

N,N-Dimethylbiguanide immobilized on mesoporous and magnetically separable silica: Highly selective and feasible organocatalyst for synthesis of β -nitroalcohols

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ABSTRACT

An organosuperbase (N,N-dimethylbiguanide) immobilized on mesoporous and magnetically separable silica supports, was found for the first time, to act as a highly-stable, scalable and efficient heterogeneous catalyst for the Henry reaction under mild and neutral condition. Several factors such as catalyst amount, solvent and reaction time concerning the reactivity were also discussed. The procedure constitutes the first immobilized biguanide promotion of selective synthesis of β -nitroalcohols without addition of stoichiometric amount of any base and showed a broad substrate scope. The uniqueness of this catalyst lay in its cleanness, cost-effectiveness, ease in removal at the end of reaction, and chemoselective formation of a wide range of β -nitroalcohols. These materials can be easily converted to other useful synthetic intermediates which many of them have been exemplified in synthetic organic chemistry and pharmaceutical industry.

Keywords: β -Nitroalcohols, Henry reaction, Magnetic catalysts, Organosuperbases, SBA-15.

1. Introduction

It is well acknowledged that there is a growing need for more cost-effective and acceptable protocols in synthetic chemical and pharmaceutical industry. One of the most important objectives now is to adapt classical processes so that pollution effects are kept to a minimum, with a reduction in energy, consumption of raw materials, and employing green and safe heterogenized catalysts. The immobilization of homogeneous catalysts on nano-scale solid supports provides an opportunity for spreading them over a large surface area, which generally increases their catalytic activity. Silica-based immobilized catalysts, as inexpensive and non-corrosive neutral solids has been well studied and shown to play a prominent role in various organic transformations under heterogeneous conditions [1-3]. One of the main purposes in organic synthetic chemistry is C-C bond formation and in this regard, Henry reaction

(an important atom-economical C-C bond-constructing methodology; also called nitroaldol reaction) [4,5] has been used extensively in many important synthetic strategies [6,7]. This reaction is simply carried out with the help of organic [4,7] and inorganic basic catalysts [8-10], quaternary ammonium salts [11] and electrochemically induced [12]. These catalysts often result in side reactions such as Cannizzaro reaction, nitroalkene formation, Michael reactions, retro-aldol, and Nef reaction [13]. Although organic bases, particularly N-containing ones [14-17], are effective for the Henry reaction, however one of the disadvantages exerted to the reaction is that acidification for removing of base in the work-up procedure is needed, which may lead to the dehydration process and the Nef reaction. Notably, heterogenation of homogeneous organobase catalyst could be an attractive solution to this problem because the heterogeneous catalysts can be easily separated from the reaction mixture [2,18,19]. Although, most of support-based catalysts are separated by filtration or centrifugation, however in these cases, expensive

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ultracentrifugation is often the only way to separate the catalyst from the product [20].

Mesoporous silica-supported catalysts are separated with simple filtration and magnetic-supported ones can be easily removed from the reaction mixture by an external permanent magnet [21,22]. Recently, we reported the synthesis of an organosuperbase (biguanide) immobilized on the silica supports such as SBA-15 (**Cat-1**) [23,24] and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell (**Cat-2**) [25,26] structures (Scheme 1). Our preliminary catalytic evaluations of these nanocomposites showed that both mesoporous SBA-15 and silica-coated magnetic nanoparticles, tethered with biguanide, could act as catalysts with high special surface area, good hydrothermal stability, large pore volume, ease of recovery, and excellent stability in reaction media. At the onset of the present study, no example of the Henry reaction catalyzed by the composite of biguanides and SBA-15 or $\text{Fe}_3\text{O}_4@\text{SiO}_2$ solid supports had been reported. Examining the scope and generality of the above mentioned catalysts, we decided to employ them for the direct Henry reaction of aromatic aldehydes with nitroalkanes and the results are being reported in this work. Our data revealed that the catalysts with considerable catalytic performance could lead to the formation of β -nitroalcohols in clean and easy recycle conditions that can be presumably suitable to produce β -nitroalcohols in large scale.

