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Green synthesis of veratraldehyde using potassium promoted lanthanum-magnesium mixed oxide catalyst

Jayaram Molleti and Ganapati D. Yadav*

Department of Chemical Engineering

Institute of Chemical Technology

Nathalal Parekh Marg, Matunga

Mumbai-400 019, India

*Author to whom correspondence be addressed.

Email: gd.yadav@ictmumbai.edu.in

Ph: +91-22-3361-1001; F: +91-22-3361-1020

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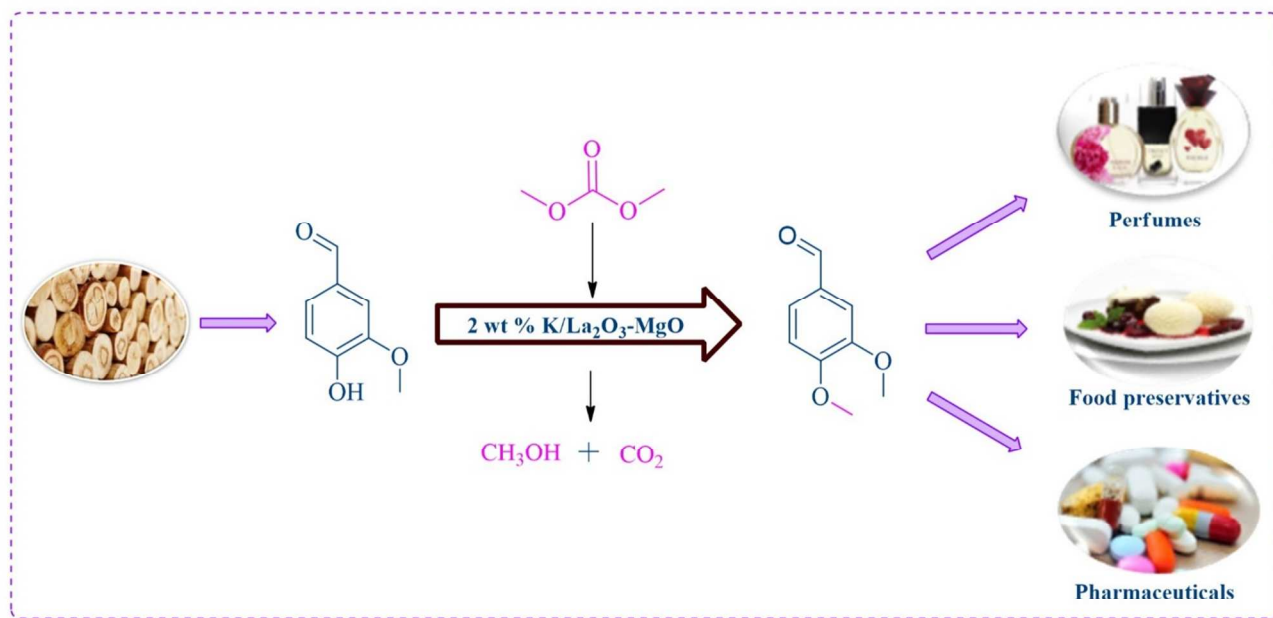
O-methylation of vanillin using DMC

ABSTRACT

Veratraldehyde is an important chemical used in perfumery, agrochemical and pharmaceutical industries. Current processes of manufacture of veratraldehyde use homogeneous catalysts which make them highly polluting creating problems of disposal effluents and product purity. In the current work, veratraldehyde was synthesized from O-alkylation of vanillin with an environmentally benign reagent, dimethyl carbonate. A series of potassium loaded La_2O_3-MgO were prepared by incipient wetness impregnation method and their performance was evaluated vis-à-vis MgO, La_2O_3, La_2O_3-MgO and a series of 1-4 wt % K/ La_2O_3-MgO. All catalysts were characterized by different techniques such as N_2 adsorption/desorption, XRD, TGA-DSC, FT-IR, CO_2-TPD and SEM techniques. Effect of different loadings (1-4 wt %) of potassium on La_2O_3-MgO was studied among which 2 wt % K/La_2O_3-MgO showed the best activity and selectivity due to high dispersion of potassium and high basicity in comparison with the rest. The activity of 2 wt % k/ La_2O_3-MgO in O-methylation of vanillin with dimethyl carbonate (DMC) was closely associated with basicity. Various parameters were studied to achieve maximum yield of the desired product. The maximum conversion was found with catalyst loading of 0.03 g/cm^3 and mole ratio of vanillin and DMC of 1:15 at 160 °C in 2 h. The reaction follows pseudo first order kinetics for the O-methylation of vanillin. The energy of activation was found to be 13.5 kcal/mol. Scale-up was done using the kinetic model to observe that the process could be scaled up using the process parameters. The overall process is clean and green.

