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Short Communication

Nanosize Co₃O₄ as a novel, robust, efficient and recyclable catalyst for A₃-coupling reaction of propargylamines

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ABSTRACT

Nanosize Co_3O_4 was prepared via hydrothermal synthesis and characterized using TEM, XRD, EDAX, XPS and BET surface area analysis. Prepared nanosize Co_3O_4 was found to be highly efficient catalyst for the synthesis of propargylamines via A_3 -coupling reaction. The catalyst was recycled up to ten consecutive cycles without any loss in its activity. The developed protocol offers efficient synthesis of diverse propargylamines eliminating the use of co-catalyst and activator as reported in earlier literature.

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1. Introduction

The catalytic applications of metal and metal oxide nanoparticles in various organic transformations have gained considerable attention in past few decades [1–3]. The differences in the activities of metal and metal oxide and their nanoparticles including catalysis are directly related to the particle size on nanometer length scale. The metallic cobalt and cobalt oxide can be considered as a one of the best example to understand the catalytic activity based on the variable particle size [4–8]. In past few years several reports showed the catalytic activity of nanosize Co_3O_4 in Fischer Tropsch synthesis and CO oxidation [8–12] reactions. However, less attention has been paid for catalytic activities of nanosize Co_3O_4 for various organic transformations. Hence, identification of new catalytic properties of nanosize Co_3O_4 for new transformations is one of the unexplored areas.

Propargylamines have wider applications in organic synthesis as they are important building blocks for the synthesis of heterocyclic compounds such as pyrrolidones, oxoazoles and pyrroles [13–15] etc. They also serve as an important intermediate for natural product synthesis [16–18]. Recently, propargylamines synthesis is carried out using an atom economic pathway from catalytic coupling of alkyne, aldehyde and amine by C–H activation wherein water is formed as theoretical by-products [19, 20]. Several homogenous catalysts like Ag, Au salts, FeCl₃, InCl₃, Ir complexes, Cu salts, Cu/Ru bimetallic



Fig. 1. TEM image of nanosize Co₃O₄ with SAED pattern inside.

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Fig. 2. Histogram of nanosize Co₃O₄ obtained from DLS measurement.



Fig. 3. X -Ray diffraction pattern of nanosize Co₃O₄.

systems [18–29] and heterogeneous systems like LDH–AuCl₃ [28], zinc dust [29], Ni–zeolite [30], Ag–SBA [31] have been developed for propargylamines synthesis. The scope of these reported methodologies are limited due to the use of an expensive, moisture sensitive reagents, toxicity, long reaction time and difficulties in catalyst recyclability. Recently, Shreedhar et al. [32] utilized Fe₃O₄ nanoparticles as a heterogeneous catalyst for propargylamines synthesis, but a high quantity of the catalyst i.e. 20 mol% was required. In present work we have developed nanosize cobalt oxide (Co₃O₄) as an

efficient, robust and recyclable catalyst for propargylamines synthesis. To the best of our knowledge this is first report for the use of nanosize Co_3O_4 catalyst for any coupling reaction or multi-component reaction.

2. Experimental

The details regarding materials, catalyst preparation, catalyst characterization and typical procedure for the A₃ coupling reactions are included in the supporting information.

2.1. Chemicals and reagents

All chemicals and reagents of A.R. grade were purchased from Spectrochem Chemicals Ltd., Mumbai, India and used without further purification.

3. Results and discussion

The Co₃O₄ nanoparticles were prepared using the different procedures mentioned in the experimental section and characterized using various techniques like TEM, EDAX, BET, XRD, and DLS histogram analysis. TEM image of cobalt oxide revealed that particles are in nanosize and SAED pattern inside TEM image indicated crystalline nature of particles (Fig. 1). The average particle size of cobalt oxide was found to be 45 nm with histogram received by DLS measurement (Fig. 2). The X-Ray diffraction pattern (Fig. 3) of cobalt oxide exhibited prominent peak of (111), (220), (311), (222), (400), (422) corresponding to spinel structure which is in agreement with ICPDS file no-421467. EDAX spectrum of cobalt oxide samples showed peaks corresponding to cobalt and oxygen only (Fig. 4a), which proves that catalyst is essentially pure. The BET surface area of catalyst was found to be 27.86 m²/g. The complete XPS survey spectrum of synthesized nanomaterials is represented in Fig. 4b. In the survey spectra, the main peaks are attributed to Co 2p and O 1 s and C 1 s region indicating absence of any other metallic or inorganic species. To conclude, by hydrothermal synthesis essentially pure Co₃O₄ obtained are well in nanoregion with average particle size 45 nm and average surface area 27 m²/g.

