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Graphical abstract

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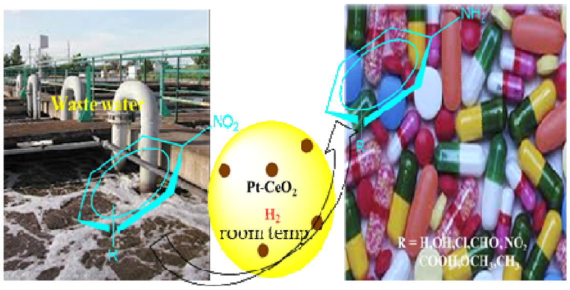


Nanocryatalline Pt-CeO_2 as an efficient catalyst for room temperature selective reduction of nitroarenes

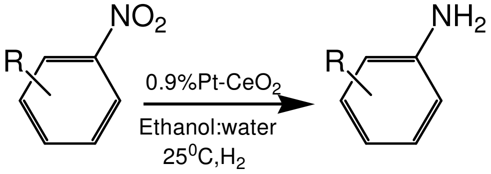
Astha Shukla,[a] Rajib Kumar Singha,[a] Takehiko Sasaki,[b] Rajaram Bal*[a]

We have developed a new synthesis strategy to prepare Pt nanoparticles with size between 2-5 nm supported on CeO_2 nanoparticle with size between 30-60 nm by hydrothermal method in presence of surfactant cetyltrimethyl ammonium bromide(CTAB) and polymer (PVP). It was found that the catalyst is highly active for the chemoselective hydrogenation of nitro compounds in aqueous medium in presence of molecular hydrogen at room temperature (25ºC). The catalyst was characterized by XRD, ICP-AES, XPS, BET-surface area measurements, SEM, TEM and EXAFS. Different reaction parameters like reaction time, catalyst ratio, Pt loading, etc. were studied in detail. The investigation revealed that the site of Pt plays a crucial role towards the activity by favouring the reduction of nitro-compounds. The catalyst shows >99.9% conversion of nitro-compounds with 99% selectivity of amino compounds. The reusability of catalyst the catalyst was tested by conducting the experiment with the same catalyst and it was found that the catalyst does not change its activity and selectivity even after five reuses.

Now-a-days, particles in nanometre regime have attracted considerable attention not only for their fundamental scientific interest but also for their many technological application, especially in the field of catalysis due to their very high accessible surface area and easily available large number of active sites.[1] The activity of the metallic nanoparticles depends on the surface structure, shape and size of nanoparticles.[2,3] The controlled synthesis of nanoparticle by simple preparation method still remains a challenge for the researchers. Among the most conventional and common synthesis route, template assisted methods have been extensively studied as an alternate route to prepare nanostructured materials.[4] In recent years, significant efforts have been devoted for the controlled synthesis of supported metal nanoparticles, but most of the preparation method are energy intensive, require substantial heat treatment and produce large particles.[5] Yet significant challenge in commercializing these materials still exist due to low symmetric yields, costly production and unreliable material application. Our group have developed a synthesis strategy for the preparation of nanostructured material by hydrothermal method in presence of surfactant.[6] We report here the successful preparation of Pt nanoparticles with size between 2-5 nm supported on CeO_2 nanoparticles with size between 30-60 nm.

Aromatic nitro-compounds are the organic pollutants present in the industrial and agricultural wastewaters as these compounds are used mainly to prepare dyes, pesticides, explosives, plasticizers and herbicides.[7] Especially, 4-nitrophenol is polluting the water and a significant threat to the environment and public health, as it is highly toxic and carcinogenic in nature. On the contrary, 4- aminophenol is an industrially important raw materials which has been widely used as the intermediate for the manufacture of many analgesic and antipyretic drugs.[8] Traditionally, the reduction from nitro to amino can be carried out by various transition metal-catalysed hydrogenation, which is considered as one of the most important and challenging tasks in synthetic organic chemistry.[9] Although various supported metal catalyst such as Au/CeO_2, Au/Al_2O_3, Pt/Al_2O_3, Au/Fe_2O_3, Au/C8, Au/TiO_2 have been effectively used to reduce nitro-compounds, but a successful catalyst system with high selectivity and yield has not been achieved.[10] Additionally, most of the cases hazardous hydrogenating agents like $LiAlH_4$ or $LiBH_4$ was used with the use of organic solvent like CH_3OH, DMF, etc. and in some cases the reaction temperature was very high. So, the development of a heterogenous catalyst for selective hydrogenation of nitrophenols to aminophenols in aqueous phase under mild condition in presence of molecular hydrogen is highly demanding. Furthermore this catalyst can be used practically for the waste water treatment containing 4-nitrophenol and other nitro compounds pollutant.

