The Preparation of Palladium –Based Catalyst via Dielectric – Barrier Discharge (DBD) for Total Oxidation of n-butanol and CO at Low Temperature

Huu Thien Pham*, Ky Duyen Vo Nguyen

Institute of Applied Materials Science - VAST, No 1A TL 29, Thanh Loc Ward, District 12, Ho Chi Minh City, Vietnam
thieniams@gmail.com

In the present study, the total oxidation of n-butanol and carbon monoxide (CO) was investigated on 1 wt% Pd/γ-Al$_2$O$_3$ catalysts which were prepared via the dielectric-barrier discharge (DBD) and wet-impregnation (WI) methods. All catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FT-IR), and Brunauer-Emmett-Teller method (BET). The catalytic activities in the total oxidation of VOCs (n-butanol) and CO under gas-phase conditions was measured. The results showed that the palladium catalysts prepared from DBD method exhibited higher activity in total oxidation of n-butanol and CO than catalysts prepared by WI method. This difference is due to better physicochemical properties of catalysts prepared by DBD method. For 1 wt% Pd loading, total oxidation of n-butanol and CO was achieved at 300 °C and 175 °C with the DBD method. Meanwhile, oxidation efficiency of the catalysts prepared by WI method is only approximately 90 % in two cases.

1. Introduction

Air pollution is becoming a serious problem and difficult to reduce. In particular, volatile organic compounds (VOC) and carbon monoxide (CO) are one of the main causes of air pollution and affects human health (Kim and Shim, 2010). So, it is very important to develop methods allowing remove or convert harmful VOC and CO into environmentally friendly products. Nowadays, there are many ways to prevent this pollution, one of which is the total oxidation by catalytic oxidation technique. In this method, the catalyst plays a major role in deciding the treatment efficiency and reaction temperature. Precious metal catalyst (Pd, Pt, Au) on different supports are often used and show high treatment efficiency (Ivanova et al., 2010). In fact, palladium-based catalysts have shown the ability to work at low temperatures of oxidation of VOCs and CO (Brummeret et al., 2015). In previous studies, palladium-based catalysts supported on a variety of supports: Al$_2$O$_3$, SiO$_2$, TiO$_2$ has been studied in pollution treatment and shown good results (Sow et al., 2017). Particularly, Al$_2$O$_3$ is a dominant material because of its low cost, porous structure and relatively high surface area.

Many studies show that Pd catalytic activity for complete oxidation of VOC and CO belongs to the preparation method. For over a decade, the non-thermal plasma technique used in the preparation process has attracted a lot of attention, because of its ability to change the catalysts properties, create nano size particle and evenly dispersed highly on the support (Hua et al., 2010). The catalysts prepared by plasma methods help to limit energy consumption heating and we also have oxidation activity and physicochemical properties different from the wet-impregnation method. Recently, dielectric barrier discharge (DBD) plasma technique has been used in catalyst preparation. For example, Ni/MgO catalyst prepared by dielectric barrier discharge plasma for CO$_2$ reforming (Hua et al.,2010), Au/P25 catalysts to treat CO prepared by the DBD plasma method (Lanbo, 2014),Fe-MOFs prepared by the DBD plasma method for efficient Fenton catalysis (Tao et al., 2019). In all cases, the DBD plasma method clearly shows its superiority with the catalytic activity of the catalysts prepared by this method.

As mentioned above,although the preparation of catalysts indicates the high effective for the different reactions. However, using Pd based catalystsprepared by the DBD plasma method to remove VOC and CO is

unprecedented. So, the aim this work was to study the effects of the preparation methods for the characterization and properties of 1 wt% Pd/Al$_2$O$_3$ catalysts. Catalytic activities of these catalysts were evaluated by the ability to oxidize n-butanol and carbon monoxide in the gas phase under atmospheric pressure.

2. Experimental

2.1 Catalyst preparation

The 1 wt% Pd catalysts were prepared by two different methods: Wet-impregnation (WI) and dielectric-barrier discharge (DBD) plasma.

WI Method: Impregnated salt solution was used as Pd (NH$_4$)$_4$(NO$_3$)$_2$, supplied by Merck. 5g Al$_2$O$_3$ (supplied by Sigma-Aldrich, S$_{BET}$ = 180 m^2/g) was dissolved in 15 mL distilled water containing Pd(NH$_4$)$_4$(NO$_3$)$_2$ before impregnation. The suspension was stirred at 80 °C for 2 h and the solid part is dried at 120 °C and heated in air at 500 °C for 4.5 h. The catalyst sample was denoted by: 1Pd1.

