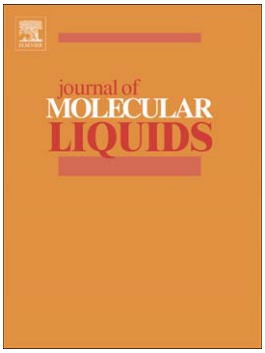


La-Sn nanocatalysts: Efficient materials for the synthesis of cyclohexanones

Ikram Ahmad, Sher Bahadar Khan, Abdullah M. Asiri, Muhammad Nadeem Arshad, Shahid Ali Khan

PII: S0167-7322(16)31526-4
DOI: doi:10.1016/j.molliq.2016.09.050
Reference: MOLLIQ 6327

To appear in: *Journal of Molecular Liquids*

Received date: 12 June 2016
Revised date: 24 August 2016
Accepted date: 18 September 2016

Please cite this article as: Ikram Ahmad, Sher Bahadar Khan, Abdullah M. Asiri, Muhammad Nadeem Arshad, Shahid Ali Khan, La-Sn nanocatalysts: Efficient materials for the synthesis of cyclohexanones, *Journal of Molecular Liquids* (2016), doi:10.1016/j.molliq.2016.09.050

La-Sn nanocatalysts: Efficient materials for the synthesis of cyclohexanones

Ikram Ahmad[a,b], Sher Bahadar Khan[a,b*], Abdullah M. Asiri[a,b], Muhammad Nadeem Arshad[a,b], Shahid Ali Khan[a,b]

[a]Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Jeddah, Saudi Arabia
[b]Chemistry Department, Faculty of Science, King Abdul Aziz University, Jeddah 21589, Saudi Arabia

* Correspondence address**:** E-mail: sbkhan@kau.edu.sa

Abstract

A series of La and Sn catalysts were synthesized by facile low temperature hydrothermal procedure La-Sn nanoparticles and characterized by x-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM) coupled with energy dispersive spectroscopy (EDS), Fourier transform infrared (FTIR) and UV-visible spectroscopy. The FESEM and XRD analysis revealed the growth of nanoparticles with homogeneous morphology, high crystallinity and particle size of < 20 nm. The synthesized nanoparticles showed excellent catalytic activity for the synthesis of cyclohexanones. The effect of variations in La and Sn contents on the progress of reaction was estimated by yield of the products. The recovery of the catalysts after the completion of reactions was also assessed.

Key words: La-Sn nanoparticles; Nano-catalyst; Cyclohexanone; Efficient catalyst

1. Introduction

Conventional heterogeneous catalysts usually consist of less active or "inert" solid carriers' and active metal phases in order to enhance available working area and material consumption. In these catalysts the metals usually show the dimensions of numerous to a few tens of nanometers,[1-3] their further processing may proceed by ion-exchange, impregnation, activation , pulverization ,coating, , drying, heat-treatment, reduction, precipitation and rewashing,[4]. This protocol can disperse the active nanoparticles or metal clusters on the carriers. But the classical procedure for catalyst mainly depends on the proficiency of process implementers. The effective catalyst is generally formed through conscientious trial-and-error experiments. Insufficient materials analysis and complicated procedures of developed routes for active catalysts are secrets of the developers for viable interests.[4, 5] The topography, facet, defect, size, shape, and compositional distinction play vital role on the efficiency of heterogeneous catalysts.[1-3]

The excellent catalytic efficiency of tin and palladium catalysts for dehydrogenation of alkanes fascinated most of the researchers in last decades.[4-6] Considerable improvements have been done experimentally and theoretically.[7-10] The bimetallic catalysts as Sn-Pt rely generally on the Pt and Sn interactions, and especially on the state of Sn.[5] It is recommended that electronic density of Pt is altered by tin by transfer of positive charge from Sn^{+} or to the other electronic structure in Sn-Pt alloys.[11] It is also reported that tin decreases the surface dimensions of Pt which helps to inhibit the isomerization, coke formation and hydro-cracking by keeping the Pt sites clean from coke.[12] However, the stabilities of the catalysts

still demand more attention. Consequently, it is vital to enhance the stability of Sn-Pt catalysts for short chain paraffin conversion.

About stability issues, developments were made and investigators reported that catalytic performance of Sn-Pt based catalysts can be improved by adding rare earth metals as they can augment thermal stabilization and reinforce metal-rare earth oxide interaction efficiently.[13-15] It has been observed that the catalytic stability of Sn-Pt/Al_2O_3 can significantly improve by adding lanthanum in propane dehydrogenation reaction because of the reticence of coke formation and reduction of Sn oxidation in the existence of La.[16] Catalytic properties selectivity and stability of Sn-Pt, Na/ZSM-5 in propane dehydrogenation process was improved by induction of La.[17] The performance of La addition illustrates that it could amend the characteristics of acid and metal function and as a consequence, the examination of La advertiser on catalyst is very crucial. Cyclohexanone derivatives play a vital role in many systems in organic synthesis and in industry.[18-20] Besides the important organic precursor, these have good antimicrobial activities such as anti-convulsant, anti-implantation, anti-asthmone, anti-bacteria, anti-fungal, and herbicidal.[21-26]

The preparation of cyclohexanone has been investigated in the presence of different catalysts.[22-24] The cascade process of ethyl acetoacetate and benzaldehyde in the presence of sodium carbonate,[23,24] piperidine,[25] triethyl amine,[26] potassium carbonate polyethylene glycol,[27] bismuth trichloride.[25] The same process in the presence of sodium hydride-butyl lithium[14] and another group studied similar reaction in the presence of potassium tetracarbonyl-hydridoferrate.[28] In recent methods cyclohexanone were reported by Knoevenagel condensation followed by Michael addition[28]. But the use of high temperatures,

expensive metal precursors, catalysts that are harmful to environment and longer reaction times limit the use of these methods. Therefore, the search for a better catalyst for the synthesis of cyclohexanone derivatives is of prime importance. Too many reactions are reported which give good yield in the presence of catalyst and also affect the reaction kinetics and mechanism.