The application of prepared nanosize Co_3O_4 for propargylamines synthesis via A₃-coupling reactions was explored (Scheme 1). The coupling of benzaldehyde, piperidine and phenyl acetylene was selected as a model reaction and the influence of various reaction parameters like solvent, catalyst loading, temperature were studied.



Fig. 4. a. EDAX spectrum of nanosize Co₃O₄. Fig. 4b. XPS spectra of nanosize Co₃O₄.



Scheme 1. Synthesis of propargylamines using cobalt oxide nanoparticles.

To obtain the optimum reaction conditions for synthesis of propargylamines, the optimization of various reaction parameters like effect of temperature, catalyst loading, solvent and time was carried out. The final optimal reaction conditions are: nanosize Co_3O_4 catalyst prepared by hydrothermal synthesis (10 mol%), solvent: toluene (3 mL), temp: 130 °C and time 15 h (Please refer Tables 1–3 for detailed study). We also studied the influence of method of catalyst preparation on model reaction. It was found that Co_3O_4 prepared by hydrothermal synthesis showed better catalytic activity than oxidation method due to larger particle size of Co_3O_4 prepared by oxidation method.(Please refer Table 1, entry 5,11 and supporting information).

The generality and efficiency of developed protocol was investigated using aldehydes with different functional groups, various amines and alkynes to understand the scope and efficiency of the nanosize cobalt oxide as a catalyst for different propargylamines synthesis (Table 4). Various amines were tested for the propargylamines synthesis, in which alicyclic amines like pyrrolidone, morpholine and piperidine gave good yield of corresponding products (Table 4, entries 1-10). It was observed that aldehydes with electron withdrawing and donating groups offers good to moderate yield. Various aldehydes with substituents at different positions were also studied. It was observed that the substituent's at para and meta position gave good yields (Table 1, entries 5-7). In case of ortho substituent lower yield (Table 4, entry 8) was obtained. This can be attributed to the steric hindrance by ortho substituent. Propargylamines synthesis involving phenyl acetylene proceeded smoothly as compared to aliphatic alkynes like 1-hexyne. Present protocol was not so compatible for aromatic amines like aniline (Table 4, entries 1-10). This may be due to difference in nucleophilicity of aniline and cyclic amines. The napthaldehyde was found to react well for present protocol providing excellent yield of desired product (Table 4, entry 11). Thus, propargylamines synthesis was found to be influenced with nature of alkynes.

An important criterion of heterogeneous catalyst is the reusability of catalyst which makes the process more economically feasible. The recyclability of nanosize Co_3O_4 was studied using the series model reaction and was found to exhibit remarkable activity up to ten recycle without any significant decrease in yield of desired product (Table 5, entry 1–10). The TEM images of the catalyst taken after 10th recycle run showed small agglomeration which can be accountable for small decrease in catalyst activity (Fig. 5).

A plausible mechanism (Scheme 2) is proposed on the basis of literature for the probable sequence of events involving activation of the C–H bond of alkyne by Co_3O_4 . The cobalt–acetylide intermediate A generated due the reaction of acetylene and Co_3O_4 . Then A

Table 2

| effect of solven | t |
|------------------|---|
|------------------|---|

| Entry | Solvent | Temperature, °C | % Yield ^b |
|-------------------|-----------------|-----------------|----------------------|
| Effect of solvent | | | |
| 1 | Water | 100 | Traces |
| 2 | Ethylene Glycol | 130 | |
| 3 | Toluene | 130 | 90 |
| 4 | Solvent free | 130 | |
| 5 | Acetonitrile | 100 | Traces |
| 6 | THF | 100 | 30 |

^a Reaction conditions : benzaldehyde (1 mmol), piperidine (1.2 mmol), phenyl acetylene (1.5 mmol), nano Co_3O_4 (20 mol%), solvent 3 mL, Time 24 h. All the reactions were performed in sealed tube. ^b GC Yield.

