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Introduction

Base-free chemoselective transfer hydrogenation of nitroarenes to anilines with formic acid as hydrogen source by a reusable heterogeneous Pd/ ZrP catalyst[†]

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A highly efficient, chemoselective, environmentally-benign method is developed for the catalytic transfer hydrogenation (CTH) of nitroarenes using FA as a hydrogen source. Various supported Pd catalysts were examined for this transformation, and Pd supported ZrP (Pd/ZrP) proved to be the best catalyst for CTH of nitrobenzene. Applicability of the Pd/ZrP catalyst is also explored for hydrogenation of various substituted nitroarenes. The Pd/ZrP catalyst showed high specificity for hydrogenation of nitro groups even in the presence of other reducible functional groups such as -C=C, $-COOCH_3$, and -C=N. To investigate the reaction mechanism, a Hammett plot was obtained for CTH of p-substituted nitroarenes. The active site is thought to be *in situ* generated Pd(0) species as seen from XRD and TEM data. The Pd/ZrP catalyst is reusable at least up to 4 times while maintaining the same activity and selectivity. To the best of our knowledge, this is one of the best methodologies for CTH of nitroarenes under base-free conditions with high activity and chemoselectivity over heterogeneous Pd-based catalysts.

Anilines are important intermediates and key precursors in the synthesis of dyes, pigments, agrochemicals, pharmaceuticals pesticides, herbicides, and fine chemicals.¹ The conventional synthesis methods for aniline are: transition metal-catalysed (a) cross-coupling reaction of ammonia with aryl halides,² phenol derivatives³ and aromatic boronic acid⁴ or (b) hydrogenation of corresponding nitroarenes.⁵ The latter approaches of catalytic reduction of nitroarenes are particularly attractive owing to their high atom efficiency and compatibility with large scale processes.

Industrial preparation of aniline performed by Bechamp process involving Fe/HCl as a reducing agent⁶ has now been replaced by more environmentally-benign catalytic protocols. Hydrogenation of nitroarenes using high pressure H₂ gas in conjunction with a range of heterogeneous catalysts has been the area of interest of a number of publications.⁷ Commercially available Ni or Pt based heterogeneous catalysts are commonly used for this transformation, however, the drawbacks of these catalysts are their poor selectivity and inapplicability for substituted nitroarenes. Great attempts for serving high selectivity in the reduction of nitro group even under the presence of other reducible functional groups have been reported by using addition of stoichiometric reducing agents such as sodium hydrosulfite,⁸ iron, tin or zinc in ammonium hydroxides,⁹ silanes,¹⁰ decaboranes,¹¹ and formates.¹² However, these processes are not environmentally sustainable, and the high selectivity is generally achieved on the expense of activity. Therefore, there is a strong incentive to develop chemoselective methods for reduction of substituted nitroarenes without using toxic additives and hydrogen gas.

Catalytic transfer hydrogenation (CTH), in which hydrogen donors are used instead of pressurized-hydrogen gas, is more advantageous way from the view point of a cost and handling; it eradicates the use of any special equipment for high pressured gas. Moreover, it is said that CTH enhances the selectivity in the reduction process *via* competitive adsorption of the liquid hydrogen donor on catalyst surface.¹³ Therefore, CTH methods induced the considerable technical improvement over the rather messy traditional reduction with homogeneous transitional metals and acid reported in previous literatures.¹⁴

A wide variety of homogeneous and heterogeneous catalytic systems are developed for CTH of nitroarenes in combination with iso-propanol–potassium hydroxide or formic acid-organic base as hydrogen source.¹⁵ Other organic compounds known as the hydrogen donor in CTH are sodium formate, methanol, hydrazine, indoline, tetrahydroquinolines, 3-pyrroline, piperidine, pyrollidine, glucose, and glycerol.¹⁶

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[†] Electronic supplementary information (ESI) available: Kinetics of nitroarenes, ¹H-NMR and ¹³C-NMR of isolated aniline, TEM images and particle size distribution of Pd supported catalysts. See DOI: 10.1039/c4ra06174h

