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Surfactant directed Ag_{1-x}Ni_x alloy nanoparticle catalysed synthesis of aromatic azo derivatives from aromatic amines

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Graphical Abstract



Highlights

- Multiply twinned AgNi bimetallic alloy nanoparticles heterogeneous catalyst
- Complete conversion of aromatic amines to the symmetric or asymmetric azobenzenes
- Breakthrough in catalytic performance, absolute selectivity (100%)
- A high stability and recyclability of the catalyst without compromising morphology

Abstract

A bimetallic and multiply twinned $Ag_{1-x}Ni_x$ (x = 0.2, 0.4, 0.6, 0.8) alloy nanoparticle (MTANP), for the first time has been explored as an efficient heterogeneous catalyst in the industrially important reaction conversion of aromatic amines to the symmetric or asymmetric azobenzenes by the activation of aerobic molecular oxygen. Here, we

demonstrated that the as-synthesized and optimized $Ag_{0.6}Ni_{0.4}$ alloy NPs showed breakthrough in catalytic performance, enabling quantitative aromatic amine conversion and absolute selectivity in azobenzenes (100%) under aerobic green reaction conditions without using the environmentally unfriendly nitrites and any other hazardous materials. A high stability and recyclability of the catalyst is observed and investigated by several instrumental techniques. The key to the effective process is found to be size effect, electronic effect and structural defect, and the presence of surfactant at the surfaces of the AgNi MTANP catalyst.

Keywords: AgNi alloy nanoparticles; oxygen activation; aniline; azobenzene

1. Introduction

Aromatic azo compounds and their derivatives are important class of commercial and high-value chemicals used as organic dyes, indicators, food preservatives, additives radical reaction initiators, polymers and therapeutic agents etc.[1-4]. Industrially azo compounds are produced by different methods like diazotization [5],[6] and coupling (coupling of primary arylamines with nitroso compounds) [7], condensation of nitro compounds with amines [8], reduction of nitro compounds [9], oxidation of amino compounds (aromatic primary amines) [10], oxidation of hydrazo derivatives [11] and reduction of azoxybenzene [12] derivatives

[6],[8]. Notably, unsymmetrical azobenzenes were synthesized in two steps by proceeding through aniline or nitrobenzene and stoichiometric amounts of nitrite salts or other oxidants via diazonium salt or nitrosobenzene intermediates, with inorganic salts as waste [13],[14]. Even though numerous efforts have been made towards the synthesis of azo derivatives but there is currently a lack of a generally applicable catalyst that is capable of oxidative coupling of aniline under green conditions for getting high yields of product (symmetric as well as unsymmetrical azobenzenes) and secondly, to prevent the use of stoichiometric and environmentally unfriendly oxidants, such as lead salts, mercury salts etc [15].

In this context, the use of molecular oxygen or the aerial oxygen as primary oxidant in the catalytic reactions will have great significance as the green chemistry point of view [16]. Oxidation of organic compounds by economical, readily available and environmental friendly oxidants such as hydrogen peroxide, molecular oxygen etc. are attractive from the perspective of industrial technology and synthetic purposes [17]. Because of the limited reports on the efficient catalyst for the activation of the molecular oxygen, there is need to explore more in this field [18]. In this process, nanoparticles (NPs) of various materials have been introduced as new catalysts in many organic transformation reactions, such as in oxidation [19],[20], C-C coupling [21],[22],[23], C-S coupling [24] etc. For the consideration of economical and green reaction protocols, first time Grirrane et al. [1] designed a route for the synthesis of aromatic azo compounds catalysed by gold NPs using O₂ (3-5 bar) as the oxidant at 100 °C. Yadav et. al.[8] have reported the silver substituted octahedral molecular sieve of cryptomelane type (Ag-OMS-2 15 wt/wt%) catalyst for the conversion of nitroareane to azobenzene with 80% selectivity. Bal group [25] have reported the use of Ag NP supported on nanostructured tungsten oxide in the oxidative coupling of aniline to azoxybenzene using H₂O₂ as an oxidant and found 87%-91% conversion and selectivity. Furthermore, singlecrystalline octahedral Au-Ag nanoframes [26] and Ag/C support [27] has been used in the formation of azobenzene in the presence of direct supply of oxygen. However, in most reports, either high temperature or high pressure was used or the yields of the reactions were very poor.

