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ORIGINAL PAPER

MgO nanoparticles as an efficient and reusable catalyst for aza-Michael reaction

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Abstract MgO nanoparticles were prepared by an improved sol–gel technique which appeared to have narrow size distributions. The synthesized magnesium oxide nanoparticles were used as an efficient catalyst in aza-Michael reaction for addition of amines to a series of α,β-unsaturated carbonyl compounds and nitro olefins under solvent-free conditions at room temperature to afford high yields of the β-amino carbonyl and β-nitro amines. The catalyst can be recovered and reused at least five successive runs without loss of activity.

Keywords MgO nanoparticles · Conjugate addition · Aza-Michael · α,β-Unsaturated compounds · Solvent free

Introduction

The aza-Michael reaction, involving the conjugate addition of nitrogen nucleophiles to α,β-unsaturated compounds, to generate a C–N bond constitutes an important step in the synthesis of bioactive natural compounds. β-Nitro amines are important intermediates for the synthesis of many organic compounds [1–3], They can be transformed into 1,2-diamines by reduction, and α-amino acids by Nef oxidation [4, 5]. β-Amino carbonyl compounds are versatile synthetic intermediates for the synthesis of a variety of biologically important natural products such as antibiotics [6], β-amino alcohols [7], β-lactams [8], β-amino acids [9, 10], heterocycles [11], peptides [12] and other nitrogen-containing molecules. These compounds also find wide applications in pharmaceuticals as antispasmodic [13], analgetic [14], local anesthetic [15] and antibacterial activity [16]. Although β-amino carbonyls and β-nitro amines can be prepared by classical Mannich reaction, it has some drawbacks, such as, harsh reaction conditions [17] and long reaction time [18, 19]. Among the different synthetic methodologies, one of the most frequently used is the conjugate addition of amines to α,β-unsaturated carbonyl compounds, which is termed as aza-Michael reaction [20].

Aza-Michael reaction protocols often employ Lewis acids (La [21], Li [21], Bi [22], Sm[23], Y [24], etc.), Brønsted acids [25, 26], base [27] and ionic liquids [28–32]. Accordingly, several other reagents have been developed as a mild promoter of the aza-Michael reaction, i.e., β-cyclodextrin [33], sodium dodecylsulfate (SDS) [34], cinchona alkaloids [35], hexafluoroisopropyl (HFIP) alcohol [36], silica-supported perchloric acid [37], alkaline Al_2O_3 [38], amberlyst-15 [39], silica gel [40], organocatalyst [41], enzyme [42, 43], tetrabutylammonium bromide [44], Dolomite ($CaMg(CO_3)_2$) [45], nanocrystalline CuO [46], $FeCl_3$/montmorillonite K10 [47], HPA/MCM-41 [48], Ps-$AlCl_3$ [49], polystyrenesupported CuI–imidazole complex [50] and MOF-199 [51]. However, some of these methods are associated with drawbacks, such as, high price and toxicity of catalyst, harmful solvents, long reaction time, low yields of the products, harsh reaction conditions, and polymerization of Michael acceptors as unexpected side reactions.

While searching for economical, cheap and better catalysts, it is worthwhile to perform a controlled reaction condition for the Michael reaction using nanoparticles.

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Nanoparticles are core base materials for implementing nanotechnology and attracted researchers in the field of chemistry because of their current promising applications in organic synthesis [52–55]. Surface of metal oxides exhibit both Lewis acid and base character which is characteristic of many metal oxides, especially TiO_2, Al_2O_3, ZnO, MgO; they are excellent adsorbents for a wide variety of organic compounds and increase reactants reactivity. The high surface area-to-volume ratio of metal oxide nanoparticles is mainly responsible for their catalytic properties [56, 57]. High yield, selectivity and recyclibility have been reported for a variety of nanocatalyst-based organic reactions [58].

Amongst these metal oxides, magnesium oxide (MgO), as an exceptionally important material for use in catalysis [59, 60], toxic waste remediation [61], or as additives in refractory, paint, and superconductor products [62, 63], has been attracting both fundamental and application studies [64, 65]. Recently, many papers have been reported for the synthesis of pyranopyrazoles derivatives [66, 67], α-sulfanyl-β-amino acid [68], α-aminoalkyl naphthol [69], organic dithiocarbamates [70], spirooxindoles [71], pyridines and 1,4-dihydropyridines [72], epoxidation, asymmetric Michael and Henry reactions, etc., using heterogeneous nanocrystalline MgO [73–81].

Availability, non-volatility, stability, non-toxicity, reusability, and low cost are advantages of this catalyst which makes it a good candidate for green processes.

To the best of our knowledge in the open literature, aza-Michael-type reactions catalyzed by the nanosized magnesium oxide have not yet been reported. The most conventional method for synthesis of Nano MgO is the decomposition of various magnesium salts or magnesium hydroxide ($Mg(OH)_2$, brucite) [64, 65, 82, 83]. Several novel methods such as controlled preparation, sol–gel route, sol–gel followed by hypercritical drying, amorphous citrate method, and preparation under hydrothermal conditions, have been reported in the literature for the preparation of nanosized MgO particles [84, 85]. Method of synthesis of NP MgO has been discussed in detail in the earlier work. We wish to report for the first time the use of nanocrystalline MgO-catalyzed Michael-type reaction between α,β-unsaturated compounds and amines following an eco-friendly pathway with high yields.

