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Green synthesis of 1,4-benzodiazepines over La_2O_3 and $\text{La}(\text{OH})_3$ catalysts: possibility of Langmuir–Hinshelwood adsorption†

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Lanthanum oxide [La_2O_3] and lanthanum hydroxide [$\text{La}(\text{OH})_3$] have been utilized as bases for the three-component reaction of aldehyde, dimedone and *o*-phenylenediamine for the synthesis of 1,4-benzodiazepine derivatives. The X-ray diffraction pattern shows pure phase formation of both catalysts. The basicity of La_2O_3 and $\text{La}(\text{OH})_3$ was measured by CO_2 -TPD (temperature programmed desorption) experiment. The measurements indicate the presence of basic sites that are useful for the reaction. Surface area measurements using Brunauer–Emmett–Teller (BET) reveal a low surface area for both the materials. TEM measurements indicate agglomerated particles with heterogeneous size distribution. The multicomponent reaction also proceeds smoothly in aqueous media as well as organic solvents. The heterogeneous catalyst was successfully recycled for 11 iterations without losing the catalytic activity. Several reactions were performed to understand the mechanism of the adsorption and the experiments suggest that the reaction may possibly proceed by a Langmuir–Hinshelwood adsorption mechanism.

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Introduction

Multi-component reactions (MCR) provide an attractive synthetic strategy to develop structurally diverse organic molecules.^{1,2} Simple experimental procedures and one-pot syntheses make MCRs highly sought after for the generation of several different structural variants of organic compounds.^{3,4} MCRs with heterogeneous catalysts offer great advantages due to atom economy, catalyst recyclability, low catalyst loading and high synthetic yields apart from the benefits that it may offer to the environment.^{5–7} Some multi-component one-pot reactions involving heterogeneous catalysts include the synthesis of 1,4-dihydropyridines,^{8,9} xanthenes,^{10,11} spirooxindole-pyrimidines,¹² pyrroles,¹³ quinoxalines,¹⁴ pyridines,¹⁵ isoquinolones¹⁶ and diazepines.^{17–20} Benzodiazepines are heterocyclic compounds with pharmacological applications^{21,22} involving anti-tumor and anti-parasitic activities.^{23–25} Synthesis of these biologically relevant benzodiazepine derivatives was achieved through ionic liquid catalysis,²⁶ solid phase synthesis,^{5,27} organometallic reagents^{28–30} and by other methods.³¹ Previous examples of heterogeneous catalysts utilized for the synthesis of

substituted benzodiazepines include ZnS nanoparticles, chitosan supported Fe_3O_4 nanoparticulate materials,³² silver salts of silico-tungstic acid, $\text{Sn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, MoO_3 – SiO_2 bifunctional catalysts, mixed-metal oxides^{33–39} etc. Solid-base catalysts involving alkaline earth metal oxides, alkali doped materials, transition metal oxides and hydrotalcites were also widely utilized for organic reactions.^{40–43} But these catalysts are limited by their recyclability. La_2O_3 and $\text{La}(\text{OH})_3$ are highly basic and cost effective basic materials which make them suitable for many organic reactions. La_2O_3 is commonly used as a support oxide in gas solid reaction in catalytic converters and methane activation.^{44–47} Recently we demonstrated the utility of lanthanum oxide and lanthanum hydroxide as recyclable catalysts for Michael addition and Hantzsch reactions.⁴⁸ The economic benefit offered by synthetic ease of the catalysts, recyclability and the removal of tedious purification procedures is key to the development of heterogeneous catalytic materials. Extending our earlier work, herein, we report one-pot green synthesis of benzodiazepine derivatives using recyclable La_2O_3 and $\text{La}(\text{OH})_3$ as heterogeneous catalysts. Mechanistic possibility involving Langmuir–Hinshelwood adsorption mechanism is also discussed.

Experimental section

All the reagents used in the synthesis were purchased from Aldrich and SD fine chemicals and were without any further purification. La_2O_3 and $\text{La}(\text{OH})_3$ that were used in the synthesis

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† Electronic supplementary information (ESI) available: Characterization spectra (^1H -NMR, ^{13}C -NMR and mass) of the synthesized molecules, catalyst removal procedure. See DOI: 10.1039/c6ra22719h



