



A Pd-Np/Ac-Catalyzed Transfer-Hydrogenation of Mesityl Oxide to Methyl Isobutyl Ketone using Sodium Formate as Hydrogen Donor

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Abstract

Methyl isobutyl ketone (MIBK) is an α,β -unsaturated carbonyl compound, which is often used as solvent and extractor for antibiotics in the pharmaceutical industry. One alternative to the synthesis of MIBK from mesityl oxide (MO) is through catalytic transfer hydrogenation (CTH) using various organic compounds as hydrogen donors in the presence of a catalyst. The purpose of this study was to synthesize MIBK from MO through the CTH reaction using sodium formate as the hydrogen donor and as the catalyst, Pd nanoparticles were used and deposited on the activated charcoal (Pd-NP/AC). Based on the Gas Chromatography-Mass spectrometer (GC-MS) analysis, the conversion value of MO was obtained in 97.3% and the yield of the MIBK formation was 10.5%. Meanwhile, the highest selectivity was obtained in 17% at 40° C. The results show that sodium formate can effectively be used to reduce MO into MIBK in the presence of Pd-NP/AC catalyst at 70° C for 5 hours.

Keywords: Catalytic transfer hydrogenation; methyl isobutyl ketone; mesityl oxide; Pd-NP/AC; sodium formate.

1. Introduction

Methyl isobutyl ketone (MIBK) is an α,β unsaturated carbonyl compound, which is often used as a solvent in paints, resins and coatings in the form of acrylanitrocellulose, acrylic and vinyl, also used as an extracting agent in the production of antibiotics and lubricating oils [1][2]. The synthesis process of MIBK is through 3 stages, the first stage is the self-condensation of acetone to diacetone alcohol (DAA, 4-hydroxy-4-methyl-2-pentanone) under acid or base catalysis; the second step is the dehydration of DAA to mesityl oxide (MO, 4-methyl-3-penten-2-one); the final step is the selective hydrogenation of the carbon – carbon double bond of MO to form MIBK [3]. However, the synthesis of MIBK requires hydrogen

gas as a reductant for MO hydrogenation, and the reaction takes place by using high temperature and pressure, which need a special equipment for the reaction due to its tendency to explode. Therefore, catalytic transfer hydrogenation (CTH) was established to reduce the risk of an explosion with the presence of a metal catalyst and hydrogen donor at low temperature - atmospheric condition [4]. The hydrogen donors are readily available, inexpensive, and easy to handle, the major side product can be recycled, and the catalysts that are involved usually are readily accessible and not sensitive [5].

The ability of a metal as a catalyst for hydrogenation reaction is related to the ability of the metal (inside the metal) to store hydrogen molecules.

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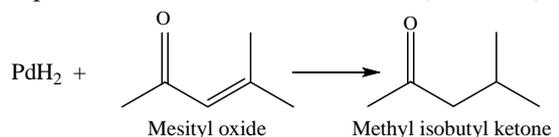
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Palladium has the ability to absorb large volumetric quantities of hydrogen at room temperature and atmospheric pressure, and subsequently forms palladium hydride (PdHx) [6][7].

The hydrogen donor that are commonly used in reducing unsaturated α , β carbonyl compounds through CTH are isopropanol, formic acid/triethylamine mixture, formic salt. However, isopropanol in the presence of Pd/C catalyst cannot reduce the carbon-carbon double bond in the MO molecule to MIBK [8]. Sodium formate, water as solvent and the presence of a Pd/C catalyst are known to reduce olefin, acetylene, and nitro compounds. The reaction proceeds mainly by a direct hydrogen transfer mechanism rather than via initial decomposition of the formate into molecular hydrogen and sodium carbonate which then decomposes to form carbon dioxide [9].

The nanometer-sized Pd catalyst metal deposit method on carbon nano is known to increase the storage capacity of hydrogen, and the size depends on the content, size and diameter of the Pd nanoparticles [10]. Palladium catalyst deposited on the Multiwall Carbon Nanotube (MWCNT) is effective in catalyzing the reaction of hydrogen donor dissociation to form hydrogen molecules [11]. Palladium nanoparticles deposited on activated charcoal, graphite and MWCNTs, and formic acid as an electron donor were known to convert styrene to ethylene benzene by 38, 38 and 68%, respectively [12]. Palladium nanoparticles deposited on graphene with their hydrogen donor sodium formate catalyze the reduction reaction of carbon double bonds in α,β unsaturated carboxylic acid with a maximum product yield (yield) of about 100% [13].