Results and discussion

In this study, nanosized magnesium oxide was synthesized and used as an efficient catalyst in the synthesis of β-amino ketones and β-nitro amines. The particle size and surface morphology of the synthesized MgO depend upon several factors such as the rate of magnesium salts hydrolysis, temperature, type of base, the salt concentration, and calcination procedure. Proper choice of these parameters can lead to particles of uniform morphology and size. In this work, nanosized MgO was prepared by improvement of the method reported by Kumar et al. [86]. Changing the parameters mentioned above resulted in the synthesis of MgO with particles size between 10 and 15 nm.

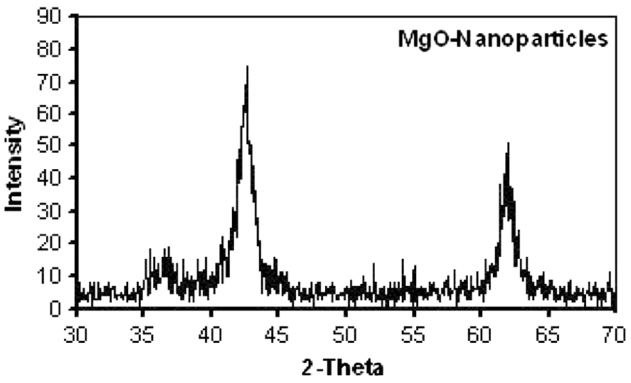


Fig. 1 X-ray diffraction pattern of synthesized MgO nanoparticles

The XRD pattern of the synthesized MgO particles in the 2θ range of 30°–70° is shown in Fig. 1. Broad and intense peaks were observed at 2θ values of 36.8, 42.7 and 62.1, corresponding to the d values of 2.43, 2.11, and 1.49 Å, respectively. These peaks indicate the presence of face centered cubic structure (fcc) of the synthesized sample.

The scanning electron micrograph (SEM) of the MgO sample is presented in Fig. 2a. As indicated in this figure, narrow size distributions with a monodisperse nature and nanoparticles of lamella-like surface morphology are observed. The transmission electron micrograph (TEM, Fig. 2b) of the MgO particles showed particles size between 10 and 15 nm.

The synthesized MgO was used as catalyst in aza-Michael reaction and compared with other catalysts. In a model reaction, chalcone (1.1 mmol) was treated with aniline (1 mmol) in the presence of different catalysts under solvent-free conditions at room temperature (Scheme 1). The results are presented in Table 1.

As it is clear in this table, TiO_2, Fe_2O_3, Al_2O_3 (nano), ZnO (nano) and commercial MgO gave a low yield of the expected product after 12 h (entries 1–5). $NbCl_5$ and KF/Al_2O_3 after a long reaction time gave only a trace amount of the product (entries 6 and 7). The aggregated MgO nanoparticles gave a moderate yield, but when this sample was sonicated for 20 min and then used as catalyst in the model reaction, the highest yield of the product was obtained (entries 8 and 9). This could be due to conversion of agglomerated MgO particles to a monodisperse nature. When aniline reacted with chalcone in the absence of the catalyst, only a trace amount of the product was formed (entry 10), implying the role of the catalyst in this reaction.

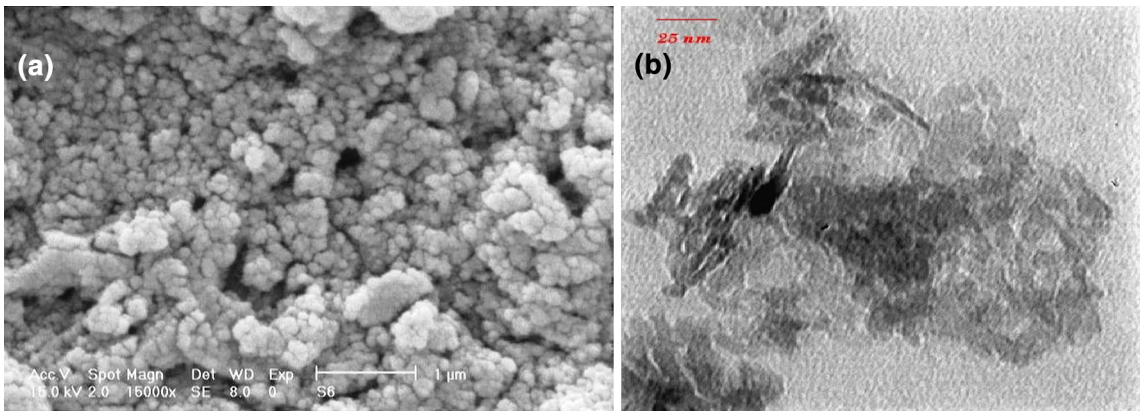


Fig. 2 **a** SEM image of MgO nanoparticles, **b** TEM image of MgO nanoparticles

Scheme1 The reaction of chalcone with aniline as a model reaction

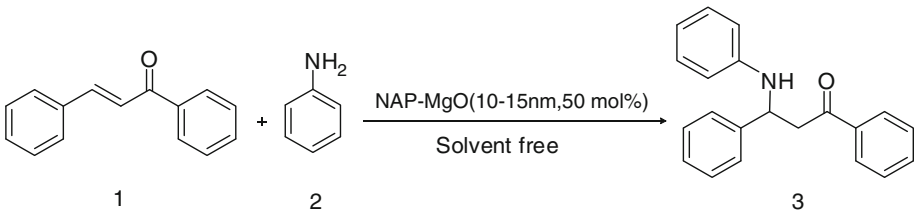


Table 1 Aza-Michael reaction of chalcone with aniline using various catalysts

Entry	Catalyst	Time (h)	Yield (%)
1	TiO_2	12	40
2	Fe_2O_3	12	30
3	Al_2O_3 (nano)	12	30
4	ZnO (nano)	12	35
5	MgO (commercial)	12	45
6	$NbCl_5$	48	Trace
7	KF/Al_2O_3	48	Trace
8	MgO (nano)[a]	7.0	68
9	MgO (nano)[b]	5.0	80
10	None	24	Trace

