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# High catalytic activity of a new Ag phosphorus ylide complex supported on montmorillonite: synthesis, characterization, and application for room temperature nitro reduction

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Abstract In this work, the phosphorus ylide, [PPh<sub>3</sub>CHC(O)CH<sub>2</sub>Cl], was reacted with AgNO<sub>3</sub> to give the  $[Ag{C(H)PPh_3C(O)CH_2Cl}_2]^+NO_3^-$  as the product. Then, it was supported on the modified montmorillonite nanoclay to prepare a new catalyst for the reduction reaction. The structure and morphology of the nanoclay catalyst were characterized by FT-IR, X-ray powder diffraction, scanning electron microscopy, energy-dispersive X-ray analysis and transmission electron microscopy techniques; also, the content of silver was obtained by inductively coupled plasma analyzer. This composition was exploited to study its catalytic activity in the reduction in aromatic nitro compounds; it displayed the high catalytic activity. Factors such as catalyst amount, solvent, temperature and reaction time were all systematically investigated to elucidate their effects on the yield of catalytic reduction in nitroarenes. This catalytic system exhibited high activity toward aromatic nitro compounds under mild conditions. The catalyst was reused five times without any significant loss in its catalytic activity.

**Keywords** Silver phosphorus ylide · Montmorillonite (MMT) · Nanocatalyst · Nitroarenes · Reduction reaction

# Introduction

In the last decade, silver has been immobilized onto various supports such as silica [1, 2], MCM and zeolite [3, 4], carbon nanotubes and activated carbon [5–8], alumina [9–11],

Kazem Karami karami@cc.iut.ac.ir titania, [12], polymeric materials [13, 14], and clay materials [15, 16]. However, clay particles at the nanosize possess some unique characteristics different from those of the other supports. Thus, they are turned into the platelet form with the thickness of only 1 nm and the width of 70–150 nm [17].

Clay minerals can be divided into four major groups including the kaolinite group, the montmorillonite (MMT)/ smectite group, the illite group, and the chlorite group. MMT nanoclay, due to high cation-exchange capacity, large specific surface, and colloidal properties that give rise to the optimum adsorbents of organic and inorganic substances [18, 19], has received much attention; it has been used as a heterogeneous catalyst for several reactions [20, 21]. These catalysts enjoy several advantages over their homogeneous counterparts in terms of recovery and recycling, as well as minimization of the undesired toxic wastes [22].

Aromatic amines are important intermediates used for the manufacture of dye stuffs, pharma, agricultural chemicals, photographic chemicals, additives, surfactants textile auxiliaries, chelating agents, and polymers [23–26]. These are essentially prepared by the reduction in nitroarene with metals [27–31]. Thus, the reduction in aromatic nitro compounds to their corresponding anilines is one of the most important transformations in the synthetic organic chemistry [32]. A plethora of methods has been used for the reduction in nitroaromatic compounds to their corresponding amines [33–35]. Among these methods, the nanocatalysts often exhibit specific physical and chemical properties [36], giving rise to their high catalytic activity for the reduction in nitrobenzenes [37].

In the present work, nanoclay (MMT) was used as a green, readily available and non-expensive support for Ag phosphorus ylide complex and the resulting hybrid material was used for hydrogen transfer reactions of aromatic nitro compounds at room temperature. According to the obtained

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data, the newly prepared nanocatalyst exhibited excellent activity for the hydrogenation of a series of nitro compounds and conversion of them to their corresponding amino derivatives. The reactions were performed at the room temperature and short reaction times. As a result, less energy and time were consumed in comparison with many other catalytic reductions of nitroarenes. At least, the catalyst was reusable five times. Please insert the reaction Scheme here.

# Experimental

#### Materials

Starting materials and solvents were purchased from Merck and Aldrich; they were used without purification. MMT-K10 with the cation-exchange capacity of 0.119 eq/100 g was provided by Aldrich chemical Co.

