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## Room temperature selective reduction of nitroarenes to a zoxy compounds over $\rm Ni\mathar{-}TiO_2$ catalyst



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### ABSTRACT

Surface tuned Ni-TiO<sub>2</sub> catalyst was prepared by hydro-solvothermal method using poly(diallyldimethylammonium chloride) (or PDADMAC) as a surfactant and hydrazine hydrate as a capping agent. Activity of catalyst was investigated for selective reduction of nitrobenzene to azoxybenzene in aqueous medium at room temperature, using hydrazine hydrate as the reducing agent for catalysis. It was observed that the catalyst prepared by hydrosolvothermal method (2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup>) showed 92 % selectivity of azoxybenzene with 89 % conversion of nitrobenzene, under mild reaction conditions, which is quite higher as compared to reported non-noble metal catalysts. Prepared catalysts were thoroughly characterized by various analytical techniques to find out the physicochemical characteristic features of the materials. 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst exhibited highly dispersed nickel nanoparticles (~6.8 nm) over TiO<sub>2</sub> surface and strong metal-support interaction due to smaller size of Niparticles, which significantly enhanced the catalytic efficiency towards selective reduction of nitroarenes to azoxy compounds. Effect of solvents on catalyst synthesis process was also investigated and reported for establishing the superiority of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst. The heterogeneous nature of highly dispersed catalyst (2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup>) was confirmed by the recyclability tests and found that the catalyst particles can be easily recovered and recycled up to four successive runs without any significant loss in its catalytic performance.

## Introduction

Nitroarenes are the organic pollutants of industrial and agricultural waste water and their transformation into industrially important products has significant importance in chemical industries [1,2]. Reduction of nitroarenes produces different products such as azo, azoxy, anilines etc. [2] and their formation often depends up on properties of catalytic materials used for catalysis as well as operating reaction conditions [2,3]. Therefore, selective production of any of these products is the real challenge for researchers. So far, significant research work has been done toward selective production of substituted anilines from nitroarenes using Pt, Pd, Ru, Rh, Au, Ag, Cu, Ni, Co etc. based nanomaterials [4-8], but very few reports are available in literature for selective production of azoxy compounds from nitroarenes. Notably, azoxy compounds can be produced from oxidation of aniline [9,10] or reduction of nitro compounds as well [11]. Azoxy compounds having conjugated system with polar functionality is a condensation product of nitroso and hydroxylamine intermediates [12]. It is also a precursor of

Wallach rearrangement, which has been particularly used in coloration of soap, resin, lacquer as well as liquid crystals in electronic display and therapeutic medicines [9,10]. Noticeably, noble metal based catalytic systems are often used for selective production of azoxy compounds, but due to their limited availability and expensiveness, development of economically viable catalyst is highly desirable. Additionally, unlike other conventional processes and as a safety viewpoint, catalytic transfer hydrogenation protocol is easy to perform without any elaborated reaction assembly or high pressure reactors [13]. For this purpose, different hydrogen donor species such as NaBH<sub>4</sub>, HCOONH<sub>4</sub>, CO +H2O, HCOOH, C3H7OH, N2H4.H2O etc. [14,15] has been constantly used for in-situ hydrogen generation for hydrogenation reaction, but most of them are hazardous, produces non-greener side products and their non-stoichiometric usage causes tedious separation process to recover the desired product. Among different hydrogen donor species, hydrazine hydrate and molecular hydrogen are considered as greener reducing agents as they do not produces harmful by-products. Moreover, pure hydrazine (100 %) is a hazardous chemical and unsafe to

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Scheme 1. Selective reduction of nitroarenes to azoxy compounds.

handle while performing a reaction, until it is used in hydrous form [14]. In this aspect, utilization of stoichiometric amount of hydrazine hydrate (it produces water and  $N_2$ ) along with the non-noble metal based catalytic system is an economic and environmentally benign approach for hydrogenation processes.

Liu et al. synthesized Ag-Cu alloy nanoparticles (NPs) for selective transformation of nitrobenzene to azoxybenzene under visible light irradiation at 60 °C within 16 h, using KOH as an additional base [16]. Gold nanoparticles (Au-NPs) supported on hydrotalcite (HT) was investigated for selective reduction of nitro to azoxy compounds in an argon atmosphere at 40 °C using isopropyl alcohol (IPA) and KOH [11]. Recently, Ferlin et al. developed Au@Zirconium-Phosphonate NPs for selective production of azoxy compounds using NaBH<sub>4</sub> as reductant in ethanolic medium at 30 °C [17]. Recently, Doherty et al. reported quite interesting results toward partial (i.e. formation of N-phenylhydroxylamine and azoxybenzene) and complete reduction (i.e. aniline) of nitroarenes using a single Au NPs supported catalyst with exceptionally high activity just by changing the reaction conditions [18]. Similarly, Ir, Rh and Ir-Rh nanosheets [19] were also reported for azoxybenzene formation, in which Ir nanosheets showed higher TOF toward azoxybenzene formation. Besides, a homogeneous diruthenium complex was investigated by Lin et al. [20] for the discussed reaction using hydrazine hydrate as reductant at 80 °C, but the reaction product was aniline derivatives. Unfortunately, utilization of noble metal catalysts limits their practical application due to their higher cost and limited availability. Moreover, Suib and co-worker fabricated sea urchin-like Ni/ Graphene nanocomposites for the synthesis of azoxy compounds from nitro compound, using hydrazine hydrate as reducing agent in ethanolic medium [12]. Furthermore, Hou et al. thoroughly investigated the formation of metastable reaction intermediate (i.e. azoxy intermediate) over Ni-Ni<sup> $\delta$ +</sup> clusters stabilized ceria catalyst at 80 °C in ethanolic medium and argon atmosphere [21]. In a recent study, Corma and coworkers investigated a bifunctional catalyst system (Ni@C-CeO<sub>2</sub>) for selective formation of azoxybenzene from nitrobenzene under base-free reaction conditions [22]. They also explored the possibility of formation of other products like azobenzene and aniline by using bifunctional catalyst. We previously reported Pt-CeO<sub>2</sub> [23] and Ni-ZrO<sub>2</sub> [24] catalyst for selective reduction of nitroarenes to corresponding anilines in aqueous medium, where molecular hydrogen was used as reductant for catalysis.