DBD plasma Method: Proceed similarly as above. However, after the drying stage, the catalyst prepared by this method was placed in a central position on the padding in the plasma-design area with a cylindrical-shaped quartz tube with a metal cover (7 mm in diameter and 400 mm in length). The vacuum pump was mounted after the reaction to ensure stable environmental conditions in the plasma projection area. The system is operated with equipment parameters: 18 kV-30 KHz. Working gas (air or argon) is supplied continuously during projection. Catalytic samples were denoted by: Pd1Ar and Pd1Air (with argon, air is the gas used to create the plasma environment). The reaction diagram is shown in the Figure 1.
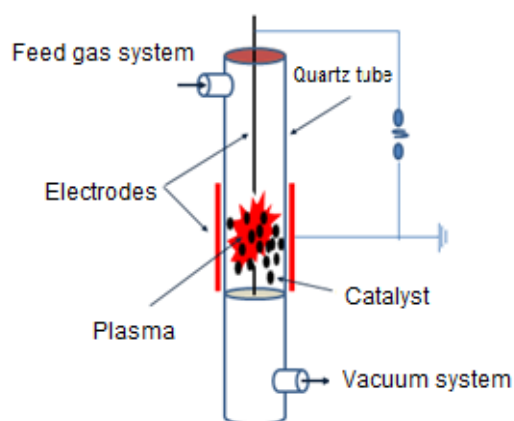

Figure 1: DBD plasma reaction diagram

2.2 Catalyst characterization

The studied catalysts were characterized by modern physicochemical methods as: XRD, FT-IR, and TEM. In particular, the X-ray diffraction (XRD) patterns of the catalyst samples were analyzed by a Bruker D5005 (Japan), scanning angle of 20 - 80 °, scanning step of 0.03 °, scanning speed of 0,7 °/sec. Fourier-transform infrared (FTIR) spectroscopy was calculated at spectral resolution of 4 cm^{-1} between 400 and 4,000 cm^{-1} using a Perkin-Elmer 1600 series spectrometer. The images of transmission electron microscope (TEM) were obtained using a TACHI H-7500 (Japan) at an acceleration voltage of 200 kV.The Brunauer-Emmett-Teller specific surface areas were determined by nitrogen adsorption data obtained at -196 °C (Nova-1000e analyzer, USA).

2.3 Catalytic performance

All chemicals were used as a model compound without further purification. The total oxidation of them was performed with a continuous flow fixed-bed with a temperature range of 50 – 300 °C with a rate of 5 °C/min. The total flow through the catalyst was kept at 6 L/h leading a gas hourly space velocity (GHSV) of about 15,000 h^{-1}. The n-butanol and CO initial concentrations were fixed at 1,000 ppm and 3,000 ppm. The concentration of inlet and outlet gases of n-butanol were analyzed GC clarus device (USA) using HP5-MS. Meanwhile, the CO concentration was analyzed in-situ by TESTO 320 LX (0563 6032 72) and then re-analyzed by a GC clarus device (USA) column packed with ZV-95, length 3 m, diameter 5.8 m.

3. Results and discussion

3.1 Catalyst characterization

Figure 2 shows characteristic peaks of crystalline Pd particles distributed on the γ-Al_2O_3.
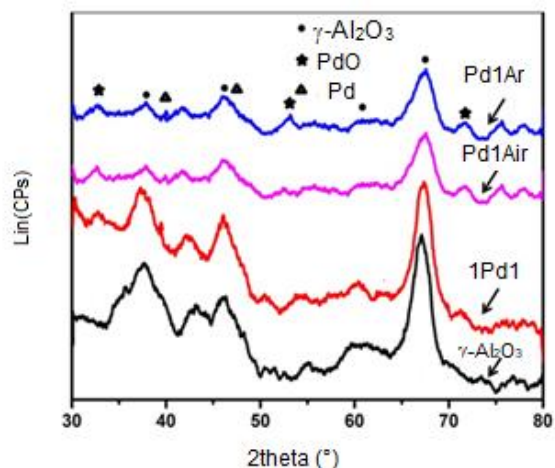

Figure 2: XRD spectra of γ-Al_2O_3, 1Pd1, Pd1 Air and Pd1Ar

The results show that the diffraction lines of PdO crystals at 2θ = 32.9 °, 55 °, 61.2 °, 72.3 ° (PDF 41-1107), Pd metallic crystals at 2θ = 40.2 °, 46.6 ° (PDF 87-0639) and Al_2O_3 at 2θ = 42.1 °, 62.3 °, 66.9 ° (PDF 79-1558).