Bimetallic alloy nanoparticles are important class of materials because of their outstanding and unique catalytic, electronic, optical, and magnetic properties arise from synergistic effect and are used in organic synthesis, fuel cell, reduction reactions, magnetic recording, antibacterial activity, etc. [28],[29],[30],[31]. However, to our knowledge, we do not see the use of low cost bimetallic alloy NPs in catalysing the subjected organic

transformation reactions in literature till date. In this context to fill the gap we wish to report the efficient catalysis of multiply twinned AgNi alloy nanoparticles in oxidative coupling of aromatic amines under green condition. AgNi alloy NPs are one of the new additions to the class of alloy particles that have recently drawn attention for their unique kinds of synthesis (complete immiscibility of metals, lower surface energy of Ag and 14% lattice mismatch) and multifunctional properties [32]. Among the as-synthesized Ag_{1-x}Ni_x NPs (where x = 0, 0.2,0.4, 0.6, 0.8, 1.0), Ag_{0.6}Ni_{0.4} alloy NP showed the best performance under mild conditions and we demonstrated that our catalyst is highly selective, efficient, easily separable and recyclable under the normal aerobic condition to give the required symmetric or asymmetric azo compounds in very high yield. In addition, Ag_{0.6}Ni_{0.4} MTANPs also catalyse oxidative coupling of benzylamine with very high selectivity (99.9%) and activity (96.0%) towards Nbenzylidene-1-phenylmethanamine formation showing wide applicability of present alloy nanocatalyst.

2. Materials and Methods

2.1. Materials

All the reagents were of analytical grade and were used without further purification. Hexadecylamine (HDA, 98%), 1-octadecene (ODE, 90%) and oleylamine (OLA, 90%) were from Sigma-Aldrich, USA. Nickel nitrate hexahydrate (Ni(NO₃)₂.6H₂O) and potassium hydroxide (KOH) were from Merck, India and silver nitrate (AgNO₃, 99.9%) from Rankem analytical reagent, India. Aniline and anisidine were obtained from SRL, India.

2.2. Synthesis of Ag_{1-x}Ni_x Alloy and Ag Nanoparticles

The one pot wet chemical co-reduction method was used to synthesize alloy nanoparticle $(Ag_{1-x}Ni_x)$ as reported in our earlier study [32]. In a typical synthesis, AgNO₃ (0.8-0.2 mmol), NiNO₃.6H₂O (0.2-0.8 mmol) and surfactant HDA (1.5 mmol) were added to 8 mL of ODE in a three necked round-bottom (RB) flask equipped with temperature controller, magnetic stirring bar and connected to a condenser. The reaction mixture was stirred vigorously and degassed at 110 °C for 30 min followed by increase of reaction temperature to 250 °C. At this temperature the reaction mixture was kept for 40 min under a continuous flow of N₂. The reaction mixture was cooled to room temperature naturally after the completion of the reaction and the product was purified by precipitation with ethanol. The as obtained precipitate was centrifuged and washed with ethanol for three times and finally dispersed in toluene for further characterizations or dried for catalytic studies. Ag NPs were synthesized

following the similar method as described above, however 1 mmol AgNO₃ was used without the addition of any Ni metal precursor while other parameters (surfactant, solvent, time, temperature, etc) were kept constant.

2.3. Synthesis of Ni Nanoparticles

Nickel NPs were separately synthesized following a similar approach as followed in our earlier report [32]. In a typical synthesis, Ni(OCOCH₃)₂.4H₂O (2 mmol) was added to OLA (16 mmol, 5.26 mL) in a three necked RB flask and degassed at 110 $^{\circ}$ C for 30 minutes. At this temperature, 1.6 mmol of TOP was injected to the reaction mixture under continuous N₂ flow and reaction mixture was brought to 220 $^{\circ}$ C and stirred at this temperature for next 2h. After completion of the reaction, product was precipitated and washed with ethanol and finally dispersed in toluene for further characterizations or dried for catalytic studies.

2.4. Characterization

The morphology and composition of the as-prepared products were characterized by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) imaging obtained from a Philips Technai G²30 transmission electron microscope operating at an accelerating voltage of 200 kV equipped with an energy dispersive X-ray spectroscopy (EDAX) attachment and elemental mapping feature. The phase and the crystallographic structure of the products were identified by X-ray diffraction (XRD, Bruker D8 Advance, Cu K α , $\lambda = 0.154\ 056\ \text{nm}$). Elemental compositions in the as-synthesized alloy samples were studied using an atomic absorption spectrometer (AAS, Zeenit 700p Analytik Jena). ¹H and ¹³C NMR spectra were recorded in DMSO on a Bruker Avance 400 MHz spectrometer. FTIR and UV-visible spectra were recorded in Perkin Elmer (Spectrum-RXI-59333, Bruker-Tensor 27) and Perkin Elmer Lambda-35 UV-Vis spectrophotometer, respectively. GC analysis was performed using a Shimadzu GC-2010 Plus instrument using N₂ as a carrier gas on FIDdetector using capillary column, Rtx-5 column (30 m x 0.25 mm x 0.25 mm, Restek, USA). GC conditions were as follows: initial oven temperature (80 °C for 3 min); ramp (15 °C/min); final temperature (180 °C); final time (10 min); injector temperature (230 °C); detector temperature (250 °C); injection volume (1 µL). An automatic micropore physisorption analyzer (Micromeritics ASAP 2020, U.S.A.) was used to determine surface areas of samples following the Brunauer-Emmett-Teller (BET) principle, and the pore parameters of the samples were determined with the Barrett-Joyner-Halenda (BJH) method, derived from N₂

