

Application of Laser Induced Breakdown Spectroscopy as a Novel Approach for Monitoring of the Activity of Nano Palladium Catalyst as Compared to Two Well-known Methods

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Abstract. Catalyst deactivation is an unavoidable process that occurs in catalytic chemical reactions. Laser Induced Breakdown Spectroscopy (LIBS) is used here as a novel approach to investigate the activity of palladium supported with carbon catalyst (Pd/C) over the hydrogenation of cinnamic acid with tetralin. Their outputs for four catalyst samples are reported for different time intervals of 0, 5, 10, 15 min during the reaction. The results of LIBS analysis are compared to Inductively Coupled Plasma Mass Spectrometry (ICP-MS), which

shows a good agreement. Experimental data specify that line intensities of palladium (Pd) are decreased significantly with an increment of the reaction time. Moreover, the Field Emission Scanning Electron Microscope with energy dispersive spectroscopy (FESEM-EDS) of catalysts samples show aggregation of palladium particles for some places in the catalyst surface. The changes of Pd content and sintering of Pd particles in the catalyst during the reaction play substantial roles in catalyst deactivation.

1 Introduction

Metal nanoparticles are suitable materials with powerful properties for applicable reactions, which are used in material design and the development of new products such as medicine, catalysis, electronics, and optics.^[1] Among metal nanoparticles, nanocatalysts have a great deal of interest due to the acceleration of chemical reactions with the use of a few amounts of the catalyst.^[2] Palladium-based catalysts are widely used for, catalytic hydro dechlorination, transfer hydrogenation reactions, methanol oxidation and explosive production.^[3] Catalyst deactivation is one critical issue associated with the catalytic processes because it shows the loss of catalyst activity over time. While catalyst deactivation is inevitable for most chemical processes, a better understanding of this issue is on focus.^[4] Monitoring and following the deactivation of the catalyst with a practical method is important for improving the reaction conditions and avoiding further costs.^[4b,5]

Catalytic Transfer Hydrogenation (CTH) has an effective rule as a suitable method for the reduction of organic substrates.^[6] In CTH reaction, hydrogen derived by an easily aromatized cyclic compound can transfer directly to an unsaturated substance with the use of catalyst.^[7] Hydrogen gas can be supplied by solvent as hydrogen donor compound using an appropriate catalyst for such reactions.^[8] With a comparison of the effectiveness of various catalysts, palladium catalysts are the most operative for hydrocinnamic production from cinnamic acid.^[9] The reduction of cinnamic acid to hydrocin-

amic acid in tetralin is one of CTH reactions in which tetralin acts as both solvent and hydrogen donor via palladium catalyst (Figure 1). In this procedure, tetralin provides hydrogen and converts to naphthalene by Pd/C catalyst in the mild condition under reflux. Derived hydrogen atoms from tetralin can reduce cinnamic acid to hydrocinnamic acid as a sequence using Pd/C catalyst.^[7,10] It is widely known that Pd catalysts can help hydrogenating double bonds well without affecting other functional groups. Since Pd catalysts are expensive, monitoring of their deactivation should be considered.

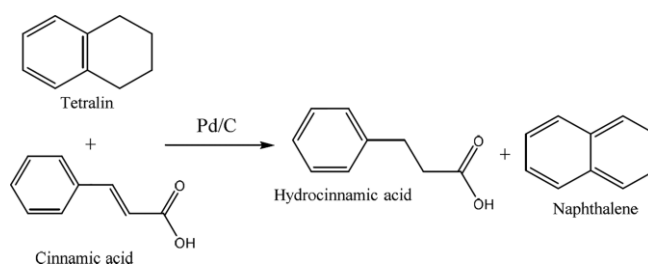


Figure 1. Catalytic transfer hydrogenation of cinnamic acid using Pd/C catalyst.

Albers et al.^[11] studied the carbon deposition on Pt/Al₂O₃ and Pd/SiO₂ catalysts through X-ray Photoelectron Spectroscopy (XPS) and Secondary-Ion Mass Spectrometry (SIMS). *Pernicone et al.*^[12] performed detailed research on commercial 0.5% Pd/C catalyst by the use several methods including Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS), CO chemisorption, and X-ray diffraction (XRD).^[12] *Koskin et al.*^[13] reported the deactivation of a palladium catalyst in the synthesis of CL-20 by hydro debenzoylation reaction over high-resolution Transmission Electronic Microscopy (TEM).^[13] *Yuan and Keane* studied deactivation of Pd/C and Pd/Al₂O₃ during the liquid