were prepared by solution combustion method using urea as a fuel.⁴⁸ Briefly, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (5 g) and urea (1.734 g) were dissolved in distilled water (20 mL) followed by heating in a muffle furnace at 500 °C. Dehydration of the solution followed by combustion gave a white powder that consisted of the mixed phases of $\text{La}(\text{OH})_3$, La_2O_3 and some unknown phases. Calcination of this powder at 700 °C for 10 h led to the formation of pure La_2O_3 phase. La_2O_3 converts back to pure $\text{La}(\text{OH})_3$ if left open in the atmosphere for 24 h. Re-calcination under similar conditions was required to regain the La_2O_3 phase. The basic property of La_2O_3 and $\text{La}(\text{OH})_3$ is investigated by using Temperature Programmed Desorption (TPD) with CO_2 gas. To determine the CO_2 desorption ability of the catalyst, flame ionization detector (FID) is used. 50 mg of the catalyst was placed in a quartz tube of (6 mm OD, 4 mm ID and 25 cm length) and flushed with N_2 gas from room temperature to 150 °C with a flow rate of 30 mL min^{-1} . This step was necessary to remove the moisture from the sample. After reaching the final temperature (150 °C), it was allowed to cool down to room temperature. The flow of nitrogen gas was stopped and the sample was flushed with CO_2 at the same flow rate for 45 min. To ensure removal of any residual gaseous phase or weakly adsorbed CO_2 gas, the sample was again flushed in nitrogen gas for 30 min at room temperature. The sample was then heated in the presence of nitrogen gas with the same flow rate from room temperature to 600 °C at the heating rate of 10 °C min^{-1} to desorb the gas. Water formation, particularly from $\text{La}(\text{OH})_3$, was removed by using anhydrous CaCl_2 tube connected in the gas line before it enters the detector. The peak area recorded for each catalyst gave an indication of the amount of CO_2 adsorbed on the catalyst and gives a measure of basicity of the catalyst.

Structural characterization of the catalysts before and after the reaction was carried out by X-ray diffraction (XRD) with Bruker D8 Discover diffractometer using $\text{Cu K}\alpha$ in the Bragg angle range of 10–80°. BET surface area were estimated using N_2 sorption isotherms obtained at 77 K using Micrometrics ASAP 2020 instrument. Samples were degassed at 90 °C for 12 h with a flow of N_2 gas. Transmission electron microscopy (TEM) for morphological characterization was carried out using Philips, Tecnai 20 microscope at 200 kV by dispersing the powdered catalyst in methanol and depositing it on a copper grid. NMR spectra of the synthesized samples were recorded using Bruker Avance (500 MHz) spectrophotometer in CDCl_3 or DMSO (D_6) as the solvent using tetramethylsilane as internal standard.

Results and discussion

Structural characterization of La_2O_3 and $\text{La}(\text{OH})_3$ was carried out using XRD (Fig. 1). The XRD pattern shows sharp, intense peaks confirming high crystallinity for both La_2O_3 and $\text{La}(\text{OH})_3$. Pure phases of both La_2O_3 (JCPDS 73-2141) and $\text{La}(\text{OH})_3$ (JCPDS 13-1481) are obtained using the solution combustion method. The particle size was estimated by using the Scherrer equation,⁴⁹ $D_p = 0.94 \left[\frac{\lambda}{\beta_{1/2} \cos \theta} \right]$. The obtained particle size for La_2O_3 is 9.55 nm and 5.41 nm for $\text{La}(\text{OH})_3$. No changes in the

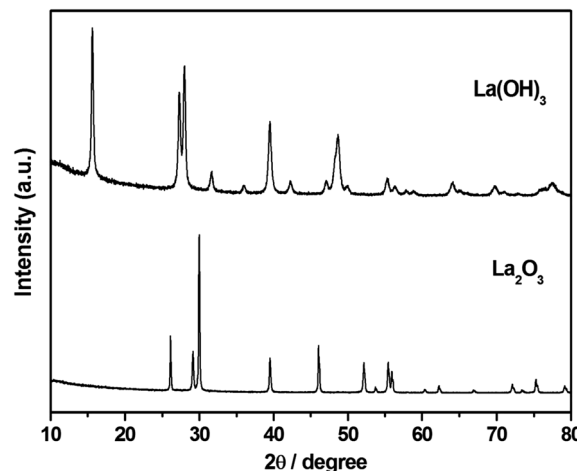


Fig. 1 XRD of combustion synthesized La_2O_3 and $\text{La}(\text{OH})_3$. La_2O_3 changes to $\text{La}(\text{OH})_3$ after the reaction while $\text{La}(\text{OH})_3$ retains the crystal structure.

crystal structure were noticed for $\text{La}(\text{OH})_3$ but La_2O_3 converts to $\text{La}(\text{OH})_3$ if kept open to atmosphere for about 24 h or after the organic synthetic reaction.⁴⁸ The BET surface area obtained was 4.70 $\text{m}^2 \text{g}^{-1}$ and 11.0 $\text{m}^2 \text{g}^{-1}$ for La_2O_3 and $\text{La}(\text{OH})_3$ respectively. The requirement of synthesis of these compounds requires high temperature (700–800 °C) calcination for a long time (10 h) causing the surface area to reduce specifically for La_2O_3 .