We report here the preparation of Pt nanoparticles supported on nanocrystalline CeO_2 for the chemoselective reduction of nitroarene containing various functional groups with molecular hydrogen at 25ºC (see scheme 1).



Scheme 1

Pt nanoparticles supported on CeO_2 nanoparticles was prepared by modifying our own preparation method using a cationic surfactant Cetyltrimethyl ammonium bromide (CTAB).

In a typical preparation method, an aqueous solution of $[Pt(NH_3)_4](NO_3)_2$ was added dropwise with aqueous solution of $Ce(NO_3)_3.6H_2O$ under vigorous stirring. Then, aqueous solution of CTAB and reducing agent hydrazine (NH_2-NH_2) was added to the mixture of two metal precursors, keeping the molar ratio of Pt: CTAB:H_2O:NH_2NH_2 =1:0.5:500:0.8. Then, few drops of Polyvinylpyrrolidone (PVP) was added to the resulting mixture and stirred for 1h. We believe in our case PVP not only act as a capping agent but also control the size of the Pt nanoparticles. The pH of the solution was maintained to 10 using Na_2CO_3 solution and stirred for another 5h to get a homogeneous mixture. The resulting mixture was transferred into a Teflon lined stainless steel autoclave and hydrothermally treated at 180ºC for 24h. The obtained material was filtered with water and ethanol and dried at 100ºC overnight. The material was finally calcined at 550ºC for 6h in air. The obtained samples were denoted as (wt%) Pt-CeO_2. Conventional impregnated Pt catalyst on commercial CeO_2 powder was also prepared by incipient wetness impregnation method using the same precursor $[Pt(NH_3)_4](NO_3)_2$ and denoted as Pt-CeO_2^{Imp}. The Pt-CeO_2 sample was also prepared by co-precipitation method and denoted as Pt-CeO_2^{CoPre}.

The amount of Pt present in the catalyst was estimated by Inductively Coupled Plasma Atomic Emission Spectra (ICP-AES). The Powder X-ray diffraction (XRD) patterns of Pt-CeO_2 catalysts along with commercial CeO_2 are shown in Fig.1, which shows the crystalline nature of the prepared catalyst. The peaks at 2θ values of 28.5º, 33.0º, 47.4º, 56.3º are attributed to those of CeO_2 (JCPDS Card No.81-0792). The peaks at 2θ values 39.8º and 46.3º are due to presence of metallic Pt (111) and (200) planes (JCPDS Card No.87-0646). All the XRD peaks for 0.9% Pt-CeO_2 are attributed to those of CeO_2 (Fig.1c) indicating the presence of very small Pt particle size. The XRD of the spent (after reaction) 0.9% Pt- CeO_2 catalyst shows characteristic peaks of CeO_2 at 28.5º, 33.0º, 47.4º, 56.3º without changing its phase confirming the thermal stability of the CeO_2 support material. The XRD pattern of spent catalysts prepared by impregnation (1%Pt-$CeO_2^{Imp.}$) and co-precipitation (1%Pt-$CeO_2^{CoPre.}$) are also shown in Fig.1. The BET surface area estimated by nitrogen adsorption of 0.9% Pt-CeO_2 was 59 m^2g^{-1}. The morphology of the 0.9%Pt-CeO_2 catalyst was determined by Scanning Electron Microscopy (SEM). The representative SEM image of 0.9%Pt-CeO_2 catalyst shows almost uniform distribution of the particle size in the range between 30-60 nm (ESI†, Fig S1). The morphology of the prepared catalyst is totally different to that of catalyst Pt-CeO_2^{Imp}, which was prepared by incipient wetness impregnation method we used the