adsorption-desorption measurements carried out at 77 K. Prior to analysis, samples were degassed in situ at 200 °C for 8 h.

2.5. Catalytic Experiments

All catalytic reactions were carried out in a RB flask. In a typical reaction for the synthesis of azobenzene, a mixture of 1 mmol aniline, 1 mmol KOH, 2.6 mg Ag_{1-x}Ni_x nanocatalyst and 2 mL of DMSO solvent were treated at 60 °C in open air. All the reactions were performed in aerial condition. The reaction mixture was vigorously stirred at the required temperature for the required time. The progression of the oxidation reactions were monitored by TLC in 5% ethyl acetate and hexane mixture and finally by GC analysis. For optimization, various catalysts (Ag, Ni and Ag_xNi_{1-x}) were applied under similar reaction condition as followed for azobenzene synthesis. The solvent variation study and catalyst loading and effect of reaction temperature study was done using Ag_{0.6}Ni_{0.4} alloy NPS, since this composition showed the best catalytic activity. The substrate scope study for oxidative coupling reaction was done using Ag_{0.6}Ni_{0.4} alloy NP under similar reaction conditions as followed for azobenzene synthesis and percentage conversion was again calculated by GC. For a symmetric and asymmetric coupling final product (azobenzene and 1-(4-methoxyphenyl)-2-phenyldiazene) was completely studied using various techniques like ¹H NMR, ¹³C NMR, IR and UV-Vis spectroscopy as shown below.

Oxidative coupling of aromatic amines to symmetric azobenzene: Ag_xNi_{1-x}, Ag or Ni NPs (2.6 mg) was added to a reaction mixture of aniline or derivatives of aniline (1 mmol, methoxyaniline, chloroaniline, thioaniline, nitroaniline), KOH (1 mmol) in DMSO (2 mL) and was vigorously stirred at 60 °C for 24 h in air. After cooling down to room temperature, the mixture was extracted with diethyl ether and purified by column chromatography to afford 84 mg (94.40%) of (E)-1,2-Diphenyldiazene. Orange solid; ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.93 - 7.91 (d, *J* = 7.6 Hz, 4H), 7.54 - 7.47 (m, 6H); ¹³C NMR (101 MHz, CDCl₃): δ (ppm) = 152.7, 131.08, 129.18, 122.93; IR (KBr): *v* = 3062, 1613, 1483, 1453, 1299, 1221, 1250, 1071, 1020, 776, 689 cm⁻¹; UV-Vis (in ethyl acetate): $\lambda_{max} = 317.5$ nm.

Synthesis of N-benzylidine-1-phenylmethanamine: Ag_{0.6}Ni_{0.4} alloy NP (2.6 mg) was added to a reaction mixture of benzylamine (1 mmol), KOH (1 mmol) in Toluene (2 mL) and was vigorously stirred at 60 °C for 24 h in air. After cooling down to room temperature, the mixture was extracted with diethyl ether and purified by column chromatography to obtain N-benzylidine-1-phenylmethanamine. In this case % conversion was calculated from NMR.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 8.34 (s, 1H), 7.71-7.70 (m, 2H), 7.40-7.25 (m, 8H), 4.76 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 161.6, 138.9, 135.6, 130.4, 128.1, 127.9, 127.6, 126.7, 126.4, 64.5.

Oxidative coupling of aromatic amines to asymmetric azobenzene. Ag_{0.6}Ni_{0.4} alloy NP (2.6 mg) was added to a reaction mixture of aniline (0.5 mmol), KOH (1 mmol), 4methoxybenzenamine (0.5 mmol) in DMSO (2 mL) and was vigorously stirred at 60 °C for 24 h in air. After cooling down to room temperature, the mixture was extracted with diethyl ether and later on the mixture was purified by column chromatography on silica gel to afford 63.1 mg (60 %) of 1-(4-methoxyphenyl)-2-phenyldiazene; yellow solid; ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 7.95 - 7.93 (m, 2 H), 7.90 - 7.88 (m, 2 H), 7.52 - 7.44 (m, 3 H), 7.03 - 7.01 (m, 2 H), 3.88 (s, 3 H); ¹³C NMR (CDCl₃, 101 MHz): δ (ppm) = 162.15, 152.85, 147.1, 130.48, 129.15, 124.87, 122.67, 114.31, 55.69; IR (KBr): v = 2962, 2923, 1601, 1501, 1252, 1140, 1029, 839, 799, 769, 688 cm⁻¹; UV-Vis (in Ethyl acetate): $\lambda_{max} = 345.0$ nm.