Morphology of La_2O_3 and $\text{La}(\text{OH})_3$ (Fig. 2) was investigated using transmission electron microscopy (TEM). $\text{La}(\text{OH})_3$ shows agglomerates of highly heterogeneous particles. Boundaries of the particles are not visible throughout and shape also cannot be defined. Black spots possibly represent stacking of the particles over each other. TEM of La_2O_3 on the other hand shows particles with well-defined shapes growing in a particular manner. Particles are still agglomerated, yet distinguishable from each other. Although crystallinity cannot be established in the absence of lattice fringes, coupled with XRD data, we can confirm that both $\text{La}(\text{OH})_3$ and La_2O_3 are well crystalline in nature.

The CO_2 -TPD experiment is performed to estimate the basicity of La_2O_3 and $\text{La}(\text{OH})_3$ at room temperature. The obtained TPD curves are shown in Fig. 3. Since these compounds are basic in nature, they show considerable CO_2 uptake even at room temperature. It has been previously reported that CO_2 desorption temperature can classify the strengths of the basic sites.⁵⁰ La_2O_3 shows two major peaks with peak temperatures 350 °C and 500 °C. This indicates that there are two different basic sites with varying strengths and the broad nature of the peak suggests that La_2O_3 has a wide range of distribution in basic site strength. Considering the amount of CO_2 adsorbed over the surface, $\text{La}(\text{OH})_3$ appear more basic as the area under the peaks is almost two times higher than La_2O_3 . However, $\text{La}(\text{OH})_3$ also has higher surface area (~2.5 times) than La_2O_3 resulting more CO_2 to adsorb on its surface. Further, considering the normalization of temperature and peak areas by BET surface area measurements, both the catalysts can be



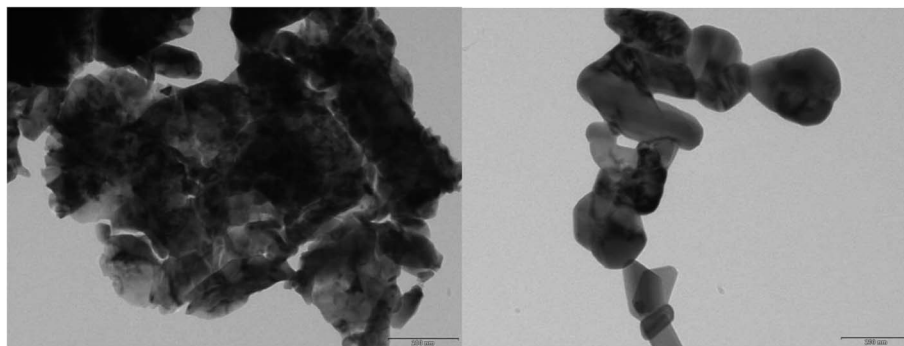


Fig. 2 TEM of combustion synthesized La(OH)_3 and La_2O_3 in the same magnification and resolution. Morphological differences are apparent.

considered equally basic with only slight difference in the energetics at higher temperature.

To demonstrate the utility of La_2O_3 and La(OH)_3 as bases, we utilized one-pot synthesis of 1,4-benzodiazepines. Table 1 lists different reactants and the products obtained. In a typical procedure, 1 mmol of *o*-phenylenediamine (OPDA) was taken in a round bottom flask and appropriate equivalents of lanthanum oxide [La_2O_3] or lanthanum hydroxide [La(OH)_3] in a suitable solvent. The contents were stirred for five minutes followed by the addition of 1 mmol of dimedone [Scheme 1]. The reaction mixture was heated to 60 °C for 15 minutes while being stirred until the observation of a new spot in thin layer chromatography [50 : 50 (ethyl acetate : petroleum ether)]. 1 mmol of a desired aldehyde derivative was then added slowly to the above reaction mixture. After completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature followed by the addition of ice cold water. The contents were filtered using a Gooch crucible and the aqueous components were discarded. The organic components were extracted with ethyl acetate and dried using sodium sulfate.

Concentration under reduced pressure followed by recrystallization in ethyl acetate yielded the desired product. No column chromatography was required. After structural confirmation of the product, 10 different experiments varying the aldehyde (aliphatic, heterocyclic or aromatic bearing electron donating or electron withdrawing groups) were performed (entries 1–10) as showed in the Table 1. In all cases, the reactions gave good to excellent yields revealing high activity of the catalysts under different substrate conditions. Similarity in the yield and reaction time confirms that the small difference in the basicity of La_2O_3 and La(OH)_3 does not affect the catalytic property of both the materials and both the materials have similar type of useful basic sites. In general, it is expected that the basic sites of lanthanum oxide or lanthanum hydroxide catalyze coupling of dimedone with *o*-phenylenediamine and subsequently the formation of seven membered cyclic product.