2. Experimental

2.1. General

All reagents and solvents were obtained from commercial sources and used without further purification. Throughout all experiments distilled water

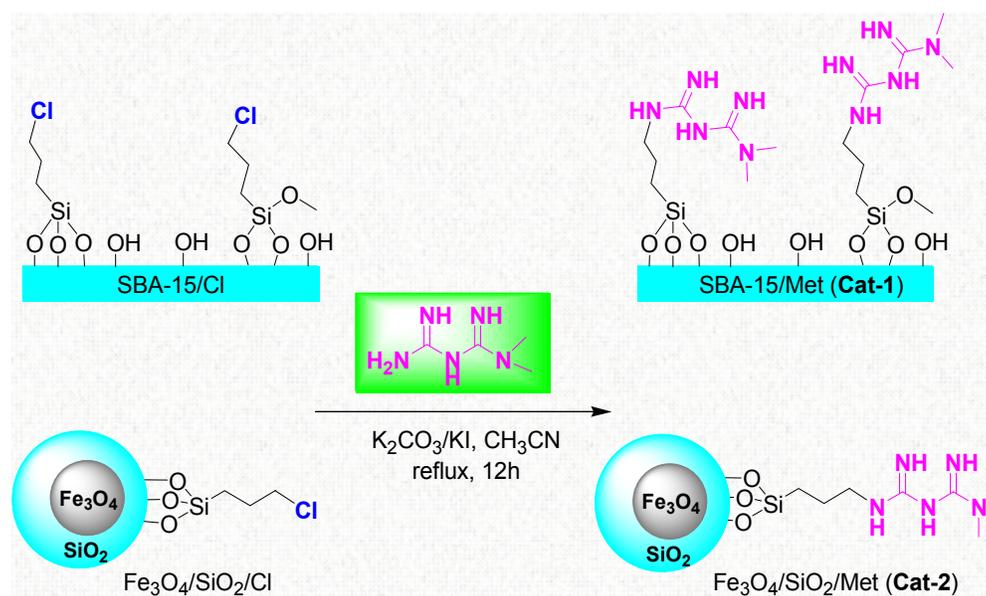
was used and all the experiments were done at room temperature. *N,N*-Dimethylbiguanide-functionalized silica SBA-15 and $\text{SiO}_2@\text{Fe}_3\text{O}_4$ nanoparticles were prepared according to the reported procedures. ^1H and ^{13}C NMR were recorded on a Bruker 200 MHz spectrometer at 200 and 50 MHz, respectively. High-resolution mass spectra (HRMS) were acquired with a MAT 8200 Finnigan instrument. Melting points were measured on a BI BransteadElectrothermal 9200 apparatus in an open glass capillary tube and are uncorrected.

2.2. General procedure for the Henry reaction of nitroalkanes with aryl aldehydes

The nitroaldol reaction (Henry reaction) was performed by mixing aldehyde (1 mmol), nitroalkane (2 mmol), optimized amount of catalyst [**Cat-1** (50 mg); **Cat-2** (100 mg)] and EtOH (2 mL) in a 15 mL round-bottom flask, and stirring the mixture for the desired time at room temperature or 45°C. After completion (monitored by TLC), the catalyst was separated from the mixture and the filtrate was concentrated in vacuum to afford the crude product. Most of the β -nitroalcohols synthesized during this study were known and characterized by comparing with those reported in the literature.

3. Results and discussion

Our investigations on the application of **Cat-1** and **Cat-2** for the Henry reaction of aldehydes and nitroalkanes began with the optimization of the reaction conditions. To evaluate the catalytic efficiency of our catalysts, 4-nitro benzaldehyde was chosen as a probe starting material to optimize the conditions for the direct Henry reaction.



Scheme 1. Schematic representation for the post-synthetic preparation steps of two types of silica-based organocatalysts.