KEYWORDS: Vanillin; Dimethyl carbonate; O-methylation; Strong base; Veratraldehyde; La_2O_3-MgO; K/ La_2O_3-MgO

INTRODUCTION

Lignocellulosic biomass, abundantly available everywhere, is a source of renewable chemicals and fuels.[1] Biomass is converted to obtain phenolic compounds, sugars, and fine chemicals via gasification, anaerobic digestion, fermentation, pyrolysis, and transesterification.[2] Lignocellulosic biomass mainly contains cellulose, hemi-cellulose and lignin. Lignin is main renewable source for chemicals such as guaiacol, vanillic acid, phenol, benzene, acetic acid and methanol.[3] Vanillin is also one of the important chemicals obtained from lignin by condensation of guaiacol with glyoxylic acid.[4] Heterogeneous catalysis has tremendous scope for conversion of biomass into value added-chemicals.[5]

Veratraldehyde is present in *Cymbopogon jevenensis* essential oil. It is extensively used in perfume compounds, food aromatizers, odorants and pharmaceutical intermediates.[6] Veratraldehyde can be obtained from O-methylation of vanillin with alkylating agents. The traditional synthesis of O-methylation reactions involved harmful alkylating agents like dimethyl sulfate,[7] methyl halides, [8] and diazomethane, [9] or nontoxic alkylating agents under harsh condition, using a solvent like dimethyl formamide.[10] These reagents are hazardous which produce a large amount of waste. These reactions are also reported with methanol as alkylating agent which require a strong acid [11] or zeolite as catalyst. Usually, they require higher temperature and produce various side products.[12] Hence, development of a green process for the synthesis of veratraldehyde is essential.

Dimethyl carbonate (DMC) is a sustainable, non-toxic, and biodegradable reagent.[13] It can be used either as a methoxycarbonylating agent (<120 °C) or as a methylating agent (>120 °C). In recent years, various applications of DMC were reported.[14] DMC was used in methylation of

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phenols,[15] indoles,[16] and anilines[17] as well as methylation of active methylene groups.[18] It is an alternative for hazardous alkylating agents.

Generally, methylation reaction by DMC requires high temperatures (>160 °C) and long reaction times. In order to attain reasonable conversion, strong organic[15,19] or inorganic bases [20,21] have been used in excess quantities which need to be neutralized at the end of reaction leading to dissolved solids in the effluent. It also adds to impurities in the desired product. The synthesis of veratraldehyde by O-methylation of vanillin with DMC as a methylating agent has been reported using homogeneous catalysts. Chern et al.[22] reported 78 % yield to veratraldehyde using K_2CO_3 as a base. Nelson et al.[23] reported 96 % yield to veratraldehyde over a base K_2CO_3 and 18-crown-6 using CH_3I as a methylating agent.

Recently Thomas[24] demonstrated this reaction with 77 % yield to veratraldehyde using 1,3-dimethylimadazolium-2-carboxylate (DMI-CO_2) catalyst in ~3h at 160 °C. The homogenous catalysts showed high catalytic performance but there are several problems such as homogeneous catalysts have to be neutralized and cannot be recycled, thereby making the process polluting. From Green Chemistry point of view, the replacement of homogeneous catalysts by heterogeneous is most desirable since the catalyst can be easily recovered, reused and also a variety of reactor configurations are possible bringing flexibility in operation. Besides, heterogeneous catalysts have many more advantages such as they present fewer disposal problems, allow easier separation and recovery of the products. They are non-corrosive and offer environmentally benign processes for the synthesis of fine chemicals. Cheaper materials of constructions can be used. Hence, there is heterogeneous catalysts are superior and needed to overcome those problems associated with homogeneous catalysts.