Screening the solvent

In order to verify the medium effects on the reaction kinetics, the reactions were performed in different solvents as listed in Table 2. The solvent screening was done using benzaldehyde, dimedone and OPDA as the reagents (entry 1: Table 1) in the presence of 0.01 equivalents of catalyst [La_2O_3 or La(OH)_3] at 60 °C. As shown in Table 2 poor yields were obtained with non-polar solvents (heptane, toluene, dioxane, THF). However, in the presence of polar solvents such as acetonitrile improved yields were obtained. Higher yields were obtained in the presence of DMSO, DMF and methanol with reduced reaction times. More importantly, the same reaction in aqueous media also gives excellent yields with comparable reaction kinetics demonstrating the greener approach of the catalysts utilized.

Catalyst loading

The reaction of benzaldehyde, dimedone and OPDA at 60 °C with water was chosen to understand the optimum catalyst loading required for the reaction. Table 3 reveals success of the reactions with 0.001 equivalents of catalyst (entry 1), although the reaction times are on a higher side. Increase in the amount of catalyst (0.01 to 0.2 equivalents), results in the decrease of reaction times but product yields do not change much (Table 4).

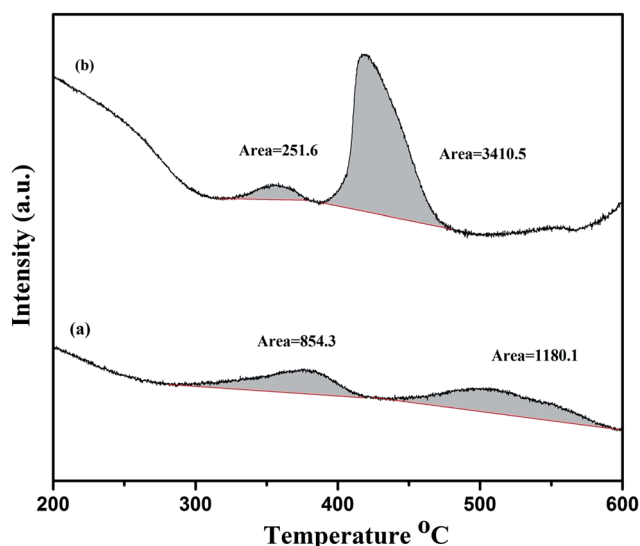


Fig. 3 Temperature programmed desorption of CO_2 . (a) La_2O_3 (b) La(OH)_3 . CO_2 adsorption is carried out at room temperature followed by desorption in the temperature range of 200 to 600 °C.



Table 1 List of the reactions performed with the different aldehydes, their reaction times and the isolated product yield