Schrerrer equation to get the CeO_2 crystallite size and found that prepared CeO_2 particles showing the size around 50 nm, which matches well with the TEM analysis (discussed later). The BET surface area of the 0.9%Pt-CeO_2 catalyst is 76 m^2/g and for 1%Pt-CeO_2^{Imp} is around 20 m^2g^{-1}. So the surface area of the hydrothermally prepared catalyst is almost four times higher than the commercial catalyst. The presence of Pt, Ce and O was confirmed by energy dispersive X-ray analysis (EDX) and detailed characterization of the distribution of the elements was carried out by means of elemental mapping which shows the homogeneous distribution Pt (ESI†, Fig S1). The elemental mapping of Pt of 1%Pt-$CeO_2^{Imp.}$ and 1%Pt-$CeO_2^{CoPre.}$ does not show homogenous distribution because of agglomeration of Pt particles(ESI†, Fig S1). Transmission Electron Microscopy (TEM) images of the 0.9%Pt-CeO_2 catalyst are shown in Fig.2. The average particle size of Pt ranges between 2-5 nm as estimated by TEM analysis. The particle size distribution histogram is also presented in Fig.2 a (inset). The Pt particle size histogram shows that 60% particles have the diameter of 2 nm, 25% particles have the diameter of 3 nm, 10% particles have the diameter of 4 nm and the rest of 5% particles have diameters of 5 nm. The lattice fringe with a d-spacing of 3.1 A° corresponding to [111] plane for CeO_2 is also presented (Fig.2b). While the lattice fringe with the d-spacing of 2.3A° corresponding to [111] plane for Pt^o is shown in Fig 2b. The HRTEM of the spent catalyst (after 5 recycle) revealed that the particle size of the 0.9%Pt-CeO_2 catalyst was remained same during the catalysis (ESI† Fig S2). The 4f XPS spectra of 0.9%Pt-CeO_2 catalyst is shown in (ESI† Fig S3). The binding energy values of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peak at 70.9 eV and 74.3 eV confirming the presence of mixed Pt species (Pt^0 and Pt^{+2}) for the fresh catalyst. Whereas the binding energy value of Pt $4f_{7/2}$ for the spent catalyst is 70.9 eV, which shows the presence of only Pt^0. We have also measured the Ce 3d binding energy for the fresh and spent catalyst. The Ce $3d_{5/2}$ binding energy in the XPS spectrum for the fresh and spent catalyst is 881.6 eV and 881.6 eV, respectively, which are similar to that of the Ce^{4+} oxide (CeO_2). EXAFS spectra was taken for the Pt L_{III}-edge to check the local environment of the species. Table 1 shows the structural parameters of the 0.9%Pt/CeO_2 catalyst determined by the curve-fitting of the PtL_{III} edge spectra. For the fresh catalyst, EXAFS shows the presence of Pt-O bond at a distance of 0.2 nm with the co-ordination number of 1.8 and Pt-Pt bond at a distance of 0.279 nm with the co-ordination number of 8.1. So, EXAFS analysis confirms the presence of both cationic Pt and metallic Pt for the fresh catalyst. During the synthesis hydrazine was used as the reducing agent, but the molar ratio of Pt to hydrazine was 1:0.8, so all the Pt was not reduced during the synthesis. For the spent catalyst, the EXAFS analysis shows the presence of Pt-Pt bond at a distance of

0.2768 nm with co-ordination number of 9.0. So, EXAFS analysis confirms the presence metallic Pt for the spent catalyst and the result are in agreement with the XPS analysis. Fourier transform Pt L_{III}-edge EXAFS spectra are shown in (ESI† Fig S5).