3. Results and Discussion

The synthesis protocol used for the synthesis of Ag_{1-x}Ni_x MTANPs was followed from our earlier report [32]. Since $Ag_{0.6}Ni_{0.4}$ composition showed the best catalytic activity as corroborated in the experimental section in the present study, characterizations of Ag_{0.6}Ni_{0.4} alloy NPs are discussed in this section as a representative case. The size, morphology and crystal structure of MTANPs was investigated by TEM analysis. Fig. 1. displays the low magnification TEM, high resolution TEM and SAED pattern for as synthesized Ag_{0.6}Ni_{0.4} alloy NPs. The low resolution TEM images of alloy NPs shows the multiple twinned nature that appears spherical at low resolution (Fig. 1a-b). The average particle diameter was found to be 20±1 nm which is consistent with our previous report. Furthermore, an image of a single isolated particle with higher magnification is shown in inset of panel b that clearly represent twinned structure in which primarily five crystalline domains oriented in different directions separated with twinned boundary are seen clearly. Therefore the particles are termed as multiply twinned alloy nanoparticles (MTANPs). The interplaner distance calculated from lattice fringes was 0.24 nm which is consistent with (111) plane of AgNi alloy NPs (Fig. 1c). SAED pattern confirms crystalline nature of alloy NPs where the (111), (200), (220) and (311) lattice planes can be ascribed to fcc structure of Ag_{0.6}Ni_{0.4} MTANPs (Fig. 1d).

The elemental composition of Ag and Ni was investigated using EDAX spectroscopy. The representative EDAX analysis of various Ag_xNi_{1-x} (X = 0.2-0.8) alloy samples is shown in Fig. 2a-d and obtained stoichiometric Ag/Ni ratios are entered in Table 1. EDAX results clearly represent expected Ag/Ni elemental ratios which indicates controlled synthesis of alloy NPs. To check the distribution of Ag and Ni elements in alloy NPs, elemental mapping in the STEM mode was carried out on $Ag_{0.6}Ni_{0.4}$ MTANPs sample which display homogeneous distributions of Ag and Ni in alloy NPs. (Fig. 1e–g). Further, we have carried out AAS measurements to determine the bulk elemental ratio of Ag and Ni in alloy samples, compositional ratios of Ag:Ni were found to be consistent with the corresponding stoichiometric elemental ratio and the ratios obtained from EDAX measurements.

In the present synthesis of MATNPs, ODE acts as solvent and HDA acts both as reducing agent and surfactant. AgNi alloy NP catalysts were conveniently prepared by the colloidal reduction method. The as-synthesized particles are stable in organic solvents and there is no secondary impurity phase present, as corroborated by powder XRD patterns as shown in Fig. 3a. These results are consistent with our previous report on the synthesis and characterization of the as-synthesized material. Powder XRD pattern for Ag_xNi_{1-x} MTANPs shows five characteristic peaks corresponding to (111), (200), (220), (311), and (222) planes of Ag fcc nanostructure but with slight deviation from the actual 20 values. With increase in Ni content, the XRD peak corresponding to (200) plane of Ag is shifted toward higher 20 values with decrease in intensity. The XRD peak corresponding to (200) plane AgNi alloy NPs can be clearly seen in between pure Ag and Ni confirming solid solution of Ag and Ni according to Vegard's law. Similar shifting towards higher 20 values and decrease in the intensity of the XRD peaks with increasing amounts of Ni content was observed for the Ag (111), (220) and (311) peaks also. However, an XRD peak centered at 52.15°, corresponding to the (200) plane of fcc Ni was not observed in MTANPs, ruling out any heterogeneous growth of Ni NPs. This observation is consistent with earlier reports of AgNi alloy particles synthesized using different methods Hence, the absence of characteristic peak of Ni (at 52.13°) and resemblance with Ag fcc structure of MTANPs confirmed the formation of solid solution in which Ni atoms are incorporated in Ag lattice.

