Palladium Supported on Mesoporous Alumina Catalyst for Selective Hydrogenation

Agrahari SK*, Lande S, Balachandran V, Kalpana G and Jasra RV

Reliance Technology Group, Reliance Industries Limited, Mumbai, Maharashtra, India

*Corresponding author: Sunil Kumar Agrahari, Reliance Technology Group, Reliance Industries Limited, Mumbai 400701, Maharashtra, India, Tel.: +91 7718859228; E-mail: sunil.agrahari@ril.com

Received date: October 3, 2017; Accepted date: October 14, 2017; Published date: October 22, 2017

Abstract

Colloidal metal nanoparticles are of great interest because of their use as catalysts, photocatalyst, adsorbent and sensors and their application in optical, electronic and magnetic devices. Capping agents are widely used in the synthesis of colloidal nano crystals for stabilizing the nanoparticles. The well dispersed Palladium nanoparticles (PdNP) supported on mesoporous γ-Al2O3 were prepared by using capping agents namely PVA, PVP, PEG and MEG using tetrahydrofuran as solvent. The catalytic properties of Pd-nanoparticle on mesoporous γ-Al2O3 were studied for hydrogenation model reaction.

The alumina supported palladium nanoparticles were characterized by using instrumental techniques namely BET surface area, HR-TEM and XRD. HR-TEM studies shows that the average particle size of Pd metal in the fresh and spent catalyst was in the range from 5 to 10 nm. The catalyst could be efficiently recycled for three times without losing catalytic activity and selectivity.

Keywords: Nanoparticles; Mesoporous alumina; Hydrogenation; Nitroaromatics

Introduction

Supported Pd nanoparticles constitute the active phase in catalysts used for energy conversion, chemical synthesis and pollution abatement. To achieve the higher selectivity and reactivity, it is desirable to have well-dispersed nanoparticles (NPs) that have similar properties and distribution of active sites [1]. Size and shape-controlled metal particles offer incentives for their wider applications as catalyst in many chemical processes [2]. It is well understood that the properties of metal nanoparticles for these applications are size and shape dependent [3]. Further, in catalysis, control of the particle size and their growth kinetics show a direct relation between the catalytic activity and the particle morphology. New synthetic approaches for size and shape-controlled nanoparticles synthesis using different ligands or capping agents are regularly investigated. Therefore, there has been considerable interest in developing colloidal routes to synthesize well-defined nanoparticles that could be used to prepare heterogeneous catalysts [4-6]. Typically, solution routes require various reducing agents such as hydrazine [7], alkalineborohydrides [8], or amine groups [9] where the particles are protected by polymer groups, surfactants or ligands to prevent agglomeration and growth [3].

Catalytic hydrogenation of aromatic nitro compounds is an industrially important process for the introduction of amino functionality into pharmaceutical and agrochemical intermediates and in the polyurethane chemistry. Aromatic nitro compounds are hydrogenated easily and hydrogenations have been carried out under a wide range of conditions including the vapor phase [10,11]. Amine production via nitroarene hydrogenation has been promoted using a range of carbon [12-14], Al2O3 [15-18], SiO2 [19], TiO2 [20], CeO2 [21], Fe3O4 [22], SnO2 [23] and CeO2 [24] supported metal Pd [25], Pt [26] and Ru [27] catalysts.

Cardenas-Lizana et al. [19] demonstrated exclusive -NO2 reduction (but at low reaction rate) in the continuous gas phase hydrogenation of substituted nitroarenes over supported Au. The role of Pd as promoter to increase activity, selective p-chloroaniline (p-CAN) production was achieved for Au/Pd ≥ 2 [18]. Increasing the Pd content delivered higher rates but with the formation of nitrobenzene (NB). This is consistent with the literature on liquid [15] phase operation that has been demonstrated nonselective CNB hydrogenation over supported Pd, generating aniline (AN) [16], NB and azo compounds as byproducts.

Al2O3 with very attractive surface and structural properties is a material of choice for the range of applications such as catalysts, catalytic supports, adsorbents, hard protective coatings, abrasives, or membrane [28]. Alumina has been extensively used as catalyst support due to high thermal stability, high purity, favorable bulk density and low price.

The present work deals with the well dispersed palladium nano particles prepared [29] and impregnated on high surface area mesoporous alumina with controlled calcination to get uniform particle size and distribution. The palladium supported catalysts were well characterized by different techniques such as BET surface area, XRD, NMR and HR-TEM. The prepared catalysts for activity and stability were tested for hydrogenation of nitrobenzene to aniline under mild conditions as model reaction. The catalysts were also tested for their activity and selectivity for the hydrogenation of other substituted nitro aromatics.

