorption isotherms at –196 °C were determined using the BEL Japan Model BELSORP-mini. The specific surface areas, the total mean pore diameters and the pore volumes were calculated by the BET method.

2.5 *General catalytic procedure*

The reaction mixture is consisted of 0.5 mmol benzyl alcohol, 2 mL H_2O_2 and Pd/Al-PILC 50 wt% to benzyl alcohol in 3 mL acetonitrile in a round bottom flask. The equation is shown in Figure 1. The mixture was continuously stirred. Afterward, the catalyst was removed from the reaction mixture by filtration. The yield of benzaldehyde product was measured by GC using cyclohexanone as the internal standard (Agilent 6890 GC; Optima-1 column, 30 m column length, 0.32 mm column diameter; isothermal at 80 °C for 1 min, ramping 10 °C/min to 230 °C and hold for 1 min).

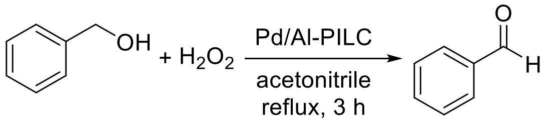


Figure 1: Synthesis of benzaldehyde from benzyl alcohol using H_2O_2 and Pd/Al-PILC.

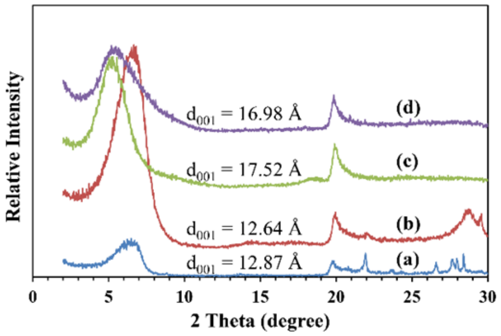


Figure 2: XRD pattern of (a) raw bentonite, (b) purified bentonite, (c) Al-PILC, and (d) Pd/Al-PILC.

3 Results and Discussion

3.1 *Catalyst characterization*

The synthesized Pd/Al-PILC was characterized by XRD. XRD was used to study the spacing between the layers of clay and the crystalline structure. XRD essentially uses the refraction of X-rays incident on the atoms in the crystal, which would cause refraction or delete stirring once. There are differences in the movement of X-rays in the horizontal plane of the atoms, which could be made to study the crystallinity and the distance between layers of the synthesized catalyst.

The patterns of XRD for Pd/Al-PILC, Al-PILC, purified bentonite and raw bentonite were compared as shown in Figure 2. The XRD pattern showed the characteristic peaks of bentonite at 2θ of 7° and 19° and quartz peaks at 2θ of 22°, 24°, and 27° disappeared in the XRD patterns of purified bentonite. The structure of bentonite clay remained and the (001) peak was found at 2θ of 7°. The XRD patterns are in good agreement with the standard JCPDS file (card no.01-088-0891) [30]. The basal spacing of Pd/Al-PILC, Al-PILC, and purified clay are illustrated in Table 1. This basal spacing of Al-PILC is shifted to the larger basal spacing as compared to the purified clay. The layer structure of clay catalysts was not demolished during the fabrication of catalysts. Nevertheless, the broad 001 peak resulted from the transformation of aluminium polyoxocations into rigid aluminium oxide pillars that increased the disordering within interlayer spacing of clay structure. The basal spacing of Pd/Al-PILC was found as a broad peak and smaller d-spacing in comparison to Al-PILC. The $PdCl_2$ impregnated on Al-PILC still had layering structure and also still possessed the large basal spacing of 16.98 Å.

Table 1 shows the comparison of the specific surface area of Pd/Al-PILC, Al-PILC, and purified clay. The BET shows that the specific surface area of Al-PILC is greater than the specific surface area of purified clay because the clay-layered structure was converted to a mesoporous structure by connecting the adjacent aluminosilicate layers with the aluminium oxide pillars in the interlayered region. Pd/Al-PILC (101.52 m^2/g of clay) exhibited a greater specific surface area than purified clay (39.58 m^2/g of clay) but it had a lower specific surface area than Al-PILC (120.26 m^2/g of clay). This is because palladium chloride deposited on the pore wall of the Al-PILC and occupied the void in mesoporous structure, causing the specific surface area to reduce. The mean pore diameters of Al-PILC and Pd/Al-PILC are lower than purified clay due to the interference of metal and calcination also causes the clay structure to have a smaller pore size.