Over the last decades, mixed oxides have been extensively used due to their distinctive physical and chemical properties. [25] Lanthanum oxide (La_2O_3) is a strongest basic oxide, but the activity of is low due to its low surface area. Its activity increased when it mixed with magnesium oxide (MgO) due to increasing basicity. [26,27] La_2O_3-MgO mixed oxide have been widely used in several chemical reactions such as Wittig reaction,[28] Michael addition reaction,[29] Wadsworth-Emmons reaction,[30] synthesis of glycerol carbonate,[31] epoxidation of an olefin [32] and

transesterification reaction.[33] Several researchers demonstrated that the use of potassium precursors such as KF.[34] K_2CO_3,[35] KNO_3,[36,37] and KOH [38] can help the formation of super base. A number of base catalyzed reactions using hydrotalcites, supported hydrotalcites, mixed metal oxides and supported mixed oxide have been studied for industrially important reactions in our laboratory.[39–44] Very recently, Yin et al.[45] demonstrated Knoevenagel condensation reaction over 10 wt % KOH/La_2O_3 as a solid super base.

Here in this report, an efficient and environmentally friendly process for solventless O-methylation of vanillin with DMC over 2 % K/La_2O_3-MgO catalyst. The fresh and spent 2 % K/La_2O_3-MgO has been fully characterized by different techniques. The catalyst activity was compared with the different solid base catalysts such as MgO, La_2O_3, and different loadings of potassium on La_2O_3-MgO support. The effect of different kinetic parameters was studied to explore the activity of catalyst in the reaction of vanillin with DMC. Plausible reaction kinetics, reaction mechanism and catalyst reusability were studied.

EXPERIMENTAL SECTION

Chemicals

Magnesium nitrate, Lanthanum nitrate, urea and potassium carbonate were procured from Thomas Baker Chemicals, Mumbai. Vanillin, dimethyl carbonate and n-decane were obtained from SD Fine chemicals limited, Mumbai.

Preparation of catalyst

Lanthanum- magnesium mixed oxide (La_2O_3-MgO) with different mole ratio of La and Mg were prepared by hydrothermal method using urea as a precipitating agent.[42] The role of urea as a precipitating agent is well described by Ogawa et al.[46] The typical process for synthesis of La-

Mg with 1:3 molar ratio is as follows, 2.1 g of La $(NO_3)_3.9H_2O$, 3.86 g of Mg $(NO_3)_3.H_2O$ and 6 g of urea were dissolved in 150 mL distilled water stirred for 1 h until the solution become homogeneous. Then it was transferred into Teflon lined bomb reactor and heated 160 ºC for 12 h in muffle furnace. After cooling the reactor to room temperature obtained solid material was washed with distilled water. After filtration, the solid material was dried at 120 ºC. MgO and La_2O_3 catalyst were prepared by same procedure and were used after calcined at 750 ºC for 4 h. Similarly, we used same method for the preparation of La_2O_3, and MgO catalysts.

The potassium modified La_2O_3-MgO was prepared by wet impregnation method. The requisite quantity of K_2CO_3 was dissolved in 2 mL of water. The resultant solution was added to 1 g of La_2O_3-MgO via wet impregnation technique, under vigorous agitation at 80 ºC. On completion of adsorption of Potassium solution onto the surface of mixed oxide, the resultant material dried at 120 ºC for 10 h then calcined at 750 ºC for 4 h in air. Here we prepared 1 to 4 wt % K on La_2O_3-MgO by taking appropriate amount of precursor and catalyst were named as 1wt % K/ La_2O_3-MgO, 2 wt % K/ La_2O_3-MgO, 3 wt % K/ La_2O_3-MgO and 4 wt % K/ La_2O_3-MgO, respectively.

General procedure for O-methylation of vanillin

A stainless-steel Amar autoclave (Mumbai, India) of 100 mL equipped with a 4 blade pitch turbine impeller was used for the reaction. The agitation speed was maintained at ±5 rpm of the experimental value. Calculated amount of reactants were taken in the autoclave. The autoclave was tightened and desired temperature was set, after attaining the temperature zero-minute sample was removed. A typical standard experiment, 0.02 mole of vanillin, 0.3 mole of DMC and 0.2 mL of n-decane as an internal standard with a catalyst loading of 0.03 g/ cm^3 against

total volume (30 cm^3) of the liquid. The reaction mass was heated at 160 °C with speed of agitation 800 rpm for 2 h.