Based on the foregoing, can methylene isobutyl ketone be synthesized through a CTH using sodium formate in a mixture of water and methanol as a hydrogen donor in the presence of a Pd catalyst deposited on various carbon materials (Scheme 1).



Scheme 1 Generation of MIBK from mesityl oxide by catalytic transfer hydrogenation (CTH).

2. Experimental

2.1. Materials and Instruments

All General Chemicals were purchased and directly used as received without further purification.

HCOONa, Pd₂(dba)₃ • CHCl₃, CHCl₃, acetone was analytical pure and was prepared by Merck Industries AG, and Activated charcoal (Fluka). The instrument used in the study was X-ray, SEM-EDX and GC-MS, X-Ray Diffraction (XRD), Bruker Advanced X-Ray Solution (AXS) model D8', Scanning Electron Microscope (SEM), Jeol JSM- IT300 (Tokyo, Japan) and GC analysis of the reactions was performed by using Agilent 7890 A (GC) and 5975 C (MS).

2.2. Methods

2.2.1. Preparation of palladium nanoparticles loaded on activated charcoal, Pd-NP/AC

Enter the screw-capped reaction vessel 25 mg Pd₂(dba)₃ • CHCl₃ as a palladium nanoparticle precursor, 300 mg of, activated charcoal and 25 mL of CHCl₃, and heated on oil bath at 80° C while shaking with a magnetic stirrer. After the dissolution of Pd₂(dba)₃, a dark red solution was formed, and stirring was performed until the red color of the solution disappeared. The Pd-NP/AC catalyst was separated from the mixture then washed with acetone to free dba, and dried at low pressure, 0.01 bar and 100 °C. The Pd-NP/AC catalyst characterization was carried out by X-Ray, SEM and EDX.

2.2.2. Catalytic Transfer Hydrogenation experiment

In a typical experiment, a screw-capped reaction vessel contains 0.24 g (2.4 mmol) mesityl oxide, 2.18 g sodium formate, mixture of 4.0 mL water and 2 mL methanol, and 0.02 g (0.19 mmol) Pd-NP/AC. The reaction vessel was then sealed and heated at 40°, 50°, 60° and 70° C, respectively for 5 h. Methyl isobutyl ketone formed was separated from the mixture was extracted with n-hexane. The product was analyzed by GC using an HP-5 column (30 m × 0.25 mm, 0.25 μm thick) to determine the conversion, yield and MIBK selectivity.

3. Result and Discussions

The Pd-NP/AC catalyst was prepared by the method described by Sergey et al. The structures of the compounds made were characterized using various techniques, including SEM, XRD and SEM-EDX. The XRD pattern of the Pd-NP / MWCNT sample is shown in Figure 1. In a spectrum of sharp and narrow peaks at $2\theta = 40^\circ, 46.8^\circ, 68.3^\circ, 82^\circ$ and 87° corresponding to (111), (200), (220), (311) and (222) crystal planes Pd, is associated with the presence of crystalline palladium and suggests that the element palladium exists in the form Pd (0). All peaks and diffraction positions for

palladium match those of the JCPDS card no. 05-0681. The average crystallite size of the palladium nanoparticles was evaluated using the Scherrer equation for the peak (111) at $2\theta = 50^\circ$ and found to be 45 nm in size.

$$D = (K \lambda) / \beta \cos \theta \dots \dots \dots \text{equation 1}$$

Where:

K is the Scherrer constant = 0.68 - 2.08

λ is the wavelength of X rays, for Cu the average = 1.54178 Å

β is the FWHM (Full Width at Half Maximum) of the peak XRD (radians)

θ is the XRD diffraction angle

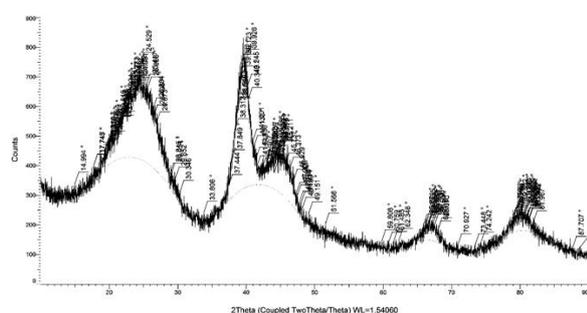


Fig. 1. XRD pattern of Pd-NP/AC catalyst.