In present investigation, we report the synthesis, characterization and catalytic effect of La-Sn nanoparticles (La-Sn/i, La-Sn/ii and La-Sn/iii) in one-pot tandem-sequence. These nanoparticles were prepared in large quantity possessing a spherical shape. La-Sn/i, La-Sn/ii and La-Sn/iii have average diameter of ~38 ± 10 nm. These catalyst were employed for the synthesis of cyclohexanones. Reaction kinetics, yield of respective products and activity factor of catalysts were determined. La-Sn nanoparticles showed efficient result with good recovery of catalyst.

2. Experimental

2.1. Reagents and Chemicals

Lanthanum carbonate, tin carbonate, ethylacetoacetate, ammonium acetate, piperidine, ethanol, and aldehydes and all other chemicals were purchased form Sigma-Aldrich. All the reagents were of analytical grade and were used without further purification.

2.2. Synthesis of La-Sn nanoparticles

The aqueous solutions of lanthanum carbonate (0.1 M) and tin carbonate (0.3 M) were mixed together and titrated by NaOH (0.5 M) solution to increase the pH above 10.0. This high basic solution was then kept for stirring at 60.0 $^{\circ}$C for 12 hours. Finally the product

was obtained by washing the precipitate several times with ethanol. The precipitate was dried and named as La-Sn/i. The La-Sn/I was calcined at 450.0 $^{\circ}$C for 6 hours and named as La-Sn/ii. For the preparation of La-Sn/iii, the same amounts of precursor materials were mixed with 5 wt% of carbon black and follow the same procedure which was used for the synthesis of La-Sn/i.

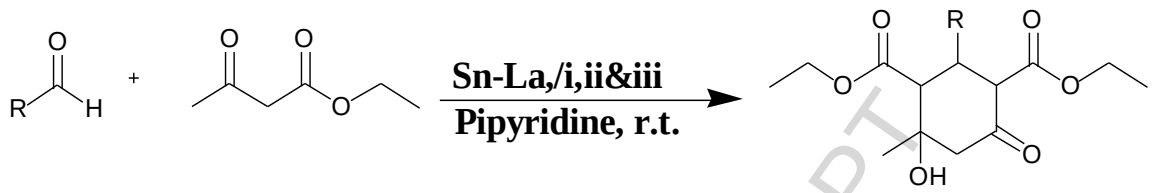
2.3. Physical Characterization of La-Sn nanomaterial

JEOL Scanning Electron Microscope (JSM-7600F, Japan) was used to analyze the morphology of the prepared material while the crystallography was studied by Thermo Scientific, ARLservice X-ray diffractometer. For compositional and optical studies of the nanoparticles, FT-IR and UV spectrum were record by a Nicolet (iS50 FT-IR) FT-IR spectrometer and UV (Evolution 300 UV-VIS) spectrometer.