Method of analysis

Samples were withdrawn periodically and analysed by GC (Chemito Model 1000 with FID detector) using a capillary column BP-1 (length 30 m and inner diameter 0.32 mm). The injector and detector temperature were programmed from 60 to 300 °C with a ramp rate of 10 °C/min. The results were based on the decrease in conversion of the limiting reagent, vanillin. Product was confirmed by GC-MS (Perkin Elmer, Clarius model 500) on Elite-1 capillary column (length 30 m and inner diameter 0.25 mm).

After completion of the reaction, the autoclave was cooled to room temperature and the catalyst separated from the reaction mixture by filtration. The catalyst was washed with methanol (4 mL x 2) to confirm that no product is adsorbed on the catalyst. The filtrate was collected and solvent was evaporated at reduced pressure to obtain oily product, which was confirmed by GC-MS. The isolated yield was 89 % because of loss of product during the isolation procedure.

Characterization methodology

Catalysts were characterized by different techniques. The detailed description of characterization methodology is published in recent literature.[47] Details is also provided in supplementary.

RESULTS AND DISCUSSION

Catalyst characterization

XRD

The XRD patterns of La_2O_3-MgO and K/ La_2O_3-MgO with 1- 4 wt % loading of potassium are showed in Figure 1. La_2O_3-MgO (Figure 1(a)) catalyst depicted the presence of La_2MgO_X (JCPDS: 42-339), La_2O_3 (JCPDS: 40-1281) and MgO (JCPDS: 27-759). The existence of La_2MgO_X confirms the interaction between the La_2O_3 and MgO constituents during the synthesis of La_2O_3-MgO.[27,48]

All potassium loaded catalysts showed similar XRD patterns of La_2O_3-MgO because potassium can be well dispersed on the La_2O_3-MgO support. Figure 1(b), (c), (d), (e) and (f) shows no typical diffraction peaks corresponding to the K_2CO_3 (2θ =12°,25°, 32°,38°and 41°), which suggest that the potassium carbonate has completely decomposed. With the loading of potassium, there was disappearance of La_2O_3 peak at 2θ=30.36° and the detection of new peak attribute to K_2O (JCPDS: 27-431).[49,50] This K_2O phase may be the origin of basicity and high catalytic activity. The crystalline size of the La_2O_3-MgO and 2 wt % K/ La_2O_3-MgO was calculated using Scherrer's formula. The average crystallite size of La_2O_3-MgO and 2 wt % K/ La_2O_3-MgO was 15.16 nm and 30.89 nm respectively. The XRD pattern of 2 wt % K/ La_2O_3-MgO and reused catalysts were compared and XRD patterns are almost same which confirms that prepared catalyst is stable.
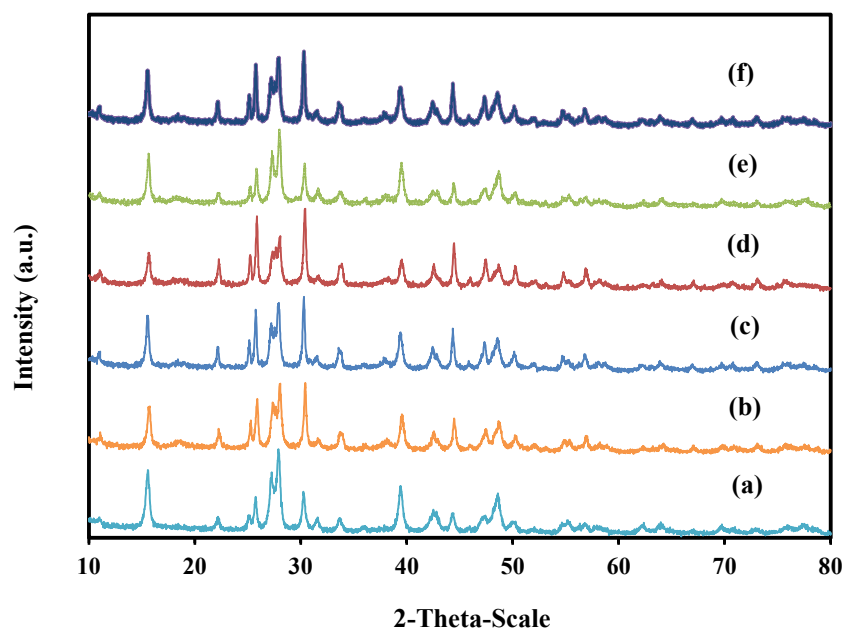
Figure 1. XRD of pattern of (a) La_2O_3-MgO, (b) 1 wt % K/ La_2O_3-MgO, (c) 2 wt % K/ La_2O_3-MgO, (d) 3 wt % K/ La_2O_3-MgO, (e) 4 wt % K/ La_2O_3-MgO and (f) reused 2 wt % K/ La_2O_3-MgO catalyst