Scheme 1

The catalyst activity was studied for liquid phase hydrogenation of p-nitrotoluene and other substituted nitroaromatics group with room
temperature at atmospheric pressure. High activity and selectivity was seen with a turn over number $1.7 \times 10^3 \text{ h}^{-1}$ under a hydrogen atmosphere in THF at room temperature. Furthermore, the catalyst could be easily recovered from reaction mixture and recycled three times without any significant loss in activity.

Materials and Chemicals

All chemicals and solvents used in this study were commercially available and used without further purification. Analytical grades Nitrobenzene, 2-nitro toluene, o-nitro anisole, p-nitro acetophenone, 4-nitro toluene, Tetrahydrofuran, Polyvinyl alcohol MW 31000, Polyvinyl pyrrolidone (MW 360,000, Polyethylene glycol (PEG) MW 20000, Ethylene glycol, Palladium (II) nitrate hydrate and Gamma alumina ($\gamma$-Al$_2$O$_3$) was prepared by reported method [30]. Silica (SiO$_2$), Zeolite and Clay.

Preparation of Pd grafted on mesoporous $\gamma$-Al$_2$O$_3$

0.108 g of Palladium (II) Nitrate was dissolved in 50 ml tetrahydrofuran (THF). The reaction mixture was stirred for 60 min at 85°C till complete dissolution. To the above mixture, mesoporous alumina powder (Al$_2$O$_3$) was added slowly in hot condition with stirring for 2 h.

Excess THF solvent was evaporated on water bath. The material was dried at 120°C followed by calcination at 550°C for 4 h in presence of air.

The Pd supported on alumina catalysts were also prepared by heat treatment method by mixing various capping agents (0.5 wt%) like PEG, PVA, PVP and EG with palladium nitrate and adopting remaining procedure as mentioned above.

Hydrogenation experimental procedure and analysis

The liquid phase hydrogenation of nitrobenzene was carried out in a 250 ml two necked round bottom flask attached to water condenser along with septum.

The catalysts were activated at 350°C in air for 2 h and cooled at room temperature prior to their use in the reaction. The reaction mixture was stirred at room temperature under hydrogen gas atmosphere.

In a typical reaction mixture consisted of 2.06 g of p-nitro toluene and 25 ml of THF with a catalyst loading of 0.5 wt%. The initial/zero time interval samples were withdrawn and catalyst was added thereafter.

Samples were withdrawn at regular intervals and analyzed periodically on a gas chromatograph (Thermo GC Trace 1310) equipped with a FID detector and TG-5MS as a capillary column.

Catalyst characterization

Following Equipment were used for catalyst characterization:

- X-ray powder diffractometer (Bruker, Model no., Advance D8) for structural analysis of alumina support.
- Specific surface area and pore volume of alumina samples were measured using ASAP 2020 (Micromeritics, USA). Inductively coupled plasma optical emission spectrometer (ICP-OES), make Perkin Elmer USA Model OPTIMA 4300 DV for chemical composition analysis.
- NMR analysis on 400 MHz AVANCE III HD, make BRUKER for determining tetrahedral and octahedral alumina phases.
- HR-TEM done with a TITAN 60-300, make FEI USA for meal particle size determination.

Surface area and pore volume

The physico-chemical properties of the catalysts are presented in the Table 1. The pure gamma alumina surface area was 248 m$^2$/g and pore volume 0.53 cc/g with pore size 68 Å.

The surface areas of palladium supported catalysts is in the range of 212 to 235 m$^2$/g and the pore volume in the range of 0.51 to 0.53 cc/g (Table 1). After loading of Pd metal, there is decrease in surface area and pore volume.

| Catalyst | Parameters | BET SA (m$^2$/g) | Pore Volume, N$_2$ (cc/g) |
|----------|------------|------------------|--------------------------|
| A        | Mesoporous $\gamma$-Al$_2$O$_3$ | 248              | 0.53                     |
| B        | PdNP (0.5%)/Al$_2$O$_3$ | 235              | 0.52                     |
| C        | PdNP (0.5% PVA)/Al$_2$O$_3$ | 212              | 0.53                     |
| D        | PdNP (0.5% PVP)/Al$_2$O$_3$ | 220              | 0.52                     |
| E        | PdNP (0.5% PEG)/Al$_2$O$_3$ | 220              | 0.53                     |
| F        | PdNP (0.5% EG)/Al$_2$O$_3$ | 222              | 0.52                     |
| G        | PdNP (0.1%)/Al$_2$O$_3$ | 223              | 0.51                     |
| H        | PdNP (0.25%)/Al$_2$O$_3$ | 215              | 0.51                     |
| I        | PdNP (1.0%)/Al$_2$O$_3$ | 230              | 0.52                     |

Table 1: BET surface area and pore volume of various prepared catalyst.