For sample 1Pd1, the characteristic peaks are still maintained but the peak intensity is reduced. The decrease in intensity may be due to the effect of dispersion of Pd oxides on the support surface. Results of Pd Air and PdAr samples are better with higher peak intensity, narrowing of the peak line, demonstrating the gradually increased crystallization of PdO on the substrate without any doping. In addition, the diffraction lines at 2θ = 40.2 °; 46.8 ° (PDF 87-0639) are characteristic of the metallic Pd phase, and this presence directly affects the activity of the catalyst oxidation (Garcia et al., 2005). Furthermore, in sample Pd1Ar, there is one peak signal at 2θ = 46.8 ° (PDF 87-0639). This is explained by the presence of active reducing agent from ionization argon in plasma treatment process, while in sample Pd1Air only NO acts as a reducing agent. As can be seen in Figure 2, the disappearance of Pd salt peaks demonstrating their complete decomposition on the surface of the material.
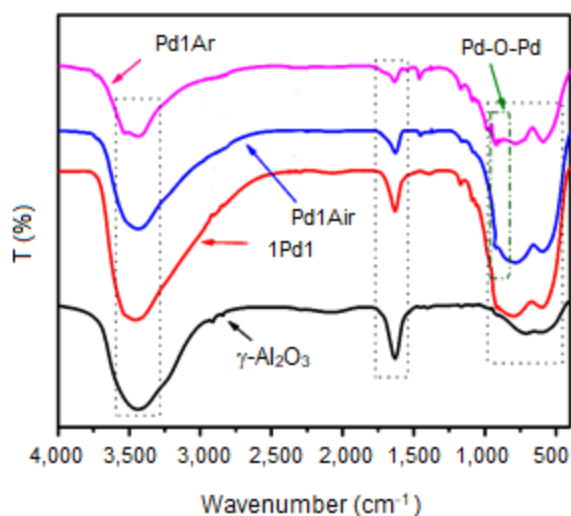

Figure 3: IR spectra of γ-Al_2O_3, 1Pd1, Pd1Air and Pd1A

Figure 3 shows IR spectra of catalysts. The band at 3,365 – 3,450 cm^{-1} và 1,639 cm^{-1} belong to the stretching vibration of O-H group absorbed on the surface or inside of the γ-Al$_2$O$_3$ support structure (Abedini et al., 2012). The band at 610 cm^{-1} can be attributed to the Pd-O vibrations, which suggests that Pd was attached to Al$_2$O$_3$. At 719 cm^{-1} was the Al-O bond represented in the support component. Similarly, in addition to the characteristic peaks, the IR spectra of the Pd1Air and Pd1Ar samples show Pd-O-Pd bond at 792 cm^{-1}. This again confirms the presence of Pd phase in the composition of the material that has been synthesized. This result was completely consistent with the XRD spectrum above.

Complementary data involving the Pd phase dispersion have been shown by TEM analysis of the Pd/γ-Al$_2$O$_3$ catalysts (Figure 4). The Pd phase crystals had a spherical morphology and a crystalline particle diameter of around 5-8 nm with catalytic sample 1Pd1, probably because of high water loadings in the sample which affects particle size. On the other hand, crystalline particles with dimensions of 4-6 nm were widely distributed on the alumina surface for Pd1Air and Pd1Ar catalysts. Furthermore, the results obtained by TEM analysis are in line with XRD, FT-IR results and the previous study (Chen et al., 2004). The results show that the DBD plasma technique intervention for catalytic preparation process will form Pd crystalline particles dispersed well with smaller particle size.
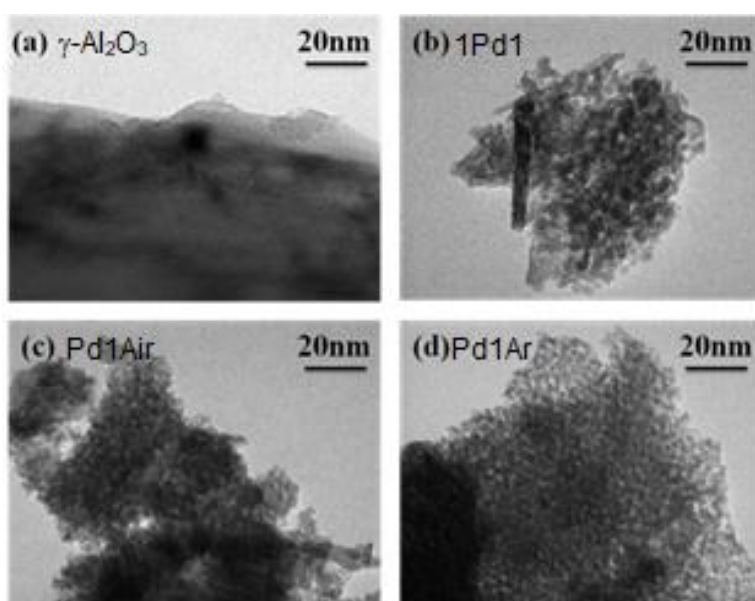