The reactions were performed using 1.1 mmol of chalcone, 1 mmol of aniline in the presence of 0.024 g catalyst under solvent-free conditions at room temperature

[a] Before sonication

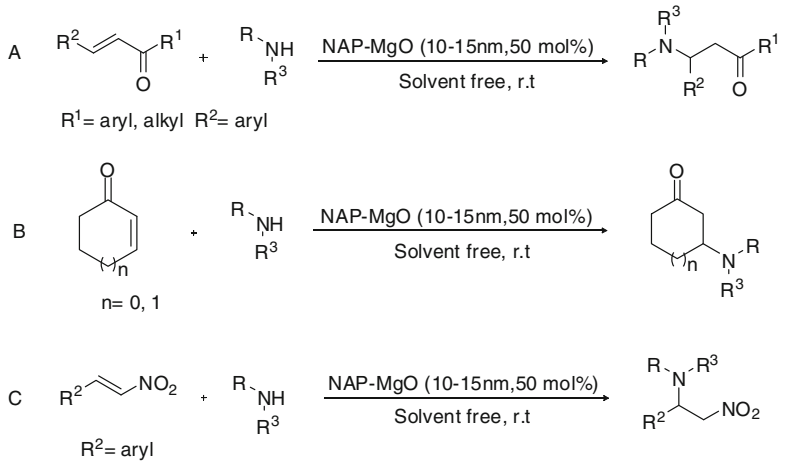
[b] After sonication for 20 min

In order to examine the applicability and generality of this method, different amines reacted with various α,β-unsaturated compounds in the presence of nanosized MgO and results are summarized in Table 2. All the reactions were performed smoothly under optimized mild reaction conditions resulting in high yields of the expected products (Table 2, entries 1–32). The cyclic enones reacted smoothly with aliphatic and aromatic amines to give high yields of the corresponding β-amino ketones (Table 2, entries 2, 4, 9, 10, 15). Acyclic enones in reaction with aromatic amines required longer time to complete the reaction (Table 2, entries 1, 3, 5–8, 11–14, 23, 24). Aliphatic and cyclic amines treated with different enones under reaction conditions to afford high yields in shorter reaction times (Table 2, entries 16, 17, 25–30). However, secondary aromatic amine (entry 18) and imidazole (entry 19) in reaction with chalcone gave the corresponding products in lower yields and required much longer reaction time. *p*-Nitroaniline did not react with chalcone and cyclohexenone even after 24 h (Table 2, entries 33 and 34). This could be due to lower nucleophilic character of the *p*-nitroaniline. Higher electrophilic character of C=C bond in nitrostyrenes resulted in a fast reaction with high yields of the corresponding β-nitro amines (Table 2, entries 8, 20-22, 31, 32).

A plausible mechanism for this reaction is shown in Scheme 2. It is assumed that coordination of the cationic center of Mg^{+2} with the carbonyl oxygen of the α,β-unsaturated carbonyl substrate on its surface could increase the electrophilicity of the β-carbon and enhance the subsequent nucleophilic attack of the amine group to form the intermediate I. Elimination of proton from intermediate I lead to formation β-amino ketones. Similar mechanism for MgO as catalyst in organic transformations reported in the literature [75].

The superiority of the present protocol over reported methods can be seen by comparing the aza-Michael

Table 2 Aza-Michael reactions of various aromatic amines with α,β-unsaturated compounds catalyzed by MgO (nano) at room temperature



Entry	Reaction	Amines	R^1	R^2	Time (min)	Yield (%)[a]	Ref.
1	A	$PhNH_2$	Ph	Ph	5 h	80	[30]
2	B	$PhNH_2$	$n = 1$	$n = 1$	70	86	[30]
3	A	p-CH_3O–$C_6H_4NH_2$	Ph	Ph	150	90	[30]
4	B	p-CH_3O–$C_6H_4NH_2$	$n = 1$	$n = 1$	90	90	[30]
5	A	p-CH_3O–$C_6H_4NH_2$	CH_3	Ph	190	88	–
6	B	p-CH_3O–$C_6H_4NH_2$	Ph	p-CH_3–C_6H_4	36	96	[91]
7	A	p-Cl–$C_6H_4NH_2$	Ph	Ph	10 h	95	[30]
8	C	p-Cl–$C_6H_4NH_2$	–	Ph	24	90	[92]
9	B	p-Cl–$C_6H_4NH_2$	$n = 1$	$n = 1$	200	96	[30]
10	B	$PhNH_2$	$n = 0$	$n = 0$	90	84	[30]
11	A	p-Cl–$C_6H_4NH_2$	Ph	p-CH_3–C_6H_4	80	95	[91]
12	A	$PhNH_2$	CH_3	Ph	5 h	70	[89]
13	A	$PhNH_2$	Ph	p-CH_3–C_6H_4	90	95	[93]
14	A	p-CH_3–$C_6H_4NH_2$	Ph	Ph	3 h	87	[30]
15	B	p-CH_3–$C_6H_4NH_2$	$n = 1$	$n = 1$	90	92	[30]
16	A	$PhCH_2NH_2$	Ph	Ph	3 h	80	[88]
17	A	$PhCH_2NH_2$	Ph	p-CH_3O–C_6H_4	100	85	[88]
18	A	$PhNHCH_3$	Ph	Ph	8 h	65	[94]
19	A	Imidazole	Ph	Ph	12 h	45	[90]
20	C	$PhNH_2$	–	Ph	24	95	[92]
21	C	p-CH_3O–$C_6H_4NH_2$	–	Ph	18	98	[92]
22	C	$PhNH_2$	–	o-O_2N–C_6H_4	30	99	[92]
23	A	$PhNH_2$	Ph	p-CH_3O–C_6H_4	80	96	[30]
24	A	$PhNH_2$	Ph	p-Cl–C_6H_4	4 h	94	[30]
25	A	$PhCH_2NH_2$	Ph	p-Cl–C_6H_4	100	93	[88]
26	B	$PhCH_2NH_2$	$n = 1$	$n = 1$	130	82	[87]
27	B	$CH_3CH_2CH_2CH_2NH_2$	$n = 1$	$n = 1$	35	65	[87]
28	A	Morpholine	Ph	p-CH_3O–C_6H_4	18	96	–
29	B	Morpholine	$n = 1$	$n = 1$	15	97	[87]
30	B	Piperidine	$n = 1$	$n = 1$	18	91	[90]
31	C	Morpholine	–	Ph	5	90	[92]
32	C	Piperidine	–	Ph	3	84	[45]
33	A	p-O_2N–$C_6H_4NH_2$	Ph	Ph	24 h	0	–
34	B	p-O_2N–$C_6H_4NH_2$	$n = 1$	$n = 1$	24 h	0	–