Powder X-ray diffraction

The representative powder XRD analysis shows that, the $\gamma$-Al$_2$O$_3$ have four characteristic peaks at 2θ = 37.4, 45.9, 66.8 which is in agreement with the standard for $\gamma$-Al$_2$O$_3$ (JCPDS no. 29-1486) as shown in Figure 1.

However, several other meta-stable aluminum oxides, known as transition alumina (such as $\kappa$, $\gamma$, $\delta$, $\eta$ and $\theta$) show similar XRD traces, which make phase identification more difficult.

The (400) and (440) peaks have a stronger intensity than the other peaks, indicating presence of gamma alumina phase.
It is also observed that PdNP does not show any significant diffraction peaks may be due to lower quantity of Pd metal supported on Al2O3.

High resolution transmission electron microscopy (HR-TEM)

Figures 2a and 2b shows representative the HAADF-STEM images of the fresh catalyst B (Pd supported on alumina without any capping agents) and spent catalysts after reaction.

The STEM images were taken before and after the reaction to see the changes in the Pd particle size along with HAADF images for both the samples.

The fresh catalyst showed Pd particles of size 10-25 nm whereas in the spent catalyst, the Pd particles were 20-25 nm in addition to few agglomerated regions of ~40 nm. The agglomeration may be due to the attrition post 3 cycles of reaction. (Figures 2a and 2b).

Figure 2c show the HRTEM images of the fresh catalyst. The images clearly show the porous nature of the γ-alumina matrix and the Pd particles are located predominantly inside the pores as well as outside the pores.

NMR analysis

The 27Al MAS NMR spectra of mesoporous γ-Al2O3 and PdNP(0.5%)/γ-Al2O3 catalyst are shown in Figure 3.

It is observed that the two signals at 7.45 and 65.47 ppm for mesoporous γ-Al2O3 and 7.06 and 64.96 ppm for PdNP(0.5%)/Al2O3 catalyst were identified, which can be related to the octahedrally co-

Catalytic activity

The prepared catalysts namely A, B, C, D, E, F and G mentioned above were used for hydrogenation of different substituted nitro aromatic viz., nitrobenzene, o-nitrotoluene, o-nitro anisole, p-nitrotoluene and p-nitro acetophenone to get respective aniline and also various process parameters were studied.

Effect of capping agents

Pd supported catalysts, PdNP(0.5% PVA)/Al2O3 (C), PdNP(0.5% PVP)/Al2O3 (D), PdNP(0.5% PEG)/Al2O3 (E) and PdNP(0.5% EG)/Al2O3 (F) were synthesized using various capping agents.

The concentration of capping agent was maintained as 0.5 wt% in all samples.

The catalytic evaluation of these catalysts was performed for liquid phase hydrogenation of nitrobenzene to aniline.

Similar reaction was also carried out using pure mesoporous gamma alumina powder, but no conversion was seen.

It is observed that catalyst B showed better hydrogenation activity for nitrobenzene to aniline. (Conversion in 3 h at RT and atmospheric pressure) compared to other catalysts as shown in Table 2.

Lower activity for PdNP supported on mesoporous γ-Al2O3 prepared by various capping agents may be due to lower dispersion.

This may result into less number of active site of Pd available on mesoporous γ-Al2O3 support with capping agent.
Table 2: Effect of different capping agents.

|       | 1    | 2    | 3    | 4    | 5    |
|-------|------|------|------|------|------|
| A     | -    | -    | -    | -    | -    |
| B     | 41.61| 94.72| 100  | -    | -    |
| C     | -    | 0.52 | 3.27 | 4.59 | 6.81 |
| D     | -    | 1.3  | 6.58 | 10.11| 13.68|
| E     | -    | 3    | 4.55 | 8.55 | 16.33|
| F     | -    | 7.66 | 10.96| 17.6 | 24.86|

Reaction conditions- 0.3 g catalyst, 1.5 mmol nitrobenzene, 50 ml THF, H₂ 1 atm at RT

Figure 4: Different wt% of Pd loading on γ-Al₂O₃. Note: Reaction conditions- 0.3 g catalyst, 1.5 mmol nitrobenzene, 50 ml THF, H₂ 1 atm at RT

Effect of Pd loading

The Pd content on mesoporous gamma alumina support was varied from 0.1 to 1.0% to study the effect of Pd loading on the rate of reaction. As the Pd loading increases from 0.1% to 0.5% conversion increases from 11% to 100%.