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phase hydro dechlorination of 2,4-dichlorophenol using Inductively Coupled Plasma (ICP) and Brunauer, Emmett and Teller (BET).^[14]

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is an analytical technique, which can be used for elemental determinations. It has been applied for the determination of trace element determination because it provides suitable advantages such as lower Limits Of Detection (LOD), multi-element and isotopic-ratio measurement capability, small sample amounts, reduced spectral interferences, high sensitivity, steadily decreasing investment costs, and *in situ*.^[15] Since spark is applied to expose the electrons of argon gas inside ICP and forming argon ions, the oscillating fields trapped them. These ions have a collision with other argon atoms, which create an argon discharge or plasma. The ICP source converts the atoms of the elements in the sample to ions. Then, the mass spectrometer separates and detects these ions. Thus, ICP-MS technology has superior detection capabilities.^[15,16]

Laser Induced Breakdown Spectroscopy (LIBS) is a rapid screening tool to evaluate the chemical constituents of materials.^[17] It was also used to assess shelf life and performance of hazardous energetic compounds.^[18] It was recently demonstrated that deactivation of Pd(OH)₂/C as fresh catalyst in debenzylolation reaction of hexabenzylhexaazaisowurtzitane (HBIW) for producing hexanitrohexaazaisowurtzitane (HNIW) can be distinguished by elemental information of analyzing the spectral content of plasma, which results from the interaction of a high power laser pulse with a sample of spent catalyst Pd/C using LIBS method.^[19] LIBS may be introduced a superior technique to others because it provides the benefits such as nondestructive, no need to initial preparation, simple, inexpensive, no spectral and matrix interference, and suitable for all types of material (solid, liquid, and gas).^[20] It is used here to permit the simultaneous analysis of the intensity of elemental and molecular emissions in the sample for confirmation of catalyst deactivation.

The purpose of this study is to extend previous work^[19] for investigation of the use LIBS technique of the deactivation of Pd/C catalyst among the catalytic transfer hydrogenation reaction of cinnamic acid. Deactivation of Pd/C catalyst has been examined among the hydrogenation transfer during time intervals of 0, 5, 10, and 15 min of reaction. Subsequently, ICP-MS carries out mapping the amount of Pd in catalyst samples. The Field Emission Scanning Electron Microscope with energy dispersive spectroscopy (FESEM-EDS) is also used to examine the catalyst surface. Measurement parameters for both the LIBS and ICP-MS are systematically optimized. A comparison is done between the result of LIBS analysis, ICP-MS, and FESEM-EDS.

2 Experimental Section

2.1. Materials and Hydrogenation Transfer

Catalytic hydrogenation transfer of cinnamic acid to hydrocinnamic acid was performed with an excess amount of tetralin as solvent and hydrogen donor via Pd/C catalyst at temperature of 190 °C. The uti-

lized catalyst was palladium (10 wt%) supported with activated carbon, which was supplied by Shaanxi Rock New Material Co., Ltd. and the reaction time was 15 min. Four samples of Pd/C catalysts in different time of hydrogenation reaction were selected for purposes of monitoring deactivation of catalyst among the reaction. Pd/C catalyst was isolated and washed with diethyl ether, water, and 10% aqueous sodium hydroxide after 5, 10, and 15 min of reaction. Then, the powdered sample of the washed catalysts dried in the oven. Due to the further analysis via LIBS technique, a binder of palmitic acid with the powdered samples was pressed to the pellets in the same conditions, which include weighing, homogenizing with palmitic acid and pressing.

2.2. LIBS Setup

All experiments were performed using a LIBS apparatus (LIB-SCAN100, Applied Photonic LTD, United Kingdom), which was equipped with Q-switched Nd:YAG laser (Quantel, USA) operating at 1064 nm with the pulse duration of 7 ± 2 ns. Laser irradiance on the sample was about 1.8 GW/cm². Samples were placed on a controlled X, Y, Z motorized translational stage that was controlled by internal software. The emitted radiation through the laser-induced plasma was transferred to the detector by an optical fiber bundle for spectroscopic analysis. The optical fiber system was connected to a detector with eight spectrometers (Avantes-20-01-13- A, Netherland), which can achieve 0.03–0.15 nm resolution for spectral analysis. The spectra were acquired at 1.27 μ s delay and 1.1 ms gate width. In our experiment, ten single-shot spectra for each sample were recorded and the resultant spectra were obtained by averaging over these measurements. A schematic diagram of the experimental setup used is shown in Figure 2. The LIBS test was done under Ar gas injection with 99.9% purity. The flow rate of 15 L·min⁻¹ was directed over the sample surface in order to reduce the effect of atmospheric gas and improve spectral peaks.^[17d,19]