Reaction condition: a mixture of amine (1.0 mmol), conjugated alkene (1.1 mmol) and 0.024 g catalyst was stirred at room temperature for appropriate time

[a] Isolated yield

Scheme 2 The proposed mechanism of aza-Michael addition catalyzed by NAP-MgO

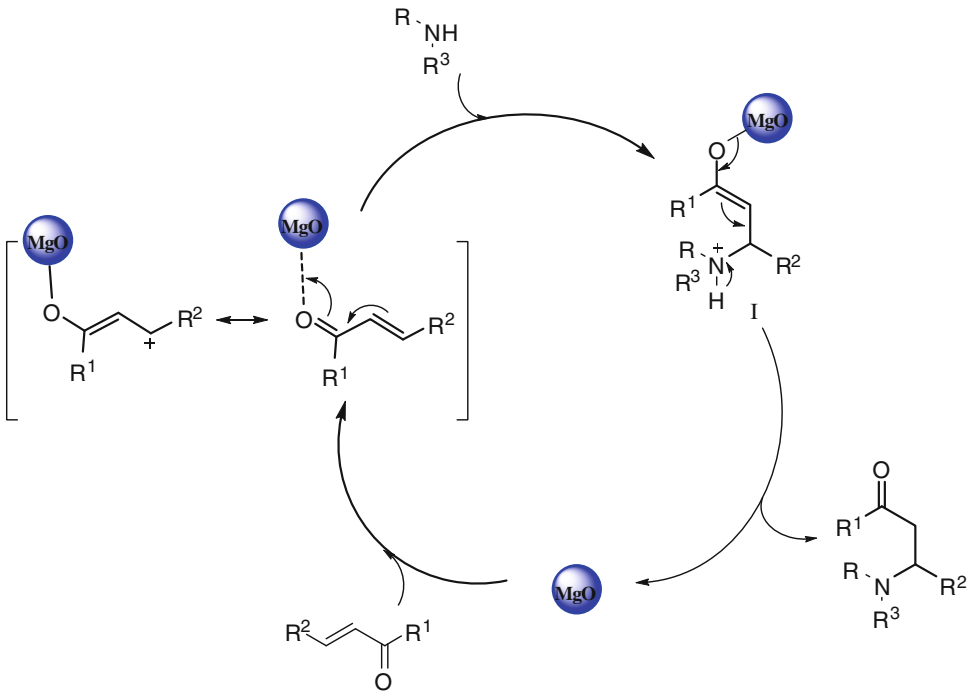


Table 3 Comparison of nanosized MgO catalyst with other reported catalysts for aza-Michael reaction

Entry[a]	Solid catalyst	Conditions	Time (h)	Yield (%) (Ref.)
1	[TMG][Lac] (0. 2 mmol)	Solvent-free, rt	8	85[a][95]
2	Catalyst-free	Glycerol (1 mL), 150 °C	36	97[a][96]
3	[emim][Gly] (0.015 mmol)	EtOH, rt	5	91[a][28]
4	DBU[Ac] (0.3 mmol)	Solvent-free, rt	8	88[a][30]
5	nano-CsPW (0.02 mmol)	EtOH, rt	8	76[a][97]
6	MgO (nano)	Solvent-free, rt	2.5	90[a]
7	$FeCl_3$/montmorillonite K10 (10 %wt/w)	Solvent-free, 60 °C	2	65[b][47]
8	Catalyst-free	Glycerol (1 mL), 100 °C	24	90[b][96]
9	$RuCl_3$ (0.05 mmol)	PEG (4 g), rt	12	87[b][87]
10	[emim][Gly] (0.015 mmol)	EtOH, rt	5	35[b][28]
11	DBU[Ac] (0.3 mmol)	Solvent-free, rt	5	89[b][30]
12	Sodium dodecyl sulfate (8×10^{-3} M)	Stirred vigorously, rt	2.30	90[b][34]
13	[TMG][Lac] (0. 2 mmol)	Solvent-free, rt	4	80[b][95]
14	MgO (nano) (0.5 mmol)	Solvent-free, rt	70 min	86[b]

TMG tetramethylguanidine

[a] Aza-Michael reaction of *p*-methoxy-aniline with chalcone

[b] Aza-Michael reaction of aniline with cyclohexenone

reaction of chalcone with *p*-methoxy-aniline and cyclohexenone with aniline using NP MgO with other catalysts reported in the literature (Table 3).