The reactivity of Henry reaction is strongly dependent upon the nature of the solvent used. Therefore, in the first step, the choice of solvent as a requisite in defining the strategies and reactions was studied under identical reaction conditions. Both protic and aprotic solvents as well as neat conditions were examined and the representative data obtained for the synthesis of 2-nitro-1-(4-nitrophenyl) ethanol under various experimental conditions are listed in Table 1. The mixture of reactants and catalyst (**Cat-1** or **Cat-2**) in 2 mL of the chosen solvent was stirred at room temperature, and the progress was monitored by TLC. It was observed that both catalysts act with excellent conversions and short reaction times in EtOH as solvent (Table 1, entry 1). Although H₂O gave promising conversion values, the reactions were sluggish and the performance of the catalysts in H₂O was not satisfactory. In the case of **Cat-1**, the conversion of starting materials to the desired product was low (68%) in H₂O, but increasing the reaction time (up to 90 min) caused complete conversion (Table 1, entry 2). The reaction in polar aprotic solvents like THF and MeCN in the presence of both catalysts showed moderate conversions (Table 1, entries 3 and 4). Surprisingly, the use of CH₃NO₂ (Table 1, entry 5) as solvent gave the worst results even after the reaction time was raised to 60 min. Furthermore, CH₂Cl₂ and Et₂O gave acceptable results only in the presence of **Cat-2** (Table 1, entries 6 and 7), however due to their volatile properties and environmental concerns cannot be considered as safe solvents in large scale transformations. As depicted in Table 1, the desired β -nitroalcohol was obtained in

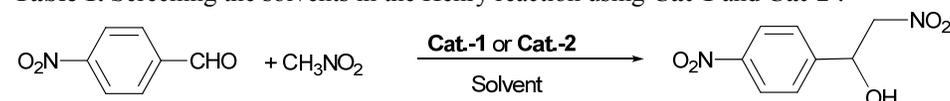
excellent isolated yield (98%) employing EtOH as solvent.

As the amount of catalyst typically plays a significant role in determining the conversion and yield values of adducts in solid catalysis, the optimization of the catalyst amount was then carried out. The catalytic reaction performed in the presence of 10 and 25 mg of **Cat-1** or **Cat-2** only resulted in moderate conversion values (10-75%) (Table 2, entries 1-4).

By increasing the amount of **Cat-1** to 50 mg, the conversion value was reached up to 100% (Table 2, entry 4). In the case of **Cat-2**, however, it was obvious that 100 mg of catalyst was the most suitable amount in view of both the conversion and the yield values (entry 6). Using less than those above-mentioned amounts of the catalysts, the quantitative conversion could not be observed and the reaction proceeded in longer times.

In the work-up step, the catalysts were easily separated either by simple filtration (**Cat-1**) or by applying an external magnet (**Cat-2**). We found that the optimum conditions required a combination of 1.0 mmol of aldehyde, 2.0 mmol of nitromethane, 50 mg of **Cat-1** or 100 mg of **Cat-2** in EtOH (2 ml) and stirring the mixture at room temperature for the desired time. All reactions proceeded cleanly under mild conditions and led to the desired β -nitroalcohols with no side products. If acidic protons are available (i.e., from protic solvent or catalyst), β -nitroalcohols tend to eliminate water to give nitroalkenes. During the course of our investigations, we did not observe any evidence of the formation of nitroalkene (by TLC monitoring), and

Table 1. Screening the solvents in the Henry reaction using **Cat-1** and **Cat-2**^a.

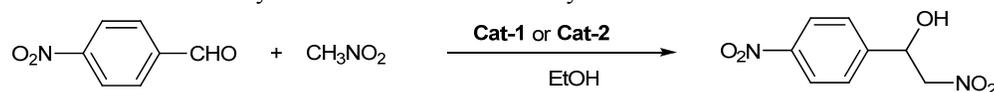


Entry	Solvent	Time (min)/Conversion ^b (%) / Yield ^c (%)	
		Cat-1	Cat-2
1	EtOH	5/100/98 ^c	5/78, (10/100/97 ^c)
2	H ₂ O	5/68, (90/100/96 ^c)	10/65
3	THF	5/55	10/60
4	MeCN	5/60	10/50
5	CH ₃ NO ₂	5/trace, (60/25)	10/trace, (60/15)
6	CH ₂ Cl ₂	5/trace	10/45
7	Et ₂ O	5/trace	10/40

^aAll reactions were carried out with 1.0 mmol of benzaldehyde and 2 mmol of nitromethane in 2 mL of solvent in the presence of 50 mg **Cat-1** or **Cat-2**.