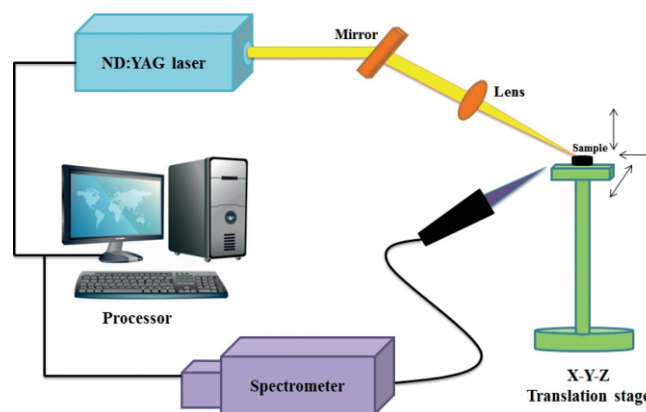


Figure 2. Schematic diagram of the experimental LIBS setup.

2.3. ICP-MS and FESEM-EDS Analysis

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a type of mass spectrometry that is highly sensitive for analyzing elements at trace levels. The capability of ICP-MS to simultaneously measure the majority of elements and can be applied to solutions, solids, and gases.^[21] Determining the concentrations of Pd in catalyst samples was greatly improved by the ability of ICP-MS to analyze the amount of Pd with high sensitivity. The palladium content in the catalyst was

determined by an Agilent 7500ce inductively coupled plasma (ICP) mass spectrometry. The catalyst samples were burned in an oxygen atmosphere furnace at a temperature of 900°C. The remainder of the catalyst samples was dissolved into aqua regia (a 1:3 mixture of nitric acid and hydrochloric acid) due to the measuring the palladium content in catalysts. The palladium content in the leached solution was measured by ICP-MS. The examination of catalyst morphology was studied by a MIRA3 TESCAN Field Emission Scanning Electron Microscope (FESEM) with energy dispersive spectroscopy (EDS).

3 Results and Discussion

3.1 LIBS Signal

The LIBS spectrum of palladium in argon ambient gas is shown in Figure 3. The spectroscopic data were extracted from the National Institute of Standards and Technology (NIST) database for identification of all of the used peaks and those related to palladium adapted with wavelengths.^[22] Every important peak of Pd and some of argon peaks are summarized in Table 1. The LIBS analyses of four sample catalysts were acquired at different times of 0, 5, 10, and 15 min from the beginning of the hydrogenation reaction. The LIBS analysis of fresh catalyst samples (0 min) with corresponding to argon emission lines are shown in Figure 4. As seen, the lines of palladium and argon are well specified in Figure 4. Moreover, in air atmosphere, due to the recombination of carbon from sample and nitrogen of the air, the molecular radiation CN violet system is seen but this radiation does not exist in the presence of argon ambient gases. These results have an agreement with other outcomes.^[19]

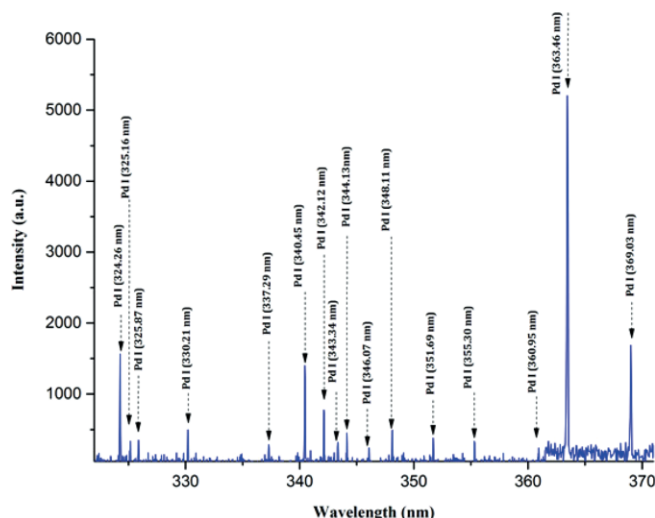


Figure 3. The LIBS spectrum of Pd.

Table 1. LIBS emission lines of palladium and argon gas.