Formic acid (FA), a non-toxic liquid at room temperature, has been suggested as the promising hydrogen donor. It can be traditionally obtained from biomass processing and produces CO₂ as sole product; *i.e.* it is a safe, cheap and high potential hydrogen donor.¹⁷ Though high efficiencies of FA as hydrogen source have been obtained in combination with a high amount of organic bases, these homogeneous bases result in increase of complexity and cost in practice. Very recently, Beller and coworkers¹⁸ reported base-free CTH reactions of nitroarenes with FA using homogeneous iron complex as catalyst affording high activity and selectivity under mild conditions. Despite accomplishment of many studies, search for an efficient, chemoselective, base-free, heterogeneously-catalysed, cost-effective and environmentally-benign procedure for CTH of nitroarenes is of continuing interest.

The extensive research on hydrogenation reactions suggested that the presence of Brønsted acid plays an crucial role for such reactions.¹⁹ We recently demonstrated zirconium phosphate (ZrP) acted as an efficient solid acid support which possessed a high ratio of Brønsted/Lewis acid sites²⁰ for Pdcatalysed hydrogenolysis of 5-hydroxymethyl furfural to 1,6hexanediol using FA as a hydrogen source.²¹ This result fascinated us to pursue potential applications of Pd/ZrP as the catalyst in CTH reactions of organic substrates such as nitroarenes.

In this study, a convenient and highly chemoselective approach is developed for base-free CTH reactions of nitroarenes under environmentally-benign conditions using FA and Pd/ZrP as a hydrogen source and a reusable heterogeneous catalyst, respectively. The catalytic system was further applied for the CTH of various substituted nitroarenes to the corresponding anilines, and a plausible mechanistic pathway is proposed based on the experimental results.

Experimental

Reagents

All reagents and solvents were obtained from commercial suppliers and used without further purification. Zirconium chloride oxide octahydrate ($ZrOCl_2 \cdot 8H_2O$), sodium dihydrogen phosphate (NaH₂PO₄ \cdot 2H₂O), nitric acid, hexane, toluene, N,Ndimethylformamide (DMF), chloroform, dichloromethane (DCM), iso-propanol (i-PrOH), methanol, butanol, ethylacetate, ethanol, and naphthalene were purchased from Kanto Chemicals Co. Inc. Methyl-3-nitrobenzoate, methyl-4-aminobenzoate and 4-chloronitrobenzene were provided by Aldrich. Formic acid, niobic acid, sulphated zirconia, palladium nitrate, nitrobenzene, aniline, 3-nitrotoluene, 3-aminotoluene, 4-chloroaniline, 2-nitroanisole, 2-anisidine, methyl-3-aminobenzoate, 4nitrobenzonitrile, 4-aminobenzonitrile, and tetrahydrofuran were supplied by Wako Chemicals. 4-Nitrostyrene, 4-aminostyrene, 2-nitrobiphenyl, 2-aminobiphenyl, 1-nitronaphthalene, and 1-aminonaphthalene were provided by Tokyo Chemical Industry (TCI) Co. Ltd. HY zeolite (Si/Al = 2.8, JRC-Z-HY-5.5), ZSM-5 (Si/Al = 45, JRC-Z5-90H(1)), and SiO₂-Al₂O₃ (Si/Al = 2.1, JRC-SAH-1) were obtained from the Catalysis Society of Japan.

Catalyst preparation

Synthesis of ZrP. Zirconium phosphate (ZrP) with a molar ratio of P/Zr = 2 has been prepared as mentioned in our previous report.²¹ An aqueous solution of 0.1 M ZrOCl₂·8H₂O (100 mL) and 0.2 M sodium dihydrogen phosphate (100 mL) was mixed at pH 1-2 dropwisely with continuous stirring at 343 K. The obtained gelatinous precipitates were digested for 1 h at 343 K, filtered, washed with water, and dried under vacuum at room temperature. The obtained material was converted to the acid form by treating with 1 M HNO3 for 30 min with occasional shaking. The sample was then separated from the acidic solution by decantation, and washed with distilled water for removal of adhering acid. This acid treatment was repeated at least five times. After final washing, the material was dried at room temperature, and then characterized with XRD, N₂ adsorption (BET surface area 140 $m^2 g^{-1}$) and applied for further studies.