^bDetermined by TLC and ¹HNMR.

^cIsolated yield.

Table 2. Effect of catalyst amount in the direct Henry reaction^a.

Entry	Catalyst amount (mg)	Time (min)/Conversion ^b (%)/Yield ^c (%)	
		Cat-1	Cat-2
1	10	5/40	5/10
2	10	10/55	10/30
3	25	5/65	5/45
4	25	10/75	10/55
5	50	5/100/98 ^c	5/77
6	50	-	10/78
6	100	-	5/90
7	100	-	10/100/97 ^c

^aAll reactions were carried out with 1.0 mmol of benzaldehyde and 2 mmol of nitromethane in 2 mL EtOH in the presence of **Cat-1** or **Cat-2**.

^bDetermined by TLC and ¹HNMR.

^cIsolated yield.

only corresponding β -nitroalcohol was obtained as the final product in a fast and one-pot pathway.

Encouraged by the preliminary results and with a reliable set of conditions in hand, our attention was next turned on the screening of the scope and generality of the above-explained catalytic reaction in more details. As summarized in Table 3, both catalysts could heterogeneously promote the Henry reaction of a series of various aryl and heteroaryl aldehydes with nitroalkanes leading to a wide variety of β -nitroalcohols in good to excellent yield. The catalysts could be applied to both electron-rich and electron-deficient aldehydes. In this way, reaction of terephthalaldehyde and isophthalaldehyde with nitromethane in the presence of both catalysts gave the desired di- β -nitroalcohols via a double cascade Henry reaction (Table 3, entries 3 and 4). When the reaction was performed with halobenzaldehydes (Table 3, entries 5-9), the corresponding 2-nitroalcohols were obtained with superior yields ranging from 78% to 95%. As it was expected, in the presence of **Cat-1** or **Cat-2**, aromatic aldehydes with electron-donating groups were more unfavorable to react with deprotonated nitromethane nucleophile than those with electron-withdrawing groups. Therefore, 2-methoxy and 2-hydroxy benzaldehydes reacted with nitromethane to give the desired products with only low or moderate yields (Table 3, entries 10 and 11).

In these cases, increasing the reaction times led to no significant increase in the conversion of starting materials to the desired products. We also evaluated the reaction of nitroalkanes with cyclic, aryl-alkyl and

conjugated ketones in the presence of **Cat-1** or **Cat-2**. Among them, only cyclohexane showed higher reactivity in short time (Table 3, entry 12) while acetophenone and 1,5-diphenyl-1,4-pentadien-3-one, both failed to give the desired products under the developed condition (Table 3, entries 13 and 14) presumably due to the preferential self-condensation process, retro-Henry reaction or resonance stability [27].

Since many reports of the Henry reaction address the stereochemical outcome (*e.g.*, diastereoselectivity in the case of nitroethane), the possible diastereoselectivity in catalytic performance of our catalysts was also evaluated. Meanwhile, because of more feasibility in separation at the end of reaction, only **Cat-2** was employed as catalyst in this part of our investigations. When nitroethane was used instead of nitromethane, even though the conversions of starting materials to the desired β -nitroalcohols were acceptable, however the longer reaction time (60 min) and higher temperature (45°C) conditions were required. Monitored by ¹HNMR spectra of the obtained β -nitroalcohols, there was a moderate to good diastereoselectivity, up to 79:21, favoring the *anti*-product more considerably for aryl aldehydes carrying either large functionality on the ring (Table 3, entries 17-19) or adjacent heteroatom with lone-pair electrons (Table 3, entry 20). We postulate that the structure of the modified catalyst (**Cat-2**) with a specific feature has a subtle influence on the mechanism of the reaction and the observed stereoselectivity may be directed with a dual activation role of the immobilized N,N-dimethylbiguanide.