The activities of the different Pt-CeO_2 catalysts for the hydrogenation of *p*-nitrophenol are shown in Table 2. All the experiment was carried out at 25ºC. Commercial CeO_2, 1%Pt-$CeO_2^{Imp.}$ (prepared by impregnation method) and 1%Pt-$CeO_2^{CoPre.}$ (prepared by co-precipitation method) do not show any activity(Table 2, entry 2, 3). We also prepared Pt nanoparticle supported on various supports like ZnO (entry 4), TiO_2 (entry 5) and found that the activity is very low. We then prepared Pt nanoparticle supported on commercial CeO_2 using literature method and denoted as 0.9% Pt-CeO_2 $^{NCo.11}$. This catalyst showed 45% conversion with 95% selectivity (entry 6). So it can be concluded that CeO_2 is the better support for Pt catalyst for the *p*-nitrophenol hydrogenation. We have also prepared different CeO_2 supports and loaded Pt on it and found that the catalyst is not active for this reaction (entry 14, Table 2). On the other hand, our hydrothermally prepared 0.9% Pt-CeO_2 catalyst shows 100% *p*-nitrophenol conversion and 99% *p*-aminophenol selectivity. Therefore, nanocrystalline CeO_2 support with size between 30-60 nm directly influencing the activity of the Pt nanoparticles for the hydrogenation reaction. Here ceria does not simply act as a carrier, but intervenes in the catalytic process. We strongly believe that a synergistic effect between nanocrystalline CeO_2 with the size between 30-60 nm and 2-5 nm Pt particles directly influence the catalytic reduction process. The reactivities of the different nitro-compounds over 0.9% Pt-CeO_2 catalyst are shown in Table 3. All the substrates like nitrobenzene (entry 1), *p*-nitrobenzaldehyde (entry 3), *p*-nitrobenzoicacid (entry 4), *m*-chloronitrobenzene (entry 5), *p*-dinitrobenzene (entry 6), *p*-nitrotoluene (entry 7), 3–methoxynitrobenzene (entry 8), 4-hydroxy-3-methoxynitrobenzene (entry 9), shows very high activity. We have examined the effect of Pt loading towards *p*-nitrophenol reduction reaction. The *p*-nitrophenol conversion and *p*-aminophenol selectivity are different as shown in Fig 3(a).when the Pt loading was 0.5%, the *p*-nitrophenol conversion was 50% and *p*-aminophenol selectivity was 99%. When the Pt loading was increased from 1.9 to 2.8%, the decrease in conversion was only marginal but selectivity decreases to 85%. We believe that with increase in Pt loading, the particle size of Pt increases (as detected by XRD and TEM), which result the decrease in *p*-aminophenol selectivity. So, it is clear that the activity of catalyst depends upon the size of Pt particle (entries 7, 8, 9 and10). The effect of run time toward the *p*-nitrophenol conversion and *p*-aminophenol selectivity is shown in Fig 3(b). It was observed that the conversion *p*-nitrophenol increases with increasing reaction time and reaches 100% within 6h. The selectivity of *p*-aminophenol was 99% throughout the run time.

There are few reports where researchers have performed some mechanistic investigation for the reduction of nitrophenol to aminophenol but the exact mechanism for the reduction process has not been fully explored.[12] We also propose a probable surface reduction mechanism which is shown in scheme 2. Initially, molecular hydrogen will dissociate on metallic Pt surface to give dissociative hydrogen species. Nitro compounds will not directly adsorb on catalyst surface but may have an interaction with the dissociative hydrogen species. The reduction occurs step by step, where initially nitro-compound will reduce to nitrosocompound which will further reduce to hydroxyamino compound. Finally, hydroxyl amine will reduce to aniline. To obtain an insight into the reaction pathway involved during the reduction process, the reaction intermediate involved in both the routes were separately subjected to a reduction process using the 0.9%Pt-CeO_2 catalyst when *p*-nitrosophenol was subjected to reduction, it gives p-aminophenol within 5h and when *p*-(hydroxyamino) phenol was subjected to a reduction it produced aminophenol within 3h (Table 2, entries-11 and 12).

The reusability of catalyst 0.9%Pt-CeO_2 was studied without any regeneration. The catalyst was repeatedly washed with ethanol and acetone and dried overnight at 100º C and used as such. It was observed that the catalyst 0.9%Pt-CeO_2 does not change its activity (conversion and selectivity) after five successive runs (ESI† Fig S4). The amount of Pt present in the catalyst after 5 runs is almost same as the fresh catalyst (estimated by ICP-AES), confirming the true heterogeneity of catalyst.