| Table I | | |
|---------------------|------------------|--------------------------|
| Effect of temperatu | ure and catalyst | screening ^a . |

| Entry | Catalyst | Temperature (°C) | Yield (%) |
|------------------------------|-------------------------------------|------------------|-----------|
| Effect of Temperature | | | |
| 1 | | 110 | |
| 2 | nano Co ₃ O ₄ | 110 | 70 |
| 3 | nano Co ₃ O ₄ | RT | |
| 4 | nano Co ₃ O ₄ | 90 | 40 |
| 5 | nano Co ₃ O ₄ | 130 | 90 |
| Effect of Catalyst Screening | | | |
| 6 | nano ZnO | 130 | 85 |
| 7 | nano Nb ₂ O ₅ | 130 | |
| 8 | bulk Co ₃ O ₄ | 130 | 43 |
| 9 | bulk CoCl ₂ | 130 | 30 |
| 10 | bulk $Co(NO_3)_2$ | 130 | 45 |
| 11 | nano Co ₃ O ₄ | 130 | 79 |

^a Reaction conditions: benzaldehyde (1 mmol), piperidine (1.2 mmol), phenyl acetylene (1.5 mmol), catalyst (20 mol%), time 24 h,toluene 3 mL All the reactions were performed in sealed tube. ^bGC Yield. ^C nanosize cobalt oxide prepared by using oxidation method.

| Table | 3 | |
|--------|---|--|
| Effect | of catalyst loading and time ^a . | |

| Entry | Catalyst Loading (mol%) | Time (h) | Yield (%) ^b |
|------------------|-------------------------|----------|------------------------|
| Effect of cataly | st loadings | | |
| 1 | 7.5 | 24 | 72 |
| 2 | 10 | 24 | 88 |
| 3 | 12.5 | 24 | 90 |
| 4 | 15 | 24 | 90 |
| 5 | 20 | 24 | 90 |
| | | | |
| Effect of time | | | |
| 6 | 10 | 9 | 75 |
| 7 | 10 | 12 | 82 |
| 8 | 10 | 15 | 88 |
| 9 | 10 | 24 | 88 |

^a Reaction conditions: benzaldehyde (1 mmol), piperidine (1.2 mmol), phenyl acetylene (1.5 mmol), nano Co₃O₄,toluene 3 mL. All the reactions were performed in sealed tube.
 ^b GC Vield

Table 4

Synthesis of different propargylamines^a.



(continued on next page)





^bGC Yield.

^a Reaction conditions : aldehyde (1 mmol), amine (1.2 mmol), acetylene (1.5 mmol), nano Co₃O₄ (10 mol%), toluene (3 mL), time (15 h). All the reactions were performed in sealed tube.

reacts with iminium ion B (generated from aldehyde and amine) to provide corresponding amine as a product.

4. Conclusion

In conclusion we have developed an efficient, simple and economical protocol for propargylamines synthesis via A_3 coupling reaction using nanosize Co_3O_4 as a heterogeneous and robust catalyst. Advantages offered by the developed methodology involve easy work up of reaction, elimination of co-catalyst or activator and divergent synthesis of propargylamines with good to moderate yield under ambient reaction conditions. The catalyst was effectively recycled up to ten consecutive runs without significant loss in the yield of desired product. We have explored catalytic activity nanosize Co₃O₄ first time ever for any multi-component reactions (MCR) or coupling reactions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10. 1016/j.catcom.2011.09.012.

Table 5Recyclability study of nano Co₃O₄ catalyst.

| | - |
|------------------|-----------|
| Recycle run (No) | Yield (%) |
| Fresh | 85 |
| 1 | 85 |
| 2 | 85 |
| 3 | 82 |
| 4 | 80 |
| 5 | 80 |
| 6 | 80 |
| 7 | 78 |
| 8 | 78 |
| 9 | 77 |
| 10 | 78 |

^aReaction condition : benzaldehyde (1 mmol), piperidine (1.2 mmol), phenyl acetylene (1.5 mmol), nano Co_3O_4 10 mol%, toluene 3 mL, time 15 h. ^bGC Yield.



Fig. 5. TEM image of catalyst recycled after 10th cycle.



Scheme 2. Mechanistic pathway of propargylamines using cobalt oxide nanoparticles.

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