Pd	324.26, 340.45, 344.13, 348.11, 363.46, and 369.03
Ar	794.81, 800.61, 801.47, 810.36, and 811.53

Since the final goal was to assess the deactivation of Pd/C catalyst among the reaction, four LIBS spectra of Pd/C were compared in 0, 5, 10, and 15 min from the beginning of the

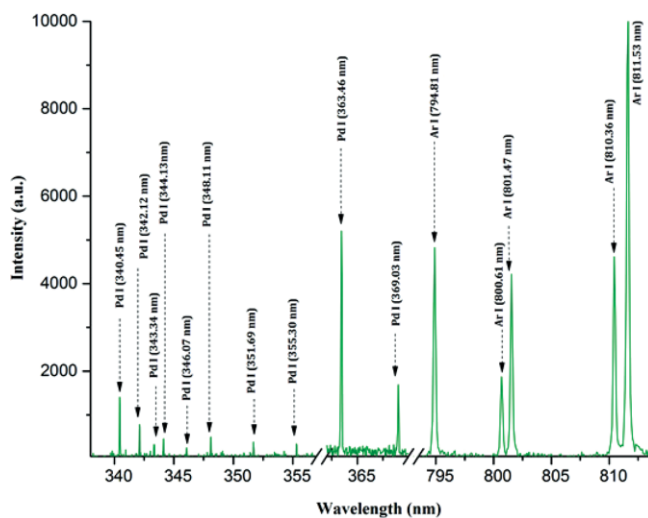


Figure 4. Emission lines of Pd I and Ar in the spectral range of 320–370 and 790–815.

reaction to end. The same conditions such as temperature, washing step, kind and amount of binder, sample amount, and flow rate of ambient gas were formed for attributing the procedure to deactivation. Figure 5 compares four samples of catalyst at different times of reaction. Due to the same condition of every LIBS analysis, all peaks were normalized to one of the argon peaks (763.57 nm) in order to reduce the effect of test parameters especially intensity shift. As seen, the intensities of spectral peaks are reduced with passing reaction time in the samples of 5, 10, and 15 min, respectively. The fresh catalyst sample (0 min) has the most intense that is seen in Figure 5. The observed trend in the intensity of spectral lines of Pd is due to the deactivation of catalyst among the catalytic transfer hydrogenation reaction.

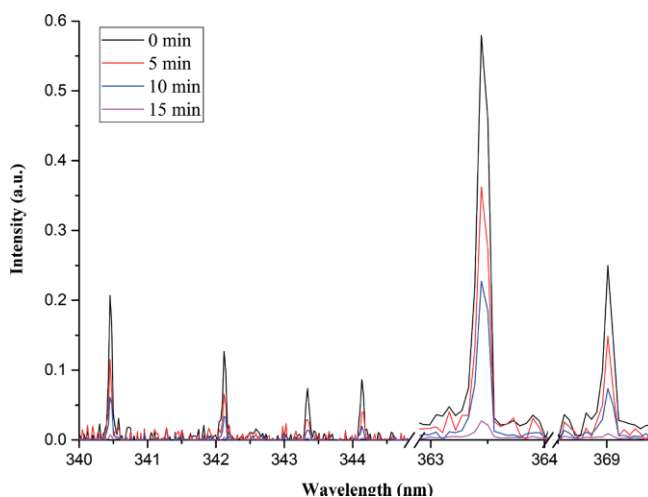


Figure 5. Comparison of Pd strong lines in four times of reaction.

3.2. ICP Analysis

The result of Pd concentrations in each of the four analyzed catalyst samples using ICP-MS are given in Table 2. The

analysis has shown that Pd concentrations were decreased by moving from sample 0 to 15 min, respectively. Comparison of the extent of Pd concentrations accumulation in the analyzed catalyst samples with ICP and LIBS analysis showed that both methods displayed a decreasing trend in the amount of Pd according to deactivation of Pd/C catalyst.

Table 2. ICP analysis of Pd concentration in four catalyst samples.

Sample	%Pd concentration
0 min	9.2
5 min	8.8
10 min	7
15 min	3.7

3.3. Change in Surface Morphology (FESEM-EDS Analysis)

The FESEM-EDS was employed to gain more insights into the deactivation of catalyst samples. It characterizes the catalyst surface before and after the catalytic transfer hydrogenation reaction. FESEM-EDS images for fresh and spent catalysts are shown in Figure 6. As shown in Figure 6a, b, c, and d for fresh catalyst (0 min) and spent catalysts after 5, 10, and 15 min, respectively, palladium particles are uniformly deposited on the surface of the activated carbon in the fresh catalyst. The palladium particles aggregate and form large particles by passing time. The size of the aggregations and the surface morphology of these catalyst samples were changed evidently before and after their use in reaction.