Figure 4: TEM images of (a)γ-Al$_2$O$_3$, (b) 1Pd1, (c) Pd1Air and (d) Pd1Ar

The specific surface area of γ-Al$_2$O$_3$ and three samples of catalyst are shown in Table 1. The synthesis method modifies undoubtedly the specific surface area and as a result, can affect the activity for n-butanol and CO total oxidation.

Table 1: The surface areas of γ-Al$_2$O$_3$ and three samples of catalysts

Sample	BET area (m^{2}g^{-1})
γ-Al$_2$O$_3$	180
1 Pd1	130
Pd1Air	142
Pd1Ar	145

3.2 Catalytic activity for n-butanol and CO oxidation

The conversion of n-butanol on different catalysts were presented in Figure 5. The result from Figure 5 shows that the oxidation reaction of n-butanol without catalysis gives a conversion rate of about 15 % at 300 °C. The Al$_2$O$_3$ catalyst shown the n-butanol conversion reached under 20 % at the same temperature. The Figure 5 also shown that the Pd1Ar was proved to be the most active catalyst for catalytic oxidation of n-butanol (100 % at 300 °C). Besides that, the Pd1Air led to n-butanol conversion of 80-99 % in the reaction temperature range (200 - 300 °C), which was lower 3-6 % than that of Pd1Ar. The lower conversion detected in the Pd1Air

can be considered by the presence of various by-products such as O_3, H_2O_2 and NOx recognized in all the range of the temperature. Some of these species can be adsorbed on the catalytic surface and affect the VOC conversion (Zhang et al., 2016). In the case of Pd1Ar catalyst, the secondary product only includes Ar gas. Subsequently, the results indicated that the activity of the 1Pd1 is lower 10-12 % than that of the Pd1Ar and Pd1Air. These results also are suitable with the TEM images, FTIR spectra and BET surface areas. The following activity was: Pd1Ar>Pd1Air>1Pd1>Al_2O_3>blank.
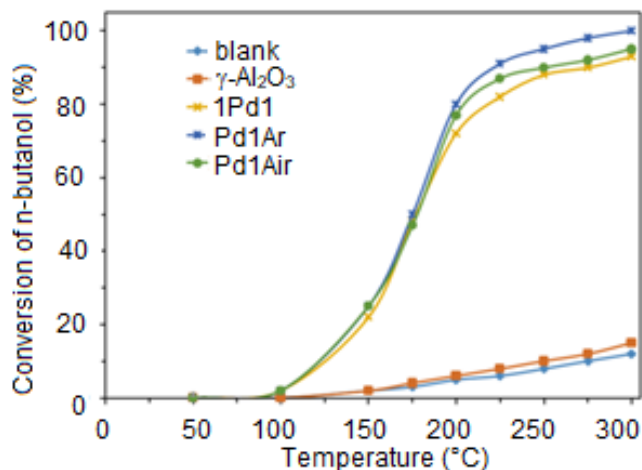

Figure 5: The conversion of n-butanol on different catalysts

Figure 6 presents the CO oxidation activity over different Pd catalysts prepared by different methods. As can be seen, the γ- Al_2O_3 was less active than that of DBD plasma and DP method, which was reached 15% at 200 °C. As a comparison, CO oxidation over Pd1Ar and Pd1Air were more active than that activated by 1Pd1. For the conversion of 100 % have been achieved on Pd1Ar and Pd1Air at 180 °C and 190 °C. Figure 5 clearly shows that the conversion of 1Pd1 is lower 6-12 % than that of two kinds of catalysts prepared by DBD plasma method. Eventually, when the temperature is more than 190 °C, the CO conversion could almost reach 100 % for all these three catalysts. The activity of the samples rank as follows: Pd1Ar> Pd1Air> Pd1> Al_2O_3>blank.
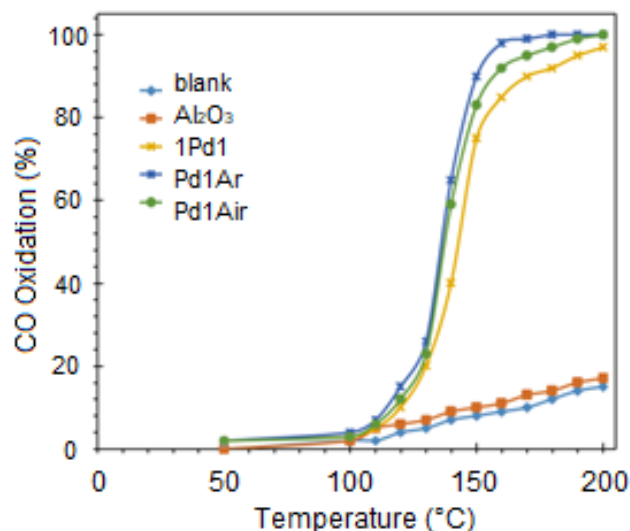