Following the SEM image and histogram of the Pd-NP/AC catalyst (Figure 2), it can be seen that the average diameter of palladium particles in activated charcoal is 92.7 ± 4.3 nm. These crystalline palladium peaks were well separated from the broad peak of AC at around $2\theta = 26^\circ$, which corresponds to the peak of graphite [14].

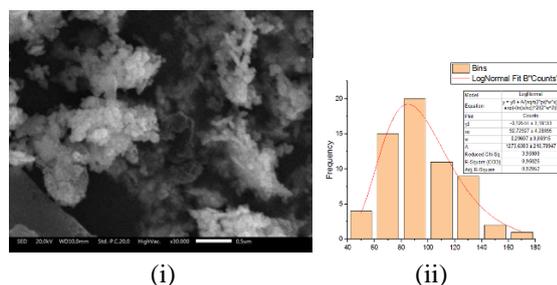


Fig. 2. SEM images of the Pd-NP/AC catalyst (i), SEM (ii) Image and size distribution (iii) of synthesized Pd-NP/AC.

In SEM-EDX (Figure 3) it is known that the palladium deposited in activated charcoal is as elemental Pd, the Pd content is 6.7 w%. The surface area of commercial activated charcoal is $820 \text{ m}^2/\text{g}$.

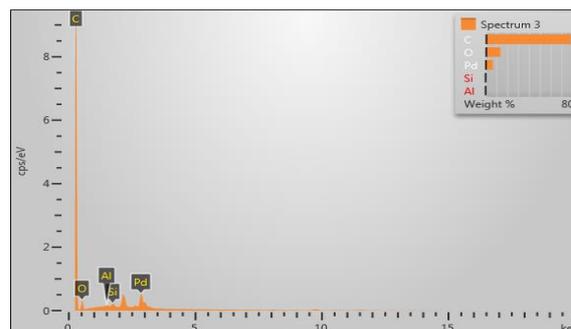


Fig. 3. SEM EDX of Pd-NP/AC catalyst

Next, we evaluate the performance of the sodium formate in the presence of the Pd-NP/AC catalyst which is the result of reducing MO to MIBK by means of a catalytic transfer hydrogenation reaction. The analysis of the reaction products was performed using GC analyzes. These assays were performed on a Gas Chromatography - Mass Spectrometry (GC-MS) Agilent Technologies type 7890A (GC) and 5975C (MS) system fitted a Agilent HP-5MS 5% Phenyl Methyl Silox column ($29.81 \text{ m} \times 250 \mu\text{m} \times 0.25 \mu\text{m}$) and an Electron Impact (EI) detector. The amount of MIBK formed is calculated from the peak area at t_R 3.78 minutes, then the MO conversion value, yield, and selectivity are calculated. The following is the equation for calculating the conversion value, yield and selectivity:

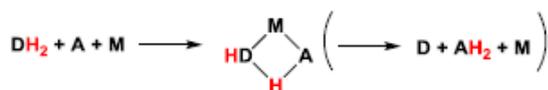
Next, we evaluate the performance of the sodium formate in the presence of the Pd-NP/AC catalyst which is the result of reducing mesityl oxide to MIBK by means of a catalytic transfer hydrogenation reaction. The analysis of the reaction products was performed using GC analyzes. These assays were performed on a Gas Chromatography - Mass Spectrometry (GC-MS) Agilent Technologies type 7890A (GC) and 5975C (MS) system fitted a Agilent HP-5MS 5% Phenyl Methyl Silox column ($29.81 \text{ m} \times 250 \mu\text{m} \times 0.25 \mu\text{m}$) and an Electron Impact (EI) detector. The amount of MIBK formed is calculated from the peak area at t_R (retention time) 3.78 minutes, then the MO conversion value, yield, and selectivity are calculated. The following is the equation for calculating the conversion value, yield and selectivity:

$$\text{Conversion (\%)} = ([\text{mol of MO loaded in the reactor-mol MO in product}]) / ([\text{mol of MO loaded in the reactor}]) \times 100$$

$$\text{Yield (\%)} = (\text{mol MIBK in product}) / ([\text{mol of MO loaded in the reactor}]) \times 100$$