To further justify the high surface area of our $Ag_{0.6}Ni_{0.4}$ MTANPs and application in catalysis, BET adsorption-desorption isotherm was performed at 77 K on the as-synthesized sample. By using the multipoint BET equation, the specific surface area of AgNi sample was found to be 76.0 m²g⁻¹. This high surface area is mainly attributed to the small sized (20±1 nm) alloy NPs. Further, the pore size distribution was calculated using the Barrett–Joyner–Halenda (BJH) method, and the maximum pore volume distribution was observed for a 1-2

nm pore radius (inset of Fig. 3b). This observation of a high number of pores could be indicative of the presence of essential dense defects on the twin boundaries.

Catalytic Study

To test the composition controlled catalytic activity, Ag, Ni and Ag_{1-x}Ni_x MTANPs were applied in coupling of aniline to azobenzene. The progress of reaction was monitored by GC analysis and obtained results were entered in Table 2 (also see Table S1 in SI). For GC analysis, final reaction solution was centrifuged at 3000 rpm to separate out the catalyst, and aliquots were then transferred to an eppendrof and 10 μ L of the aliquot was diluted with the 1.5 mL of ethylacetate. The diluted solution was then run through the GC column. The oxidation products were identified by their retention times in comparison with standard samples. Each peak of the GC chromatogram was integrated and the actual concentration of each component was obtained from the pre-calibrated plot of peak area against concentration. The yields of azo compounds were calculated with reference to product selectivity and product yield were calculated from the GC data as follows:

$$Substrate Conversion(\%) = \frac{moles of converted substrate \times 100}{moles of reactant in feed}$$
(1)

$$Product selectivity(\%) = \frac{moles of product formed \times 100}{moles of reactant converted}$$
(2)

$$Product \ yield \ (\%) = \frac{Substrate \ conversion \ (\%) \times Product \ selectivity \ (\%)}{100}$$
(3)

From obtained results it was found Ag metal have higher activity over Ni for oxidative coupling reaction which can be due to high electron density of Ag metal which help in faster oxygen activation over metallic surface. From initial study, it has been investigated that catalytic property of Ag can be enhanced by doping of Ni atoms in Ag lattice and hence synergistic effect between more electronegative noble Ag and less electronegative transition metal Ni. This metal-metal synergistic effect of Ag and Ni metals may be resulted into optimum adsorption-desorption behaviour of substrate and product over catalyst surface as per Sabatier principle [33]. As per the volcano plot drawn according to the Sabatier principle, Ag is on the left side of the volcano maximum and Ni is on the right side. Thus Ag is limited by desorption of product and Ni is limited by activation of reactants. Therefore, an optimum adsorption-desorption characteristics could be expected from a proper combination or

alloying of both metals. Thus following this assumption, we found that $Ag_{0.6}Ni_{0.4}$ composition demonstrated the best catalytic activity towards the oxidative coupling of aniline (1 mmol) in DMSO (2 mL) at 60 °C in aerobic condition with excellent conversion (94.4%) and azobenzene selectively (99.9%) (See Fig. S2). The decrease in activity for $Ag_{0.2}Ni_{0.8}$ may be attributed to the excess content of Ni (more than alloying limit for AgNi alloys) which gets oxidized and passivate the surface for catalysis. To further gain insight, physical mixture of Ag and Ni (60/40 %) was used in similar catalytic reaction conditions which showed 67 % conversion confirms the synergistic effect of Ag and Ni in alloy NPs.

This is a first report where such kind of low cost alloy nanoparticle catalyst is used under very mild reaction condition and obtained excellent yield and absolute selectivity. To confirm this optimum condition, several controlled reactions have been carried out using Ag_{0.6}Ni_{0.4} MTANPs and the results are summarized in Fig. 4 and Table 3. The effect of solvent was first investigated, keeping the catalyst loading (2.6 mg) and time (24 h) intact. Fig. 2a shows that only DMSO solvent demonstrated the best yield of azobenzene, whereas no progression of reaction in other mentioned solvents. Other than DMSO, DMF is another possible solvent matching properties with DMSO. However here too, the activity of the catalyst and conversion of aniline depend on the interaction of solvent-catalyst, solubility of air and interaction of solvent-aniline in the solution phase. We assume that, in the strong basic condition amidate formed from the DMF binds to the AgNi alloy and inhibits the catalytic process. On the other hand since the polarity of DMSO is higher than isopropanol and at the same time it is aprotic solvent than water, it is assumed that DMSO is showing the best result. Further reaction time was varied keeping the catalyst loading (2.6 mg) in DMSO intact (see Fig. 2b, Table S3). Maximum product was obtained after 24 h of reaction time. Notably, AgNi alloy NPs catalysts have been tested in various conditions such as with and without base, at different temperature and different amount of catalyst loading. However, no product has been detected without the use of KOH and also maximum conversion of substrate and maximum yield obtained when the catalyst loading was 2.6 mg and the reaction temperature was 60 °C as seen in Table 3. However, in particular, effect of catalyst loading was studied by varying catalyst amount from 1.3-7 mg and obtained results were entered in Table 3. It seems that 2.6 mg catalyst loading is the optimum condition, as increase of catalyst amount is not enhancing the conversion efficiency. However, no other product formed in these higher catalysts loading other than azobenzene. On the other hand, higher

reaction temperature leads to over oxidation of substrates/intermediate and yields multiple by-products (GC data is not shown).