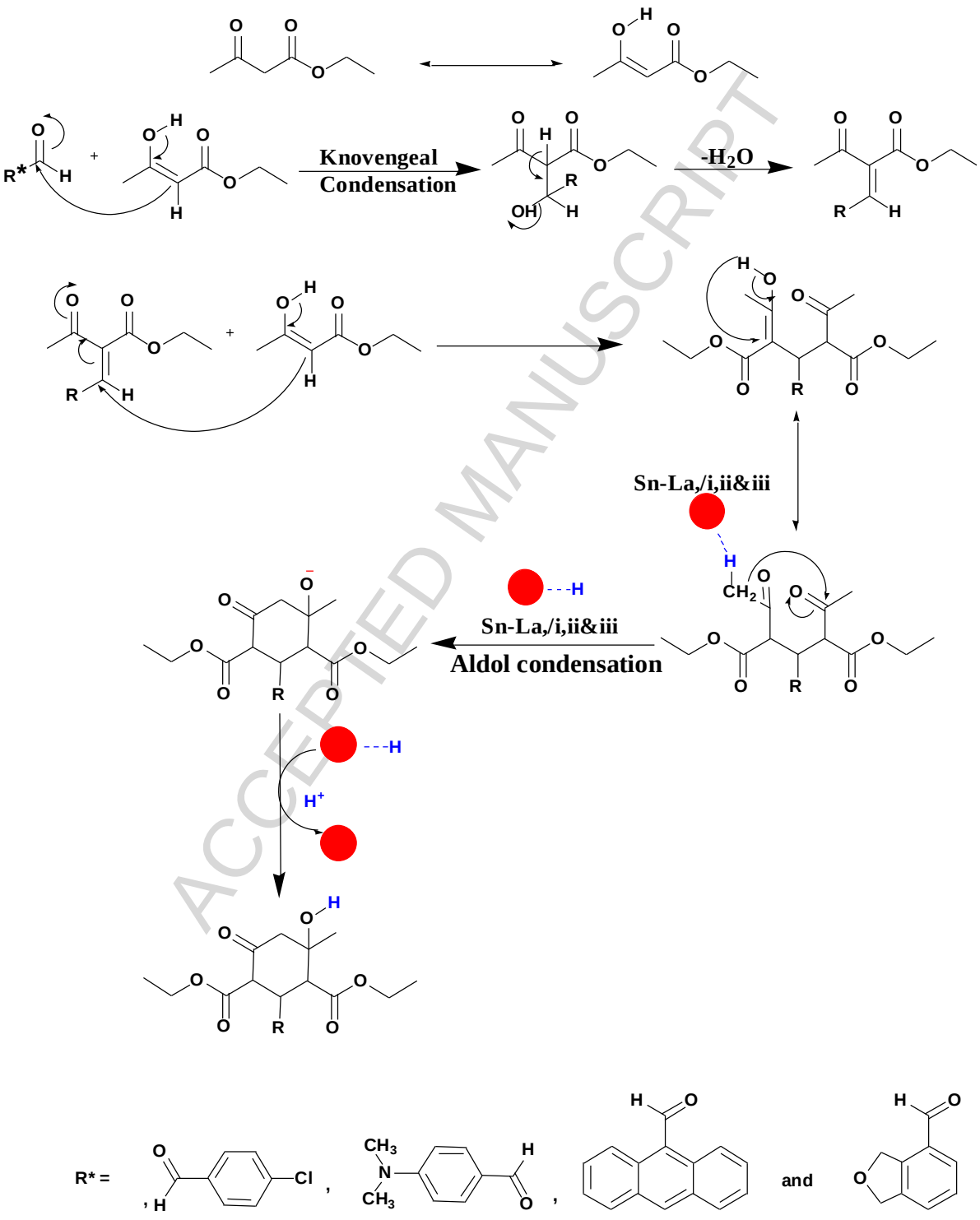
2.4. Catalytic activity

The catalytic activity of the prepared nanomaterial was determined by applying in the tandem Knoevenagel condensation followed by aldol condensation reaction of aromatic aldehyde with ethyl acetoacetate in the presence of piperidine as base (Scheme 1) and proposed mechanism showed in scheme 2. The reaction was carried out at room temperature and pressure (RTP), monitored by thin layer chromatography (TLC) and product was purified by column chromatography. As the two of main product were crystalline so the confirmation was done by single crystal XRD technique and non-crystalline were confirmed by NMR. The reaction was repeated, monitored by TLC and determined the reaction kinetics by UV (Evolution 300 UV-VIS). Same protocol was applied for different catalysts and

determined the catalytic activity by calculating slope. Activity factor of catalysts was compared and yield of product was calculated to sort out the best catalyst.



Scheme 1: Catalyzed tandem Knoevenagel condensation followed by Aldol condensation reaction.



Scheme 2: Proposed Mechanism for the synthesis of cyclohexanones.

3. Results and Discussion

3.1 \Physical characterization of La-Sn nanoparticles

The FESEM images of the synthesized La-Sn nanoparticles are presented in Fig. 1 were utilized to explore the morphology and size of all La-Sn nanoparticles. It is evident from the FESEM images that La-Sn/i, La-Sn/ii and La-Sn/iii are grown in the form of particles. These nanoparticles are grown in large quantity possessing a spherical shape. La-Sn/i, La-Sn/ii and La-Sn/iii nanoparticles are grown in the size of < 20 nm.

