

Palladium Supported on Mesoporous Alumina Catalyst for Selective Hydrogenation

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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], Fe₂O₃ [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 \geq 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.

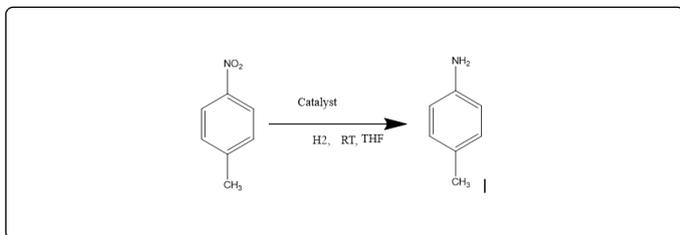
Al₂O₃ with very attractive surface and structural properties is a material of choice for the range of applications such as catalysts, catalytic supports, adsorbents, hard protective coatings, abrasives, or membrane [28]. Alumina has been extensively used as catalyst support due to high thermal stability, 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, Poly vinyl pyrrolidone (MW 360,000, Polyethylene glycol (PEG) MW 20000, Ethylene glycol, Palladium (II) nitrate hydrate and Gamma alumina ($\gamma\text{-Al}_2\text{O}_3$) was prepared by reported method [30]. Silica (SiO_2), Zeolite and Clay.

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

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_2O_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 $248 \text{ m}^2/\text{g}$ and pore volume 0.53 cc/g with pore size 68 \AA .

The surface areas of palladium supported catalysts is in the range of 212 to $235 \text{ m}^2/\text{g}$ 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 $\gamma\text{-Al}_2\text{O}_3$	248	0.53
B	PdNP(0.5%)/ Al_2O_3	235	0.52
C	PdNP (0.5% PVA) / Al_2O_3	212	0.53
D	PdNP (0.5% PVP)/ Al_2O_3	220	0.52
E	PdNP(0.5% PEG)/ Al_2O_3	220	0.53
F	PdNP(0.5% EG)/ Al_2O_3	222	0.52
G	PdNP (0.1%)/ Al_2O_3	223	0.51
H	PdNP (0.25%)/ Al_2O_3	215	0.51
I	PdNP (1.0%)/ Al_2O_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 $\gamma\text{-Al}_2\text{O}_3$ have four characteristic peaks at $2\theta \approx 37.4, 45.9, 66.8$ which is in agreement with the standard for $\gamma\text{-Al}_2\text{O}_3$ (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 θ) 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.

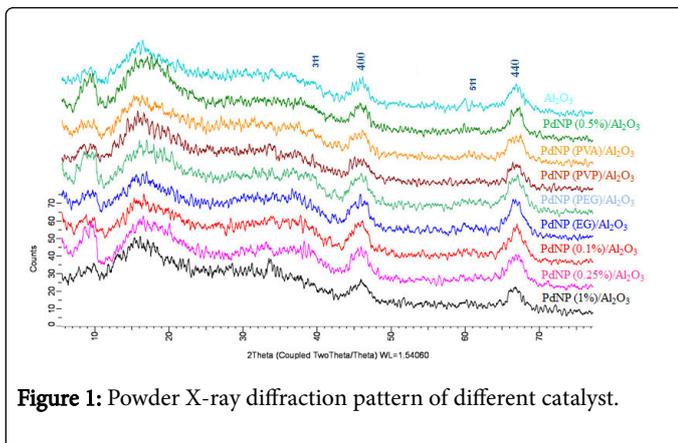


Figure 1: Powder X-ray diffraction pattern of different catalyst.

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.