Synthesis of Pd/ZrP. Pd/ZrP was prepared by an adsorption method as mentioned in our previous $report^{21}$ with some modification. $Pd(NO_3)_2$ (46.1 mg) was resolved into an aqueous solution (20 mL), and then ZrP (1 g) was mixed under stirring for 2 h at room temperature. The solid was filtered, washed with water and dried at room temperature for overnight under vacuum. Then, 2.1 wt% Pd/ZrP catalyst as a brown coloured powder was obtained.

Characterization

Characterization of the catalyst was conducted using several techniques. X-ray diffraction pattern (XRD) was recorded with a Rigaku Smart Lab diffractometer using Cu Ka radiation within $2\theta = 2-80^{\circ}$ range. Transmission Electron Microscopy (TEM) study was carried out in a Hitachi H-7100 instrument operating at an accelerating voltage at 100 kV. TEM samples were prepared by dispersing the catalyst powder in ethanol under ultrasonic radiation for 1-2 min, and then the resulted solution was dropped on a copper grid followed by slow evaporation of solvent under vacuum at room temperature. Inductive Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) for determination of the actual amount of metal loading and metal leaching test of reaction mixture was measured on Shimadzu ICPS-7000 Ver. 2. Nuclear Magnetic Resonance (NMR) spectroscopy was executed on Brücker advance 400 MHz instrument using CDCl₃ as a solvent.

Catalytic reactions

Reaction of various nitroarenes was performed in a Schlenk glass tube attached to a reflux condenser. In a typical CTH reaction, requisite amounts of substrate and catalyst were weighed and mixed in ethanol solvent in the presence of FA. The reactor was heated on an oil bath at 313 K for t h. After the completion of reaction for desired time, the reactant was cooled to room temperature, and naphthalene was added as an internal standard. The filtrate was analysed by a Shimadzu gas chromatography (GC-17A) with an Agilent DB-1 column and a flame ionization detector. Conversion, yield and selectivity were

calculated using the calibration curve method following these equations:

% Conversion =
$$100 - \left(\frac{\text{mmol of reactant detected}}{\text{mmol of reactant taken}} \times 100\right)$$

% Yield =
$$\frac{\text{mmol of product formed}}{\text{mmol of reactant taken}} \times 100$$

% Selectivity =
$$\frac{\% \text{ yield}}{\% \text{ conversion}} \times 100$$

Results and discussion

Our own experience²¹ and literature survey²² of Brønsted acidmediated CTH reaction served as the starting point of our studies. Pd was selected because it is known as an active metal for several hydrogenation reactions.²³ Initial experiments were conducted to explore the role of support for Pd using FA for CTH of nitrobenzene to aniline at 313 K. Numerous supports including ZrP with high number of Brønsted acid sites,²⁰ zeolites, niobic acid, sulphated-zirconia, and γ -alumina having moderate Brønsted acid sites were chosen.

As shown in Table 1, all catalysts promoted the formation of aniline to a considerable extent under the general condition (1 mmol, 313 K, 2 h). Especially, Pd/ZrP and Pd/ZSM-5 stand out with the high activities towards aniline as the sole product (entries 1 and 6), which could be attributed to high amount of Brønsted acid sites of these catalysts. It has been understood that with the increase in Si/Al ratio, the Brønsted acid sites increases due to extra framework aluminium, thus the activity is associated with the tetrahedrally coordinated aluminium species in close proximity to Brønsted acid sites in ZSM-5.24 Pd supported on HY and SiO₂-Al₂O₃ having low Si/Al ratio were also found to be fairly active (entries 8 and 11). Though the number of Brønsted acid sites owing to Si-O-Al units would increase with decrease of Si/Al ratio, Pd/HY zeolite (Si/Al = 2.8) showed little higher activity than $Pd/SiO_2-Al_2O_3$ (Si/Al = 2.1). It is known that not only the amount of Brønsted acid sites but also the hydrophobicity derived from Si/Al ratio and topology strongly contributed on the catalysis over Si-O-Al type of materials. These factors also supposedly influenced on their catalytic activities for the reaction. Notable yields (79-84%) of aniline were attained with Pd supported on Nb2O5 and Y-Al2O3 having moderate Brønsted acid sites (entries 9 and 10). Surprisingly, Pd supported on SO₄²⁻/ZrO₂ was found to be least active for this CTH. It has been reported that there is high probability of leaching of Brønsted acid sites of SO₄²⁻/ZrO₂ in polar protic solvents.²⁵ The Pd loading onto SO₄²⁻/ZrO₂ was carried out in water in our case. This catalyst synthetic methodology is believed to result in loss of Brønsted acid sites of SO_4^{2-}/ZrO_2 in accordance with previous literatures. Additionally, the sulfate ions may also act as poison for the active Pd. It is well known that BaSO₄ poisons Pd's activity in the Rosenmund

