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MoO₃ Nanoparticles Synthesis via Hydro-Solvothermal Technique and Its Application as Catalyst for Efficient Ring Opening of Epoxides With Amines Under Solvent-Free Conditions

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Molybdenum trioxide nanoparticles were synthesized using ammonium heptamolybdate tetrahydrate (AHM) through a facile hydro-solvothermal technique. The materials were characterized via X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The mean diameter of semispherical α -MoO₃ nanoparticles was determined to be 20 \pm 5 nm. The catalytic performance of obtained products was examined in the ring opening of epoxides with diverse amines under solvent-free conditions in excellent yields and short period of times.

Keywords β -aminoalcohol, metal oxide nanoparticles, molybdenum trioxide, solvent-free

INTRODUCTION

Research on metal oxide nanoparticles has become more intense due to their interesting physicochemical properties in comparison with their bulk counterparts.^[1] These functional materials are in use as adsorbents, sensors, photo devices, catalysts, etc.^[2] One of the most important metal oxides is molybdenum trioxide (MoO₃) that is a wide band-gap n-type semiconductor. This material has received many attentions such as investigation of its photo- and electrochromic properties,^[3] catalytic behavior,^[4] sensor,^[5] lubricant,^[6] using in smart windows,^[3] lithium battery,^[7] etc. Also molybdenum trioxide is used as a good precursor for synthesizing other significant compounds, such as MoS₂^[8] and MoO₂.^[9]

Molybdenum trioxides can be found in three polymorphisms, one stable orthorhombic (α -MoO₃) phase, two metastable mon-

oclinic (β -MoO₃) phases, and hexagonal (h-MoO₃) phase. It was shown that β -MoO₃ can be converted into α -MoO₃ at temperature around 400°C.^[10]

Previously, crystalline MoO₃ nanoparticles were prepared through various routes such as microplasma process,^[11] ultrasonic,^[12] electrospinning,^[13] electrodeposition,^[14] template,^[15] chemical vapor deposition (CVD),^[16] aerosol-assisted CVD,^[17] thermal evaporation,^[18] hot plate,^[19] solvothermal,^[20] and hydrothermal techniques,^[21–26] incorporation with all citations therein.^[27,28]

On the other hand, β -amino alcohols are an important class of organic compounds.^[29] They are found in a wide variety of biologically active alkaloids and peptides.^[30] Amino alcohols are also useful as chiral auxiliaries and as ligands for transition metals for asymmetric synthesis and catalysis.^[31] They are easily converted into many other molecules, including amino acids and amino sugars.^[32] The transformation of an epoxy ring to the respective β -amino alcohol is also a crucial step in the synthesis of anti-HIV agents,^[33] the protein kinase C inhibitor,^[34] and antimalarial agents.^[35] Several methods have been reported in the literature for the synthesis of β -amino alcohols using several catalysts including sulfamic acid,^[36] amberlist-15,^[37] metal triflates,^[38] metal alkoxides,^[39] transition metal salts,^[40] heteropolymolybdate or tungstate,^[41] monodispersed silica nanoparticles,^[42] zeolites,^[43] montmorillonite clay,^[44] and MCM-41.^[45] In many of these cases, the ring opening of epoxides is carried out in a solvent, and normally requires many hours at reflux temperature under environmentally unfriendly conditions.

Accordingly, here we report the synthesis of MoO₃ nanoparticles through a simple solvo-hydrothermal approach via acidification of ammonium heptamolybdate tetrahydrate (AHM), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in ethanol and subsequently adding 1octadecene, oleic acid, and oleylamine as surfactants. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques. To the best of our

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knowledge, this catalyst has not been reported for the ring opening of epoxides with aromatic amines (Scheme 1).

EXPERIMENTAL

Oleylamine was purchased from Aldrich Company (Netherlands) and AHM, oleic acid and 1-octadecene were purchased from Merck Company (Darmstadt, Germany). All materials were used without further purification.

A Bruker D8-advance X-ray diffractometer was used to record XRD data with Cu K α radiation ($\lambda = 1.5406$ Å). Data were recorded with a speed of 2° min⁻¹ and a step of 0.05°. Using a CamScan MV2300 scanning electron microscope operating at 30 kV and a Philips CM10 transmission electron microscope operating at 100 kV, SEM and TEM images were imaged, respectively. Fourier transform infrared spectroscopy (FT-IR) spectra of the samples were recorded on a Bruker Tensor 27 spectrometer. Melting points were measured using Barnstead Electrothermal. GC Mass analysis was performed using Agilent 6890 GC system Hp-5 capillary 30 m × 530 μ m × 1.5 μ m nominal. ¹H NMR spectra were recorded on a Bruker AQS-AVANCE Spectrometer at 500 MHz, using tetramethylsilane (TMS) as an internal standard.

Synthesis of MoO₃ Nanoparticles

In a typical procedure, absolute ethanol (10 mL) was mixed with 1-octadecene (20 mL), oleic acid (10 mL), and oleylamine (1 mL) under magnetic stirring for a few minutes to form a homogenous solution. Then, 0.1765 g of AHM was dissolved in 4 mL of distilled water in a separate beaker, using 2M nitric acid, the pH value of the solution was adjusted to 3, and this solution was added slowly into the first solution under mechanical stirring condition for 2 h. The obtained solution was transferred into 90 mL teflon-lined stainless-steel autoclave and maintained at 180°C for 24 h. After cooling to room temperature, the precipitated solid was harvested by centrifugation, washed thoroughly with distilled water, methanol, and toluene, and dried at vacuum desiccator. Finally, this compound was annealed at 450°C in air for 2 h.