Due to low cost and high abundance, synthesis of non-noble metal based heterogeneous systems with unique physico-chemical properties, tuned structural geometry and improved catalytic performance has great importance in both fundamental studies as well as industrial applications. So far, significant research work has been introduced for the synthesis of supported non-transition metal oxide catalysts [25], but synthesis of smaller metal NPs over transition metal oxides support is quite challenging because lower surface area of transition metal oxides leads to agglomeration of metal NPs and consequently decreases catalytic efficiency. However, several other factors, such as active metal particle size, accessibility of metal-metal oxide (as a support) interfacial sites, synergy between active metals-metal oxides, metal-support interactions etc. are also responsible for altering the catalytic efficiency

[26]. All these properties are strongly influenced by catalyst synthesis procedures [24,26a]. Hence, by varying the synthesis procedure one can easily alter the physicochemical characteristics of prepared nanomaterials. Again, problem associated with most of the synthesis procedures are utilization of excessive energy, special equipments, expensive metal precursors along with the complicated synthesis procedure and also some of them have inability [26a] to synthesize smaller nanoparticles, which is desirable for catalysis. From last decade, TiO<sub>2</sub> has been considered to be one of the most promising support material for the synthesis of various noble and non-noble metal based nanomaterials, which exhibited outstanding performance toward several catalytic processes (especially in photocatalysis) [27]. Even bare  $TiO_2$  was also reported for photocatalytic reduction of nitroarenes [28]. Variety of synthetic protocols [29] have been reported for Ni/TiO2 catalysts but in most of the cases, post-synthesis methods [29] were applied where nickel was incorporated after preparing the TiO<sub>2</sub> support (or commercial TiO<sub>2</sub>). Hence, controlled synthesis of smaller NPs by using single-step synthesis procedure still remains a challenge for scientific community. Therefore, we aimed to develop a simplified, efficient, highly selective and cost-effective single-step preparation method for synthesis of supported transition metal oxide catalyst.

In present work, we prepared Ni-TiO<sub>2</sub> catalyst (2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup>) by single-step hydro-solvothermal (mixture of ethylene glycol and water) method using poly(diallyldimethylammonium chloride) (or PDADMAC) as a surfactant and hydrazine hydrate as a capping agent. The role of hydrazine hydrate as a capping agent is reported in our previously published articles [26a,c]. Performance of the catalyst was examined for selective reduction of nitrobenzene to azoxybenzene and it was observed that the catalyst prepared by hydro-solvothermal method (2.6 % Ni-TiO2<sup>EG-W-H</sup>) was highly efficient for room temperature selective production of azoxy derivatives in aqueous medium, using stoichiometric amount of hydrazine hydrate as reductant (Scheme 1). 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst showed higher TON than other reported non-noble metal-based systems and our catalyst maintained its heterogeneous nature throughout the reaction. To further explore the superiority of our (2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup>) system, we have investigated the solvent effects for catalyst synthesis process and also prepared another Ni-TiO<sub>2</sub> catalyst by wetness impregnation method and their activity was compared for the reduction processes.

### Experimental

Materials used for catalyst synthesis, catalyst synthesis procedures and catalyst characterization equipments/techniques are mentioned/ described in detail in the Electronic Supplementary Information (ESI) of this manuscript.

### Catalyst synthesis

Ni-TiO<sub>2</sub> catalyst was synthesized by hydro-solvothermal method using ethylene glycol and water as mixture of solvents. Synthesis methods for other Ni-TiO<sub>2</sub> catalysts prepared for the study can be found in the ESI of this manuscript.



**Fig. 1.** A] BET adsorption-desorption isotherms and corresponding pore size distribution (inset) of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst; B] XRD patterns of a] NiO<sup>Com.</sup>; b] TiO<sub>2</sub><sup>Com.</sup>; c] 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup>; d] 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup>; e] 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup>; e] 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-S</sup> catalysts.

## Synthesis of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst

Initially, 5 mL PDADMAC [poly (diallyldimethylammonium chloride)];  $M_w = 100,000-200,000$ ] was added to mixture of ethylene glycol (100 mL) and distilled water (100 mL) and dissolved well by stirring. After 15 min., required amount of titanium (IV) isopropoxide (17.8 g) and nickel chloride hexahydrate (0.61 g i.e.  $\sim$  3 wt. %) was added. The solution was allowed to stir for 15 min. and hydrazine hydrate (0.52 g) was added to above solution keeping the Ni:N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O mole ratio was 1:1. The whole solution was vigorously stirred for 2 h. The pH of solution was maintained  $\sim 10$  using ammonium hydroxide (25 %) and again the solution was stirred for 3 h. The resulting mixture was transferred into Teflon lined stainless steel autoclave for 90 h at 150 °C. After cooling the autoclave at room temperature, the formed precipitate was thoroughly centrifuged and washed with excess of distilled water. The centrifuged cake was then dried at 80 °C for 12 h. Obtained material was calcined at 550 °C for 6 h in air. Prepared powdered material was designated as 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst, where 2.6 % is the wt.% of nickel (as determined by ICP-AES). Catalysts of lower and higher loading were also prepared, designated as 1.3 % Ni- $\text{TiO}_2^{\text{EG-W}}$  and 5.3 % Ni-TiO $_2^{\text{EG-W}}$  catalysts (as determined by ICP-AES). Fresh or the catalysts without H2-pretreatment were designated as X% Ni-TiO2<sup>EG-W</sup>, H2-pretreated catalysts were designated as Y% Ni-TiO2<sup>EG-</sup> W-H and the spent catalyst or the catalyst after catalysis, was designated as Z% Ni-TiO<sub>2</sub><sup>EG-W-S</sup> catalyst, where X, Y and Z are the wt. % of Ni in the catalyst. We have followed the similar designations for all the respective catalysts also.

Pure TiO<sub>2</sub> was prepared by opting the above mentioned synthesis procedure (i.e. similar to 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst), eliminating the nickel addition step, which was designated as TiO<sub>2</sub><sup>P</sup>. For comparison, we have also prepared catalysts using water and ethylene glycol as solvents i.e. 2.7 % Ni-TiO<sub>2</sub><sup>W</sup> (water as solvent) and 2.8 % Ni-TiO<sub>2</sub><sup>EG</sup> (ethylene glycol as solvent). We have also synthesized a catalyst (2.6 % Ni-TiO<sub>2</sub><sup>Imp.Com.</sup>) by conventional wetness impregnation method using commercial TiO<sub>2</sub>. The details can be found in the ESI.

### Catalytic activity measurement

#### Selective reduction of nitroarenes

Catalytic reduction experiments were conducted in closed vessel using magnetic stirrer bar. All the reduction experiments were carried out at room temperature in aqueous medium. H<sub>2</sub>-pretreated catalysts (450 °C for 2 h, using 10 % H<sub>2</sub> balanced He) were used for catalysis. In a typical reduction experiments, 1 g of reactant dissolved in  $10 \text{ mL H}_2\text{O}$  (in case of water insoluble reactants, 2 mL ethanol was added with 8 mL of water) and then, 0.10 g of catalyst (10 wt. % w.r.t reactant amount) was added to it. Hydrazine hydrate were used as hydrogen donor species for catalysis and used reactant:hydrazine hydrate mole ratio was 1:1.5. During ongoing reaction, aliquots were withdrawn from reaction mixture periodically for analysis and progress of reaction was monitored by Gas chromatography (Agilent 7890) having HP-5 (length 30 m, id.0.28 mm, 0.25 µm film thickness) column equipped with FID (flame ionization detector). At the end of reaction, solid catalysts were centrifuged and washed with acetone to remove the surface adsorbed organic molecules. The catalyst particles were dried at 80 °C for 6 h and reused for next catalytic cycle. The obtained reaction products were further confirmed by GC–MS.