Table 1 Nitrobenzene reduction using various palladium catalysts and FA^a



Entry	Catalyst	Particle size ^b /nm	NB	AN	
			Conv./%	Yield/%	Sel./%
1	Pd/ZrP	3.5	>99	>99	>99
2^{c}			>99	>99	>99
3 ^d			99	99	100
$4^{\rm e}$			99	99(97 ^g)	100
5^{f}			<1	0	0
6	Pd/ZSM-5	2.8	100	98	98
7 ^c			61	59	97
8	Pd/HY zeolite	3.8	98	92	94
9	Pd/Nb ₂ O ₅	H.D.	90	84	93
10	Pd/γ - Al_2O_3	H.D.	87	79	91
11	Pd/SiO ₂ -Al ₂ O ₃	3.5	87	75	86
12	$Pd/SO_4^{2-}/ZrO_2$	H.D.	8	4	_
13	ZrP		5	4	_
14	Blank		<1	0	0
$15^{\rm f}$	Blank		<1	0	0

^{*a*} Reaction conditions: nitrobenzene (NB, 1 mmol, ^c5 mmol, ^e20 mmol), ethanol (5 mL, ^c20 mL, ^e50 mL), FA (3 mmol, ^c15 mmol, ^e60 mmol), temp. (313 K, ^d353 K), time (2 h, ^c3 h, ^d15 min, ^e12 h), 2.1 wt% Pd catalyst (20 mg, ^{c,e}50 mg). ^bDetermined by TEM observation (See Fig. S3, ESI). ^fWithout FA. ^gIsolated yield. H.D.: Hardly distinguished.

reduction. Thus leaching of Brønsted acid sites and poisoning of Pd by sulfate ions could be one of the reasons for low activity of $Pd/SO_4^{2-}/ZrO_2$.

Though many supports including ZrP can afford small size particles between 2.8 and 3.8 nm, it was observed that there is no correlation between Pd mean particle size and the activity of catalyst. This fact suggested that the high number of Brønsted acid sites of support is one of the key factors for novel activity in CTH reaction of NB using FA. The high activities of the Pd/ZrP and Pd/ZSM-5 lead us to further examine the 5 mmol-scale CTH of nitrobenzene. Remarkably, Pd/ZrP catalyst showed higher activity than Pd/ZSM-5 (entries 2 and 7).

The metal-free ZrP showed very less activity with only 4% conversion of nitrobenzene (entry 13), resultantly, clarifies the necessity of metal for the CTH process with FA. Furthermore, the CTH reaction was also examined in the absence of Pd/ZrP catalyst and/or FA (entries 5, 14 and 15). In all three cases, the reaction scarcely occurred. It follows that, the observed high catalytic activity could be accounted for the presence of both Pd/ZrP and FA. Moreover, the present transfer hydrogenation methodology is so effective that it can completely reduce nitrobenzene in just 15 minutes at 353 K without any loss in selectivity (entry 3).