As the Pd content increases beyond 0.5% there is decrease in the conversion. This decrease could be due to bigger particle size of Pd metal with higher loading and also lower metal dispersion. Therefore, all further experiments were carried out using 0.5% Pd supported catalyst as shown in Figure 4.

Effect of different catalyst support

In order to compare the effect of supports on rate of the reaction, various catalyst supports such as SiO₂, Zeolite and Clay were evaluated for liquid phase hydrogenation of nitrobenzene to aniline.

It is observed that PdNP/SiO₂ and PdNP/Zeolite showed 15 and 17% conversion respectively in 5 hour at RT with respect to 100% conversion in 3 hour in case of Pd-NP on mesoporous γ-Al₂O₃ support. PdNP/clay catalyst does not show significant conversion as shown in Figure 5. This is may be due to lower metal dispersion of Pd on other mentioned supports.

Hydrogenation of different nitroaromatics

Catalyst B showed excellent activity for nitrobenzene hydrogenation. So we have extended this study for hydrogenation using other substituted nitro aromatics such as o, and p-nitro toluene, o-nitro anisole, and p-nitro acetoephone under identical reaction conditions. The hydrogenation activity for various nitro aromatics is shown in Table 2. It is observed that the initial rate of the reaction, i.e., 1 hour for hydrogenation of o, p-nitro toluene and p-nitro anisole are comparatively lower than that of nitro benzene. But in case of p-nitro acetoephone, the rate of reaction was very slow and the reaction started only after ~2 hour. Similar type of observation are also reported [33,34].

Turn over number (TON) and Turn over frequency (TOF)

The palladium nanoparticles supported on alumina catalysts showed excellent activity compared to other studied supports for hydrogenation of nitrobenzene. The catalytic activity values of various nitro substituted aromatic compound over nitro aromatic have been compared in terms of TOF at different time interval with identical reaction parameters at room temperature. The TON and TOF calculated for B catalyst is mentioned in Table 3. It is observed that nitrobenzene shows higher TON and TOF compared to other substrate studied in this report [33,34].

Table 3: % conversion of different nitroaromatics. Note: Reaction conditions-0.3 g catalyst, 1.5 mmol reactant, 50 ml THF, H₂ 1 atm at RT.
capping agent showed good catalytic activity for hydrogenation of nitro benzene and other substituted nitro aromatics. Finally, the catalyst could be recovered in a facile manner from reaction mixture and recycled three times without any significant loss in activity and stability.

This approach could be used for the development of selective hydrogenation catalysts (Acetylene, MAPD and C4 hydrogenation streams) which are used mainly for the purification of steam-cracker streams although they are also employed to treat FCC effluents.

Acknowledgement

Authors wish to acknowledge technical support rendered by Ms. Rashmi Dave in XRD analysis, Ms. Sangita Rathod for textural Analysis and Dr. Rudra for NMR analysis. Finally authors are grateful to Reliance R and D management for providing the facilities and infrastructure and encouragements for carrying out this study.