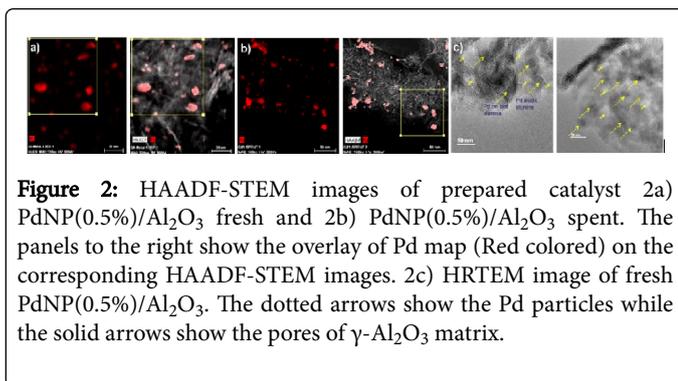


Figure 2: HAADF-STEM images of prepared catalyst 2a) PdNP(0.5%)/Al₂O₃ fresh and 2b) PdNP(0.5%)/Al₂O₃ spent. The panels to the right show the overlay of Pd map (Red colored) on the corresponding HAADF-STEM images. 2c) HRTEM image of fresh PdNP(0.5%)/Al₂O₃. The dotted arrows show the Pd particles while the solid arrows show the pores of γ -Al₂O₃ matrix.

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 65.47ppm 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-

ordinated AlO₆ and the tetrahedrally coordinated AlO₄ sites in the alumina matrix respectively.

Penta-coordinated alumina often associated to the presence of amorphous alumina phase is absent.

The ratio of tetrahedral to octahedral Al is about 1:3, which is characteristic of γ -Al₂O₃ phase [31,32]. The relative intensities of tetrahedral and octahedral components are 23 and 77% [31].

From NMR studies, it is observed that there is no major change in chemical shift of alumina co-ordination sites after impregnation of active Pd metal prepared catalyst may be due to lower Pd loading as shown in Figure 3.

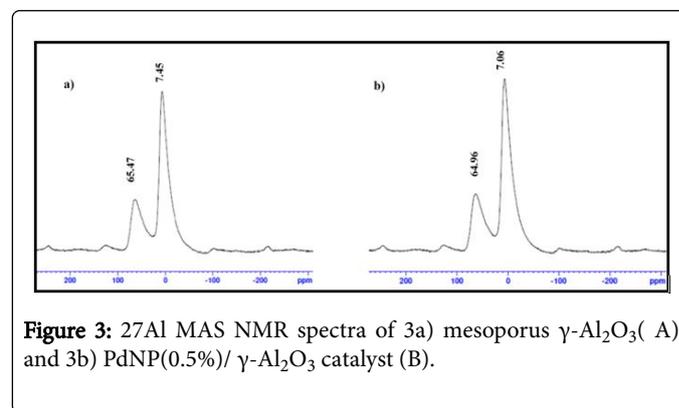


Figure 3: ²⁷Al MAS NMR spectra of 3a) mesoporous γ -Al₂O₃ (A) and 3b) PdNP(0.5%)/ γ -Al₂O₃ catalyst (B).

Results and Discussion

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.

Catalyst	% Conversion
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	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

Table 2: Effect of different capping agents.

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.

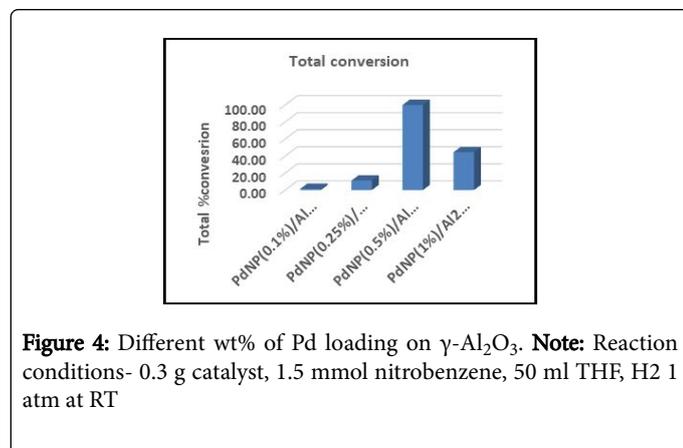


Figure 4: Different wt% of Pd loading on γ -Al₂O₃. **Note:** Reaction conditions- 0.3 g catalyst, 1.5 mmol nitrobenzene, 50 ml THF, H₂ 1 atm at RT

Effect of 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.