In the UV-Vis spectrum (Fig. 5a), the optical absorption peak at 317 nm suggested the formation of *trans*-azobenzene as the only product. The FTIR data of azobenzene (I) in Fig. 5b show a band at 1613 cm⁻¹ confirming the synthesis of the azo (N=N) group. In the ¹H-NMR spectrum (Fig. 5c), the protons of the aromatic ring appeared at 7.00–8.00 ppm, however, there is no peak for the NH group in the product; proving the formation of azobenzene. Further, this is confirmed from ¹³C-NMR analysis, where four signals for the aromatic ring carbons in the range of 165-114 ppm shown in Fig. 5(d). The reason behind the excellent conversion of aniline to azobenzene with complete selectivity in the present study is the multiply twinned nature of AgNi alloy NPs catalyst and the controlled aerial oxidation facilitate by it. In addition the observed efficiency comes from size effect (high surface area), structural effect (defects generated from twinned structure) and electronic effect (difference in oxidation potential of Ag/Ni) offered by AgNi MTANPs [32]. In most of the previous reports [1], [34] over oxidation of the hydrazine intermediate occurred to form azoxy benzene and nitroso benzene as by-products. However in the present case over oxidation is not observed, hence absolute selectivity in product formation.

In a measure to check the reaction process, catalytic reactions were carried out in three more conditions. Interestingly, in these cases no product was detected in the absence of catalyst, under a nitrogen atmosphere and surfactant removed AgNi MTANPs (entry 1-3 in Table 3). Thus based on all the above experimental facts we found the key to the effective process can be divided to four factors: (a) the activation of molecular oxygen in air in the presence on the surface of AgNi NPs (no reaction under inert atmosphere, entry 2 Table 3), (b) size effect, availability of high effective surface area for catalysis due to small sized alloy NPs (BET measurements showed high surface area, Fig. 3b), (c) electronic effect, the electronegativity difference between Ni (1.91) and Ag (1.93) metals would cause electron transfer to Ag from Ni resulting in the creation of electron rich and electron poor regions on the bimetallic surface and last but not the least (d) presence of surfactant and structural defect at the surfaces due to twinned morphology (corroborated from the Table 2 and 3). The importance of twinning effect can be ascertain from entry 7 Table 2, where % of conversion was very less for physical mixture as compared to twinned alloy NPs catalyst. In addition, it is found in entry 3 Table 3 that, when the HDA surfactants on the surface of AgNi NPs were removed by annealing no reaction occurs under comparable reaction conditions demonstrating the function of long chain hydrocarbon. The removal of HDA surfactant from the surface of AgNi NPs is ascertain from Fig. 6, where C-N, C-H and N-H stretching and bending frequencies related to the amine molecules are absent on the annealed sample. Since the polar amine group is bounded to inorganic metal alloy surface, the hydrophobic chains

make the NPs dispersible in DMSO. Further these hydrocarbon ends of HDA plays an important role for aniline substrates to get oxidized on the AgNi NP catalyst surface with adsorbed oxygen (transformed to superoxide radical) due to easy access through hexadecyleamine as proved earlier in different reactions [32][35][36]. These factors give the evidence about the mechanism of reaction which cannot be possible without oxygen and a mechanistic model can be proposed as shown in Scheme 1, based on the earlier work by Dutta et al. and Cai et al. [37][38]

Recyclability and stability of catalyst

Stability and reusability of the alloy NP catalyst were measured in subsequent batches of catalytic cycles using the recovered catalyst, in identical reaction condition set up by adding fresh aniline (1 mmol), KOH and DMSO (2 mL). At the end of the reaction, the reaction mixture was collected, tested by TLC in 5% ethylacetate and hexane mixture and finally analyzed by GC. The results (as shown in Fig. 7, Table S4) suggest that the catalyst can be reused up to minimum 5 cycles with negligible decrease in conversion of aniline to azobenzene.