Table 3. Biguanide-functionalized silica SBA-15 and magnetite composites catalyzed Henry reactions of nitroalkanes with different aldehydes and ketones.^a

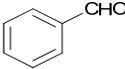
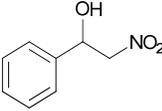
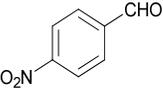
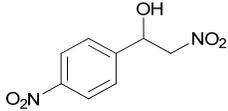
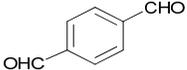
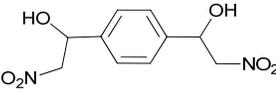
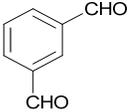
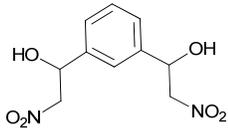
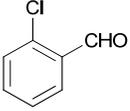
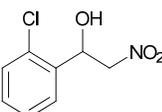
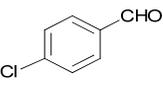
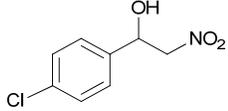
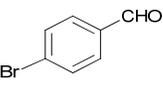
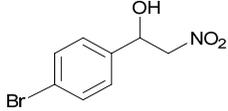
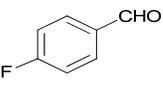
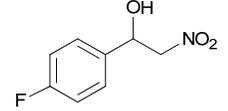
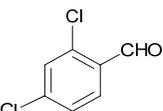
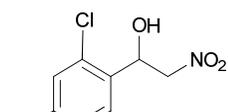
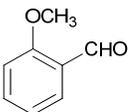
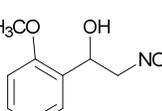
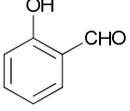
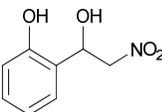
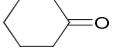
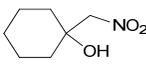
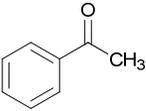
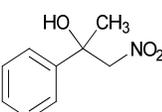
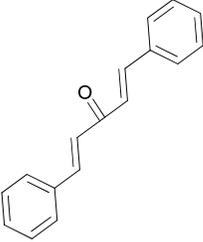
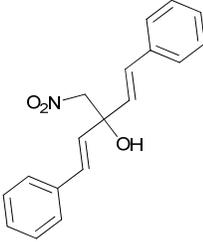
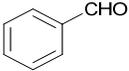
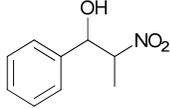
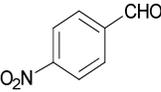
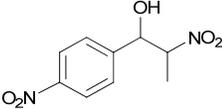
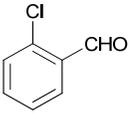
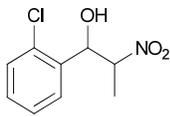
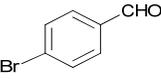
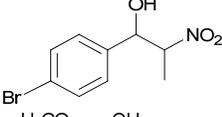
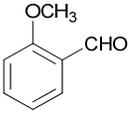
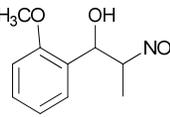
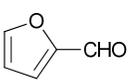
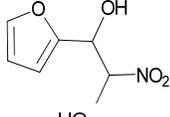
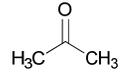
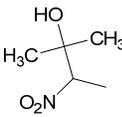
Entry	Substrate	Product	Time (min)/Yield ^b (%)		dr (<i>syn/anti</i>) ^c	
			Cat-1	Cat-2	Cat-2	Cat-2
1			5/91		10/90	
2			5/98		10/97	
3			5/93		10/98	
4			5/90		10/96	
5			5/86		10/88	
6			5/78		10/85	
7			5/86		10/90	
8			5/88		10/92	
9			5/85		10/95	
10			5/40 (60/41) ^d		10/41 (60/49) ^d	
11			5/48 (60/50) ^d		10/52 (60/55) ^d	
12			5/75		10/88	
13			N.R. ^e		60/trace	

Table 3. (Continued).