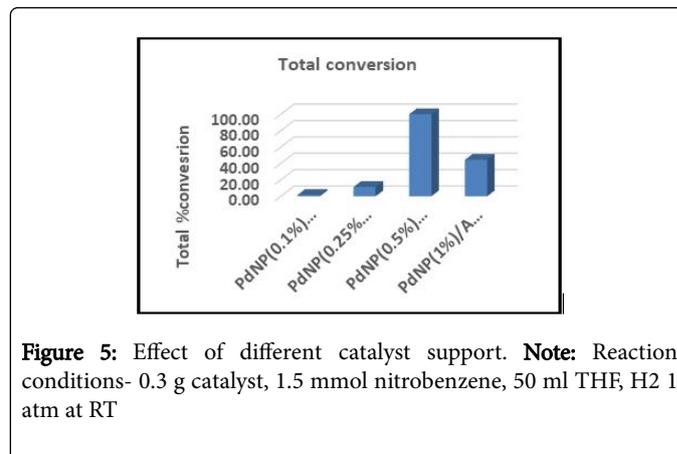


Figure 5: Effect of different catalyst support. **Note:** Reaction conditions- 0.3 g catalyst, 1.5 mmol nitrobenzene, 50 ml THF, H₂ 1 atm at RT

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 acetophenone 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 acetophenone, 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 4).

PdNP (0.5%)/Al ₂ O ₃	% Conversion				
	1	2	3	4	5
Time (hrs)					
Nitrobenzene	42	95	100	-	-
o-nitrotoluene	21	49	75	96	100
o-nitroanisole	15	35	91	100	-
p-nitrotoluene	16	35	43	62	77
p-nitro acetophenone	-	-	38	54	70

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.

Substrate	Palladium Wt%	TON	TOF (Time-1)	Time for reaction (min)
Nitrobenzene	0.5	1.75×10^3	9.71	180
2-nitrotoluene	0.5	1.73×10^3	5.79	300
o-nitro anisole	0.5	1.74×10^3	7.28	240
p-nitro toluene	0.5	1.73×10^3	5.79	300
p-nitro acetophenone	0.5	1.23×10^3	4.12	300

Table 4: TON and TOF data.

This is defined as the number of molecules of nitrobenzene converted per Pd atom per hour. It is calculated as equation 1 and 2.

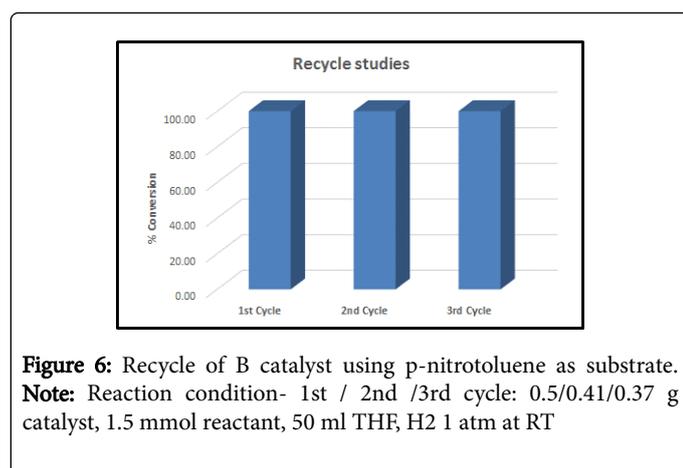
$$\text{TON} = \frac{\text{Moles of Aniline formed}}{\text{Number of surface Pd sites}} \quad (1)$$

$$\text{TOF} = \frac{\text{TON}}{\text{Time of reaction}} \quad (2)$$

It is observed that nitrobenzene to aniline shows higher TON and TOF compared to other substrates studied as mentioned earlier on B catalyst.

Catalyst recyclability studies

The regeneration and recyclability of catalyst B were investigated by recycling the catalytic reaction for three times. After completion of the reaction, the catalyst was filtered for next reaction cycle followed by drying and calcination at 520°C. This step was carried out to burn off any adsorbed molecules and coke deposits. For each cycle, the nitrobenzene to aniline conversion was 100% within three hours run time. Therefore, the B catalyst is a promising catalyst with good reusability as shown in Figure 6.



Conclusion

Palladium nanoparticles prepared by using PVA, PVP, EG and PEG as capping agent were grafted on mesoporous alumina. The prepared catalysts were well characterized by XRD, HR-TEM, NMR and BET surface area. The HR-TEM studies shows that Pd metal is uniformly dispersed on mesoporous γ -Al₂O₃ with average particle size of 5 to 10 nm. The Pd supported on alumina catalyst prepared without any

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.

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