## Characterization

Infrared spectra were recorded on a FT-IR JASCO 680 spectrophotometer in the range of 400–4000 cm<sup>-1</sup> using KBr pellets. Gas chromatography (GC) data for the reduction reaction were recorded by 6890 N Technologies from Agilent Company, using the FID detector and N<sub>2</sub> as the carrier gas. Column chromatography with 28.5 m length, 320 µm inner diameter, and 0.25  $\mu$ m thickness (the HP + 5 types) was used. X-ray diffraction (XRD) analysis was carried out to measure the change in the interlayer spacing of the clay mineral based on Bragg's law for confirming the intercalation of complexes into the galleries of the Ag/MMT nanocatalyst. The XRD analyses were performed via the X-ray diffractometer (Bruker, D8 Advance) with CuKa characteristic radiation (wavelength k = 0.154 nm at 45 kV, 100 mA, with a step size of  $0.02^{\circ}$  and at the range of  $2\theta = 1.2 - 10^{\circ}$ ). The dispersion morphology of the samples was observed using field-emission scanning electron microscope [(FE-SEM) HITACHI: S-4160]. Energy-dispersive X-ray analysis (EDX) results were obtained at 20 kV using Philips (Model XL-30) instrument. Transmission electron microscopy (TEM) images were obtained using a Philips CM 120 microscope with an accelerating voltage of 100 kV. NMR spectra were recorded in DMSO- $d_6$  at room temperature on a Bruker spectrometer at 400.13 MHz ( $^{1}$ H) and 100.61 MHz ( $^{13}$ C). The silver content of the catalyst was measured by inductively coupled plasma (ICP) analyzer (Varian-vista-pro-CCD simultaneous ICP-OES inductive genoppeltes plasma).

#### Preparation of the Ag phosphorus ylide complex

First, the phosphorus ylide, [PPh<sub>3</sub>CHC(O)CH<sub>2</sub>Cl], was prepared according to our previous study [38]. Then, the

[PPh<sub>3</sub>CHC(O)CH<sub>2</sub>Cl] was reacted with AgNO<sub>3</sub> (2:1) in acetone (10 mL) at room temperature in dark. The resulting solution was stirred for 4 h; then, the reaction mixture was concentrated under reduced pressure to yield a white solid. The residue was purified by re-precipitation from ethyl acetate and *n*-hexane, which were collected and air-dried (Scheme 1). Yield is 64%.

# Preparation of the Ag complex/MMT nanohybrid catalyst

The original MMT-K10 powder samples were sieved, and the fraction < 40 mm was used as a host matrix for the preparation of the Ag/MMT. The clay mineral sample was stirred in 30 mL DI water for 8 h at 90 °C. Then, it was dispersed in the 0.1 M aqueous solution of Ag complex, and the mixture was stirred at 60 °C for 6 h. The product was filtered through a plug of glass fiber filter paper and washed with distilled water several times. It was dried for 24 h at 80 °C.

#### General procedure for the reduction in nitroarenes

First, NaBH<sub>4</sub> (1 mmol) was used as a reducing agent for the conversion of Ag (+ 1) to Ag (0) in methanol at room temperature for 2 h. After that, the Ag/MMT was filtered and used as a catalyst. Then, in a typical procedure, a mixture of 4-nitrophenol (0.1 mmol), KOH (0.15 mmol), isopropyl alcohol (3 mL), and Ag/MMT catalyst (50 mg) 1.01 wt% was stirred at room temperature for an appropriate time (Scheme 2). After the completion of the reaction (monitored by GC), the catalyst was separated by filtration. The ensuing product was extracted with ethyl acetate and repeatedly washed with water (3–4 times) to remove KOH. The resulting solvent was evaporated to dryness in vacuum.