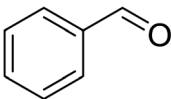
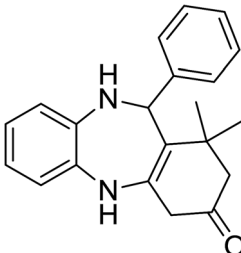
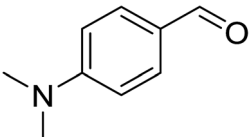
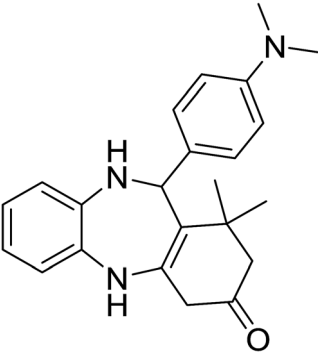
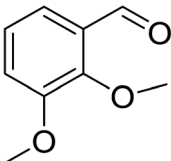
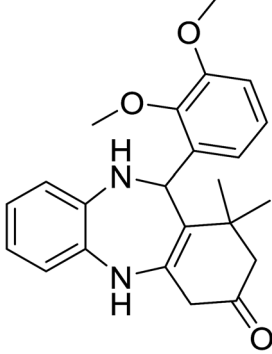
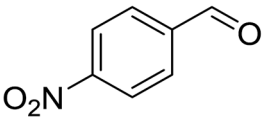
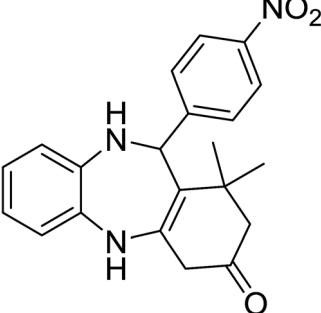
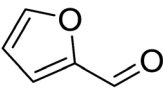
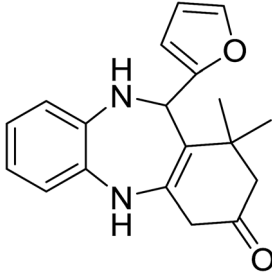
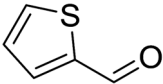
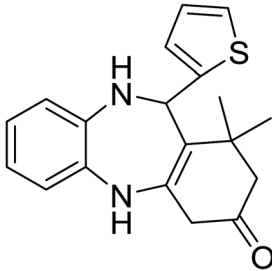
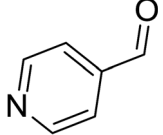
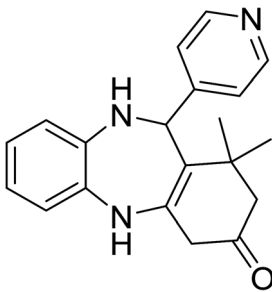
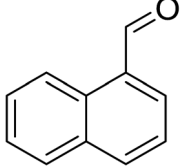
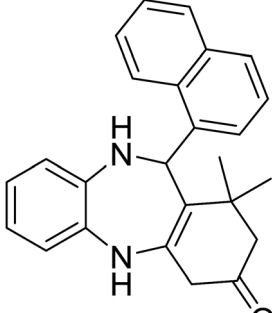
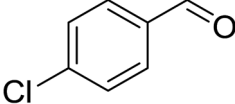
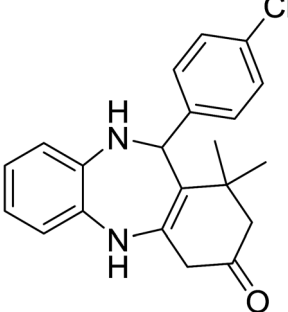
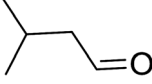
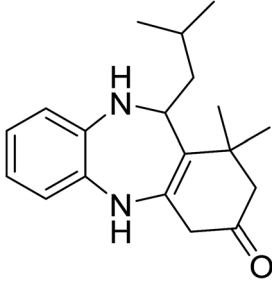
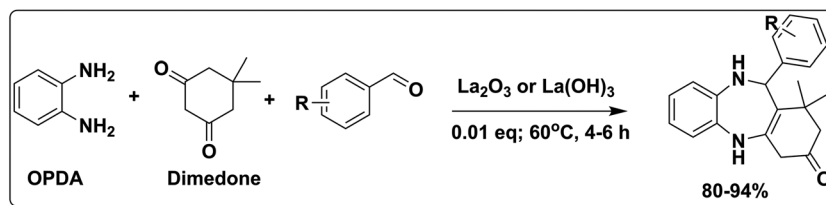
Entry	Reactant A	Reactant B	Reactant C	Product	Time (h) La ₂ O ₃ /La(OH) ₃	Yield (%) La ₂ O ₃ /La(OH) ₃
1	OPDA	dimedone			4/3.5	81/76
2	OPDA	dimedone			4.6/5	79/82
3	OPDA	dimedone			4.5/4.5	80/76
4	OPDA	dimedone			3.5/3	83/85
5	OPDA	dimedone			4.5/5	81/79



Table 1 (Contd.)

Entry	Reactant A	Reactant B	Reactant C	Product	Time (h) La ₂ O ₃ /La(OH) ₃	Yield (%) La ₂ O ₃ /La(OH) ₃
6	OPDA	dimedone			4.8/5	76/79
7	OPDA	dimedone			5/4.5	74/76
8	OPDA	dimedone			4/3.5	69/71
9	OPDA	dimedone			3.6/4	84/81
10	OPDA	dimedone			5/4.5	75/70





Scheme 1 Schematic of a synthetic strategy for preparation of 1,4-benzodiazepine derivatives.

Recyclability of the catalyst

Compared to the homogeneous catalysts, heterogeneous catalysts have an advantage of reusability, hassle-free catalyst removal providing a cost-effective method in the industrial scale production. The reaction given in entry 1, Table 1 was used to understand the catalyst recyclability. Fig. 4 illustrates that the catalyst can be recycled for 11 cycles without any loss of activity. Further reactions could not be conducted because of the gradual loss of catalyst in each cycle.

Table 2 Solvent screening in the presence of 0.01 equivalents of catalyst

S. no.	Solvent	Reaction time (in hours)	Yield (%)
1	Heptane	8.7	41
2	Toluene	9	39
3	Dioxane	7.8	45
4	THF	8.3	48
5	Acetonitrile	6	67
6	DMSO	4.5	82
7	Methanol	4	79
8	Water	4	81

Table 3 Effect of catalyst loading on reaction kinetics

S. no.	Catalyst loading	Reaction time (hours)	Product yield (%)
1	0.001	8.5	79
2	0.005	7	75
3	0.01	4	81
4	0.05	3.5	80
5	0.1	3	78
6	0.2	3	82

Table 4 Mechanistic understanding of reactions

Reaction no.	Reagent addition sequence	Reaction time (hours)	Yield (%)
1	A, B, C	4	81
2	A, C, B	5	56
3	B, A, C	4.5	77
4	B, C, A	—	—
5	C, A, B	—	—
6	C, B, A	—	—

Understanding the adsorption of the reactants over the catalyst surface

Heterogeneous catalysis is primarily based upon the adsorption phenomenon. There are two major mechanisms involved in the adsorption processes; Langmuir–Hinshelwood and Eley–Rideal mechanisms. In the former, all the three reactants are required to adsorb on the catalyst surface while in the latter, adsorption of all the reactants is not needed. To gain further insight of the type of adsorption mechanism, we performed one reaction (entry 1, Table 1) in six different ways [Fig. 5].