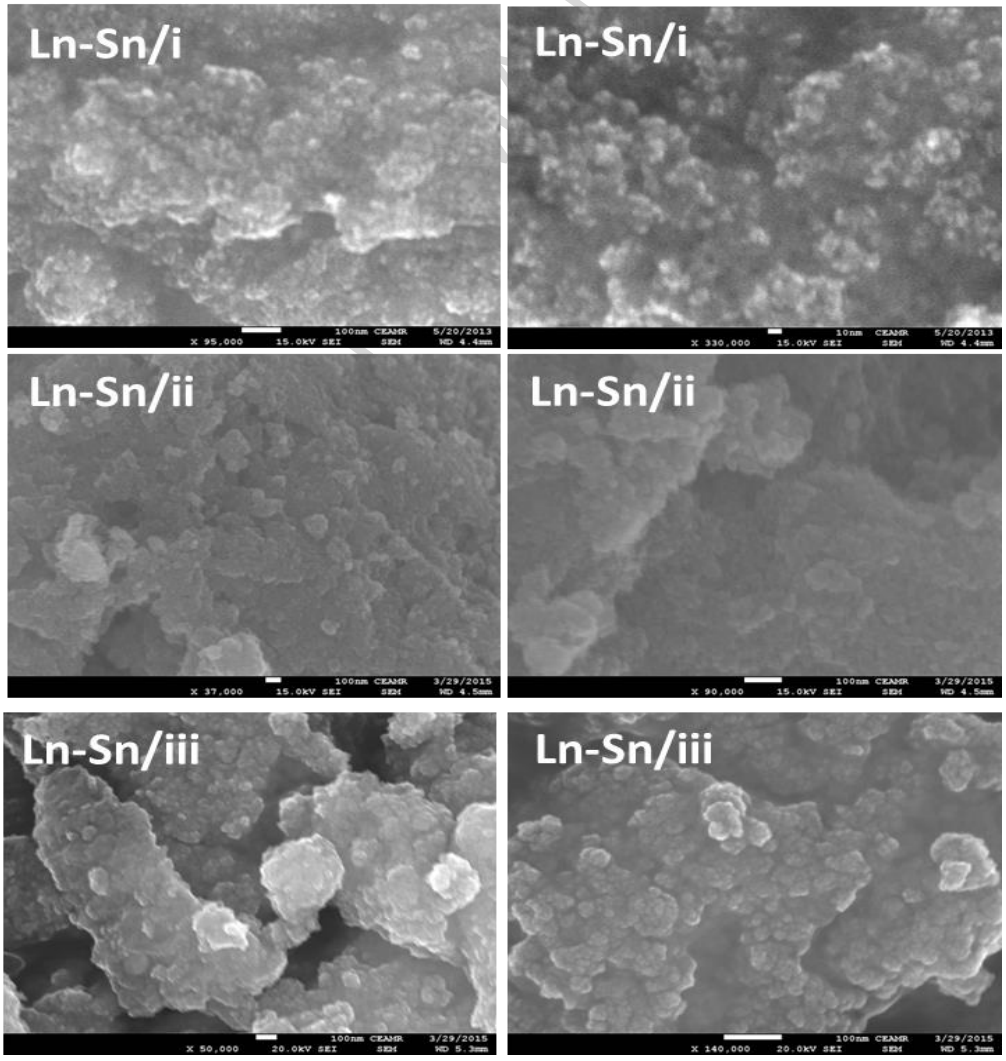


Figure: 1. Typical FESEM images of Ln-Sn/i, Ln-Sn/ii and Ln-Sn/iii.

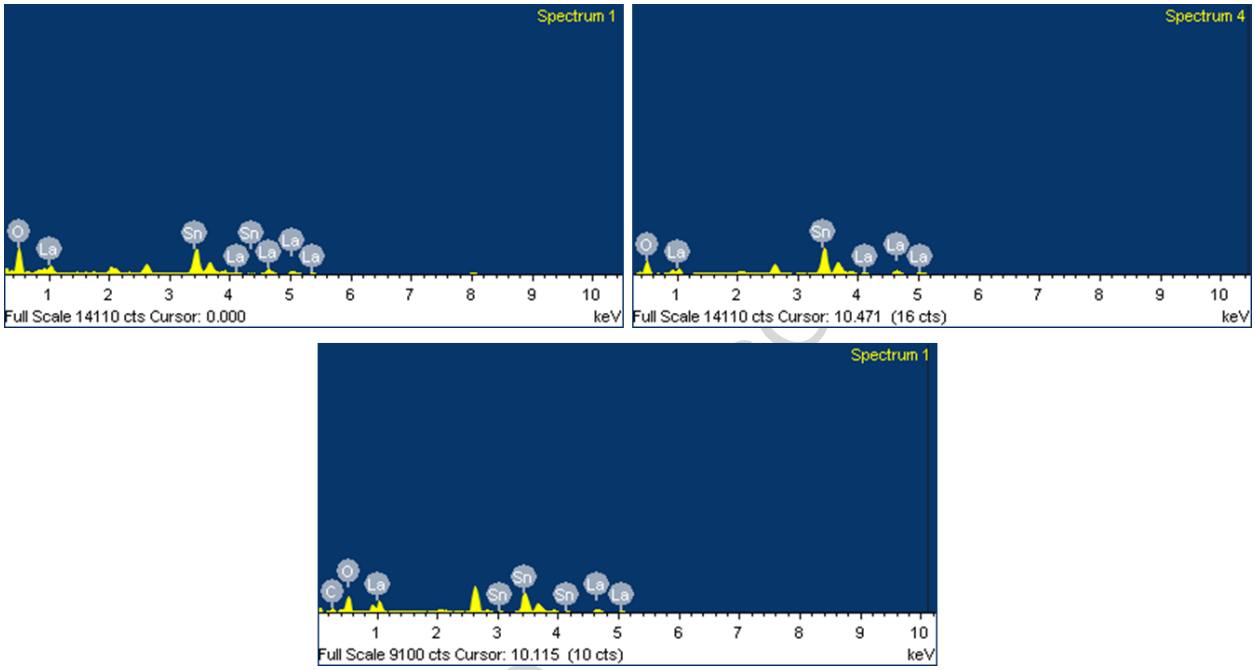


Figure: 2.Typical EDS spectrum of Ln-Sn/i, Ln-Sn/ii and Ln-Sn/iii.

The elemental composition was determined from the EDS spectrum. The EDS analysis indicating the presence of O, Ln and Sn elements as showing in Fig. 2.

The crystallographic information of the all La-Sn based nanoparticles was corroborated by X-ray diffraction (Fig. 3 (a)). All the characteristic diffraction peaks coincided with those for well-crystalline hexagonal La_2O_3 as well as tetragonal SnO_2.[34,35] The SnO_2 peaks at 2θ values of 26.6°, 33.9°, 38.0°, 51.7°, and 65.9° can be associated with (110), (101), (200), (211) and (112) respectively. The La_2O_3 peaks at 2θ values of 27.3°, 31.6°, 45.5°, and 56.6° can be associated with (100), (101), (110), and (112) respectively.