#### **Results and discussion**

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the Ag complex were recorded in CDCl<sub>3</sub>. The <sup>1</sup>H NMR spectrum of Ag complex displayed two sets of signals for the methylene protons and acrylic protons. The <sup>13</sup>C NMR spectrum of the Ag complex showed aliphatic and aromatic regions. MMT had a crystal lattice unit formed by one alumina octahedral sheet sandwiched between two silica tetrahedral sheets. The elementary structural units were silica tetrahedron and aluminum octahedral [39, 40]. The cation Si<sup>+4</sup> was fourfold and possessed tetrahedral coordination with oxygen, while the cation, Al<sup>+3</sup>, occurred in the sixfold or octahedral coordination. The ion substitution or the site vacancies at the tetrahedral and/or octahedral sheets could result in a negatively charged surface. The exchangeable cations between the layers could compensate for the



on the modified Ag/MMT-K10 nanocatalyst

Fig. 1 FT-IR spectra of (a) MMT-K10 and (b) Ag/MMT hybrid

Wavenumber [ Cm<sup>-1</sup>]

negative charge and might be easily exchanged by other metal cations accounting for the high ion-exchange capacities of these clay minerals [41]. Due to this crystalline arrangement, MMT could expand and contract the interlayer while maintaining the two-dimensional crystallographic integrity. The interlayer between units contained positive cations and water molecules.

According to ICP analysis, the silver content of the catalyst was obtained to be 1.01 wt%.

#### **FT-IR** analysis

The FT-IR spectrum of the MMT-K10 and Ag/MMT hybrid is shown in Fig. 1. The FT-IR spectra for MMT-K10 showed a broadband in the range of  $2700-3600 \text{ cm}^{-1}$  that was related to the interlayer absorbed water molecules (Fig. 1a). A weak band that appeared at 1645 cm<sup>-1</sup> was related to the OH bending vibration. The Si-O stretching band was in the range of 1300–900  $\text{cm}^{-1}$ . The bands at 463 and 529  $\text{cm}^{-1}$ were related to Mg–O and Al–O bonds, respectively [42]. The FT-IR spectrum of Ag/MMT showed characteristic bands due to the clay mineral (Si–O) at 1100 cm<sup>-1</sup>. The IR spectrum of ligand showed a band at 1575 cm<sup>-1</sup> that could be assigned to  $\nu$  (C=O); for the Ag complex, the absorption was in the range of  $1670-1675 \text{ cm}^{-1}$  in the region typical for the C-bonded phosphorus ylides [43]. The three bands corresponded to P–C bonds at 700–800  $\text{cm}^{-1}$  (Fig. 1b). Carbonyl-stabilized phosphorus ylides could behave as C or O donors owing to the delocalization of the ylidic electron pair The FT-IR spectra confirmed that the ligand was bound through the carbon of ylide to the Ag (I) center. The FT-IR data exhibited that the Ag complex and then MMT/Ag were synthesized, confirming the presence of the Ag complex intercalated between the MMT layers.

#### X-ray diffraction analysis

Figure 2 shows the XRD pattern of pristine MMT and Ag/ MMT hybrids. The pristine MMT showed a diffraction peak at  $2\theta = 8.7^{\circ}$  with the d-spacing of 1.051 nm (Fig. 2a). After the treatment of MMT by cation-exchange with the Ag complex, the X-ray reflections were shifted to a lower angle position. The XRD pattern of the Ag/MMT exhibited a diffraction peak at about  $2\theta = 2.3^{\circ}$  that corresponded to an interlayer distance of 3.84 nm (Fig. 2b). An increase in the interlayer distance led to a shift of the diffraction peak toward the lower angles, confirming that the intercalation reaction and surface modification of MMT had occurred. This implied that the basic structures of the MMT were kept, the layers were only propped open, and the basal distances were increased significantly, thereby providing evidence that the intercalation reaction had occurred successfully. It



**Fig. 2** X-ray powder diffraction pattern of (*a*) MMT-K10 and (*b*) Ag/ MMT

could be regarded as a good sign, revealing that complex had entered into the interlayer space of MMT.