### **Results and discussion**

## Catalyst characterization

Our best catalyst (2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup>) was characterized (with and without H<sub>2</sub>-pretreatment and after catalysis) thoroughly and all other characterizations for other catalysts (synthesized by changing solvents as well as by different synthesis procedure) were also performed to compare with the properties of the best one. The characterization details of other catalysts are described in ESI.

## N<sub>2</sub>-physisorption and X-ray diffraction analysis

 $N_2$  adsorption-desorption isotherm and respective pore size distribution of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst are represented in Fig. 1A. Brunauer-Emmett-Teller (BET) surface area of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> was found to be 67 m<sup>2</sup> g<sup>-1</sup>. Results obtained from N<sub>2</sub> physisorption studies revealed that the catalyst (2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup>) prepared using mixture of solvents (water and ethylene glycol) have higher surface area than other synthesized catalysts including catalysts prepared by only ethylene glycol (2.8 % Ni-TiO<sub>2</sub><sup>EG</sup>) and water (2.7 % Ni-TiO<sub>2</sub><sup>W</sup>) as solvents (Fig. S1, Table S1). According to IUPAC classification of gas-solid adsorption isotherms, N<sub>2</sub>-adsorption desorption isotherm of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst showed typical Type IV isotherm with a noticeable hysteresis loop (H1 type) [30], which is a characteristic of mesoporous material [31]. We have observed that Ni loading affected the surface area of catalysts. On increasing the Ni loading of catalysts [X% Ni-TiO<sub>2</sub><sup>EG-W</sup> (X = 1.3, 2.6, 5.3)], increasing trend of BET surface area (61

## Table 1Physicochemical properties of 2.6 % Ni-TiO2 $^{EG-W}$ catalyst.

Catalyst	$S A (m^2 g^{-1})$	Particle size (by TEM) <sup>\$</sup>		Crystallite size (by XRD)*		MD
		Active metal (nm) NiO	TiO <sub>2</sub> (nm)	Active metal (nm) NiO	TiO <sub>2</sub> (nm)	
2.6 % Ni-TiO <sub>2</sub> <sub>EG-W</sub>	67	6.8	16	ND	15.8	14.9

\*- Crystallite size by using Scherrer equation; SA - surface area; ND - not determined; \$ - average particle size; MD- metal dispersion (%).

 $m^2 g^{-1}$ , 67  $m^2 g^{-1}$ , 71  $m^2 g^{-1}$ ) of respective catalysts were observed, as it is reported in various literature reports [32–34]. Furthermore, 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst showed higher metal dispersion than the other prepared catalysts as shown in Table 1 and Table S1.

Fig. 1B shows XRD pattern of NiO<sup>Com.</sup> (commercial NiO) (Fig. 1Ba), TiO<sub>2</sub><sup>Com.</sup> (commercial TiO<sub>2</sub>) (Fig. 1Bb), 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> (Fig. 1Bc), 2.6 % Ni-TiO2<sup>EG-W-H</sup> (Fig. 1Bd) and 2.6 % Ni-TiO2<sup>EG-W-S</sup> (spent) (Fig. 1Be) catalysts. Typically, TiO<sub>2</sub> can be present in form of three different phases i.e. anatase, rutile and brookite. The distinct anatase phase of TiO<sub>2</sub> was observed in all the XRD pattern of prepared materials (Fig. 1B and Fig. S2). Broadness in XRD peaks of TiO<sub>2</sub> for synthesized catalyst as compared to commercial TiO2<sup>Com.</sup> indicated that the crystallite size of TiO<sub>2</sub> for respective catalysts was smaller than commercial TiO<sub>2</sub>, which was further confirmed by calculating the crystallite size using Scherrer equation (Table 1 and Table S1). XRD pattern of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst showed peaks at 20 values 25.51°, 38.07°, 48.15°, 54.19°, 55.27°, 62.91° and 75.24°, which are the characteristic peaks of anatase phase of TiO<sub>2</sub> (JCPDS Card no.-84-1286) (Fig. 1Bc). The most exposed plane of anatase TiO<sub>2</sub> was (101), which was observed in all the prepared samples. 2.6 % Ni-TiO2<sup>EG-W</sup> catalyst also showed a peak at 20 value 43.56° corresponding to (200) plane of NiO (JCPDS Card no.-78-0643). Presence of NiO peak in 2.6 % Ni-TiO2<sup>EG-W</sup> catalyst confirmed the existence of NiO crystals larger than 5 nm [34].

Meanwhile, XRD analysis of reduced (2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup>) catalyst was also performed to examine the changes after H<sub>2</sub>-pretreatment and before catalysis (Fig. 1Bd). We observed that 20 values of 2.6 % Ni-TiO2<sup>EG-W-H</sup> catalyst belongs to anatase phase of TiO2 as that of fresh 2.6 % Ni-TiO2<sup>EG-W</sup> catalyst, while NiO was reduced to Ni° (metallic) as depicted in the XRD pattern with the peaks at  $2\theta$  values of  $44.50^{\circ}$  and 51.84° for (111) and (200) crystal faces (JCPDS Card No- 04-0850). Spent catalyst (2.6 % Ni-TiO2 EG-W-S) showed the characteristic peaks of anatase TiO<sub>2</sub> along with Ni° (metallic nickel) peaks in the corresponding XRD pattern (Fig. 1Be). Since, H<sub>2</sub>-pretreated catalyst was used for catalysis, it might be the possible reason for presence of metallic nickel in spent catalyst and/or utilization of hydrazine hydrate during catalysis, could be another possibility. Furthermore, recyclability of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst substantiated the absence of leaching phenomenon, which was further confirmed by ICP-AES analysis. The crystallite size of TiO<sub>2</sub> in 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup>, 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> and 2.6 % Ni- ${\rm TiO_2}^{\rm EG-W-S}$  catalysts were calculated by using Scherrer equation and found to be 15.8 nm, 15.8 nm and 16 nm, respectively.