The reactants OPDA, dimedone and benzaldehyde were labeled A, B and C respectively for simplicity. For this, water was used as the solvent with 0.01 equivalents of the catalyst and the reaction was performed at 60 °C. Each reactant was added step by step with a time gap of 15 minutes.

Method 1. First A was added followed by addition of B and C with 15 minutes gap of each addition. We identified the disappearance of A in 15 minutes (by TLC), indicating the adsorption of A on the catalyst surface. After addition of B, in 15 minutes a new TLC spot was noticed that indicates the reaction has taken place between A and B, then we have added C. The reaction was smooth and completed in 4 h. The product was isolated, crystallized and characterized by NMR. The synthetic yield was 81%.

Method 2. In this, the sequence of the reagents is A, C followed by B. A was added first and in 15 minutes C was added to the reaction mixture. After the addition of C, TLC showed three

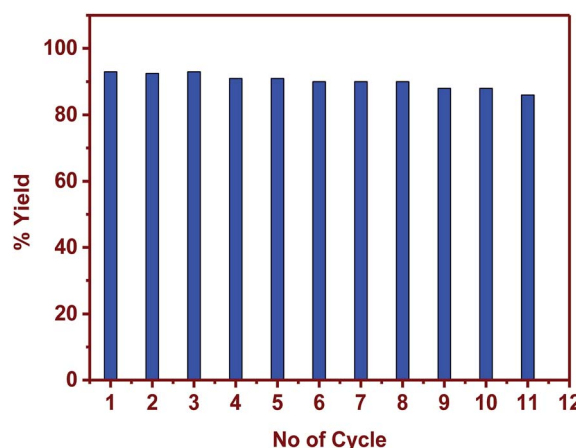


Fig. 4 Reusability of the catalyst and the corresponding yields (reaction conditions: temperature 60 °C, catalyst loading 0.01 equiv., solvent water, reaction entry 1, Table 1).



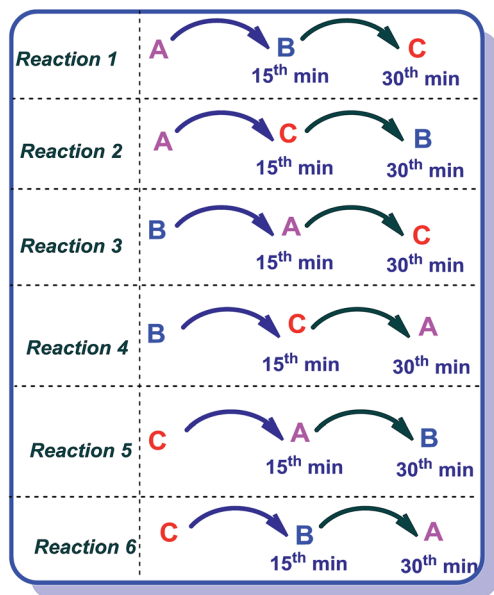


Fig. 5 Reactions performed to understand the mechanism involved.

spots. Reagent B was subsequently added in 15 minutes and the product was isolated as described earlier in the experimental section. The overall reaction time is 5 h but the yields of this reaction dropped to 56%.

Method 3. Sequence of reactants B, A and C were followed for Method 3, which gave similar reaction kinetics as reaction 1, but time of reaction was slightly extended to 4.5 h. However, the isolated product shows comparable yields (77%) similar to that obtained in Method 1.

Method 4. In Method 4, the reagents were added in the sequence of B, C and A with 15 minutes gap for addition of each reagent. The crude reaction mixture gave a complex TLC and the product was not isolated as isolation was difficult.

Methods 5 and 6. In 5th and 6th methods, C was the first reactant; both the reactions resulted in dark brown reaction mixture with traces of product formation. Many crystallization procedures were tried to isolate the product but were unsuccessful because of multiple product formation. From all these set of reactions, we concluded that the best order of reactant addition for smooth reaction is A followed by B and C. The details are summarized in Table 4.