# **TEM analysis**

Figure 3 shows the TEM images of the Ag/MMT nanocatalyst. In the TEM image of the hybrid, the presence of Ag (0) nanoparticles based on the sizes more than 235 resulted in 45.89-nm particles in the presence of MMT platelet fragments; however, they were separated from each other. Probably, they originated from the collapse of MMT-K10 structure during the ion-exchange process, confirming the damage of the MMT-layered morphology by the ion-exchange process, as already shown by XRD analysis.

#### **FE-SEM** analysis

The FE-SEM images of the Ag/MMT catalyst were studied by the SEM technique (Fig. 4). According to the SEM images, the Ag/MMT catalyst had a layer structure.

#### **Energy-dispersive X-ray spectroscopy**

The energy-dispersive X-ray spectroscopy (EDX) showed the presence of Ag and P atoms as well as Al, Si, Fe, Cl, and O atoms in the structure of the MMT-supported Ag catalyst (Fig. 5).

# Catalytic activity of Ag/MMT for the reduction in aromatic nitro compounds

The Ag/MMT material was explored as a nanocatalyst for hydrogen transfer reactions of aromatic nitro compounds using isopropyl alcohol (IPA) as the hydrogen donor (Table 1). First, the catalytic activity of the prepared nanocatalyst was tested for the reduction in 4-nitrophenol to yield 4-aminophenol under various reaction conditions. In the hydrogen transfer reaction, different parameters including the effects of the type of bases, temperature, solvent, and the amount of the catalyst were tested. So, three different amounts of catalyst 1 (25, 50, and 100 mg) were used, keeping all other reaction parameters including room temperature, IPA (3 mL), KOH, and reaction time (2 h) fixed (Table 2, entries 5, 11, and 12). Consequently, 50 mg of the catalyst 1 was taken to be ideal with higher conversion. Different reactions were used in order to choose the suitable base in the reduction reaction (Table 2, entries 6–10). Therefore, a high yield was gained in the presence of KOH in IPA. Moreover, we tested various solvents in the presence of KOH, using the appropriate time reaction; it was evident that the catalytic activity in isopropanol was greater than that in CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>OH, and ethanol (Table 2, entries 1-4) and IPA was the best selection for this reduction



Fig. 3 TEM images of Ag/MMT at different magnifications of a 150 nm, b 80 nm, and histogram illustrating the Ag nanoparticles size distribution

reaction (Table 2, entry 5). In addition, the effect of reaction temperature was investigated at two different temperature intervals (room temperature and 60 °C) (Table 2, entries 5, 6). At room temperature, the reaction showed the ideal yield after 2 h (Table 2, entries 6). After the optimization of the reaction conditions, the catalytic activity of the catalyst with other nitro substrates was further explored. Notably, transfer hydrogenation over the modified clay mineral as the nano-catalyst exhibited excellent activity for the hydrogenation of a series of nitrobenzenes. All nitroarenes were reduced in excellent yields (Table 1, yield 80–98%) affording a single

product, thereby minimizing the efforts to separate the unreacted starting compounds. As the solvent used was IPA, without any harmful group such as Cl, the reaction was safe. The nature and position of the substituents on the aromatic nitro compounds did not significantly influence the catalytic performance of the synthesized nanocatalyst. For example, electron-donating and electron-withdrawing groups such as -Cl, -F, -Br, -NO<sub>2</sub>, -NHNH<sub>2</sub>, and -OCH<sub>3</sub> did not have any significant influence on the reduction reaction. Notably, transfer hydrogenation over Ag/MMT nanocatalyst exhibited excellent activity and selectivity (Table 2, entries 4–6, 8–10)



Fig. 4 FE-SEM images corresponding to the Ag (0) complex/MMT before reaction



Table 1Optimizing o thereaction conditions for thereduction in 4-nitrophenol,using the Ag/MMT nanocatalyst