The values for recovery, selectivity and synthesis conversion of MO to MIBK at reaction temperatures of 40°, 50°, 60° and 70° C are shown in Figure 3 showing the higher the reaction temperature, the greater the MO conversion. The highest value of product, selectivity and conversion was at the reaction temperature of 70° C, which is 66.06%. This is because (1) the increase in temperature will increase the reaction speed according to the Arrhenius equation or (2) the increase in temperature can increase the solubility of sodium formate in water. Following are the solubility data of sodium formate in water at 0, 20 and 100° C, respectively 43.82, 97.2 and 160 g / 100 mL. Based on these data, it shows that the solubility of sodium formate in water increases with increasing temperature, so that the decomposition of HCOONa forms hydrogen molecules which are used for the hydrogenation reaction of MO to be more abundant. Based on the value of recovery, conversion and selectivity, the optimum temperature of MIBK synthesis through the catalytic reaction of hydrogenation transfer from MO using a Pd-NP/AC catalyst is 70°C. The hydrogen molecule for hydrogenation of the double bond in MO is produced from the dissociation of sodium formate in a mixture of water in methanol and the presence of a Pd-NP/AC catalyst at 70°C for 5 hours, as in the following reaction Formate salts are known hydrogen carriers and donors [15][16] and generally decompose to molecular hydrogen and bicarbonate salt in presence of water and a Pd/C catalyst. Thus, the reversible Pd/C-catalyzed decomposition of sodium formate to hydrogen and sodium bicarbonate [9] can be represented as shown in Scheme 2.

(A) Direct transfer pathway



M: metal, A=acceptor dan DH_2 = hydrogen donor
 $\text{HCOONa} + \text{H}_2\text{O} + \text{A} + \text{M} \rightleftharpoons \text{AH}_2 + \text{NaHCO}_3 + \text{M}$
 Scheme 2. Pd/C – catalyzed transfer hydrogen

Pd/C-catalyzed hydrogen transfer reactions to sodium format also occur with an acceptors (A) such as nitroarenes, haloarenes, olefins and aldehydes [17] can be shown as written in Scheme 1. The products are the hydrogenated form of the starting materials and bicarbonate salts. It is realized that the in situ generation of bicarbonate salts during Pd / C catalyzed transfer-hydrogenation reaction of olefin to alkane via

hydrogen transfer from formate salts is beneficial for enhancing the selectivity to alkene. This indeed is the case as we characterize the salt obtained after the reaction as NaHCO_3 (Scheme 1). The role of water is important not only as a stoichiometric reagent but as a contact medium on the surface of the catalyst between the hydrogen donor and the metal and the substrate by forming a layer of sodium formate solution [9]. The highest selectivity occurs at 60° C.

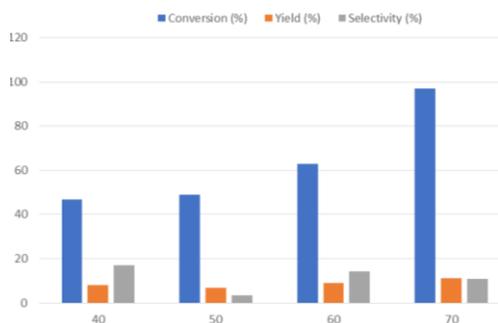


Fig.4 Value of Yield, Conversion and Selectivity Synthesis of MIBK from MO via CTH using sodium formate and Pd-NP/AC

Reaction conditions: 2.4 mmol MO; 32 mmol HCOONa (in 4mL water); 0.002 g Pd-NP/AC.

Note: Gas Chromatography - Mass Spectrometry (GC-MS) Agilent Technologies type 7890A (GC) and 5975C (MS) with helium gas mobile phase, Agilent HP-5MS 5% Phenyl Methyl Silox stationary phase 29.81mx 250µm x 0.25µm, and source of Electron Impact (EI) ions.

Sodium formate in the presence of Pd-NP/AC catalyst preparation results act as a hydrogen donor in the reaction of mesityl oxide into methyl Isobutyl ketone. The optimum conversion values of MO and the MIBK yield occurred at 70°C temperatures were obtained in 97.3% and 10.5%, respectively. Reaction temperature affects conversion value and yield but the selectivity value is less influential, with a maximum value at 40°C is 17.0 %.

4. Conclusion

Pd-NP/AC catalyst has been successfully synthesized on carbon with the average size of the palladium particles in the catalyst of 92.7 ± 4.3 nm and the crystallite size of 45 nm. The catalyst performance in the synthesis of MIBK from MO via the catalytic transfer hydrogenation using sodium formate as hydrogen donor showed the optimum conversion values of MO and the MIBK yield at 70 °C were 97.3% and 10.5%, respectively. The highest selectivity was 17% at 40 °C.

5. Conflicts of interest

There is no conflict of interest.

6. Funding sources

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