Thus, we see that if we add A or B first (in any order), reaction occurs smoothly and reaction kinetics and the yield are similar. In all the other cases, either the reaction rate is affected or the reaction stops completely. Thus, adsorption of A and B is essential for the reaction to proceed. Initial adsorption of A and B leads to the formation of the intermediate and further addition of C yield the final reaction product. In fact adsorption of A seems most important as its adsorption in the beginning gives greater yield and faster kinetics (Method 1). It is important to note that if adsorption of only A and C was important and not B, reaction Method 2 would have given the same kinetics and yield as reaction 1, but it is significantly affected. If adsorption of only A and B was important and not C, reaction number 4, 5 and 6 would also give the yields and kinetics similar to reaction 1 but

it does not even react. Finally, if adsorption of only B and C was important and not A, reaction number 6 will also give the reaction but it does not react either. Adsorption of C is further verified by carrying out a variation in Method 1. After adding A and B, the catalyst is removed from the reaction through simple filtration followed by the addition of C. After this, the reaction is allowed to continue in a usual manner as mentioned above. The time for the reaction was very large and the obtained product yield was also poor (15%). From these observations, we conclude that all the steps in the reaction require catalyst *i.e.*, the adsorption of all the reactants was necessary. Therefore, the reaction mechanism may possibly be the Langmuir–Hinshelwood type where the adsorption of all the reactants is necessary. This is an important observation which makes this heterogeneous catalysis over $\text{La}_2\text{O}_3/\text{La}(\text{OH})_3$ different from homogeneous catalysis where the sequence of addition has a lesser role to play.

Conclusions

In conclusion, La_2O_3 and $\text{La}(\text{OH})_3$ are used as efficient catalysts for the synthesis of 1,4-benzodiazepine derivatives from various substituted *o*-phenylenediamines in water. This is a simple and efficient synthesis method for the three-component one-pot green synthesis using heterogeneous catalysis. Kinetics of the reactions is comparable with both La_2O_3 and $\text{La}(\text{OH})_3$ which means that the useful basic sites on the both the materials are similar. The reaction appears to follow the Langmuir–Hinshelwood adsorption model which is deciphered by running the reaction in different sequences. The use of water as a solvent enables greener synthetic methodology. Easy work up procedure, low catalyst loading, high product yields, avoidance of the column purification and catalyst recyclability provides an eco-friendly and environmentally benign process.

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References

- 1 S. Brauch, S. S. Van Berkel and B. Westermann, *Chem. Soc. Rev.*, 2013, **42**, 4948–4962.
- 2 J. Zhu and H. Bienaymé, *Multicomponent reactions*, John Wiley & Sons, 2006.
- 3 M. Jose Climent, A. Corma and S. Iborra, *RSC Adv.*, 2012, **2**, 16–58.
- 4 A. Maleki, Z. Alrezvani and S. Maleki, *Catal. Commun.*, 2015, **69**, 29–33.
- 5 M. J. Climent, A. Corma, S. Iborra and L. L. Santos, *Chem.–Eur. J.*, 2009, **15**, 8834–8841.
- 6 M. B. Gawande, P. S. Branco and R. S. Varma, *Chem. Soc. Rev.*, 2013, **42**, 3371–3393.
- 7 F. Zaera, *Chem. Soc. Rev.*, 2013, **42**, 2746–2762.