As it is clear from Table 3, the present method gives high yields of the products in shorter reaction times under very mild reaction conditions (entries 6 and 14).

The reusability of the catalyst was examined for the model reaction (Table 2, entry 1). After completion of the reaction, ethylacetate (5 mL) was added to the reaction mixture, the catalyst was removed by filtration, washed with methanol (3×10 ml) and dried at 150 °C overnight. The recovered catalyst could also be activated by heating at 450 °C for 2 h. The reactivated catalyst was reused for five subsequent runs without significant loss of its activity (Table 4).

Table 4 Reusability of the catalyst for the synthesis of 1,3-diphenyl-3-(phenylamino)propan-1-one (Table 2, entry 1)

Number of runs	Fresh	1	2	3	4	5
Isolated yield (%)	80	80	80	78	78	75

Reaction condition: aniline (1 mmol) with chalcone (1.1 mmol) at room temperature for 5 h

Experimental section

General procedure

Melting points were measured on a Micro Scientific Works apparatus and are uncorrected. IR spectra were recorded on a JASCO IR spectrophotometer using KBr pallets. ^{1}H and ^{13}C NMR spectra were recorded with Bruker NMR spectrometer at 300 MHz using TMS as internal standard. Reactions were monitored by thin layer chromatography (TLC) on 0.2 mm silica gel F254 plates. All the products are known compounds and are characterized by comparing their IR, ^{1}H NMR, and melting points with those reported in the literature. The XRD pattern of the MgO sample was recorded in the 2q range of 30°–70° using a Shimadzu XD-D1 diffractometer employing Cu Kα radiation ($\lambda = 1.5418$ Å). Scanning electron micrograph pictures were taken using Jeol JSM-5300 microscope (acceleration voltage 10 kV). The sample powder was deposited on a carbon tape before mounting on a sample holder. In order to reduce the charge developed on the sample, gold sputtering was done for 3 min. The transmission electron micrographs (TEM) were obtained with a Jeol-1200EX microscope. The MgO sample for TEM was prepared by dispersing the powdered sample in ethanol by sonication and then drop drying on a copper grid (400 mesh) coated with carbon film.

Modified procedure to synthesize nanosized MgO

MgO nanoparticles were synthesized by modification of the procedure reported by Kumar et al. [86]. In a typical procedure, $Mg(NO_3)_26H_2O$ is used as the magnesium source. MgO nanoparticles were obtained by precipitation of the magnesium hydroxide gels in aqueous solution using Mg $(NO_3)_2$ as salt and liquid ammonia as the precipitating agent. Initially, the pH of 200 ml of distilled water was adjusted to 10.5 by addition of liquid ammonia. To this solution, 0.2 M magnesium nitrate solution was added dropwise with continuous stirring. The rate of addition of the salt solution was kept at 30 ml/h. During the addition, the pH of the mixture decreased due to hydrolysis of the salt. The pH was maintained at 10.5 by controlled addition of liquid ammonia solution. The hydration water in Mg $(NO_3)_2.6H_2O$ seems enough to ensure a completion of this reaction. After completion of the precipitation procedure, the mixture was stirred at room temperature for 20 h Then the sample was kept at room temperature for 10 h, filtered, were repeatedly washed with distilled water and dried at 150 °C to give a white powder. The white powders were calcined in air in a muffle furnace using a step temperature controller. The temperature of the furnace was raised linearly from room temperature to 450 °C with an increment of 10 °C/min and finally at 450 °C for 2 h. The temperature was increased very slowly to maximally avoid the sudden collapse of the brucite structure, so as to preserve the morphological features in the final MgO sample. Finally, the sample was sonicated to convert the agglomerated MgO particles to the lamellar structures.

General procedure for the aza-Michael additions

A mixture of amine (1 mmol) and α,β-unsaturated compounds (1.1 mmol) and NAP-MgO (0.024 g) was stirred at 25 °C for appropriate time (Table 2). After completion of the reaction (monitored by TLC), ethylacetate (5 mL) was added, and MgO was removed by filtration. The solvent was evaporated under reduced pressure. Further purification was achieved by crystallization from dicholoromethane:petroleum ether (single spot on TLC) or by column chromatography using ethyl acetate/hexane gradient. The structure of the products was confirmed by physical data, ^{1}H and ^{13}C NMR spectra and comparison with authentic samples.

4-(4-Methoxyphenylamino)-4-phenylbutan-2-one (Table 2, entry 5, a yellow oil, yield 88 %)

IR: 3346 (NH), 1683 (CO) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.1, 2.2 (6H, 2S, $2CH_3$), 2.98–3.01 (2H, m, CH), 4.81 (1H, $J = 8.7$ Hz, CHN), 6.54 and 6.91 (4H, $J = 103$ Hz, 4CH), 7.23–7.39 (5H, m, Ar–H).^{13}C NMR ($CDCl_3$, 75 MHz): δ 30.7, 51.3, 55.7, 113.9, 114.1, 126.3, 127.1, 127.3, 136.3, 141.9, 152.1, 207.2. MS (EI, *m/z*) 269 (M^+). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.78, H, 7.09, N, 5.22.