## Transmission electron microscopy

In the TEM images of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst (Fig. 2), irregular shaped catalyst particles was observed with the size of around 16 nm–60 nm and the d-spacing values of 0.21 nm and 0.35 nm belongs to (200) plane of NiO and (101) plane of anatase TiO<sub>2</sub> (Fig. 2b), respectively. SAED pattern further confirmed the polycrystalline [35] nature of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst (Fig. 2b-inset). TEM-elemental mapping of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst showed the uniform distribution of Ni over the TiO<sub>2</sub> support, i.e. no agglomeration was observed

(Fig. 3). The average particle size of NiO in the 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst was found to be 6.8 nm. Use of ethylene glycol (50 %) during synthesis, might have played a significant role in controlling the size [36] of active metal (i.e. nickel) in case of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst. However, TEM images of H<sub>2</sub>-pretreated (2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup>) and spent (2.6 % Ni-TiO<sub>2</sub><sup>EG-W-S</sup>) catalysts confirmed the presence of metallic Ni in the respective catalysts as shown in Fig. 2 c - Fig. 2e.

We have also performed morphological analysis by scanning electron microscopy (SEM) for 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup>, 2.7 % Ni-TiO<sub>2</sub><sup>W</sup> and 2.8 % Ni-TiO<sub>2</sub><sup>EG</sup> catalysts (Fig. S3) and TEM analysis for 2.7 % Ni-TiO<sub>2</sub><sup>W</sup> and 2.8 % Ni-TiO<sub>2</sub><sup>EG</sup> catalysts, which can be found in ESI (Figs. S4 and S5).

# X-ray photoelectron spectroscopy (XPS) and temperature programmed reduction (TPR) analysis

XPS is a surface analysis technique and Ni 2p core level spectra of fresh and spent catalysts showed the presence of different nickel species over the catalyst's surface (Fig. 4A). Ni 2p XP spectra characterized by two spin-orbit components (i.e. Ni 2p<sub>3/2</sub> and Ni 2p<sub>1/2</sub>), which are separated by 17.4 eV–18.4 eV. Ni 2p XP spectra of fresh (2.6 % Ni-TiO<sub>2</sub><sup>EG–W</sup>), reduced (i.e. 2.6 % Ni-TiO<sub>2</sub><sup>EG–W-H</sup>) as well as spent (2.6 % Ni-TiO2<sup>EG-W-S</sup>) catalysts showed well defined Ni 2p<sub>3/2</sub> peaks with their respective satellite peaks. In the fresh 2.6 % Ni-TiO $_2^{EG-W}$  catalyst, Ni 2p3/2 peak consists three component peaks with binding energy values at 854.6 eV, 856.1 eV and 857.5 eV, which can be assigned for NiO, Ni<sub>2</sub>O<sub>3</sub> and Ni(OH)<sub>2</sub> (Fig. 4Aa), respectively [24,33,37-39]. Meanwhile, Ni 2p XP spectra of reduced (i.e. 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup>) catalyst was also recorded and Ni2p3/2 binding energy values centred at 852.5 eV and 855.4 eV were assigned for Ni<sup>0</sup> and NiO, respectively (Fig. 4Ab) [24,38]. Presence of oxide form of nickel was due to re-oxidation of surface Ni<sup>0</sup> (metallic) before XPS analysis [24,38] or due to the interaction of surface metallic Ni atoms with the surface oxygen of TiO<sub>2</sub>. Spent (2.6 % Ni-TiO<sub>2</sub><sup>EG-W-S</sup>) catalyst exhibited three component binding energy values of Ni2 $p_{3/2}$ , centred at 852.6 eV, 854.5 eV and 856.2 eV with the corresponding satellite peaks (Fig. 4Ac). In the spent catalyst, binding energy values at 852.6 eV and 854.5 eV can be assigned for Ni<sup>0</sup> and NiO, respectively. While the binding energy value at 856.2 eV could be assigned for Ni<sub>2</sub>O<sub>3</sub> as reported in literature [24]. From TEM analysis, it can be easily seen that the active Ni-species was present at the catalyst surface, interacting with TiO2. Now, if we look at the XPS analysis, our target was not the quantification of Ni but the investigation of the Ni-species present at the catalyst surface. From XPS analysis of 2.6 % Ni-TiO2<sup>EG-W</sup> catalyst and analysing the intensity and area under the peaks, we can say that a good amount of Ni-species was present at the surface. Also, from metal dispersion analysis we have found that the Ni-species size was smallest for 2.6 % Ni-TiO2<sup>EG-W</sup> catalyst. In this case, Ni-atom of the Ni-species interacts with the surface O-atom of TiO<sub>2</sub> and the electron transfers between Ni-atom and O-atom of TiO<sub>2</sub> creates metal-support interaction. As the size of the Ni-species decreases, the interfacial surface ratio of Ni-species to TiO<sub>2</sub> increases and the interaction between Ni-species and TiO<sub>2</sub> becomes stronger, which is actually the case for 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst. In the fresh 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst, Ti  $2p_{3/2}$  represented

In the fresh 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst, Ti  $2p_{3/2}$  represented binding energy values centred at 457.4 eV and 459.5 eV (Fig. 4Ba). First peak could be assigned for Ti<sup>+3</sup> species which is close to reported literature [40]. The second peak at 459.5 eV was assigned for Ti<sup>+4</sup> which is also consistent with the reported literature [41]. Similarly, 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst did not show any change in Ti-2p spectra (Fig. 4Bb) and confirmed the presence of Ti<sup>+3</sup> and Ti<sup>+4</sup>, after H<sub>2</sub>-pretreatment. While 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-S</sup> catalyst exhibited binding energy value at 458.3 eV indicating the presence of Ti<sup>+4</sup> in the spent catalyst (Fig. 4Bc) [42]. O 1s spectra of fresh (2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst exhibited binding energy values which were located at 529.4 eV and 530.9 eV (Fig. 4Ca). O 1s spectra of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst showed binding energy values at 528.1 eV, 529.8 eV and 531.5 eV (Fig. 4Cb). After deconvolution, spent (2.6 % Ni-TiO<sub>2</sub><sup>EG-W-S</sup>) catalyst displayed binding



Fig. 2. TEM images of 2.6 % Ni-TiO2<sup>EG-W</sup> (a and b), 2.6 % Ni-TiO2<sup>EG-W-H</sup> (c), 2.6 % Ni-TiO2<sup>EG-W-S</sup> (d and e) catalysts and corresponding SAED patterns (inset).

energy values at 529.4 eV, 531.1 eV and 532.8 eV (Fig. 4Cc). The binding energy values at 529.4 eV, 529.8 eV and 529.4 eV for fresh, reduced and spent catalysts were assigned for lattice oxygen of metal oxides (NiO<sub>x</sub> and TiO<sub>2</sub>) [9,24]. Binding energy values at 530.9 eV, 531.5 eV and 531.1 eV for fresh, reduced and spent catalysts were assigned for adsorbed surface oxygen or hydroxyl species [9,24]. For reduced and spent catalysts, binding energy values at 528.1 eV and 532.8 eV can be assigned for O atoms present at top layer of the surface metal oxide and O atoms of adsorbed water molecule [38], respectively.