In summary, Pt-nanoparticles with size between 2-5 nm supported on nanocrystalline CeO_2 were prepared by hydrothermal method in presence of surfactant. 0.9 (wt%) Pt supported on CeO_2 support shows a *p*-nitrophenol conversion of 100% with 99% *p*-aminophenol selectivity after 6h at 25ºC in presence of molecular hydrogen. This catalyst shows very good activity towards chemoselective reduction for different nitro-compounds. The catalyst can be reused several times without any considerable decrease in their physiochemical property and reactivity. This catalyst could replace the existing hydrogenation process where the hazardous hydrogenating agents like $LiAlH_4$, $NaBH_4$ can be avoided and to make this process environmentally friendly. This catalyst can be used for the removal of harmful pollutants from the waste water at 25ºC.

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Notes and references

[a] Refining Technology Division
CSIR-Indian Institute of Petroleum, Dehradun 248005, India
Tel: +91-135-2525917, Fax:+91-135-26660202
Email address: raja@iip.res.in
[b] Department of Complexity Science and Engineering, Graduate school of Frontier Sciences, The University of Tokyo, Kashiwanoha Kashiwa-Shi, Chiba, 277-8561, Japan.

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Figure 1. XRD patterns of (a) com.CeO_2, (b) prepared CeO_2, (c) 0.9%Pt-CeO_2 and (d) 1.9%Pt-CeO_2, e) 0.9%Pt-CeO_2 (spent catalyst after 5 successive reuses), (f) 1% Pt-CeO_2^{CoPre} (spent catalyst), (g) 1% Pt-CeO_2^{Imp} (spent catalyst).

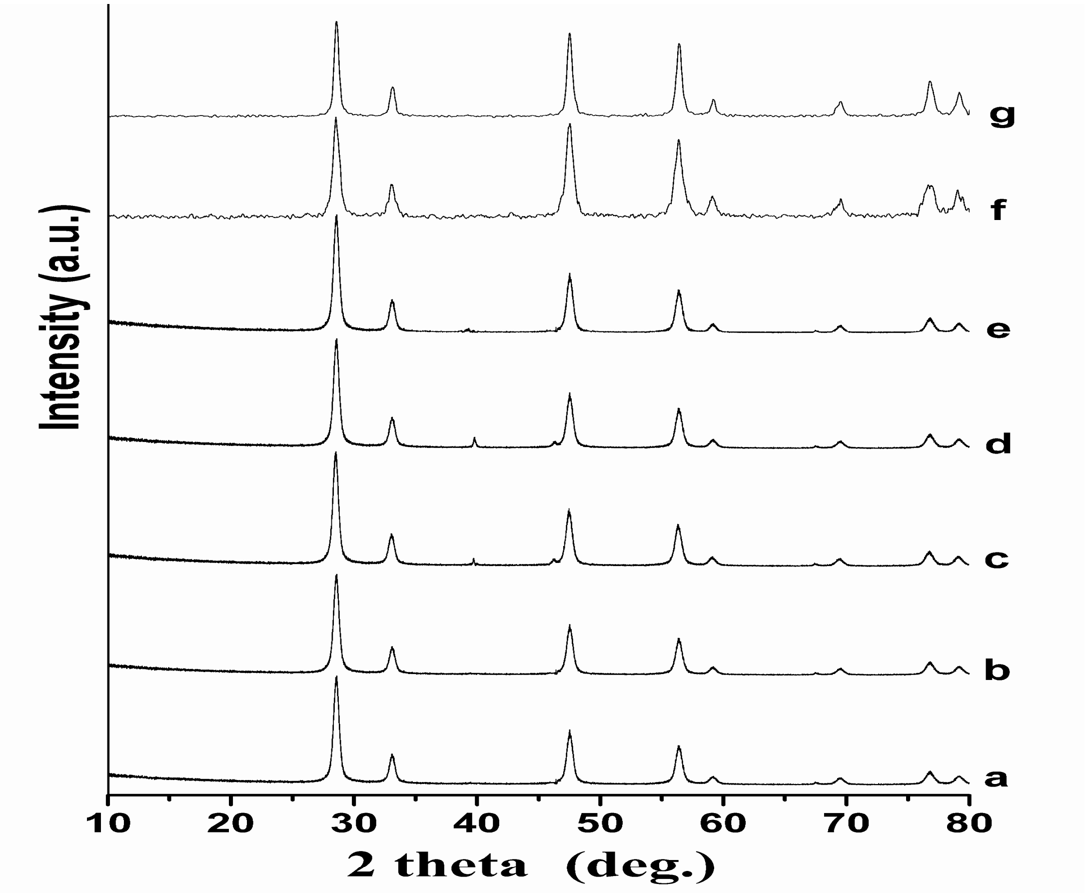

Figure 2. (a) TEM images of (a) fresh catalyst, histogram of Pt particle size (inset), (b) Lattice fringe of CeO_2 and Pt.