N-2-Nitro-2-(o-nitrophenyl)ethylaniline (Table 2, entry 22, yellow oil, yield 99 %)

IR: 3446 (NH), 1640, 1605, 1475, 1352 (NO_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.78–5.03 (2H, m, CH_2), 5.8–5.88 (1H, m, CH), 7.73-8.09 (9H, m, Ar–H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 50.9, 78.4, 112.8, 117.5, 125.0, 128.8, 129.1, 129.5, 133.8, 134.2, 146.1, 148.6. MS (EI, *m/z*) 287 (M^+). Anal. Calcd for $C_{14}H_{13}N_3O_4$: C, 58.53; H, 4.56; N, 14.63. Found: C, 58. 54, H, 4.53, N, 14.62.

3-(p-Methoxyphenyl)-3-morpholino-1-phenylpropan-1-one (Table 2, entry 28, white solid, m.p. 150-152, yield 96 %)

IR (KBr): 3386 (NH), 1671 (CO) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.31 (3H, s, CH_3), 2.36–2.55 (4H, m, $2CH_2$), 3.55–3.64 (4H, m, $2CH_2$), 4.41 (1H, t, $J = 8.9$ Hz, CH), 7.44–7.57 (5H, m, Ar–H), 7.9 and 8.02 (4H, 2d, $J = 905$ Hz, 2CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1,

42.2, 50.9,65.3, 67.2, 126.3, 128.0, 128.3, 119.1, 132.2, 136.6, 138.4, 141.1, 198.4. MS (EI, *m/z*) 325 (M^+). Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found: C, 73. 80, H, 7.10, N, 4.28.

Conclusions

A narrow size range MgO nanoparticles (10–15 nm) was synthesized by sol–gel technique and used as a catalyst in the aza-Michael reaction of various aliphatic or aromatic amines with a variety of structurally diverse α,β-unsaturated cyclic and acyclic compounds. The attractive features of this protocol are: simple procedure, operable under solvent-free conditions at room temperature, cost effectiveness, use of recyclable and environmentally benign catalyst, and in most cases good to excellent yields of the desired 1,4-adducts and its adaptability for the synthesis of a diverse set of β-amino carbonyls and β-nitro amines.