Reducibility behaviour of particular system is directly influenced by the size of metal nanoparticles and catalyst synthesis procedure [26a,43]. In addition, interaction between active metal and support of a supported catalyst can be also determined by its respective TPR profile. H<sub>2</sub>-TPR profiles of TiO<sub>2</sub><sup>P</sup> and 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst are shown in Fig. 4D. Literature reports revealed that pure TiO<sub>2</sub><sup>P</sup> exhibited a broad low intensity H<sub>2</sub>-consumption peak at ~570 °C (Fig. 4 Da), which was likely due to reduction of surface Ti<sup>+4</sup> to Ti<sup>+3</sup> [44–46]. From the TPR profile of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst, different interaction pattern between Ni-oxide and TiO<sub>2</sub> nanoparticles can be clearly observed. TPR profile of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst exhibited three H<sub>2</sub>-consumption

peaks which were centred at 252 °C, 327 °C and 406 °C, indicating three different sized NiOx species interacting with the support in different manner i.e. different metal-support interaction (Fig. 4Db). As reported in literature [26a,47], the surface particles are easily reduced than bulk structures because of their accessibility for reduction. Moreover, core species are not readily exposed for reduction during the diffusion of molecular hydrogen over the surface of active species and hence, it requires higher temperature to reduce completely [26a]. In our case, first smaller H2-consumption peak at 252 °C was ascribed for smaller easily reducible surface NiOx particles [24] and second peak located at 327 °C was due to a little bit bigger NiO<sub>x</sub> particles, while the third one H<sub>2</sub>-consumption peak located at 406 °C can be ascribed for larger NiO<sub>x</sub> particles and/or may be due to two step reduction [24] of Ni<sub>2</sub>O<sub>3</sub> species  $(Ni_2O_3 \rightarrow NiO \rightarrow Ni^\circ)$  which matched well with the XPS results of fresh  $(2.6 \% \text{ Ni-TiO}_2^{\text{EG}-\text{W}})$  catalyst. Hence, different metal-support interactions due to different sized Ni-oxide particles are evidenced from the TPR profile. In the TPR profile of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst, a smaller hump at higher temperature region (without clear T<sub>max</sub>, value) was also observed which was probably due to reducible surface Ti<sup>4+</sup> species [45]. TPR profiles of 2.7 % Ni-TiO<sub>2</sub><sup>W</sup> and 2.8 % Ni-TiO<sub>2</sub><sup>EG</sup> catalysts



Fig. 3. Elemental mapping of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> [a-d] catalyst.



Fig. 4. A] Ni-2p; B] Ti-2p; C] O-1 s XP spectra of a] 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst; b] 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst; c] 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-S</sup> catalyst; D] TPR profiles of a] TiO<sub>2</sub><sup>P</sup>; b] 2.6 % Ni-TiO<sub>2</sub> <sup>EG-W</sup> catalyst.

were also recorded and described in the ESI (Fig. S6A).

### RAMAN spectroscopy

Raman spectra of TiO<sub>2</sub><sup>P</sup>, 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup>, 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> and 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-S</sup> catalysts are represented in Fig. 5A and Fig. 5B. In the Raman spectra of TiO<sub>2</sub><sup>P</sup>, bands centred at 144.9 cm<sup>-1</sup>, 198.1 cm<sup>-1</sup>, 396.7 cm<sup>-1</sup>, 515.2 cm<sup>-1</sup>, 518 cm<sup>-1</sup> (superimposed on 515.2 cm<sup>-1</sup>), 638.9 cm<sup>-1</sup> were attributed to E<sub>g</sub>, E<sub>g</sub>, B<sub>1g</sub>, A<sub>1g</sub>, B<sub>1g</sub>, E<sub>g</sub> vibrational modes of anatase TiO<sub>2</sub> (Fig. 5Aa) [48,49]. Literature report revealed that characteristic Raman band for anatase TiO<sub>2</sub> (~144.9 cm<sup>-1</sup>) has tenfold greater intensity than any other phonons of this phase [50]. 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst showed shifts in bands position which were centred at 151.7 cm<sup>-1</sup>, 201.7 cm<sup>-1</sup>, 396.3 cm<sup>-1</sup>, 512.3 cm<sup>-1</sup>, 518.6 cm<sup>-1</sup> (superimposed on 512.3 cm<sup>-1</sup>), 632.2 cm<sup>-1</sup> (Figs. 5Ab, 5Bb), which is due to phonon confinement and surface stress [48b].

After H<sub>2</sub>-pretreatment, slight change in band position was observed in the 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst (Fig. 5Ac). Such spectra of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst indicated that no other phase of TiO<sub>2</sub> (i.e. rutile, brookite) was observed i.e. only anatase phase was predominating phase before catalysis (after H<sub>2</sub>-pretreatment) [49a]. Raman spectra of spent (2.6 % Ni-TiO<sub>2</sub><sup>EG-W-S</sup>) catalyst exhibited all the six Raman active bands for anatase TiO<sub>2</sub> except very minute shifting in band position toward higher wavenumber (i.e. 152, 204, 399, 515.5, 519.2 and 634.3 cm<sup>-1</sup>) from the fresh one (2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst), indicating stability of the catalyst after catalysis (Fig. 5Ad).

As reported in literature [24,51], NiO exhibits four Raman active bands centred at around 420 cm<sup>-1</sup>, 500 cm<sup>-1</sup>, 708 cm<sup>-1</sup> and 1075 cm<sup>-1</sup> for NiO vibration mode, in which band at ~420 cm<sup>-1</sup> and ~500 cm<sup>-1</sup> (intense bands) were assigned to first order transverse optical (TO) and longitudinal optical (LO) phonon modes of NiO. The other two Raman active bands at ~708 cm<sup>-1</sup> and ~1075 cm<sup>-1</sup> were assigned for combination of 2TO and 2LO, respectively [51]. In our case, the bands corresponding to NiO vibration mode, were not separately distinguishable in 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup>, 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> and 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-S</sup> catalysts. The possible reason behind this might be due to very low Ni loading (2.6 %) in the catalysts or there might be overlapping of NiO (weak) bands with A<sub>1g</sub> + B<sub>1g</sub> band of TiO<sub>2</sub> which is indicated by broadness in A<sub>1g</sub> + B<sub>1g</sub> band of TiO<sub>2</sub> in the synthesized catalysts as compared to pure TiO<sub>2</sub><sup>P</sup> [Fig. 5A (b, c, d)]. For comparison purpose, Raman spectra of 2.7 % Ni-TiO<sub>2</sub><sup>W</sup> and 2.8 % Ni-TiO<sub>2</sub><sup>EG</sup> catalysts were also recorded and it is provided in the ESI (Figs. S6B & S6C).