Table 1: Data analysis from XRD and BET of catalysts

Clay Catalyst	d_{001} (Å)	S_{BET} (m^2/g)	d_p (nm)	V_p (cm^3/g)
Purified clay	12.64	39.58	7.04	0.05
Al-PILC	17.52	120.26	3.92	0.12
Pd/Al-PILC	16.98	101.52	4.41	0.11

S_{BET}: specific surface area
d_p: mean pore diameter
V_p: total pore volume

3.2 *Catalytic activities of Pd/Al-PILC in the oxidation of benzyl alcohol*

To test the catalytic activity of Pd/Al-PILC, the synthesis of benzaldehyde from benzyl alcohol with hydrogen peroxide was chosen. The reaction temperature, reaction time, amount of Pd/Al-PILC, and solvent were varied to determine the best reaction condition.

3.2.1 Catalytic activities of Na-clay, Al-PILC and Pd/Al-PILC clay catalysts

In the first part, the catalytic activity of Pd/Al-PILC was compared to the activity of Na-clay, Al-PILC, and reaction without a catalyst. When the synthesis of benzaldehyde was performed without a catalyst, the yield was only 8% as shown in Table 2 (entry 1). Therefore, experiments were performed to investigate whether Na-clay, Al-PILC, and Pd/Al-PILC can act as a catalyst in this reaction to increase the yield and shorten the reaction time. The reactions were performed using 5 mmol benzyl alcohol, 85 mmol (2 mL) H_2O_2, and 50 wt% of the catalyst compared to benzyl alcohol in refluxing acetonitrile for 24 h or 3 h. When Na-clay was used, the yield increased only slightly to 11% (entry 2). Al-PILC performed better but the yield was still quite low at 18% (entry 3). Pd/Al-PILC exhibited the highest yield at 82% in only 3 h (entry 4). In addition, benzoic acid was not detected. $PdCl_2$ itself has been reported to be able to catalyze the oxidation of benzyl alcohol to provide benzaldehyde product but with low yield [31], [32]. This can be concluded that Pd/Al-PILC is an effective catalyst for the synthesis of benzaldehyde from benzyl alcohol.

Table 2: Effect of different types of clay catalysts

Entry	Clay Catalyst	Yield (%)
1	None	8
2	Na-clay	11
3	Al-PILC	18
4	Pd/Al-PILC	88

Reaction conditions: benzyl alcohol (5 mmol), H_2O_2 (85 mmol, 2 mL), acetonitrile (3 mL), catalyst (50 wt% to benzyl alcohol) at refluxing acetonitrile (82 °C) for 24 h.

3.2.2 Effect of reaction temperature and reaction time

One significant factor is the temperature used in the reaction. An experiment was performed to investigate whether the reaction carried out at room temperature using Pd/Al-PILC can produce the product. After 24 h, only a moderate yield (44%) was obtained as shown in Table 3 (entry 1). In addition, attempts were also made to reduce the reaction time and to track the progress of the reaction at refluxing temperature. When the reaction was run for 1 h, 48% of benzaldehyde was obtained (entry 2). Increasing the reaction time to 2 h, the yield was 73% (entry 3), while at 3 h, the yield was 82% (entry 4), and, as stated previously, when performed for 24 h, the yield slightly increased to 88% (entry 5). Therefore, based on these results, a reaction time of 3 h was selected as the optimum time.

Table 3: Effect of temperature and reaction time

Entry	Temp.	Time	Yield (%)
1	Room temp.	24 h	44
2	Reflux temp.	1 h	48
3	Reflux temp.	2 h	73
4	Reflux temp.	3 h	82
5	Reflux temp.	24 h	88

Reaction conditions: benzyl alcohol (5 mmol), H_2O_2 (85 mmol, 2 mL), acetonitrile (3 mL), Pd/Al-PILC 50 wt% to benzyl alcohol at room temperature (30 °C) and refluxing temperature (82 °C).