14			N.R. ^e	N.R. ^e
15			-	60/85 43:57
16			-	60/88 41:59
17			-	60/66 37:63
18			-	60/60 34:66
19			-	60/58 38:62
20			-	60/78 21:79
21			-	N.R. ^e -

^aThe reaction of aldehydes or ketones (1.0 mmol) and nitroalkane (2.0 mmol) in the presence of Cat-1 or Cat-2 were carried out either at room temperature or 45°C.

^bIsolated yield.

^cDiastereoselectivity was determined by ¹H NMR spectroscopy.

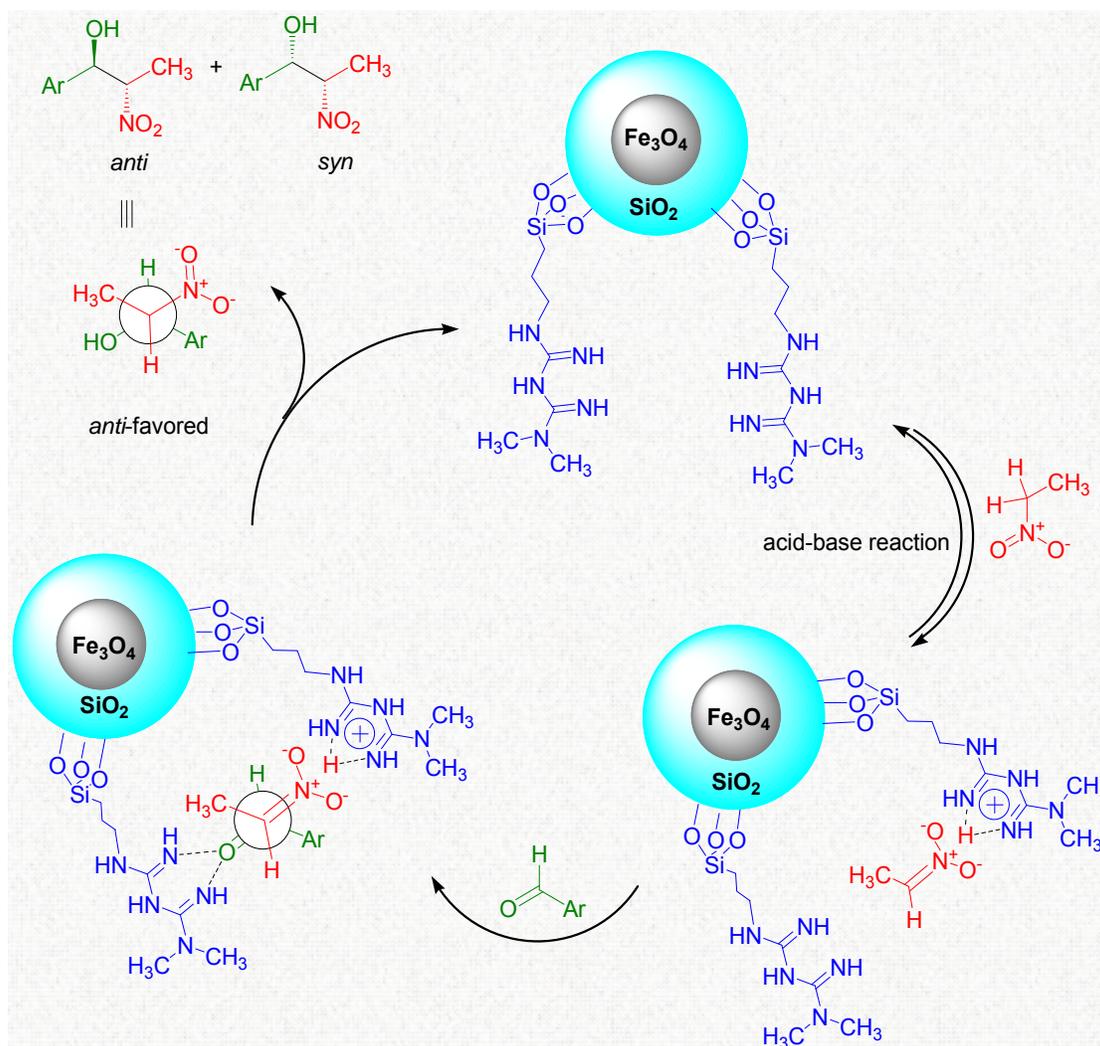
^dThe yields were low even after increasing of reaction time to 60 min.