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References

1. R. Bloch, Chem. Rev. **98**, 1407–1438 (1998)
2. S. Kobayashi, H. Ishitani, Chem. Rev. **99**, 1069–1094 (1999)
3. A. Acc, Cordova. Chem. Res. **37**, 102–112 (2004)
4. E. M-López, P. Merino, T. Tejero, R.P. Herrera, Eur. J. Org. Chem. **2009** , 2401–2420 (2009)
5. E. Foresti, G. Palmieri, M. Petrini, R. Profeta, Org. Biomol. Chem. **1**, 4275–4281 (2003)
6. M. Liu, M.P. Sibi, Tetrahedron **58**, 7991–8035 (2002)
7. G. Nagendra, C. Madhu, T.M. Vishwanatha, V.V. Sureshbabu, Tetrahedron Lett. **53**, 5059–5063 (2012)
8. S. Comesse, M. Sanselme, A. Daïch, J. Org. Chem. **73**, 5566–5569 (2008)
9. K. Damera, K.L. Reddy, G.V.M. Sharma, Lett. Org. Chem. **6**, 151–155 (2009)
10. B. Weiner, W. SzymaĔski, D.B. Janssen, A.J. Minnaarda, B.L. Feringa, Chem. Soc. Rev. **39**, 1656–1691 (2010)
11. L. Elkaim, L. Grimaud, N.K. Jana, F. Mettetal, C. Tirla, Tetrahedron Lett. **43**, 8925–8927 (2002)
12. C. Palomo, M. Oiarbide, A. Landa, M.C. G-Rego, J.M. García, A. González, J.M. Odriozola, M. M-Pastor, A. Linden, J. Am. Chem. Soc. **124**, 8637–8643 (2002)
13. J.J. Denton, R.J. Turner, W.B. Neier, V.A. Lawon, H.P. Scliedl, J. Am. Chem. Soc. **71**, 2048–2050 (1949)
14. F. Felluga, G. Pitacco, E. Valentin, C.D. Venneri, Tetrahedron:Asymmetry **19**, 945–955 (2008)
15. J.G. Baker, S.J. Hill, R.J. Summers, Trends Pharmacol. Sci. **32**, 227–234 (2011)
16. W.L. Nobles, B.B. Thompson, J. Pharm. Sci. **68**, 1554–1555 (1964)
17. C. Palomo, M. Oiarbide, A. Laso, R. Lo'pez, J. Am. Chem. Soc. **127**, 17622–17623 (2005)
18. X.C. Wang, L.J. Zhang, Z. Zhang, Z.J. Quan, Chinese Chem. Lett. **23**, 423–426 (2012)
19. J.C. Anderson, P. Gareth, G.P. Howell, M. Ron, R.M. Lawrence, C.S. Wilson, J. Org. Chem. **70**, 5665–5670 (2005)
20. A.Y. Rulev, Russ. Chem. Rev. **80**, 197–218 (2011)
21. A.V. Narsaiah, Lett. Org. Chem. **4**, 462–464 (2007)
22. R. Varala, M.M. Alam, S.R. Adapa, Synlett **5**, 720–722 (2003)
23. I. Reboule, R. Gil, J. Collin, Tetrahedron Lett. **46**, 7761–7764 (2005)
24. M.J. Bhanushali, N.S. Nandurkar, S.R. Jagtap, B.M. Bhanage, Catal. Commun. **9**, 1189–1195 (2008)
25. S.A. Fernandes, R. Natalino, P.A.R. Gazolla, M.J.D. Silva, G.N. Jham, Tetrahedron Lett. **53**, 1630–1633 (2012)
26. S. Azad, T. Kobayashi, K. Nakano, Y. Ichikawa, H. Kotsuki, Tetrahedron Lett. **50**, 48–50 (2009)
27. X.J. Tang, Z.L. Yan, W.L. Chen, Y.R. Gao, S. Mao, Y.L. Zhang, Y.Q. Wang, Tetrahedron Lett. **54**, 2669–2673 (2013)
28. N. Morimoto, Y. Takeuchi, Y. Nishina, J. Mol. Catal. A: Chem **368**, 31–37 (2013)
29. A.K. Verma, P. Attri, V. Chopra, R.K. Tiwari, R. Chandra, Monatsh. Chem. **139**, 1041–1047 (2008)
30. A.G. Ying, L. Liu, G.F. Wu, G. Chen, X.Z. Chen, W.D. Ye, Tetrahedron Lett. **50**, 1653–1657 (2009)
31. S.R. Roy, A.K. Chakraborti, Org. Lett. **12**, 3866–3869 (2010)
32. X. Chen, X. Li, H. Song, Y. Qian, F. Wang, Tetrahedron Lett. **52**, 3588–3591 (2011)
33. K. Surendra, N.S. Krishnaveni, R. Sridhar, K.R. Rao, Tetrahedron Lett. **47**, 2125–2127 (2006)
34. H. Firouzabadi, N. Iranpoor, A.A. Jafari, Adv. Synth. Catal. **347**, 655–661 (2005)
35. D. Perdicchia, K.A. Jørgensen, J. Org. Chem. **72**, 3565–3568 (2007)
36. K. De, J. Legros, B. Crousse, D. ele Bonnet-Delpon, J. Org. Chem. **74**, 6260–6265 (2009)
37. C. Mukherjee, A.K. Misra, Lett. Org. Chem. **4**, 54–59 (2007)
38. X. Ai, X. Wang, J.M. Liu, Z.M. Ge, T.M. Cheng, R.T. Li, Tetrahedron **66**, 5373–5377 (2010)
39. A.P. Esteves, M.E. Silva, L.M. Rodrigues, A.M.F. Oliveira-Campos, R. Hrdina, Tetrahedron Lett. **48**, 9040–9043 (2007)
40. L. You, S. Feng, R. An, X. Wang, D. Bai, Tetrahedron Lett. **49**, 5147–5150 (2008)
41. J. Lv, H. Wu, Y. Wang, Eur. J. Org. Chem. **11**, 2073–2083 (2010)
42. K.P. Dhake, P.J. Tambade, R.S. Singhal, B.M. Bhanage, Tetrahedron Lett. **51**, 4455–4458 (2010)
43. L.N. Monsalve, F. Gillanders, A. Baldessari, Eur. J. Org. Chem. **6**, 1164–1170 (2012)
44. G. Imanzadeh, F. Ahmadi, M. Zamanloo, Y. Mansoori, Molecules **15**, 7353–7362 (2010)
45. F. Tamaddon, M. Tayefi, E. Hosseini, E. Zare, J. Mol. Catal. A: Chem. **366**, 36–42 (2013)
46. M.L. Kantam, S. Laha, J. Yadav, S. Jha, Tetrahedron Lett. **50**, 4467–4469 (2009)
47. V.R. Choudhary, D.K. Dumbre, S.K. Patil, RSC Adv. **2**, 7061–7065 (2012)
48. S.L. Xie, Y.H. Hui, X.J. Long, C.C. Wang, Z.F. Xie, Chinese Chem. Lett. **24**, 28–30 (2013)
49. L. Dai, Y. Zhang, Q. Dou, X. Wang, Y. Chen, Tetrahedron **69**, 1712–1716 (2013)
50. L. Li, Z. Liu, Q. Ling, X. Xing, J. Mol. Catal. A: Chem. **353**, 178–184 (2012)
51. L.T.L. Nguyen, T.T. Nguyen, K.D. Nguyen, N.T.S. Phan, Appl. Catal. A **425**, 44–52 (2012)
52. M. Filice, M. Marciello, M.D.P. Morales, J.M. Palomo, Chem. Commun. **49**, 6876–6878 (2013)
53. A. Fihri, M. Bouhrara, B. Nekoueishahraki, J.-M. Basset, V. Polshettiwar, Chem. Soc. Rev. **40**, 5181–5203 (2011)
54. L. Yip, T.M. Kubczyk, T.E. Davies, S.H. Taylor, D.C. Apperley, A.E. Graham, Catal. Sci. Technol. **2**, 2258–2263 (2012)