A 20 mmol-scale transfer hydrogenation was also performed to check the viability of the process. Remarkable activity (yield > 99%) was observed at 313 K with a TON of 1977 (entry 4). After completion of the reaction, the catalyst was simply removed by a filtration method. The filtrate was condensed under reduced pressure to obtain aniline as crude product. Aniline was obtained in 97% as isolated yield (entry 4g). ¹H- and ¹³C-NMR were conducted with the crude product only (see ESI, Fig. S1 and S2†) and compared with NMR of authentic aniline. NMR analysis confirms that the NMR of crude product exactly matches with authentic aniline and no extra peak was observed. ¹H-NMR (CDCl₃, TMS, 400 MHz): δ 3.5 (s, 2H, amino), 6.6–7.1 (m, 5H, phenyl ring) ppm.

Type of solvent was found to be crucial in transfer hydrogenation of nitrobenzene under our reaction conditions. Various aprotic and protic solvents were attempted to use for the CTH reaction of nitrobenzene over Pd/ZrP with FA as shown in Table 2. Alcoholic solvents showed good activity for the CTH, among which ethanol led to the near full conversion of nitrobenzene with almost 100% yield of aniline (entry 1). iso-Propanol which would act both as a solvent and hydrogen donor²⁶ showed good activity with 76% conversion but with low selectivity (entry 2). Butanol and methanol also gave mild or low activity (entries 3 and 4).

It is known that alcohols can serve as a hydrogen source in transfer hydrogenation,²⁷ however, the reaction without FA in ethanol solvent did not give any product in our case (Table 1, entry 5). Accordingly, the contribution from alcohol solvents as the hydrogen source in this reaction system is negligible. None of the aprotic solvent catalysed the CTH of nitrobenzene to a significant extent (entries 5–10) under present reaction conditions.

Time course of the reaction

To investigate the route of the reaction, the yield and selectivity of aniline were monitored as a function of reaction time, as shown in Fig. 1. Nitrobenzene conversion and aniline formation exactly follows each other and selectivity was near 100% throughout the reaction process under present reaction conditions. Remarkably, no intermediate was detected; this suggests

Table 2 Screening of different solvents in the CTH reaction of nitrobenzene towards aniline over Pd/ZrP^{a}

		NB	AN		
Entry	Solvent	Conv./%	Yield/%	Sel./%	
1	Ethanol	>99	>99	>99	
2	iso-Propanol	76	60	79	
3	<i>n</i> -Butanol	54	47	87	
4	Methanol	40	27	67	
5	Toluene	40	5	_	
6	Tetrahydrofuran	10	5	_	
7	<i>N</i> , <i>N</i> -Dimethylformamide	7	5	_	
8	Ethylacetate	7	3	_	
9	Chloroform	6	2	_	
10	Dichloromethane	4	2		

^a Reaction conditions: NB (1 mmol), 2.1 wt% Pd/ZrP (20 mg), solvent (5 mL), FA (3 mmol), 313 K, 2 h, 500 rpm. NB: nitrobenzne; AN: aniline.



Fig. 1 Time course for transfer hydrogenation of nitrobenzene. Reaction conditions: nitrobenzene (1 mmol), 2.1 wt% Pd/ZrP (20 mg), ethanol (5 mL), FA (3 mmol), 313 K.

that either there is no formation of intermediates or they react immediately on catalytic surface before desorbing.

Reusability

Recyclability of the catalyst is an important criteria in heterogeneous catalytic system. On that account, the reusability of catalyst for CTH of nitrobenzene was investigated. In each run, after the reaction, the catalyst was separated by centrifugation, washed thoroughly with ethanol, dried in vacuum for overnight, and then the dried catalyst was used for further reaction.

The results in Fig. 2 indicated that the Pd/ZrP catalyst can be reused at least 4 times without losing the activity and selectivity. The aliquots of the reaction mixture after first and fourth run were analysed by ICP-AES, no Pd was detected in the solutions.



Fig. 2 Reusability of Pd/ZrP for transfer hydrogenation of nitrobenzene. Reaction conditions: nitrobenzene (1 mmol), 2.1 wt% Pd/ZrP (20 mg), ethanol (5 mL), FA (3 mmol), 313 K, 2 h.

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The hot filtration test was also conducted in order to re-affirm the ideal heterogeneity of Pd/ZrP. For this, the catalyst was removed after 1 h and reaction was continued with the filtrate. The results showed that the reaction didn't proceed. These confirmed that there was no significant leaching of metal from the catalyst surface and the reaction is truly heterogeneous.