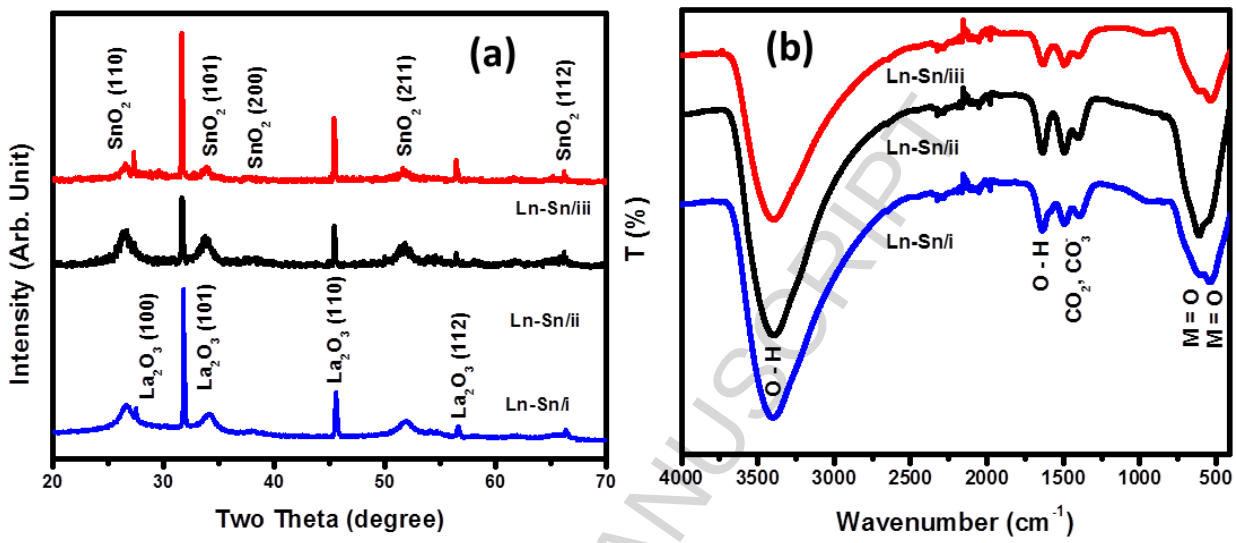


Figure: 3. Typical (a) XRD pattern and (b) FTIR spectrum of Ln-Sn/i, Ln-Sn/ii and Ln-Sn/iii.

The chemical structure of La-Sn/i, La-Sn/ii and La-Sn/iii nanoparticles was also examined by FTIR analysis which was recorded in the range of 400 ~ 4000 cm^{-1} and shown in Fig. 3 (b). An intense broad peak exhibited at 3350 cm^{-1} recommended the presence of OH stretching vibration. The very intense bands observed at 525 and 621 cm^{-1} were attributed to M–O (M = Sn, La) and M-O-M bonds, respectively. Supplementary peaks centered at 1369, 1636 and 3412 cm^{-1} were assigned to CO_2, CO_3^-, H_2O absorbed from the environment, respectively[36],[37]

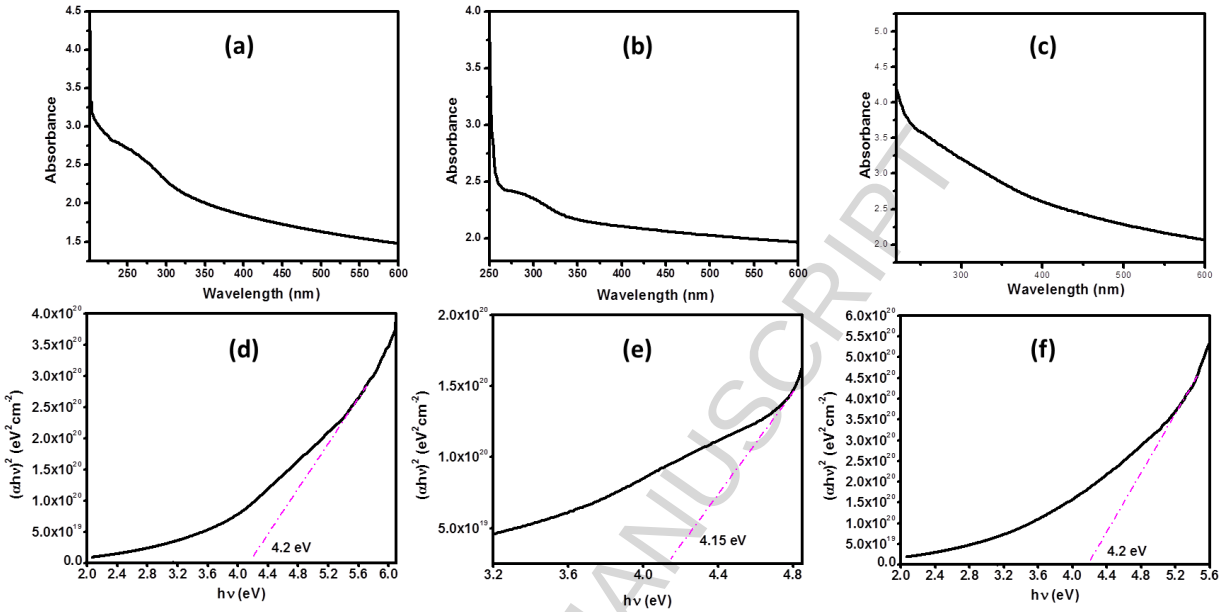


Figure: 4. Typical UV spectrum of (a) Ln-Sn/i (b) Ln-Sn/ii, (c) Ln-Sn/iii and $(\alpha h\nu)^2$ vs. hν plots of (d) Ln-Sn/I, (e) Ln-Sn/ii, (f) Ln-Sn/iii.