Entry	Solvent	Catalyst (g)	Base	Temp. (°C)	Time (h)	Conv. (%) <sup>a</sup>
1	CH <sub>3</sub> CN	0.05	КОН	60	6	40
2	CH <sub>3</sub> OH	0.05	KOH	60	6	45
3	Ethanol	0.05	KOH	60	4	70
4	$CH_2Cl_2$	0.05	KOH	60	5	60
5	Isopropanol (IPA)	0.05	KOH	60	2	97
6	IPA	0.05	KOH	R.T	2	95
7	IPA	0.05	Na <sub>2</sub> CO <sub>3</sub>	R.T	4	85
8	IPA	0.05	NaOAC	R.T	3	90
9	IPA	0.05	NaOH	R.T	4	30
10	IPA	0.05	K <sub>2</sub> CO <sub>3</sub>	R.T	3.5	87
11	IPA	0.1	KOH	R.T	2	95
12	IPA	0.025	KOH	R.T	2	75

Reaction conditions: 4-nitrophenol (0.1 mmol), base (0.15 mmol), solvent (3 mL), and catalyst <sup>a</sup>Determined by GC

Table 2Ag (0) complex/<br/>montmorillonite catalyzed by<br/>the hydrogen transfer reaction<br/>of aromatic nitroarene



Reaction conditions: nitroarene (0.1 mmol), KOH (0.15 mmol), IPA (3 mL), and 50 mg of catalyst 1.01 (wt%) Ag  $^{\rm b} Determined$  by GC



Fig. 6 FE-SEM images corresponding to the Ag (0) complex/MMT after the fifth run



Scheme 3 The possible mechanism for hydrogen transfer reactions over Ag complex/montmorillonite



**Fig. 7** Recyclability tests for the catalyst in the reduction in 4-nitrophenol (reaction conditions were the same as those given in Table 2)



Fig. 8 Kinetic profiles of the Ag catalyst in the reduction reaction. (*a*) Normal reaction kinetics in the presence of catalyst; (*b*) reaction kinetics in the absence of the catalyst. Reaction conditions: nitroarene (0.1 mmol), KOH (0.15 mmol), IPA (3 mL), 50 mg of catalyst, room temperature, 2 h

for the hydrogenation of a series of halogenated nitrobenzenes to their corresponding halogenated amines, without any dehalogenation product. The stability and reusability of the catalyst at room temperature could be important from the viewpoint of a green sustainable protocol, in the heterogeneous catalysis. So, the stability of the Ag/MMT nanocatalyst was tested by recycling and reusing the catalyst (five times) without any significant loss in the catalytic activity. After each cycle, the catalyst was separated and used for the next cycle to check the efficiency of this protocol in the reduction in 4-nitrophenol. After using this catalyst for nitro reduction, the SEM images did not show any changes in the surface morphology and the layered structure was confirmed (Fig. 6).

In order to show the improvement in this heterogeneous reaction, a typical experiment was conducted. The model reaction of the reduction in 4-nitrophenol was proceeded. The mixture was stirred without the catalyst for 24 h. No formation of product was observed. Also, a standard reaction of the reduction was proceeded by 4-nitrophenol in the presence of the Ag complex. The mixture was stirred for 12 h; notably, no product was observed even after 12 h, indicating that no homogeneous catalyst was involved in the reaction. The reduction in 4-nitrophenol was done without the intercalated Ag complex, such that no formation of the product was observed.

The proposed mechanism for the reduction in aromatic nitro compounds is depicted in the Scheme 3 [44]. After the reaction between NaBH<sub>4</sub> and the prepared complex and the conversion of Ag (+ 1) to Ag (0), as a result of the adsorption of IPA on the Ag/MMT nanocatalyst surface, a hydride was transferred to the nitro group with the concomitant formation of acetone 1, 2. Meanwhile, the rate of reaction could show the dependence on the strength of the adsorption of both isopropanol and the nitro compound. The nitroso intermediate 3, which was formed upon the elimination of water adsorbed on the Ag/MMT nanocatalyst, was again reduced by the hydride transfer from IPA to the hydroxylamine 4, which was further reduced to the amine group 5. Mainly, phosphorus ylides show interesting properties such as high stability and resistance as ligands. Phosphorus ylides could be used as the chiral auxiliary reagents, reaction intermediates, or starting materials in a wide variety of processes due to their nucleophilic nature, particular bonding properties, and diverse coordination modes. In our work, it is shown that the phosphorus vlide could be a stable agent for the Ag nanoparticles. Notably, we synthesized a heterogeneous catalyst by using the Ag phosphorus ylide complex that was