CTH of substituted nitroarenes

After optimizing the conditions for CTH reaction of nitrobenzene over Pd/ZrP, we further examined the scope of this catalytic system for CTH reactions of various substituted nitroarenes. The results shown in Table 3 are under optimum rFeaction conditions for each substrate. It was seen that longer reaction time is required for CTH reaction of substituted nitroarenes to achieve >90% yield of the corresponding anilines. Entries 2 and 3 are for 3-nitrotoluene and 4-chloronitrobenzene, respectively. Notably, this catalyst system can efficiently transfer hydrogen to produce substituted anilines at 313 K. Halo-nitroarenes have tends to undergo hydrogenolysis (of C–X bond), but in our case no hydrogenolysis was proceeded and 4-chloroaniline was formed in 93% yield with >99% selectivity. Nitro groups attached to a naphthalene and biphenyl ring were also successfully reduced with excellent yield and selectivity of the

Entry	Reactant	Product	Time/h	Conv./%	Yield/%	Sel./%
1	nitrobenzene	aniline NH2	2	>99	>99	100
2	3-nitrotoluene	3-aminotouene	6	92	92	100
3 ^{<i>b</i>}	CI NO ₂ 4-chloronitrobenzene	CI NH ₂ 4-chloroaniline	18	94	93	99
4	2-nitrobiphenyl	2-aminobiphenyl	16	96	94	99
5	I-nitronaphthalene	NH ₂ I-aminonaphthalene	16	94	93	98
6	2-nitroanisole	2-anisidine	24	94	91	96
7	methyl-3-nitrobenzoate	methyl-3-aminobenzoate	12	>99	99	>99
8	methyl-4-nitrobenzoate	methyl-4-aminobenzoate	20	98	95	97
9	4-nitrobenzonitrile	4-aminobenzonitrile	18	93	91	97
10 ^c	4-nitrostyrene	4-aminostyrene	6	97	90	92

^{*a*} Reaction conditions: substrate (1 mmol), 2.1 wt% Pd/ZrP (20 mg), FA (3 mmol), ethanol (5 mL), temp. (313 K), 500 rpm. ^{*b*} Temp. (333 K). ^{*c*} 2.1 wt% Pd/ZrP (10 mg).

corresponding anilines (entries 4 and 5). Reductions of nitro groups in the presence of other functional groups such as $-OCH_3$, $-COOCH_3$ (entries 6–8) proceeded with high tolerance for these functional groups to afford the corresponding anilines with >90% yield and selectivity.

The nitro group was selectively hydrogenated in the presence of easily reducible nitrile group with 91% yield (97% selectivity) of 4-aminobenzonitrile (entry 9). The most challenging task was the chemoselective reduction of nitro group in the presence of -C=C as the reactivity order for hydrogenation of olefins are next to nitro group. 4-Nitrostyrene was chemoselectively transformed to 4-aminostyrene as major product with 92% selectivity (entry 10); in this case, the by-product of 4-ethylaniline was detected. The cause for the high chemoselectivity might be explained in terms of high electrostatic interactions of polar nitro group with the catalyst surface as compared to non-polar -C=C bond.²⁸

Hammett plot

The reactivity of substrates in heterogeneous catalysis mainly depends on the charge density at the reaction centre and steric factor of substrates. Therefore, to study the reaction mechanism of CTH, the initial rate for various substituted nitroarenes with electron-withdrawing groups (EWG) like $-\text{COOCH}_3$, -Cl, $-\text{C}\equiv\text{N}$ at para position were measured. Initial rates and rate constants are shown in Table S1, in ESI.[†]

The graph is plotted for $\log(K/K_0)$ against the Hammett substitution constants (sigma)²⁹ in Fig. 3, where *K* is an initial rate constant for substituted nitrobenzene and K_0 is an initial rate constant for nitrobenzene. The plot shows a linear relationship with a slope of -1.0. The negative slope with such a high value indicates that the present CTH proceeds *via* cationic intermediate and EWG hinders the rate of reduction of nitrobenzene.³⁰