^eNo reaction was carried out after 24 h.

It is believed that the deprotonation of nitroalkanes in Henry reaction is necessary for the proceeding of reaction. In the present study, the immobilized biguanide as an organosuperbase with $pK_a = 10.8$ [15,23], can simply deprotonate the nitroethane to nitronate anion. Additionally, the selectivity is presumably due to the controlled and directed settlement of the starting materials toward active site of the catalyst. In one hand, an acid-base reaction of nitroethane (with acidic protons) and immobilized organosuperbasebiguanide leads to the formation of nitronate anion followed by an electrostatic interaction between this anion and protonated form of catalyst. On the other hands, hydrogen bonding-assisted positioning of aldehyde through its oxygen terminus onto the biguanide moiety on catalyst provides an *anti*-selective arrangement for the intermediates and eventually for

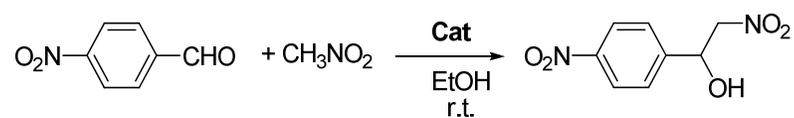
the final products. A hypothesized mechanism for these immobilized biguanide-catalysed reactions is depicted in Scheme 2.

Finally, reusability of the catalysts was evaluated by carrying out repeated runs of the reaction on the same batch of the catalyst in the case of the model reaction. Upon completion of each reaction, the catalyst was easily separated, washed copiously and heated at 80°C for 6 h. Then, it was reused in the reaction with a fresh mixture of starting materials. The results showed that both catalysts could be reused several times without any modification and no significant loss of activity performance was observed. In the case of **Cat-1**, the performance slightly decreased after 5th run, mainly due to the partially blockage of the SBA-15 pores. However, catalyst **Cat-2** worked without significant degradation in the catalytic performance (Table 4).



Scheme 2. Proposed catalytic cycle for the diastereoselective formation of β -nitroalcohols catalyzed by **Cat-2**.

Table 4. Yield of the model reaction with the recycling of **Cat-1** and **Cat-2**.



Run	Yield (%) ^a	
	Cat-1	Cat-2
1	98	97
2	97	96
3	96	96
4	93	95
5	91	93
6	70	92
7	63	92
8	58	88

^aIsolated yield.

Conclusion

In summary, an organic superbase (*N,N*-dimethyl biguanide), immobilized on mesoporous silica SBA-15 and magnetically separable nanoparticle supports was found, for the first time, to act as efficient catalyst for the Henry reaction under mild conditions. Employing these new nanocatalysts, the reactions were carried out in fast (5-10 min), clean and cost-effective manner with possible reusability of the catalysts for several runs. Avoiding of organic volatile solvents and toxic catalysts enabled an operationally green new portal to β -nitroalcohols. In the case of magnetite support, ease in separation of the catalyst with an external magnet simply eliminates the filtration process and make the condition even greener. Additionally, there was a good stereoselectivity in the formation of β -nitroalcohols obtained from the reaction of nitroethane with aldehyde which was believed due to the dual activation role of the catalyst.

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