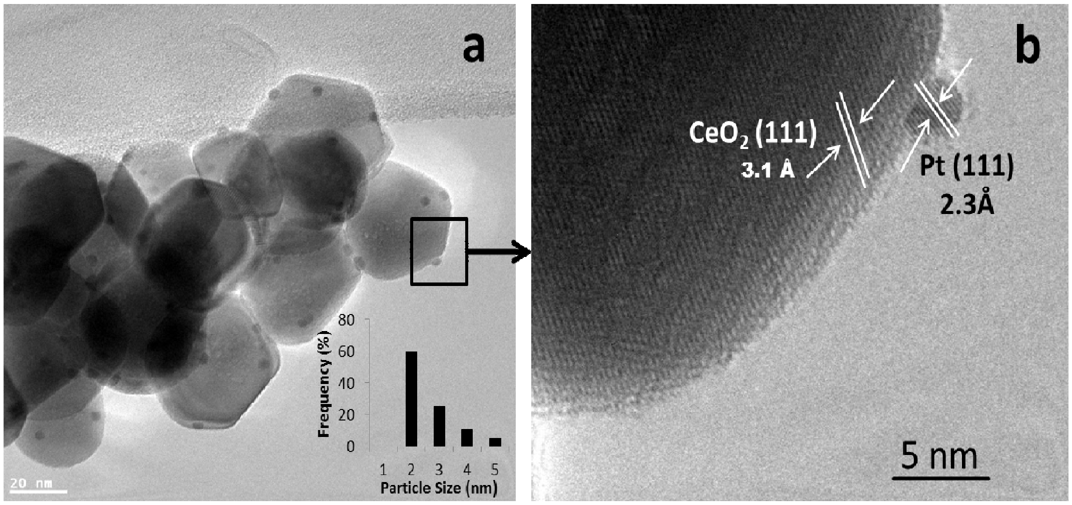

Figure 3. (a) Effect of Pt loading on *p*-nitrophenol hydrogenation, (b) Effect of time on *p*-nitrophenol hydrogenation.

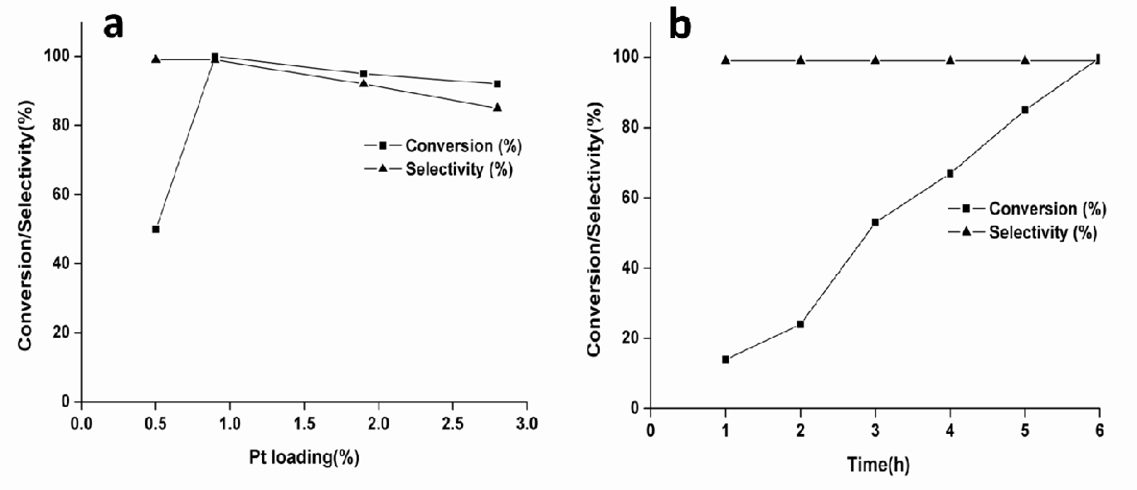

Table 1 EXAFS curve-fitting parameters at Pt L_{III}-edge of the 0.9%Pt-CeO_2 catalyst