Catalytic Reactions

Reaction of Epoxides With Amines: Typical Reaction

To a mixture of epoxide (1 mmol) and amine (1 mmol), MoO_3 nanoparticles (0.01 g) were added and the reaction mix-

ture proceeded at 120°C for corresponding time in Table 1. After completion of the reaction as indicated by thin layer chromatography (TLC), hot ethanol was added to the mixture, the catalyst was filtered, and solvent was evaporated under reduced pressure. The crude products were purified by re-crystallization from ethanol.

RESULTS AND DISCUSSION

The expected reaction in acidic medium for isopolymolybdate anion is as follows^[26]:

$$Mo_7O_{24}^{6-} + 6H^+ \rightarrow 7MoO_3 = 3H_2O$$

In fact, increasing in the concentration of $Mo_7O_{24}^{6-}$ or $6H^+$ leads to shift the equilibrium reaction to the right incorporated with some halfway steps. In our synthesis, the intermediate compounds including ammonium tetramolybdate, $(NH_4)_2Mo_4O_{13}$, and ammonium octamolybdate, $(NH_4)_4Mo_8O_{26}$, were obtained.

Figure 1 shows the XRD of the intermediate compounds (containing $(NH_4)_2Mo_4O_{13}$ and $(NH_4)_4Mo_8O_{26})$ and MoO_3



FIG. 1. XRD patterns of (a) mixture of $(NH_4)_2Mo_4O_{13}$ and $(NH_4)_4Mo_8O_{26}$, and (b) α -MoO₃ nanoparticles.

Entry	Epoxide	Amine	Product	Time (min)	Yield (%)	mp (°C)		
						Found	(Lit.)	Ref.
1	O	NH ₂ NH ₂	1a	45	88	69–72	73–74	[46c]
2	O	CI NH ₂	1b	40	85	101–103	102–104	[47]
3	O	OMe NH ₂	1c	40	85	57–58	59	[46a,b]
4	O	NH ₂	1d	45	85	67–69	68–70	[48]
5	O	Br NH ₂	1e	45	80	120–121	122–123	[47]
6	\bigcirc	NH ₂	1f	45	85	52–53	54–55	[46a,b]
7	Ph ^O	NO ₂ NH ₂	1g	40	80	103–105	104–106	[45]
8	Ph ^O	NO ₂	1h	40	80	100–102	101–103	[45]

 TABLE 1

 MoO₃ nanoparticles catalyzed ring opening of epoxides with amines

nanoparticles. It is shown that after calcinations at 450°C, the intermediate compounds decompose into pure α -MoO₃ which is in good agreement to the data (JCPDS No. 05-0508). The widths of MoO₃ XRD peaks in comparison with their corresponded ones in the intermediates are larger, which may originate from ammonia and water releasing.^[25] Scherrer formula also estimates the MoO₃ particles with average size of 30 nm.

SEM and TEM images of MoO₃ nanoparticles are depicted in Figure 2 respectively. TEM image reveals the presence of dispersed semispherical particles with the average size of 20 ± 5 nm without any aggregation, which is in agreement with XRD data.

In continuation of our interest in the synthesis of organic compounds under solvent-free condition^[49] herein, we report a simple, environment-friendly, and proficient method for the preparation of β -amino alcohols in the presence of catalytic amounts of MoO₃ nanoparticles as a green, reusable, and efficient catalyst. In a typical procedure, cyclohexene oxide (1 mmol) and WD28

a

epoxypropyl phenyl ether, and their corresponding results are summarized in Table 1. Epoxide opening in entries 7 and 8 in Table 1 took place exclusively at the less-hindered carbon. It is worthwhile to mention that desired regioselective transformation of epoxides to corresponding β -amino alcohols in high yields was achieved by MoO₃ nanoparticles and product **2** was not observed (Scheme 1).

All reaction products were known and characterized by ¹H NMR, IR, GC mass, and melting point as comparing with those obtained from authentic samples.

CONCLUSION

We present a novel and facile synthesis of pure molybdenum trioxide nanoparticles $(20 \pm 5 \text{ nm})$ via a solvo-hydrothermal method. Final products were characterized using XRD, SEM, and TEM techniques. To our knowledge, compared with other similar previous works, our products have smaller size. Also the catalytic performance of nanoparticles for the first time was examined in the ring opening of epoxides with aromatic amines. These reactions offer several advantages in preparative procedures such as environmental compatibility, simplification of work-up, formation of cleaner products, enhanced selectivity, reduction of by-products, reduction in waste produced, and low catalyst loading.

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FIG. 2. (a) SEM and (b) TEM images of MoO_3 nanoparticles.

aniline (1 mmol) in the presence of 0.01 g MoO₃ nanoparticles under solvent-free conditions afforded the desired product (**1a**) in 88% yield.

The reaction was well performed with aliphatic epoxides catalyzed by MoO_3 nanoparticles. In all cases, the corresponding amino alcohols were obtained in excellent yields. The reaction takes place in the solid phase, in an open vessel, and the products can be extracted from the support by solvent. Various aromatic amines were treated with cyclohexene epoxide or 2,3-



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1406

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