### UV-vis DR spectroscopy

To demonstrate the optical properties of prepared catalyst, UV-vis



Fig. 5. A] Raman spectra; B] Raman shifts of Eg mode of a] TiO<sub>2</sub><sup>P</sup>; b] 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup>; c] 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup>; d] 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-S</sup> catalysts.



Fig. 6. UV-vis DR spectra of TiO<sub>2</sub><sup>P</sup> and 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst.

DR spectra were recorded for  $\text{TiO}_2^{P}$  and 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst and depicted in Fig. 6. Pure  $\text{TiO}_2^{P}$  exhibited strong absorption band at 312 nm, which corresponds to  $\text{O}^{2-} \rightarrow \text{Ti}^{4+}$  charge transfer interaction [52].

On the other hand, Ni loaded catalyst such as 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> showed an absorption band at 300 nm. Noticeable shift in absorption edge toward higher wavelength was observed in case of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst than pure TiO<sub>2</sub><sup>P</sup>, which might be due to charge transfer interaction between NiO and TiO<sub>2</sub> particles. In the visible region, band from 600 – 800 nm is the characteristic of coloured species present in the sample [53]. Therefore, 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst also exhibited a weak broad absorption band (~720 nm) in visible region which is responsible for coloured species (i.e. NiO). UV–vis-DR spectra of 2.7 % Ni-TiO<sub>2</sub><sup>W</sup> and 2.8 % Ni-TiO<sub>2</sub><sup>EG</sup> catalysts were also recorded and described in the ESI (Fig. S6D).

The k<sup>3</sup>-weighted Fourier transform of Ni k-edge EXAFS spectra of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> and 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-S</sup> catalysts are shown in Fig. S7 and Table S2. For comparison and to know about more characteristic differences, we have performed the EXAFS analysis of 2.7 % Ni-TiO<sub>2</sub><sup>W</sup> and 2.8 % Ni-TiO<sub>2</sub><sup>EG</sup> catalysts also and it is provided in the ESI (Fig. S7 and Table S2).

Catalytic performance

Catalytic performance of different Ni-TiO<sub>2</sub> catalysts was examined for selective reduction of nitrobenzene to azoxybenzene at room temperature in aqueous medium and at atmospheric pressure. Generally, metallic nickel is more reactive than its oxide form for hydrogenation reactions [54]. Therefore, H<sub>2</sub>-pretreated catalysts were used for catalysis. Number of experiments were conducted to find the most efficient system after examining the reactivity of different synthesized Ni-TiO<sub>2</sub> catalysts as a function of reaction time, reactant:reducing agent mole ratio, temperature, solvents, and active metal loading etc. (Tables 2 and S3, Figs. 7, 8, S8-S10). Hydrazine hydrate was used as transfer hydrogenating agent for reduction of nitro-compounds, where in-situ generated active hydrogen species reduced the nitro-compounds and produced water and N<sub>2</sub> as by-products, after catalysis. Nitrobenzene was considered as a reference compound for optimization and comparison (Scheme 2). Catalytic activities of synthesized catalysts were thoroughly investigated and compared (see ESI) to establish the most efficient catalyst system (2.6 % Ni-TiO2<sup>EG-W</sup>) for selective reduction of nitrobenzene to azoxybenzene.

Initially, the reaction was carried out in presence of commercial NiO and commercial TiO<sub>2</sub>, but these metal oxides did not initiate the reaction as depicted in Table 2, entries 1 and 2. At room temperature, 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> (H<sub>2</sub>-pretreated) catalyst exhibited 89 % nitrobenzene conversion with 92 % azoxybenzene selectivity at room temperature within 12 h, using 1:1.5 nitrobenzene to hydrazine hydrate mole ratio (Table 2, entry 3). Furthermore, we extended the time of ongoing reaction up to 16 h to observe the changes in reactivity of synthesized catalyst. No specific change in reactivity of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst was observed up to 16 h of reaction time (Fig. 7A).

Effect of temperature studies for 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst revealed that the rate of reaction was increased with increasing temperature (Fig. 7B). On increasing the temperature from RT to 80 °C, decrease in product selectivity was observed at higher temperature over 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst. At 80 °C, 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst showed ~96 % conversion of nitrobenzene with 82 % selectivity of azoxybenzene. Higher selectivity of azoxybenzene (92 %) was observed at room temperature for 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst (Fig. 7B). Reaction data of synthesized 2.7 % Ni-TiO<sub>2</sub><sup>W-H</sup> and 2.8 % Ni-TiO<sub>2</sub><sup>EG-H</sup> catalysts is also provided in the ESI (Figs. S8–S10 and Table S3).

After that, we altered the nitrobenzene:hydrazine hydrate mole ratio (1:0.5, 1:1.5 and 1:2.5) without changing the other reaction parameters such as temperature (RT), time (12 h) and solvent (water)



**Fig. 7.** A] Effect of run time over 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst [Reaction condition: Nitrobenzene = 1 g; solvent (water) = 10 mL; catalyst used = 10 wt. % w.r.t. reactant; 25 °C; time = 16 h; Nitrobenzene : N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O = 1:1.5 (mole ratio)]; B] Effect of temperature over 2.6% Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst [Reaction condition: Nitrobenzene = 1 g; solvent (water) = 10 mL; catalyst used = 10 wt. % w.r.t. reactant; variable reaction temp. (25 °C, 40 °C, 60 °C, 80 °C); time = 12 h; Nitrobenzene:N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O = 1:1.5 (mole ratio)].



**Fig. 8.** A] Effect of nitrobenzene:hydrazine hydrate mole ratio over 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst [Reaction condition: Nitrobenzene = 1 g; solvent (water) = 10 mL; catalyst used = 10 wt. % w.r.t. reactant; 25 °C; time = 12 h; variable Nitrobenzene to  $N_2H_4$ . $H_2O$  mole ratio (1:0.5, 1:1.5, 1:2.5); B] Effect of Ni loading (wt. %) over X % (X = 1.3, 2.6, 5.3) Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalysts [Reaction condition: Nitrobenzene = 1 g; solvent (water) = 10 mL; catalysts used = 10 wt. % w.r.t. reactant; 25 °C; time = 12 h; Nitrobenzene = 1 g; solvent (water) = 10 mL; catalysts used = 10 wt. % w.r.t. reactant; 25 °C; time = 12 h; Nitrobenzene = 1 g; solvent (water) = 10 mL; catalysts used = 10 wt. % w.r.t. reactant; 25 °C; time = 12 h; Nitrobenzene: $N_2H_4$ . $H_2O$  = 1:1.5 (mole ratio)].

(Fig. 8A). On increasing nitrobenzene to hydrazine hydrate mole ratio, the conversion of nitrobenzene was increased to some extent but the selectivity of azoxybenzene was dropped for 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst. When we used nitrobenzene to hydrazine hydrate mole ratio 1:2.5, conversion of nitrobenzene was found to be ~90 % with 75 % azoxybenzene selectivity for 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> system. Higher selectivity of azoxybenzene was observed using nitrobenzene to hydrazine hydrate mole ratio 1:1.5 for 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst. It was observed that formation of aniline was taking place in case of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> while using 1:2.5 nitrobenzene to hydrazine hydrate mole ratio (Fig. 8A).