The band gap was determined from UV-Vis data. The catalyst Ln-Sn (i, ii and iii) indicating a band gap at 4.2, 4.15 and 4.2 eV as depicted in Fig. 4d-4f respectively.

3.2. Catalytic activity

The catalytic efficiency of La-Sn/i, La-Sn/ii and La-Sn/iii nanoparticles were evaluated in tandem reaction for the synthesis of cyclohexanone derivatives at room temperature using different aromatic aldehydes, ethyl acetoacetate and piperidine in ethanol as the starting materials. The experiment was carried out at room temperature. The aromatic aldehyde (3 mmol), piperidine (3 mmol), ethylacetoacetate (6 mmol) and 10 mol% of La-Sn/i or La-Sn/ii or La-Sn/iii nanoparticles were taken in reaction flask having 2ml ethanol and stirred for a certain period of time. The reaction was monitored by collecting the sample after each periodically to observe reaction kinetics through UV/VIS spectrophotometer. The product

was also confirmed by TLC. When the reaction completed, the contents were filtered and washed with ethanol to recover the catalyst, the components of filtrate were purified by column chromatography. The main fraction of column crystallized out after 24 hrs in 5% ethyl acetate ethanol solvent system and the structure was examined by single crystal XRD and NMR. The % yields were calculated which are given in Table 1. The formation of product was also monitored by UV/vis analysis. After treating the reactants in the presence of catalyst, the UV absorbance was gradually increased with the passage of time. Figure 5 is showing the UV analysis of the products for catalysts La-Sn/i,La-Sn/ii and La-Sn/iii, respectively.

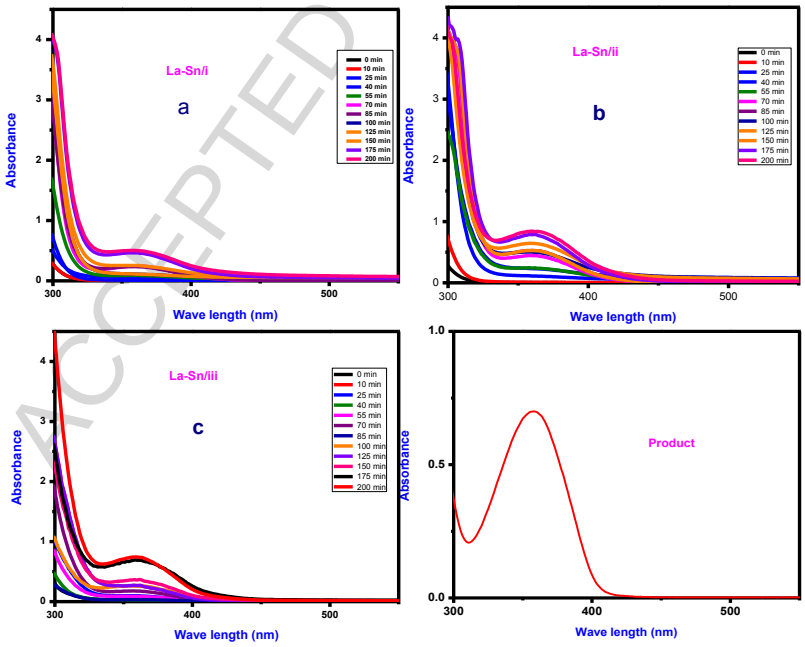


Figure: 5. Absorbance spectra of the synthesis of Cyclohexanone derivatives through tandem Knoevenagel condensation followed by aldol condensation in the presence of **a)** Sn-La/i nanoparticles. **b)** Sn-La/ii nanoparticles. **c)** Sn-La/iii nanoparticles. **d)** 2-(4-Chloro-phenyl)-4-hydroxy-4-methyl-6-oxo-cyclohexane-1,3-dicarboxylic acid diethyl ester).

The results showed that La-Sn/ii is the most efficient catalyst and it also gave no side product i.e. cyclohexanone derivative which was purified by column chromatography, as the product was crystalline, single crystal XRD technique was used for their structure analysis. The % yield of crystalline product was calculated which was extra ordinary good. Table 2, 3, 4 and 5 is showing the excellent results of the catalysts. . (not clear)

Table: 2. % yield of Molecule 1 by using Sn-La/i, Sn-La/ii and Sn-La/iii nanomaterial.

Sr#	Catalysts	Reaction Time (±5 min.)	Literature Time[28]	% Yield	Literature Yield[28]
1	Sn-La/ii	200*	2 days	91%*	66%
2	Sn-La/iii	230	2 days	84%	66%
3	Sn-La/i	300	2 days	76%	66%

Table: 3. % yield of Molecule 2 by using Sn-La/i, Sn-La/ii and Sn-La/iii nanomaterial.