References

1. Park J, Aliaga C, Renzas J, Lee H, Somorjai G (2009) The Role of Organic Capping Layers of Platinum Nanoparticles in Catalytic Activity of Co-oxidation. Catal Lett 129: 1-6.
2. Harada T, Ikeda S, Miyazaki M, Sakata T, Mori H, et al. (2007) A Simple Method for Preparing Highly Active Palladium Catalysts Loaded On Various Carbon Supports For Liquid-Phase Oxidation And Hydrogenation Reactions. J Mol Catal A: Chem 268: 59-64.
3. Rodriguez A, Amiens C, Chaudret B, Casanove MJ, Lecante P, et al. (1996) Synthesis and Isolation of Cuboctahedral and Icosahedral Platinum Nanoparticles. Ligand-Dependent Structures. Chem Mater 8: 1978-86.
4. Hirai H (1979) Formation and Catalytic Functionality of Synthetic Polymer-Noble Metal Colloid. J Macromol Sci Part A Pure Appl Chem 13: 633-49.
5. Esumi K, Itakura T, Torigoe K (1994) Preparation Of Organo Palladium Solis from Palladium Complexes in Various Alcohols. Colloids Surf A 82: 111-3.
6. Bradley JS, Hill EW, Klein C, Chaudret B, Duteil A (1993) Synthesis of Monodispersed Bimetallic Palladium-Copper Nanoscale Colloids. Chem Mater 5: 254-6.
7. Underhill RS, Liu G (2000) Preparation and Performance of Pd Particles Encapsulated on Block Copolymer Nanospheres as A Hydrogenation Catalyst. Chem Mater 12: 3633-64.
8. Brust M, Walker M, Bethell D, Schiffrin DJ, Whyman R (1994) Synthesis of Thiol-Derivatised Gold Nanoparticles in a Two-Phase Liquid-Liquid System. J Chem Soc Chem Comm 7: 801-2.
9. Compton OC, Osterloh FE (2007) Evolution of Size and Shape in the Colloidal Crystallization of Gold Nanoparticles. J Am Chem Soc 129: 7793-8.
10. Vogt PF, Gerulis JJ, Ullmans (1985) Encyclopaedia of Industrial Chemistry (5th edn.). Verlag Chemie,Weinheim.
11. Baumeister P, Studer N, Roessler F (1999) Handbook of Heterogeneous Catalysis.
12. Saif BN, Grange P, Verhasselt P, Addoun F, Dubois V (2005) Effect of Oxidant Treatment of Date Pit Active Carbons used as Pd supports in Catalytic Hydrogenation of Nitrobenzene. Appl Catal A 286: 167-74.
13. Kratký V, Králik M, Mecarova M, Stolcova M, Zalbera L, et al. (2002) Effect of Catalyst and Substituents on the Hydrogenation of Chloronitrobenzenes. Appl Catal A 235: 225-31.
14. Neri G, Musolino MG, Milone C, Pietropaolo D, Galvagno S (2001) Particle Size Effect in the Catalytic Hydrogenation of 2,4-Dinitrotoluene over Pd/C Catalysts. Appl Catal A 208: 307-16.
15. Vishwanathan V, Jayasri V, Basha PM (2007) Vapor Phase Hydrogenation of o-Chloronitrobenzene (o-CN) over Alumina supported Palladium Catalyst — A Kinetic Study. React Kinet Catal Lett 91: 291-98.

16. Xu Q, Liu XM, Chen JR, Li RX, Li XJ (2006) Modification Mechanism of Sn⁴⁺ for Hydrogenation of p-Chloronitrobenzene over PVP-Pd/γ-Al₂O₃. J Mol Catal A: Chem 260: 299-305.

17. Meng X, Cheng H, Akiyama Y, Hao Y, Qiao W, et al. (2009) Selective Hydrogenation of Nitrobenzene to Aniline in Dense Phase Carbon dioxide over Ni/γ-Al₂O₃: Significance of molecular interactions. J Catal 264: 1-10.

18. Cárdenas LF, Gómez-Quero S, Hugon A, Delannoy L, Louis C, et al. (2009) Pd-promoted Selective Gas Phase Hydrogenation of p-Chloronitrobenzene over Alumina supported Au. J Catal 262: 235-43.

19. Cárdenas-Lizana F, Gómez-Quero S, Keane MA (2008) Clean Production of Chloroanilines by Selective Gas Phase Hydrogenation over Supported Ni Catalysts. Appl Catal A 334: 199-206.

20. Meng XC, Cheng HY, Fujita SI, Hao YF, Shang YL, et al. (2010) Selective Hydrogenation of Chloronitrobenzene to Chloroaniline in Supercritical Carbon dioxide over Ni/γ-Al₂O₃: Significance of molecular interactions. J Catal 269: 131-39.

21. Cárdenas-Lizana F, Gómez-Quero S, Perret N, Keane MA (2011) Gold Catalysis at the Gas-Solid Interface: Role of the Support in Determining Activity and Selectivity in the Hydrogenation of m-Dinitrobenzene. Catal Sci Technol 1: 652-61.

22. Zhang J, Wang Y, Ji H, Wei Y, Wu N, et al. (2005) Magnetic Nanocomposite Catalysts with High Activity and Selectivity for Selective Hydrogenation of Ortho-Chloronitrobenzene. J Catal 229: 114-18.

23. Zuo B, Wang Y, Wang Q, Zhang J, Wu N, et al. (2004) An Efficient Ruthenium Catalyst for Selective Hydrogenation of o-Chloronitrobenzene prepared via Assembling Ruthenium and Tin Oxide Nanoparticles. J Catal 222: 493-98.

24. Cárdenas-Lizana F, Gómez-Quero S, Perret N, Keane MA (2009) Support Effects in the Selective Gas Phase Hydrogenation of p-Chloronitrobenzene over Gold. Bull Geol 42: 124-32.