FT-IR

Figure 2 shows FT-IR spectra of La_2O_3-MgO, 1 wt % K/ La_2O_3-MgO, 2 wt % K/ La_2O_3-MgO, 3 wt % K/ La_2O_3-MgO, 4 wt % K/ La_2O_3-MgO and reused 2 wt % K/ La_2O_3-MgO catalyst. The strong band at 650 cm^{-1}, which is attributable to the lattice vibration of Lanthanum oxide bond. The band at 3560 cm^{-1} indicates the presence of hydroxide species of adsorbed water molecule and two bands at 1460 and 1380 cm^{-1} due to the carbonate species. The weak band at 1080 cm^{-1} indicates the presence of symmetric $(CO_3)^{2-}$. The band at 1460 cm^{-1} reveals that the inclusion of potassium promotes the formation of basic sites and the adsorption of carbon dioxide on the surface of La_2O_3-MgO. FT-IR spectra virgin and used catalysts were signifying that there were no structural changes. It also indicates that there were no externally adsorbed species on the surface of the 2 wt % K/ La_2O_3-MgO catalyst.
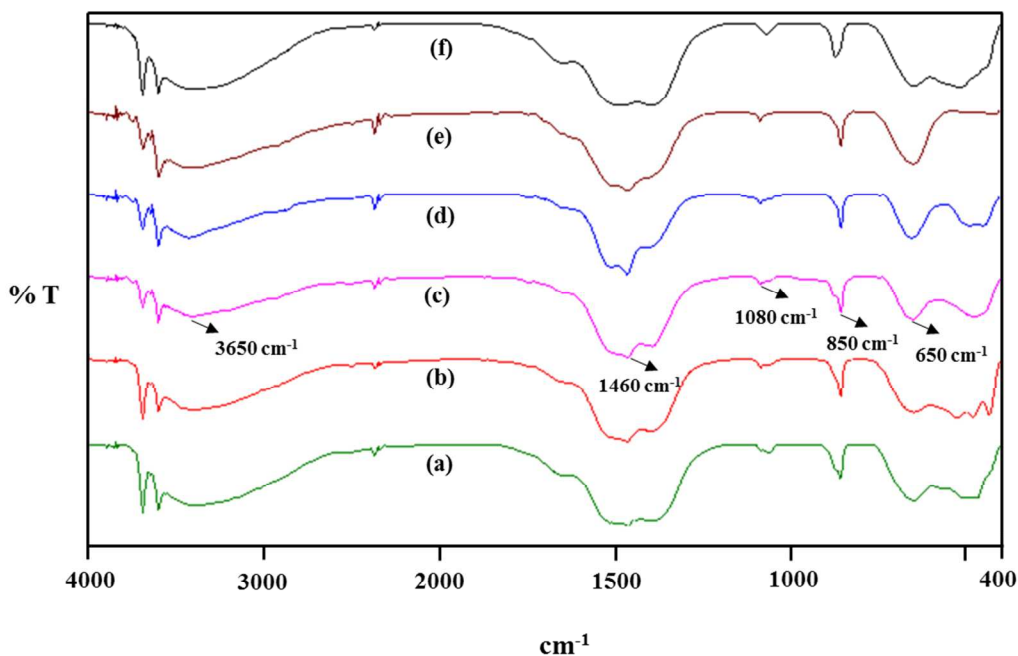
Figure 2. FTIR of (a) La_2O_3-MgO, (b) 1 wt % K/ La_2O_3-MgO, (c) 2 wt % K/ La_2O_3-MgO, (d) 3 wt % K/ La_2O_3-MgO, (e) 4 wt % K/ La_2O_3-MgO and (f) reused 2 wt % K/ La_2O_3-MgO catalyst