- 8 M. Dixit, A. Menon, R. Baruah, A. Bhargav and S. Sharma, *React. Kinet., Mech. Catal.*, 2015, **115**, 611–624.
- 9 R. Pagadala, S. Maddila, V. D. B. C. Dasireddy and S. B. Jonnalagadda, *Catal. Commun.*, 2014, **45**, 148–152.
- 10 B. Karami, S. J. Hoseini, K. Eskandari, A. Ghasemi and H. Nasrabadi, *Catal. Sci. Technol.*, 2012, **2**, 331–338.
- 11 T. S. Rivera, A. Sosa, G. P. Romanelli, M. N. Blanco and L. R. Pizzio, *Appl. Catal., A*, 2012, **443**, 207–213.
- 12 J. Deng, L.-P. Mo, F.-Y. Zhao, Z.-H. Zhang and S.-X. Liu, *ACS Comb. Sci.*, 2012, **14**, 335–341.
- 13 H. Ueda, M. Yamaguchi, H. Kameya, K. Sugimoto and H. Tokuyama, *Org. Lett.*, 2014, **16**, 4948–4951.
- 14 A. Huang, Y. Chen, Y. Zhou, W. Guo, X. Wu and C. Ma, *Org. Lett.*, 2013, **15**, 5480–5483.
- 15 A. Hakki, R. Dillert and D. W. Bahnemann, *ACS Catal.*, 2013, **3**, 565–572.
- 16 A. Maleki, *RSC Adv.*, 2014, **4**, 64169–64173.
- 17 A. Maleki, *Tetrahedron*, 2012, **68**, 7827–7833.
- 18 A. Maleki, *Tetrahedron Lett.*, 2013, **54**, 2055–2059.
- 19 V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara and J.-M. Basset, *Chem. Rev.*, 2011, **111**, 3036–3075.
- 20 C. S. Radatz, R. B. Silva, G. Perin, E. J. Lenardão, R. G. Jacob and D. Alves, *Tetrahedron Lett.*, 2011, **52**, 4132–4136.
- 21 W. Hunkeler, H. Mohler, L. Pieri, P. Polc, E. P. Bonetti, R. Cumin, R. Schaffner and W. Haefely, *Nature*, 1981, **290**, 514–516.
- 22 W. Wisden and D. N. Stephens, *Nature*, 1999, **401**, 751–752.
- 23 D. E. Thurston, H. Vassoler, P. J. M. Jackson, C. H. James and K. M. Rahman, *Org. Biomol. Chem.*, 2015, **13**, 4031–4040.
- 24 N. Maheshwari, A. Goyal, S. Jain, D. Jain and N. S. H. N. Moorthy, *Med. Chem. Res.*, 2014, **23**, 765–774.
- 25 A. Kamal, R. V. Shetti, M. J. Ramaiah, P. Swapna, K. S. Reddy, A. Mallareddy, M. P. N. Rao, M. Chourasia, G. N. Sastry and A. Juvekar, *MedChemComm*, 2011, **2**, 780–788.
- 26 A. H. Jadhav, A. Chinnappan, R. H. Patil, S. V. Kostjuk and H. Kim, *Chem. Eng. J.*, 2014, **240**, 228–234.
- 27 B. Lemrová and M. Soural, *ACS Comb. Sci.*, 2012, **14**, 645–650.
- 28 J. Qian, Y. Liu, J. Cui and Z. Xu, *J. Org. Chem.*, 2012, **77**, 4484–4490.
- 29 J. D. Neukom, A. S. Aquino and J. P. Wolfe, *Org. Lett.*, 2011, **13**, 2196–2199.
- 30 M. W. Gribble, J. A. Ellman and R. G. Bergman, *Organometallics*, 2008, **27**, 2152–2155.
- 31 N. Kaur and D. Kishore, *Synth. Commun.*, 2013, **44**, 1375–1413.
- 32 A. Maleki, N. Ghamari and M. Kamalzare, *RSC Adv.*, 2014, **4**, 9416–9423.
- 33 M. Jeganathan and K. Pitchumani, *ACS Sustainable Chem. Eng.*, 2014, **2**, 1169–1176.
- 34 A. Maleki and M. Kamalzare, *Catal. Commun.*, 2014, **53**, 67–71.
- 35 A. Maleki and M. Kamalzare, *Tetrahedron Lett.*, 2014, **55**, 6931–6934.
- 36 H. Naeimi and H. Foroughi, *New J. Chem.*, 2015, **39**, 1228–1236.
- 37 P. Hazarika, P. Gogoi, S. Hatibaruah and D. Konwar, *Green Chem. Lett. Rev.*, 2011, **4**, 327–339.
- 38 K. D. Parghi and R. V. Jayaram, *Catal. Commun.*, 2010, **11**, 1205–1210.
- 39 M. B. Gawande, P. S. Branco, K. Parghi, J. J. Shrikhande, R. K. Pandey, C. A. A. Ghumman, N. Bundaleski, O. M. N. D. Teodoro and R. V. Jayaram, *Catal. Sci. Technol.*, 2011, **1**, 1653–1664.
- 40 A. Kawashima, K. Matsubara and K. Honda, *Bioresour. Technol.*, 2008, **99**, 3439–3443.
- 41 A. F. Lee, J. A. Bennett, J. C. Manayil and K. Wilson, *Chem. Soc. Rev.*, 2014, **43**, 7887–7916.
- 42 H. Hattori, *Appl. Catal., A*, 2001, **222**, 247–259.
- 43 A. Guida, M. H. Lhouty, D. Tichit, F. Figueras and P. Geneste, *Appl. Catal., A*, 1997, **164**, 251–264.
- 44 Y. Sekine, K. Tanaka, M. Matsukata and E. Kikuchi, *Energy Fuels*, 2009, **23**, 613–616.
- 45 J. A. Kurzman, L. M. Misch and R. Seshadri, *Dalton Trans.*, 2013, **42**, 14653–14667.
- 46 M. S. Palmer, M. Neurock and M. M. Olken, *J. Am. Chem. Soc.*, 2002, **124**, 8452–8461.
- 47 M. Dixit, A. Menon, R. Baruah, A. Bhargav and S. Sharma, *React. Kinet., Mech. Catal.*, 2015, **115**, 611–624.
- 48 B. P. Gangwar, V. Palakollu, A. Singh, S. Kanvah and S. Sharma, *RSC Adv.*, 2014, **4**, 55407–55416.
- 49 A. L. Patterson, *Phys. Rev.*, 1939, **56**, 978–982.
- 50 O. V. Manoilova, S. G. Podkolzin, B. Tope, J. Lercher, E. E. Stangland, J.-M. Goupil and B. M. Weckhuysen, *J. Phys. Chem. B*, 2004, **108**, 15770–15781.