55. Q. Zhang, H. Su, J. Luo, Y. Wei, Catal. Sci. Technol. **3**, 235–243 (2013)
56. F. Tamaddon, F. Aboee, A. Nasiri, Catal. Commun. **16**, 194–197 (2011)
57. J. Mu, L. Zhang, M. Zhao, Y. Wang, J. Mol. Catal. A: Chem. **378**, 30–37 (2013)
58. M. L. Kantam, S. V. Manorama, P. Basak, V. R. Chintareddy, S. K. Bhargava, in Nanoscale oxides in catalysis: "Manipulation of Nanoscale Materials: An Introduction to Nanoarchitectonics" ed. By K. Ariga (RSC, 2012), p. 129-164
59. V.R. Chintareddy, M.L. Kantam, Catal. Surv. Asia **15**, 89–110 (2011)
60. C.H. Xu, J.K. Bartley, D.I. Enache, D.W. Knight, G.J. Hutchings, Synthesis **19**, 3468–3476 (2005)
61. A. Zare, A. Hasaninejad, A. Khalafi-Nezhad, A.R. Moosavi Zare, A. Parhami, Arkivoc **2007**, 105–108 (2007)
62. N. Na, S. Zhang, S. Wang, X. Zhang, J. Am. Chem. Soc. **128**, 14420–14421 (2006)
63. M. Bag, S. Adak, R. Sarkar, Ceram. Int. **38**, 2339–2346 (2012)
64. X.S. Ye, J. Sha, Z.K. Jiao, L.D. Zhang, Nanostruct. Mater. **8**, 945–951 (1997)
65. M. Sterrer, O. Diwald, E. Knozinger, J. Phys. Chem. B **104**, 3601–3607 (2000)
66. M. Babaie, H. Sheibani, Arab. J. Chem. **4**, 159–162 (2011)
67. H. Sheibani, M. Seifi, A. Bazgir, Synth. Commun. **39**, 1055–1064 (2009)
68. M.L. Kantam, K. Mahendar, B. Sreedhar, B.M. Choudary, S.K. Bhargava, S.H. Priver, Tetrahedron **66**, 5042–5052 (2010)
69. B. Karmakar, J. Banerji, Tetrahedron Lett. **52**, 4957–4960 (2011)
70. B. Karmakar, J. Banerji, Tetrahedron Lett. **52**, 6584–6586 (2011)
71. B. Karmakar, A. Nayak, J. Banerji, Tetrahedron Lett. **53**, 5004–5007 (2012)
72. M.L. Kantam, K. Mahendar, S. Bhargava, J. Chem. Sci. **122**, 63–69 (2010)
73. M.L. Kantam, K. Mahendar, B. Sreedhar, B.M. Choudary, S.K. Bhargava, S.H. Priver, Tetrahedron **66**, 5042–5052 (2010)
74. B.M. Choudary, M.L. Kantam, K.V.S. Ranganath, K. Mahendar, B. Sreedhar, J. Am. Chem. Soc. **126**, 3396–3397 (2004)
75. B.M. Choudary, K.V.S. Ranganath, U. Pal, M.L. Kantam, B. Sreedhar, J. Am. Chem. Soc. **127**, 13167–13171 (2005)
76. Y. Xi, R.J. Davis, J. Mol. Catal. A: Chem. **341**, 22–27 (2011)
77. L. Chakrapani, M. L-Kantam, Synth. Commun. **41**, 3442–3447 (2011)
78. V.K. Das, A.J. Thakur, Tetrahedron Lett. **54**, 4164–4166 (2013)
79. M.L. Kantam, K. Mahendar, B. Sreedhar, K. Kumar, B.M. Choudary, Synth. Commun. **38**, 3919–3936 (2008)
80. M.B.M. Reddy, S. Ashoka, G.T. Chandrappa, M.A. Pasha, Catal. Lett. **138**, 82–87 (2010)
81. V.K. Das, R.R. Devi, A.J. Thakur, Appl. Catal. A: Gen. **456**, 118–125 (2013)
82. S. Ardizzone, C.L. Bianchi, B. Vercelli, Appl. Surf. Sci. **126**, 169–175 (1998)
83. D. Beruto, R. Botter, A.W. Searcy, J. Am. Ceram. Soc. **70**, 155–160 (1987)
84. Y. Ding, G. Zhang, H. Wu, B. Hai, L. Wang, Y. Qian, Chem. Mater. **13**, 435–440 (2001)
85. O.B. Koper, I. Lagadic, A. Volodin, K. Klabunde, J. Chem. Mater. **9**, 2468–2480 (1997)
86. D. Kumar, V.B. Reddy, B.G. Mishra, R.K. Rana, M.N. Nadagouda, R.S. Varma, Tetrahedron **63**, 3093–3097 (2007)
87. H. Zhang, Y. Zhang, L. Liu, H. Xu, Y. Yang, Synthesis **13**, 2129–2136 (2005)
88. M. Zahouily, B. Mounir, H. Charki, A. Mezdar, B. Bahlaouan, M. Ouammou, Arkivoc **2006**, 178–186 (2006)
89. C.R. Brindaban, S. Sampak, K.G. Sakar, Tetrahedron **58**, 983–988 (2002)
90. C. Mukherjee, A.K. Misra, Lett. Org. Chem. **4**, 54–59 (2007)
91. J.S. Yadav, A.R. Reddy, Y.G. Rao, A.V. Narsaiah, B.V.S. Reddy, Synthesis **22**, 3447–3450 (2007)
92. G. Choudhary, R.K. Peddinti, Green Chem. **13**, 276–282 (2011)
93. R. Qiu, X. Xu, L. Peng, Y. Zhao, N. Li, S. Yin, Chem. Eur. J. **18**, 6172–6182 (2012)
94. L. Yang, L.W. Xu, W. Zhou, L. Li, C. Gu-Xia, Tetrahedron Lett. **47**, 7723–7726 (2006)
95. A. Ying, M. Zheng, H. Xu, F. Qiu, C. Ge, Res. Chem. Intermed. **37**, 883–890 (2011)
96. A. Ying, Q. Zhang, H. Li, W. Gong, M. He, Res. Chem. Intermed. **39**, 517–525 (2013)
97. Z. Shobeiri, M. Pourayoubi, A. Heydari, T.M. Percino, M.A.L. Ramırez, C. R. Chimie **14**, 597–603 (2011)