Surface area and pore size analysis

The BET N_2 adsorption/desorption isotherms of La_2O_3-MgO and different loadings of potassium (1-4 wt %) on La_2O_3-MgO are shown in Figure 3. All catalysts showed a type IV isotherm and type H3 hysteresis loop, indicative of the formation of mesoporous material. The surface area, pore volume and average pore diameter of La_2O_3-MgO catalyst are 48 m^2 g^{-1}, 0.13 cm^3 g^{-1} and 11 nm, respectively (Table 1). After the introduction of potassium, there is a decline in surface area as well as pore volume. Diez and coworkers[51,52] reported that the introduction of alkali metals on MgO would result in a decrease in surface area and pore volume. The decline in pore volume and surface area upon potassium loading observed over La_2O_3-MgO and K/ La_2O_3-MgO catalysts are in good agreement with the results of SEM and CO_2-TPD analysis. The

porous parameters of 2 wt % K/ La$_2$O$_3$-MgO and reused 2 wt % K/ La$_2$O$_3$-MgO catalysts were

observed almost same.

Table 1. Surface properties of various synthesized catalysts for O-methylation of vanillin

No.	Catalysts	BET surface area (m^2/g)	Average pore diameter (nm)	BJH pore volume (cm^3/g)
1	La$_2$O$_3$-MgO	48	11	0.13
2	1 wt % K/ La$_2$O$_3$-MgO	22	25	0.12
3	2 wt % K/ La$_2$O$_3$-MgO	20	28	0.11
4	3 wt % K/ La$_2$O$_3$-MgO	18	21	0.09
5	4 wt % K/ La$_2$O$_3$-MgO	13	23	0.07
6	Reused 2 wt % K/ La$_2$O$_3$-MgO	19	26	0.10
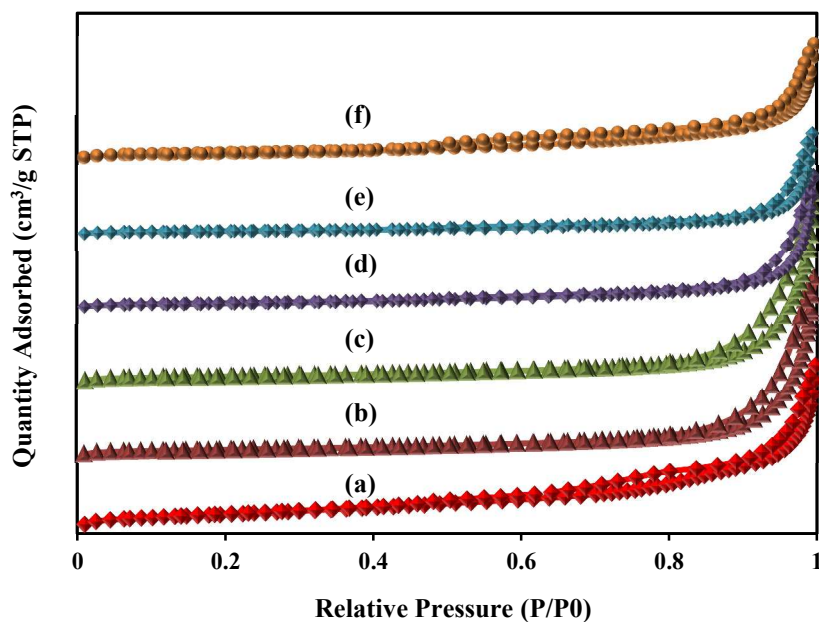
Figure 3. N_2 adsorption-desorption plot for the (a) La_2O_3-MgO, (b) 1 wt % K/ La_2O_3-MgO, (c) 2 wt % K/ La_2O_3-MgO, (d) 3 wt % K/ La_2O_3-MgO, (e) 4 wt % K/ La_2O_3-MgO and (f) reused 2 wt % K/ La_2O_3-MgO catalyst