Sr#	Catalysts	Reaction Time (±5 min.)	Literature Time[28]	% Yield	Literature Yield[28]
1	Sn-La/ii	70*	2 days	96%*	86%
2	Sn-La/iii	75	2 days	91%	86%
3	Sn-La/i	100	2 days	76%	86%

Table: 4. % yield of Molecule 3 by using Sn-La/i, Sn-La/ii and Sn-La/iii nanomaterial.

Sr#	Catalysts	Reaction Time (±5 min.)	Literature Time	% Yield	Literature Yield
1	Sn-La/ii	110	--	92%	--
2	Sn-La/iii	150	--	81%	--
3	Sn-La/i	180	--	72%	--

Table: 5. % yield of Molecule 4 by using Sn-La/i, Sn-La/ii and Sn-La/iii nanomaterial.

Sr#	Catalysts	Reaction Time (±5 min.)	Literature Time	% Yield	Literature Yield
1	Sn-La/ii	120	--	87%	--
2	Sn-La/iii	165	--	71%	--
3	Sn-La/i	200	--	66%	--

4. Conclusions

In conclusion efficient La-Sn/i, La-Sn/ii and La-Sn/iii nanoparticles catalysts were developed, characterized and determined their catalytic activity towards synthesis of cyclohexanone derivatives through tandem Knoevenagel condensation followed by aldol route. The catalyst helped to increase the yield, reduce time, decrease the side products and gave a different route than classical mechanism by which cyclohexanone derivative compounds were prepared more conveniently and were easy to purify. The yield and time of tandem Knoevenagel condensation followed by aldol route by these catalysts is strong evidence that the traditional catalysts could be replaced by nanocatalysts to improve the shortcomings in organic synthesis of vital compounds by which standards of health and food can be increased because of their versatile applications of products.

Acknowledgment

The authors are grateful to the center of excellence advance material research King Abdulaziz University, Saudi Arabia for providing research facility.

Authors' contributions

Ikram design and carried out all experiments and write the manuscript. Sher and Nadeem help in experiment and revised the manuscript Abdullah also revised the manuscript and provide experimental facilities while Shahid help in experiment. All the authors read and approved the final manuscript.

Conflict of interest

The authors confirms that this article content has no conflict of interest.

References:

1. J. C. Serrano-Ruiz, A. Sepúlveda-Escribano and F. Rodríguez-Reinoso, *Journal of Catalysis*, 2007, **246**, 158-165.
2. S. T. Korhonen, S. M. K. Airaksinen, M. A. Bañares and A. O. I. Krause, *Applied Catalysis A: General*, 2007, **333**, 30-41.
3. M. Tasbihi, F. Feyzi, M. A. Amlashi, A. Z. Abdullah and A. R. Mohamed, *Fuel Processing Technology*, 2007, **88**, 883-889.
4. M. Ohta, Y. Ikeda and A. Igarashi, *Applied Catalysis A: General*, 2004, **266**, 229-233.
5. G. J. Siri, G. R. Bertolini, M. L. Casella and O. A. Ferretti, *Materials Letters*, 2005, **59**, 2319-2324.
6. S. A. Bocanegra, S. R. de Miguel, I. Borbath, J. L. Margitfalvi and O. A. Scelza, *Journal of Molecular Catalysis A: Chemical*, 2009, **301**, 52-60.
7. G. J. Siri, J. M. Ramallo-López, M. L. Casella, J. L. G. Fierro, F. G. Requejo and O. A. Ferretti, *Applied Catalysis A: General*, 2005, **278**, 239-249.

8. A. B. Merlo, V. Vetere, J. F. Ruggera and M. L. Casella, *Catalysis Communications*, 2009, **10**, 1665-1669.

9. M. Womes, F. Le Peltier, S. Morin, B. Didillon, J. Olivier-Fourcade and J. C. Jumas, *Journal of Molecular Catalysis A: Chemical*, 2007, **266**, 55-64.

10. Y. Zhang, Y. Zhou, H. Liu, L. Bo and M. Tang, *Fuel Processing Technology*, 2009, **90**, 1524-1531.

11. C. Kappenstein, M. Guerin, K. Lazar, K. Matusek and Z. Paal, *Journal of the Chemical Society, Faraday Transactions*, 1998, **94**, 2463-2473.

12. A. Iglesias-Juez, A. M. Beale, K. Maaijen, T. C. Weng, P. Glatzel and B. M. Weckhuysen, *Journal of Catalysis*, 2010, **276**, 268-279.

13. G. Del Angel, A. Bonilla, Y. Peña, J. Navarrete, J. L. G. Fierro and D. R. Acosta, *Journal of Catalysis*, 2003, **219**, 63-73.