3.2.3 Effect of amount of Pd/Al-PILC

The amount of Pd/Al-PILC for the synthesis of benzaldehyde was varied and the results are summarized in Table 4. Generally, the more catalyst used, the faster the reaction. However, it would cost more as well. Therefore, experiments were performed to reduce the amount of catalyst used. For all reactions, the yields of benzaldehyde increased with increasing the amount of catalysts. The amount of Pd/Al-PILC was reduced to 10% and 30%, the yields of benzaldehyde were only 29% and 59%, respectively. Therefore, 50% of Pd/Al-PILC was still selected as the optimum amount of catalyst.

Table 4: Effect of amount of Pd/Al-PILC

Entry	Pd/Al-PILC (wt%)	Yield (%)
1	10%	29
2	30%	59
3	50%	82

Reaction conditions: benzyl alcohol (5 mmol), H_2O_2 (85 mmol, 2 mL), acetonitrile (3 mL), Pd/Al-PILC (wt% to benzyl alcohol) at refluxing acetonitrile for 3 h.

3.2.4 Effect of solvent

Solvent is an important factor in the reaction. It affects the solubility of reactants and catalysts. Its parity could also affect the amounts of products. Various types of solvents, such as tetrahydrofuran, acetone ethyl acetate, methanol, and acetonitrile were studied and the results are shown in Table 5. When using acetonitrile, it was found to give higher yield of benzaldehyde than methanol, ethyl acetate, acetone and tetrahydrofuran. Acetonitrile has more polarity than tetrahydrofuran, acetone, and ethyl acetate but has less polarity than methanol. This means that in this reaction, solvent with medium polarity is better for the reaction.

Table 5: Effect of solvent

Entry	Solvent	Yield (%)
1	Tetrahydrofuran	15
2	Acetone	18
3	Ethyl acetate	20
4	Methanol	26
5	Acetonitrile	82

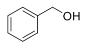
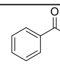
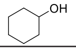
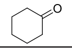
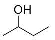
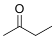
Reaction conditions: benzyl alcohol (5 mmol), H_2O_2 (85 mmol, 2 mL), solvent (3 mL), Pd/Al-PILC 50 wt% to benzyl alcohol at refluxing solvent for 3 h.

The benzaldehyde yield of 82% after 3 h was better than some other catalysts reported in the literature. For example, the best Au-Pd catalyst prepared by sol immobilization by Pritchard et al. produced benzaldehyde product for only 63% after 6 h [33], while the one prepared by Tareq et al. gave only 39% after 6 h [34]. In addition, Pt/TiO_2 catalyst prepared by Kunene *et al.* only gave a 7.2% conversion of benzyl alcohol to benzaldehyde after 5 h [35].

3.2.5 Substrates catalyzed by Pd/Al-PILC

Three other alcohols including cyclohexanol, sec-butanol, and sec-propanol were chosen to observe the action of Pd/Al-PILC catalyst. The results are summarized in Table 6. Cyclohexanol was chosen as a representation of cyclic alcohol. The oxidation of cyclohexanol with H_2O_2 furnished cyclohexanone with a good yield. The oxidation of sec-butanol and sec-propanol as substrate can synthesize 2-butanone and propanone in 59% and 51% yield, respectively. All products were identified by GC by comparing with authentic samples.

Table 6: Variation of substrate

Entry	Substrate	Product	Yield (%)
1			82
2			62
3			59
4			51

Reaction conditions: substrate (5 mmol), H_2O_2 (85 mmol, 2 mL), acetonitrile (3 mL), Pd/Al-PILC 50 wt% to benzyl alcohol at refluxing acetonitrile for 3 h.

5 Conclusions

Pd/Al-PILC has been proven to be an effective catalyst for the synthesis of benzaldehyde. The optimized condition was using hydrogen peroxide and 50 wt% of Pd/Al-PILC to benzyl alcohol in acetonitrile under refluxing condition for 3 h. The reaction furnished benzaldehyde in very good yield under extremely mild reaction conditions. In addition, this experimental procedure was applied to some other alcoholic substrates and the experiments produced good yields of the desired products.

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Author Contributions

P.T.: conceptualization, methodology, validation, formal analysis, investigation, data curation, writing an original draft; writing-reviewing and editing, supervision, project administration, funding acquisition; D.S. and N.A.: conducting experiments, data acquisition, figure preparation; K.C.: data analysis, reviewing and editing; R.R. and M.S.: editing an original draft. All authors have read and agreed to the published this version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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