	Shell	CN	R (10^{-1} nm)	DW (10^{-5} nm^2)	ΔK (10 nm^{-1})	Δr (10^{-1} nm)	S_0^2	ΔE_0 (eV)	R_f (%)
fresh	Pt-O	1.8±0.6	2.00±0.016	4.3±2.6	3-13.5	1.2-3.0	0.95	10.9±1.5	1.21
	Pt-Pt	8.1±1.2	2.79±0.005	4.7±0.6					
spent	Pt-Pt	9.0±1.4	2.77±0.068	4.2±0.6	3-14	1.4-3.0	0.95	6.7±2.0	2.20

Table 2. Activities of different catalyst on *p*-nitrophenol hydrogenation to *p*-aminophenol.

Entry	Catalyst	Catalyst loading (wt%)	Time (h)	C_{PNP} (%)	S_{PAP}(%)	Y_{PAP} (%)
1	$CeO_2^{Com.}$	-	6	-	-	-
2	$PtCeO_2^{Imp.}$	1	6	-	-	-
3	$PtCeO_2^{CoPre.}$	1	6	-	-	-
4	Pt-ZnO	1	6	12	75	9
5	Pt-TiO_2	1	6	15	82	12.3
6	Pt-$CeO_2^{NCo.}$	1	6	45	95	42.8
7	Pt-CeO_2	0.5	6	50	99	49.5
8	Pt- CeO_2	0.9	6	100	99	99
9	Pt- CeO_2	1.9	6	95	90	85.5
10	Pt-CeO_2	2.8	6	90	85	76.5
11	Pt- CeO_2^{NSP}	0.9	5	100	99	99
12	Pt- CeO_2^{HAP}	0.9	3	100	99	99
13	$PtCeO_2^{r}$	0.9	6	100	99	99
14	$PtCeO_2^{d}$	1	6	-	-	-

Reaction conditions: Substrate (*p*-nitrophenol) = 1gm; solvent (ethanol+ water) = 2:1; 25ºC; time = 6h ; H_2 = 1.5MPa; Catalyst used is 5wt %, C_{PNP}(%):conversion of PNP based on FID –GC result = moles of PNP reacted/initial moles of PNP used] × 100; S_{PAP}(%): selectivity of product calculated by total moles of product formed/total moles of PNP converted ×100; Y_{PAP}: yield of PAP= conversion × selectivity/100; Com. = commercial; Imp.=impregnation method on comm. CeO_2 powder; NCo. = nanoparticles by post synthesis over commercial CeO_2; CoPre. = co-precipitation method; NSP = 4-nitrosophenol; HAP = 4-(hydroxyamino) phenol; [d] Pt loading on CeO_2 support prepared by different method; [r] Catalyst after 5 reuses.

Table 3 Reactivities of the nitro- compounds over 0.9%Pt-CeO_2.

Entry	Substrate	Product	C_R. (%)	S_P(%)	Y_P (%)
1	Nitrobenzene	Aniline	100	98	98
2	*p*-Nitro phenol	*p*-Amino phenol	100	99	99
3	*p*-Nitro benzaldehyde	*p*-Amino benzaldehyde	100	99	99
4	*p*-Nitro benzoic acid	*p*-Amino benzoic acid	100	99	99
5	*m*-Chloro nitrobenzene	*m*-Chloro aminobenzene	100	99	99
6	*p*-Dinitro benzene	*p*-Diamino benzene	100	98	98
7	*p*-Nitro toluene	*p*-Amino toluene	100	98	98
8	3 –Methoxy nitrobenzene	3-Methoxy aminobenzene	100	98	98
9	4-Hydroxy-3-methoxy nitrobenzene	4-Hydroxy-3-methoxy aminobenzene	100	97	97

Reaction conditions: Substrates = 1gm; solvent (ethanol + water) = 2:1; catalyst used is 5wt % (0.9%Pt CeO_2); 25°C; time = 6h; H_2 1.5MPa; C_R(%): Conversion of reactant; S_P(%): Selectivity of product; Y_P(%):Yield of product.

Scheme 2. Probable mechanistic pathway