In this study, 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst showed metal (Ni) dispersion of 14.9 % which is highest among other synthesized catalysts. Metal dispersion analysis showed the percentage of surface Ni particles of the respective catalysts, which also indicated that with decreasing metal dispersion, size of Ni particles increases [26a,33,34]. TPR patterns of the other synthesized catalysts (by changing solvents during synthesis) also showed that with decreasing Ni-dispersion, reducibility

of the Ni-oxide particles decreased, which showed higher temperature reduction peaks [26a,33,34]. Among the synthesized catalysts, 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst showed most easily reducible Ni-oxide particles [47b] and these particles are the smallest compared to other synthesized catalysts, according to metal dispersion analysis. Smaller surface Ni-species generated higher metal-support interfacial surface area, making the interaction very strong which effected on the catalyst's activity [26a,33,34]. Our characterization results suggested that 2.6 % Ni-TiO<sub>2</sub><sup>EG-W</sup> catalyst having smallest Ni-species among the synthesized catalysts with stronger metal-support interactions and the catalyst showed superior catalytic activity as compared to others.

We have also thoroughly examined the activity results by changing reaction time, reactant to reductant mole ratio and temperature for other two synthesized catalysts (i.e. by changing solvents) (Figs. S8–S9). Additionally, activity result of catalyst synthesized by conventional wetness impregnation method (2.6 % Ni-TiO<sub>2</sub><sup>Imp.Com.</sup>) is also shown in ESI (Table S3, entry 1). 2.6 % Ni-TiO<sub>2</sub><sup>Imp.Com.</sup> catalyst showed very low reactivity with 5% nitrobenzene conversion. During study, we



Scheme 2. Selective reduction of nitrobenzene to azoxybenzene.

Table 2		
Activities of Ni-TiO2 nanocr	ystals for reduction	n of nitrobenzene.

S. No.	Catalysts <sup>@</sup>	Hydrogen source	Solvent	C <sub>NB</sub> (%)	S <sub>P</sub> (%)	S <sub>P</sub> (%)		
					Azo (1)	Azoxy (2)	Aniline (3)	
1	NiO <sup>Com.</sup>	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	H <sub>2</sub> O	-	-	-	-	-
2	TiO2 <sup>Com.#</sup>	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	$H_2O$	-	-	-	-	-
3	2.6 % Ni-TiO <sub>2</sub> <sup>EG-W-H</sup>	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	$H_2O$	89	4	92	4	1008
4	2.6 % Ni-TiO <sub>2</sub> <sup>EG-W-H</sup>	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	DMF, EtOH	~ 87	4	~ 91	5	~975
5	2.6 % Ni-TiO <sub>2</sub> <sup>EG-W-H</sup>	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	TOL	~12	14	76	10	~112
6	2.6 % Ni-TiO <sub>2</sub> EG-W-H*	H <sub>2</sub>	$H_2O$	90	_	1	99	11
7	2.6 % Ni-TiO <sub>2</sub> EG-W-R	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	H <sub>2</sub> O	88	4	91	5	986

Reaction conditions: Nitrobenzene = 1 g; solvent = 10 mL; catalyst used = 10 wt. % w.r.t. reactant; 25 °C; time = 12 h; Nitrobenzene :  $N_2H_4$ . $H_2O$  = 1:1.5 (mole ratio);  $C_{NB}$ (%): Conversion of nitrobenzene;  $S_P$ (%): Selectivity of different products; TOL = toluene; @ =  $H_2$ -pretreated catalysts were used; # = without  $H_2$ -pretreatment; \* = reaction performed in high pressure Parr reactor using 1.0 MPa  $H_2$ ; R = catalyst after four recycle; TON (Turnover number) = [moles of desired product (azoxybenzene) formed]/[moles of nickel used].

have found that 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst showed higher activity among different synthesized catalysts at room temperature in 10 mL of solvent (water) within 12 h of reaction time, using 1:1.5 reactant to reductant mole ratio (Table 2, entry 3). Therefore, we targeted the most efficient 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst to further optimize the other parameters such as solvent effect and active metal loading (Ni wt.%) etc. To check the effect of solvent over 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst, we used variety of polar and non-polar solvents (Table 2, entries 4 and 5) and found that polar solvents such as ethanol, DMF, etc. showed higher yield of desired product whereas, non-polar solvent such as toluene showed moderate yield of corresponding product.

Thereafter, effect of active metal loading studies revealed that on increasing the active metal (Ni) content (wt.%), conversion of nitrobenzene was increased as the number of available active sites was increased for catalysis, but the selectivity of desired product was decreased (Fig. 8B). 1.3 % Ni-TiO<sub>2</sub>  $^{EG-W-H}$  catalyst showed ~43 % conversion of nitrobenzene with 64 % azoxybenzene selectivity, probably due to presence of lesser number of active site for catalysis (Table S3, entry 2). Higher loading of catalyst (5.3 % Ni-TiO $_2^{EG-W-H}$ ) showed higher conversion (98 %) but the selectivity of azoxybenzene was decreased (35 %) which is the drawback of system (Table S3, entry 3). Although, 5.3 % Ni-TiO $_2^{\rm EG-W}$  catalyst have higher surface area with more Ni contents but it showed comparatively lower selectivity of azoxybenzene than 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst which might be due to presence of bigger, agglomerated NiOx crystals (as reflected in respective XRD pattern, Fig. S2e) and lower metal dispersion. Hence, from the effect of active metal loading studies, 2.6 % (wt. %) Ni loading was found to be optimum loading to get maximum yield of desired product (i.e. azoxybenzene).

Performance of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst was also tested under 1.0 MPa H<sub>2</sub> pressure, which produced aniline selectively (Table 2, entry 6). This showed that under H<sub>2</sub> pressure azoxybenzene could further reduce to aniline. Therefore, it can be concluded from the experiment that operating reaction conditions is also responsible to move the path of reaction. To compare the catalytic activities of other catalysts with 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst, please see the Table S3 in the ESI. Furthermore, we did the kinetic calculations for selective reduction of nitrobenzene to azoxybenzene over 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst. As reported in literature [12,55], selective reduction of nitrobenzene follows the pseudo-first order kinetics. We calculated rate constant values for selective reduction processes and plotted ln ( $C_t/C_0$ ) verses time for 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst (Fig. S11A). We calculated activation energy by using Arrhenius equation, which was found to be around 6.2 kJ mol<sup>-1</sup> for 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst (Fig. 9) and it is much lower than the other synthesized catalysts (Fig. S12), indicating the superiority of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> system.