These results concluded recyclability of alloy NPs with the minor decrease in product yield after five successive cycles. This trifling decrease in efficiency may be attributed to catalyst lost and removal of capping surfactant lost during successive cycles. After each test, the catalyst was recovered by centrifugation followed by washing with diethyl ether, distilled water and drying. For a heterogeneous catalyst it is important to retain original properties. Therefore, to check the structural changes in crystal structure, morphology and surface capping agents of the recovered AgNi catalyst after five catalytic runs, we have carried out post-characterization of recovered catalyst using FT-IR, XRD and TEM analysis and the results are shown in Fig. 6 (FT-IR) and 8 (XRD and TEM). FT-IR results shows that surfactant was not removed from NPs surface even after 5th catalytic cycle indicating consistent catalytic activity, strong attachment of surfactant molecules to NPs surface and stability of alloy NPs towards azobenzene synthesis. It can be seen from XRD pattern of reused Ag_{0.6}Ni_{0.4} MTANPs (Fig. 8a) that peak positions remain unchanged and matching well with the fresh AgNi MTANPs, which presents the structural stability of present sample. However, the peak intensity is found to be reduced in the case of reused catalyst. This observation can be understood from the TEM micrograph as shown in Fig. 8b, where slight reduction in particle size of the reused AgNi alloy NP is manifested. This might be due to removal (leaching) of some AgNi surface atoms during repeated cycles.

Substrate scope of the Ag0.6Ni0.4 MTANPs catalyst

We have in addition evaluated the generality of AgNi alloy NPs as catalyst for oxidative coupling of amines. Aniline afforded product symmetric azobenezene in 94.4% yield with 99.9% selectivity (Table 4, entry 1). In case of electron donating groups on aniline also afforded corresponding aromatic azo compounds in good to excellent yield with 99.9% selectivity (Table 4, entries 2-4). The catalyst was unable to catalyse the reaction of 4-nitroaniline (electron withdrawing group on aniline) (Table 4, entry 5). We have also carried out the oxidative coupling reaction of benzylamine in toluene and azomethine compound was obtained in 96% yield with 99.9% selectivity (Table 4, entry 6). See Fig. S2-S8 for detail characterizations.

Later, $Ag_{0.6}Ni_{0.4}$ alloy NPs was also tested for oxidative coupling of asymmetric aniline. The oxidative coupling of anilines and *p*-anisidine was studied and major product 1-(4-methoxyphenyl)-2-phenyldiazene was obtained in 60% yield (Scheme 2) and the diazobenzene was a minor product. The major product was characterized using FTIR, UV-Vis and NMR measurements and the spectra are shown in Fig. S9-S12. This result further corroborates the usefulness of $Ag_{0.6}Ni_{0.4}$ MTANPs catalyst in the efficient production of symmetric and asymmetric azo compounds with considerable recyclability and stability.

4. Conclusions

In summary, we demonstrated that optimized $Ag_{0.6}Ni_{0.4}$ MTANPs efficiently catalyse oxidative coupling of aromatic amines to form azo compounds under mild reaction conditions. The synthesis reaction was catalysed by using the alloy NPs (2.6 mg loading) at 60 °C in open air, which results in symmetrical and asymmetrical azobenzene with 99.9% selectivity. Excellent recyclability of the catalyst, with only 5% activity loss after five cycles, makes the process environmentally and economically sustainable. This advanced catalytic activity of the present catalyst is due to its smaller size, presence of twinned defect, activation of molecular oxygen effectively at the surface and electronic effect from two different metals. We expect that such alloy nanoparticle will open the way for a variety of catalysis reactions for the synthesis of important organic compounds.

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Fig. 1. (a-b) Low resolution TEM images (Inset: single isolated alloy nanoparticle showing five-fold twinning), (c) HRTEM image and (d) SAED pattern for of Ag_{0.6}Ni_{0.4} MTANPs.



Fig. 2. EDAX analysis of (a) Ag_{0.8}Ni_{0.2}, (b) Ag_{0.6}Ni_{0.4}, (c) Ag_{0.4}Ni_{0.6}, (d)Ag_{0.2}Ni_{0.8} samples. (e) Dark-field TEM image and (f-g) elemental maps of Ag and Ni of Ag_{0.6}Ni_{0.4} MTANPs.



Fig. 3. (a) Powder XRD pattern of pure Ag, Ni and synthesized alloy compositions. (b) BET



Fig. 4. (a) Amount of azobenzene yield vs. the variation of reaction solvent. (b) Progress of reaction at different time interval.



Fig. 5. (a) UV-Vis spectrum and (b) FTIR spectrum of as-obtained azobenzene dissolved in ethyl acetate. (c) ¹H-NMR and (d) ¹³C NMR spectrum of as-obtained azobenzene dissolved in CDCl₃.