Figure 6: The conversion of CO on different catalysts

4. Conclusion

In this work, 1 wt% Pd/γ-Al$_2$O$_3$ catalysts have been prepared by two different methods: DBD and WI. The characteristic morphology of these catalyst was also determined by XRD, FT-IR and TEM. First of all, the results indicated that with DBD method, the particle size is small and uniformly distributed on the surface of Al$_2$O$_3$. Pd1Ar and Pd1Air catalysts supported on alumina gave better conversion efficiency when compared with catalyst 1Pd1, best with Pd1Ar catalyst. Thus, the plasma technical intervention in the catalytic preparation process brings remarkable processing efficiency. Last, but not least, this result promises to improve catalytic conversion of n-butanol and CO to limit environmental pollution.

Acknowledgments

References

Abedini A., Saion E., Larki F., Zakaria A., Noroozi M., Soltani N.,2012, Room Temperature Radiolytic Synthesized Cu@CuAlO$_2$-Al$_2$O$_3$ Nanoparticles International Journal of Molecular Sciences,13, 11941-11953.

Brummer V., Jecha D., Martinec J., Lestinsky P., Skryja P., Stehlík P., 2015, Impact of catalytic oxidation operating conditions on VOC and CO conversions on the Pt-Pd/Al$_2$O$_3$ catalyst, Chemical Engineering Transactions, 45, 1009-1014.

Chen M. H., Chu. W., Dai X. Y., Zhang X. W., 2004, New palladium catalysts prepared by glow discharge plasma for the selective hydrogenation of acetylene,Catalysis Today, 89, 201–204.

Garcia T., Solsona. B., Murphy D.M., Antcliff K.L.,Taylor S.H., 2005,Deep oxidation of light alkanes over titania-supported palladium/vanadium catalysts, Journal of Catalysis, 229, 1-11.

Hua W.,Jin L., He X., Liu J.,Hua H.,2010,Preparation of Ni/MgO catalyst for CO$_2$ reforming of methane by dielectric-barrierdischarge plasma, Catalysis Communications, 11, 968–972.

Ivanova, A. S., Slavinskaya, E. M., Gulyaev, R. V., Zaikovskii, V. I., Stonkus, O. A., Danilova, I. G.Boronin, A. I.,2010. Metal–support interactions in Pt/Al2O3 and Pd/Al2O3 catalysts for CO oxidation. Applied Catalysis B: Environmental, 97(1-2), 57–71.

Kim, S. C., Shim, W. G., (2010). Catalytic combustion of VOCs over a series of manganese oxide catalysts. Applied Catalysis B: Environmental, 98(3-4), 180–185.

Koo, K. Y., Jung, U. H., Yoon, W. L., (2014). A highly dispersed Pt/γ-Al2O3 catalyst prepared via deposition–precipitation method for preferential CO oxidation. International Journal of Hydrogen Energy, 39(11), 5696–5703.

Lanbo D., 2016, Preparation of Au/P25 catalysts for removal of CO by dielectric barrier discharge plasma, Advanced Material Research, 989, 344 – 347.

Li, Z., 2004, Plasma treatment of Ni catalyst via a corona discharge. Journal of Molecular Catalysis A: Chemical, 211(1-2), 149–153.

Sow Lock I.M., Sow Lock S.M., Dai-Viet V.N., Abdullah B., 2017, Influence of palladium on ni-based catalysts for hydrogen production via thermo-catalytic methane decomposition, Chemical Engineering Transactions, 57, 343-348.

Xumei T., Chao S., Liang H., Yuanyuan H., Dongyan X., 2019, Fe-MOFs prepared with the DBD plasma method for efficient Fenton catalysis, Royal Society of Chemistry, 9, 6379 – 6386.

Zhang Z.X., Wenfeng S., 2016, Low-temperature catalysis for VOCs removal in technology and application: a state-of-the-art review, Catalysis Today, 264, 270-278.