As shown in FESEM-EDS images (Figure 6), the morphology of catalyst surface has been changed by using in reaction. Due to the deactivation of catalyst in hydrogenation reaction, palladium nanoparticles coalesce and make large units. Furthermore, the acidic environment of reaction can leach the palladium particles from the catalyst into the liquid phase. Hence, it can be concluded that the sintering and leaching of palladium particles has a significant effect on the catalyst deactivation.

4 Conclusions

Catalyst deactivation through the chemical reaction is an inevitable process. In order to monitor the change in palladium content in the catalyst and deactivation of the catalyst, the catalytic hydrogenation transfer of cinnamic acid reaction was performed at different time intervals. Deactivation of the catalyst with an increment of reaction time was investigated by LIBS analysis. Due to the advantages of the LIBS method including nondestructive, no need for initial preparation, consumption small amount of sample, and fast detection, it can be used as a capable method to study the deactivation of Pd/C catalyst. The result of LIBS was compared to ICP-MS analysis. Moreover, FESEM-EDS images of catalyst samples were acquired to study the morphology of the surface. These results can be explained that three methods demonstrated the decrease in Pd amount because of Pd leaching and sintering with an increment

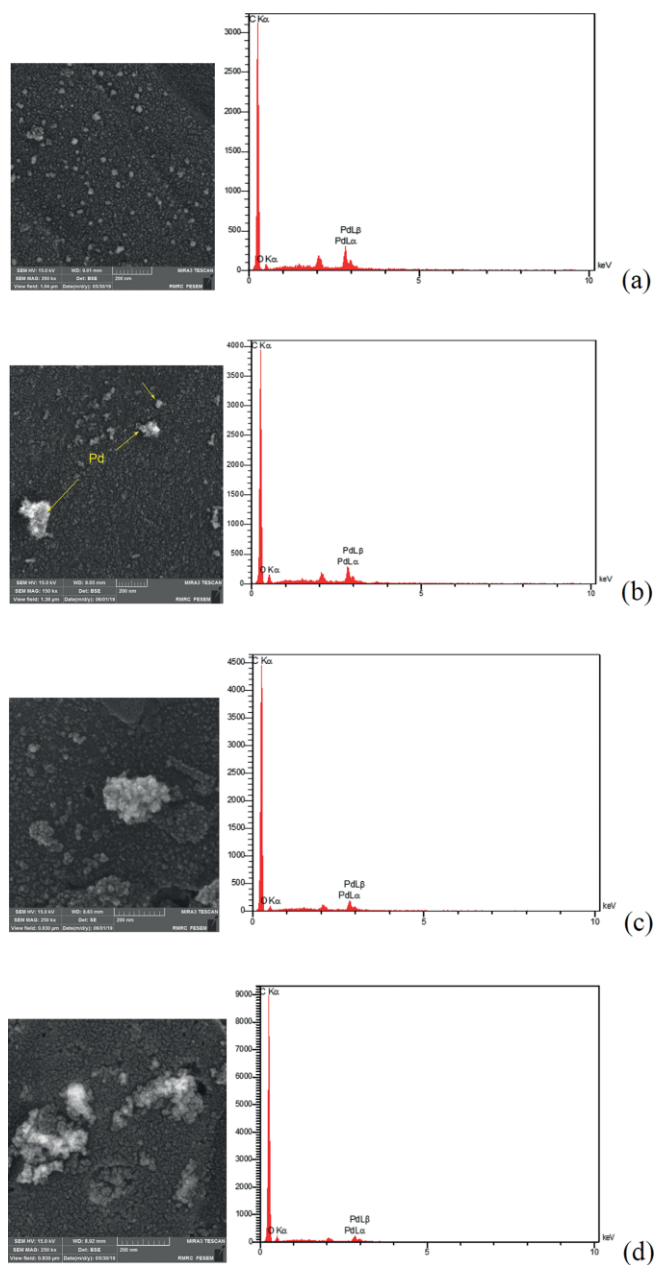


Figure 6. FESEM-EDS images of (a) fresh catalyst (0 min), (b) catalyst after 5 min of reaction, (c) catalyst after 10 min of reaction and (d) spent catalyst after the reaction is over (15 min).

of reaction time. Although the leaching of palladium particles is the main reason for catalyst deactivation, the growing up of palladium particles and forming large units can also cause catalyst deactivation.

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