14. A. Trovarelli, *Catalysis Reviews*, 1996, **38**, 439-520.

15. F. Oudet, P. Courtine and A. Vejux, *Journal of Catalysis*, 1988, **114**, 112-120.

16. R. Xiang Li, N. Bew Wong, K. Chung Tin, J. Ru Chen and X. Jun Li, *Catalysis Letters*, 1998, **50**, 219-223.

17. Y. Zhang, Y. Zhou, H. Liu, Y. Wang, Y. Xu and P. Wu, *Applied Catalysis A: General*, 2007, **333**, 202-210.

18. M. T. Musser, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000, DOI: 10.1002/14356007.a08_217.

19. M. Kamal Nasar, R. Ranjith Kumar and S. Perumal, *Tetrahedron Letters*, 2007, **48**, 2155-2158.

20. T. C. W. Paul T. Anastas, 1998.

21. P. T. W. Anastas, J. C, 1998.

22. D. Enders, S. Müller and A. S. Demir, *Tetrahedron Letters*, 1988, **29**, 6437-6440.

23. B. C. Siebenhaar, Bruno; Studer, Martin; Blaser, Hans-Ulrich, *Canadian Journal of Chemistry*, 2001, **79**, 566.

24. B. C. Siebenhaar, B. Synth. Meth. Organomet, *inorganic Chemistry*, 2002, **10**, 114.

25. J. S. S. Dipak Prajapati, *Chemical letters*, 1992, **10**, 1945-1946.

26. G. F. Cainelli, M. Panunzio and A. Umani-Ronchi, *Journal of the Chemical Society, Perkin Transactions 1*, 1975, DOI: 10.1039/P19750001273, 1273-1275.

27. Z. D. Yu-Qing Cao, Rui Zhang, Bao-Hua Chen, *Synthetic communications*, 2004, **34**, 2965-2971.

28. M. Srinivasan and S. Perumal, *Tetrahedron*, 2006, **62**, 7726-7732.

29. Agilent, *CrysAlis PRO*, 2012, Yarnton, England.

30. G. M. Sheldrick, *Acta Crystal*, 2008, **A64**, 112-122.

31. L. J. Farrugia, *Journal of Applied Crystallography*, 2012, **45**, 849-854.

32. L. J. Bourhis, Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H,, *Acta Crystal*, 2015, **A71**, 59-75.

33. A. L. Spek, *Utrecht University*, *Utrecht* 2005.

34. R. Shi, F. Wang, Tana, Y. Li, X. Huang and W. Shen, *Green Chemistry*, 2010, **12**, 108-113.

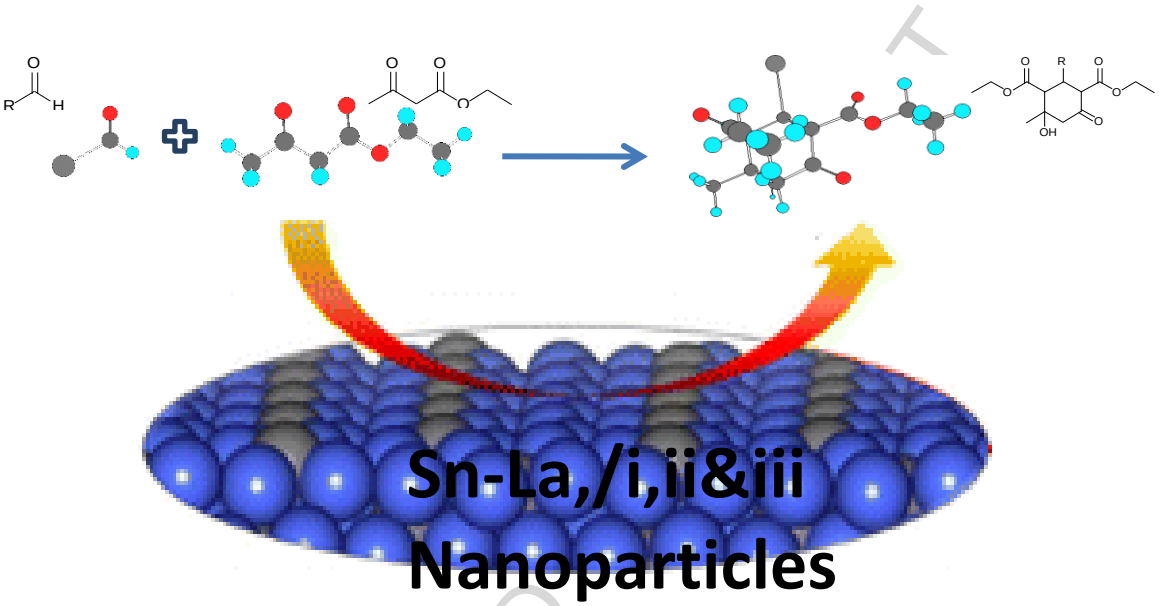
35. S. B. Khan, A. M. Asiri, M. M. Rahman, H. M. Marwani and K. A. Alamry, *Physica E: Low-dimensional Systems and Nanostructures*, 2015, **70**, 203-209.

36. M. T. S. Chani, S. B. Khan, A. M. Asiri, K. S. Karimov and M. A. Rub, *Journal of the Taiwan Institute of Chemical Engineers*, DOI: http://dx.doi.org/10.1016/j.jtice.2015.02.005.

37. S. B. Khan, M. T. S. Chani, K. S. Karimov, A. M. Asiri, B. Mehran and T. Rana, *Talanta*, 2014, **120**, 443-449.

38. S. Asif, S. Khan and A. Asiri, *Nanoscale Res Lett*, 2014, **9**, 1-9.

Graphical abstract



Highlights

- Low temperature synthesis of La-Sn nanoparticles
- La-Sn nanoparticles as efficient nano-catalyst
- Synthesis of cyclohexanone
- High yield