XRD and TEM



Fig. 4 shows the XRD pattern for fresh as well as used catalysts. The XRD pattern clearly demonstrates that there is no structural

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Fig. 4 (a) XRD patterns for (1) ZrP support, (2) fresh Pd/ZrP, and Pd/ZrP after (3) first run and (4) fourth run. (b) & (d) are TEM images and (c) & (e) are particle size distribution for Pd/ZrP prior and after the reaction respectively.

deterioration of catalyst after the reaction. However, an additional peak at 40 degree was observed for post reaction catalysts, which corresponds to Pd(0). This indicates that Pd(n) is reduced to Pd(0) during the reaction.

While performing the reaction, it was also seen that the catalyst colour changes to black from its initial brown colour within a few minutes of the reaction. The high reusability of catalyst without any oxidation treatment of catalyst (shown in Fig. 2) hints that the active site for transfer hydrogenation is *in situ* formed Pd(0) instead of Pd(π). From decades, it's known that the catalytic hydrogenation reaction requires metal (in reduced form). FA has the ability and can convert Pd(π) from Pd(0).³¹ Very recently, Wang *et al.*, synthesised Pd nanoclusters from Pd(π) using FA as a reducing agent at room temperature.³¹

From Fig. 4(b–e), we observed that the average particle size which was 3.5 nm for catalyst prior to reaction increases to 5.4 nm after the catalytic run. An increase in particle size after

reaction observed by TEM measurements may account the reduction of ionic Pd into Pd(0) nanoparticles in accordance with the XRD measurements.

Proposed mechanism

A reaction mechanism is proposed for the CTH of nitroarenes with FA as a hydrogen source as shown in Fig. 5 based on the experimental results mentioned above. At the initial stage, FA decomposes on the Pd/ZrP surface into CO₂ and H⁺, H⁻ (1 in Fig. 5), CO₂ evolution is confirmed by GC-8A (TCD detector) of collected gas from the reaction.³²

The H⁻ adsorbs on Pd surface to reduce Pd(n) into Pd(0) (2 in Fig. 5). Since the nitro group attached to the benzene ring can pull electrons more strongly from benzene ring, and can easily be adsorbed on the surface of catalyst. Consequently, nitroarenes adsorbs on the catalyst surface by electrostatic interaction as shown in **3** (Fig. 5).

Thereafter, H^+ from Brønsted acid sites of ZrP and H^- (from FA) adsorbed on Pd are transferred to electron rich O and

electron deficient N of nitro group, respectively, to form 4 (Fig. 5). One of the hydroxyl group in 4 attacks on the H^+ (from FA) to generate 5 eliminating a water molecule. Further protons are trapped and the free aniline is desorbed from catalytic surface as shown in 5 and 6 (Fig. 5).

A high value negative slope was observed in the Hammett plot signifies a well-developed positive charge on the transition state as discussed in Fig. 3. Thus, in strong agreement to the Hammett plot a cationic intermediate was proposed for the transformation.

The high activity of Pd/ZrP catalyst may be attributed to its high capacity of holding nitroarenes by electrostatic interactions between polar nitro group with H^+ and H^- on Pd/ZrP. This strong interaction leads to direct reduction of nitroarenes to anilines without the formation of any intermediates.

Conclusions

In summary, a highly efficient, base-free, heterogeneously-catalysed, and chemoselective CTH methodology is developed for



Fig. 5 Proposed mechanism for transfer hydrogenation of nitroarenes over Pd/ZrP.

the synthesis of industrially important anilines. The Pd/ZrP catalyses the selective transfer hydrogenation of various functionalized nitroarenes to the corresponding anilines with excellent yields at 313 K. Solid catalyst could be used repetitively without any obvious loss in activity. The reaction mechanism involving cationic intermediate has been proposed based on the above characterizations and the slope of Hammett plot. The presence of both high amount of Brønsted acid sites (of ZrP) and efficient reducing property (of Pd(0)) in Pd/ZrP forms the key factors for efficacious fixation of hydrogen species from FA in this study.

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