Fig. 6. FTIR spectra of as-synthesized (black curve), reused (blue) and annealed (red curve) $Ag_{0.6}Ni_{0.5}$ MTANPs showing the presence, retainment and removal of hexadecyle amine surfactant at three different conditions.



Fig. 7. Recyclability study of the Ag_{0.6}Ni_{0.4} MTANPs catalyst for aniline oxidation in DMSO at 60 °C.



Fig. 8. Characterization result of $Ag_{0.6}Ni_{0.4}$ nanocatalyst after 5th cycle (a) XRD pattern, (b) low magnification TEM image.



Scheme 1. Proposed mechanistic model of the oxidation of aniline into azobenzene over AgNi alloy NP catalyst.



Scheme 2. Synthesis of asymmetric 1-(4-methoxyphenyl)-2-phenyldiazene in the identical reaction condition using AgNi alloy NPs as catalyst.

Sr.	Ag/Ni	Ag/Ni	Ag/Ni
No.	(Precursors	(EDS atomic	(AAS atomic
	composition)	percentage)	percentage)
1	Ag _{0.8} Ni _{0.2}	81.5/18.5	83.6/16.4
2	Ag _{0.6} Ni _{0.4}	60.3/39.7	61.2/38.8
3	Ag _{0.4} Ni _{0.6}	41.9/58.1	40.8/59.2
4	Ag _{0.2} Ni _{0.8}	18.1/81.9	17.2/82.8

Table 1. Comparison of stoichiometric elemental ratios with EDAX and AAS results.

Table 2. Studies on the variation of catalyst and catalyst composition in the oxidative coupling of aniline to azobenzene.^a

$$\bigcup^{\text{NH}_2} + \bigcup^{\text{NH}_2} \frac{\text{KOH, Ag}_{0.6}\text{Ni}_{0.4} \text{ MTANPs}}{\text{air, 60 °C, DMSO, Entry 3}} \bigcup^{\text{N}_{\text{N}}}$$

Entry	Nanocatalysts composition	Conversion (%)
1	Ag	64.4
2	$Ag_{0.8}Ni_{0.2}$	94.0
3	$Ag_{0.6}Ni_{0.4}$	94.4
4	$Ag_{0.4}Ni_{0.6}$	93.0
5	$Ag_{0.2}Ni_{0.8}$	71.3
6	Ni	15.3
7	Physical mixture of Ag and Ni NPs	67

^{*a*}Aniline (1 mmol), KOH (1 mmol), DMSO (2 mL) were taken in a reaction flask (at 60 °C) and composition of $Ag_{1-x}Ni_x$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0) catalyst (2.6 mg) was added and stirred for 24 h.

Entry	Catalyst	T (°C)	Variation in	Conversion
	loading		solvents	(%) ^b
1	No catalyst	60	DMSO	0
2°	2.6 mg	60	DMSO	trace
3 ^d	2.6 mg	60	DMSO	trace
4	2.6 mg	60	O-Xylene	0
5	2.6 mg	60	Toluene	0
6	2.6 mg	60	Acetonitrile	0
7	2.6 mg	60	Water	0
8	2.6 mg	60	DMF	0
9	2.6 mg	60	Isopropanol	20.0
10	2.6 mg	60	DMSO	94.4
11	1.3 mg	60	DMSO	68
12	4.3 mg	60	DMSO	90.5
13	7.0 mg	60	DMSO	85.0
14	2.6 mg	30	DMSO	40.0
15	2.6 mg	100	DMSO	20.2

Table 3. Controlled reactions at indicated conditions^a.

^aAniline (1 mmol), $Ag_{0.6}Ni_{0.4}$ (indicated amount) and KOH (1 mmol) were taken in solvent (2 mL) and stirred at specified temperature. ^bThe conversion was determined by GC and product was characterized by NMR. ^cReaction under nitrogen environment. ^dSurfactant stripped (annealed under N₂ atmosphere) catalyst.

Entry	Reactant	Product	Conversion ^b (%)	Selectivity (%)
1	NH ₂		94.3	99.9
2	MeO NH2	MeO Nan OMe	87	99.9
3	CI NH2		72.8	99.9
4	HS NH2	HS NSN SH	100	99.9
5°	O ₂ N-	No product		
6 ^d	NH ₂		96	99.9

Table 4. Substrate scope for oxidative coupling of amine catalysed by Ag_{0.6}Ni_{0.4} MTANPs.^a

^aAmine (1 mmol), Ag_{0.6}Ni_{0.4} (2.6 mg) and KOH (1 mmol) were taken in DMSO (2 mL) and stirred at 60 °C for 24 h. ^bThe conversion and selectivity was determined by GC and product was characterized by NMR. ^cOrtho and para derivatives. ^dToluene was used as a solvent in place of DMSO.