For catalyst recyclability, repeated use of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst was carried out under optimized reaction conditions (Fig. S13). Recycling experiments were also conducted up to four successive cycles for other two catalysts (Fig. S13). It was found that 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst showed negligible loss in reactivity (Table 2 entry 7, Fig. S13) than others, which is an indication of its heterogeneous nature. Catalytic activities of the synthesized catalysts were found to be dependent on surface area, metal dispersion, active metal species size and formation of solid solution phase of the catalysts (see ESI, Figs. S2–S4, S6, Table S1 & S3).

According to Haber's mechanism [56], nitro group containing



Fig. 9. Plot of ln k vs. 1000/T ( $K^{-1}$ ) for 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst.

compounds are reduced to anilines in stepwise manner by forming nitroso and hydroxylamine intermediates. Meanwhile, when these intermediates undergo condensation step, then formation of azoxy and azo compounds takes place [12,56-58]. From last few years, Corma and coworkers [59] continuously working on selective reduction of nitroarenes over various catalytic systems (mainly gold as active metal) and emphasized the role of support for selective reduction processes. During their studies, they investigated the effect of support by using Au/CeO2 and Au/TiO<sub>2</sub> (with same Au particle size) catalysts and found that support does not act as a simple carrier but also intervene in the reaction during catalysis. Previously, we reported Pt-CeO<sub>2</sub> [23] and Ni-ZrO<sub>2</sub> [24] catalyst for the selective reduction of nitroarenes to corresponding amines using molecular hydrogen and found that reaction was proceeding via direct route. But in present case, the reaction proceeded through condensation route, where nitroso intermediate condensed with hydroxylamine intermediate to form azoxy compound selectively. The azobenzene and aniline were formed in very less amount. To investigate the reaction pathway, we subjected the reaction intermediates (nitrosobenzene, phenylhydroxylamine, nitrosobenzene + phenylhydroxylamine, azoxybenzene, azobenzene) as reactants, under optimized reaction condition (Table S4). During the study, it was found that when we introduced nitrosobenzene as a reactant then good yield of azoxybenzene was formed within 8h of reaction time. Moreover, when mixture of nitrosobenzene and phenylhydroxylamine was subjected then higher yield of azoxybenzene was obtained within 5 h of reaction time. While phenylhydroxylamine, azoxybenzene and azobenzene reduced to aniline with a poor yield i.e. only trace amount of aniline was detected, which indicated that further reduction of azoxybenzene to azobenzene and azobenzene to aniline was not favourable with 2.6 %  $\rm Ni\math{-}TiO_2^{EG-W-H}$  catalyst. In our case, strong metal-support interaction (SMSI) favoured the rapid dissociation of hydrazine hydrate at the metal support interfaces and the formation of active hydrogen species take place. After that, nitrobenzene gets physisorbed over the active surface of the catalyst and the subsequent conversion of nitrosobenzene to phenylhydroxylamine occurs. As soon as phenylhydroxylamine form, it immediately reacts with nitrosobenzene to form dihydroxy intermediate [11], which get dehydrated to form azoxybenzene. Further reduction of azoxybenezene to azobenzene and azobenzene to aniline does not proceed under optimized reaction conditions, which might be due to much higher hydrogenation barrier of these steps than previous steps (up to azoxybenzene formation) [11]. Therefore, we can conclude that the reduction of nitrobenzene followed the condensation route over 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst.

Turnover number (TON) is an important factor to measure the efficiency of catalytic system. The higher TON of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst again confirmed the superiority of system than other prepared catalysts (Tables 2 & S3) and reported non-noble metal based catalyst systems (Table S5). It was found that with increasing metal dispersion and decreasing Ni-species size of the catalyst, catalytic activity increased. So, it is obvious and also supported by different literature reports that active Ni-species sites at the catalyst's surface are the active centres for the reaction. Here, strong metal-support interaction at the catalyst surface is generated by electron transfer between metal (Ni) and support (TiO<sub>2</sub>) but not due to solid solution and/ or encapsulation phenomena.

To further elucidate the applicability of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst, the reaction was extended to different nitroarenes, under optimized reaction condition. It was noted that 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst showed excellent yield of azoxy compounds with *para*-substituted (electron withdrawing or electron donating) nitro compounds. 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst showed 78 %–89 % conversion of different nitro compounds with the 84 %–92 % selectivity of corresponding azoxy compounds (Table S6).

### Conclusions

We have developed a facile, cost-effective, selective and efficient Ni-TiO<sub>2</sub> catalyst system for the removal of organic pollutants. The catalyst  $(2.6 \% \text{ Ni-TiO}_2^{\text{EG}-\text{W}})$  synthesized by hydro-solvothermal method using poly (diallyldimethylammonium chloride) and hydrazine hydrate was highly active for hydrogenation process. It was observed that 2.6 % Ni-TiO2<sup>EG-W-H</sup> catalyst exhibited very high activity (high TON and low activation energy) for room temperature selective reduction of nitrobenzene to azoxybenzene, in aqueous medium using hydrazine hydrate as a reductant and conversion of nitrobenzene was found to be 89 % with 92 % selectivity of azoxybenzene. In addition, 2.6 % Ni-TiO $_2^{EG-}$ <sup>W-H</sup> catalyst also showed good yield of azoxy compounds with different substituted nitroarenes, under optimized reaction conditions. Probable reason for excellent activity of 2.6 % Ni-TiO<sub>2</sub><sup>EG-W-H</sup> catalyst was due to presence of highly dispersed ( $\sim 6.8 \text{ nm}$ ) Ni nanoparticles over TiO<sub>2</sub> nanocrystals, providing large number of active sites for catalysis and strong metal-support interaction at the catalyst surface, which prevented the leaching of active species during catalysis. Hence, 2.6 % Ni- $\mathrm{TiO}_{2}^{\mathrm{EG-W-H}}$  catalyst maintained heterogeneity throughout the reaction and recycled up to several successive runs without significant loss in reactivity. Performing number of experiments, we concluded that the reduction of nitrobenzene to azoxybenzene occurs via condensation route instead of direct route. During the study, it was also found that the catalyst preparation methods and solvents used during catalyst synthesis significantly altered the physicochemical characteristics as well as reactivity of respective catalyst system.

## **Declaration of Competing interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### CRediT authorship contribution statement

Astha Shukla: Investigation, Formal analysis, Validation, Writing original draft. Rajib Kumar Singha: Visualization, Writing - review & editing. Takehiko Sasaki: Formal analysis, Writing - review & editing. Shubhadeep Adak: Formal analysis. Sonu Bhandari: Validation. V.V.D.N. Prasad: Writing - review & editing. Ankur Bordoloi: Writing - review & editing. Rajaram Bal: Conceptualization, Writing - review & editing, Supervision.

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### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.110943.

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