Table 3Comparison with
the reported results for the
reduction reaction on the
supported Ag catalysts

Entry	Catalyst	Reaction conditions solvent/ base/temp./time/oxidant	Yields (%)	References
1	Ag-Ni core-shell nanoparticles	IPA/KOH/80 °C/2 h	96	[44]
2	AgNPs@CeO <sub>2</sub>	Dodecane/110 °C/24 h/H <sub>2</sub>	98	[45]
3	Ag-MPTA	NaOH/i-PrOH/80 °C/10 h/N <sub>2</sub> atmosphere	96	[46]
4	SiO <sub>2</sub> Ag (nano), NaBH <sub>4</sub> , H <sub>2</sub> O	H <sub>2</sub> O/NaBH <sub>4</sub> /Reflux/1 h/-	100	[47]
5	Ag/HT (Ag: 0.02 mmol)	DMA, H <sub>2</sub> O/150 °C/CO/3 h	> 99	[48]
6	Complex 1/clay	IPA/KOH/RT/2 h/-	98	This work

facile, simple, and inexpensive; it could be used in a green protocol for nitro reduction.

## **Recycle procedure**

To confirm the recyclability of the nanocatalyst in the reduction in nitroarenes, 4-nitrophenol was used. After the completion of the first reaction cycle, the catalyst was separated and washed several times with ethyl acetate and water. The catalyst was dried overnight at 80 °C before being reused. For the other runs, the fresh 4-nitrophenol was added while the other conditions were the same as the first reaction cycle.

A little decrease in the conversion was observed with no significant change in selectivity, which exhibited that the catalyst was stable and could be reused. The results are shown in Fig. 7.

According to ICP analysis, the silver content of the catalyst after the fifth run was obtained to be 0.5 wt%. Furthermore, the reaction kinetics of the reduction reaction of 4-nitrophenol with the Ag catalyst was investigated. The results are shown in Fig. 8. A control experiment indicated that the reduction in 4-nitrophenol did not occur mostly in the absence of the catalyst. The yield of the product was increased quickly with the reaction time until it reached 97% after 2 h.

#### Comparison with the other studies

The catalytic performance of the catalyst for the reduction in nitrobenzene was compared with various silver catalysts. As shown in Table 3, comparison exhibited comparable yields, in a short reaction time. The catalytic activity of the current catalyst was at room temperature. Furthermore, the preparation process of the catalyst was very simple and green.

### Conclusions

To conclude, a new complex was obtained through the reaction of the phosphorus ylide,  $[PPh_3CHC(O)CH_2Cl]$ , with AgNO<sub>3</sub>, giving  $[Ag\{C(H)PPh_3C(O)CH_2Cl\}_2]^+NO_3^-$ . Then, the synthesized Ag complex was supported on the surface of MMT-K10 to prepare Ag/MMT as a new heterogeneous nanocatalyst. Reduction in aromatic nitro compounds by this catalyst occurred at room temperature in IPA, showing the green conditions for this reaction. The structure and morphology of the new catalyst were characterized by TEM, XRD, and FE-SEM. The Ag/MMT catalyst was found to be active for the reduction in several aromatic nitro compounds to their corresponding amino derivatives. The catalyst could be separated easily and reused several cycles without any decrease in the catalytic activity. Furthermore, this catalyst could be applicable for large-scale synthesis. **Acknowledgments** We wish to express our gratitude to the Research Affairs Division of Isfahan University of Technology (IUT), Isfahan, for the partial financial support. Further financial support from Iran Nanotechnology Initiative Council (INIC) is also gratefully acknowledged.

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