CO$_2$-TPD

CO$_2$-TPD analysis was used to measure the basic nature of sites generated on the surface of the samples. As showed in Figure 4 La_2O_3-MgO catalyst CO$_2$ desorption peaks were observed at 285 ºC and 470 ºC corresponds moderate /strong basic sites, and the quantity of CO$_2$ was 0.36 and 0.38 mmolg^{-1}. The introduction of potassium results in increase in the desorption temperature and enhancement in the amount of CO$_2$ desorption. 2 wt % K/ La_2O_3-MgO catalyst showed desorption peaks at 106 ºC, 324 ºC, 498 ºC and 745 ºC corresponds to weak, moderate, strong and super basic sites and the quantity of CO$_2$ desorbed were 0.15, 0.21, 0.05 and 1.09 mmolg^{-1}, respectively. The desorption peak at 745 ºC is a clear indication of super basic sites.[53] Further increasing concentration of potassium, there is a decline in the basicity of 3 and 4 wt % K/ La_2O_3-MgO catalysts (Table 2). This is due to the coverage of excess potassium on the surface of basic sites. The basicity of fresh and used catalyst shows almost similar results.

Table 2. CO$_2$-TPD analysis for various synthesized catalysts

No.	Catalysts	CO$_2$-TPD analysis Basicity (mmol g^{-1})		
		Weak	Moderate/strong	Total
1	La_2O_3	0.02	0.25	0.27
2	MgO	0.05	0.31	0.36
3	La_2O_3-MgO	0.04	0.70	0.74
4	1 wt % K/ La_2O_3-MgO	0.10	0.88	0.98

5	2 wt % K/ La$_2$O$_3$-MgO	0.15	1.35	1.50
6	3 wt % K/ La$_2$O$_3$-MgO	0.09	1.17	1.26
7	4 wt % K/ La$_2$O$_3$-MgO	0.08	1.05	1.13
8	Reused 2 wt % K/ La$_2$O$_3$-MgO	0.13	1.33	1.46
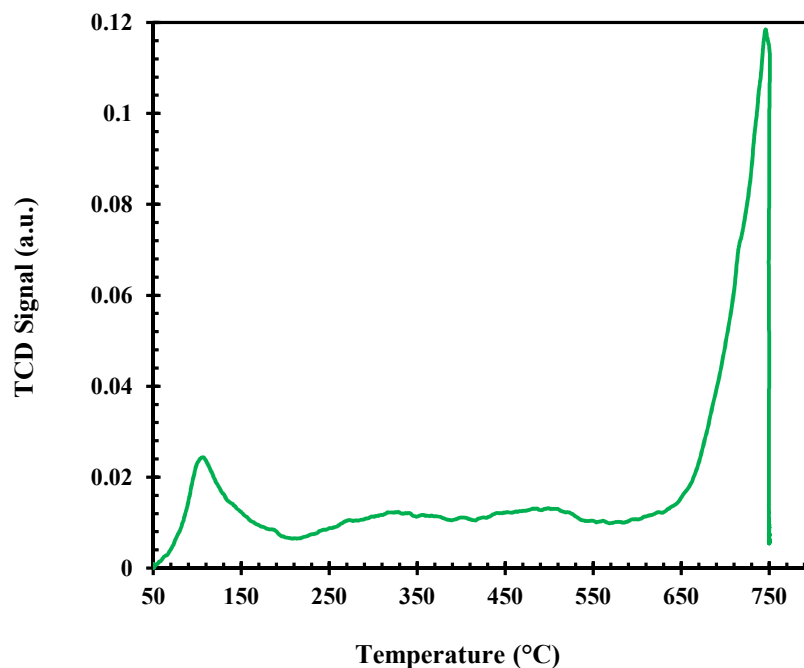
Figure 4. CO$_2$-TPD pattern of 2 wt % K/ La$_2$O$_3$-MgO

TGA-DSC

TGA-DSC analysis of 2 wt % K/ La$_2$O$_3$-MgO catalyst was carried out from 50 to 700 ºC (Figure 5). Two endothermic peaks were observed in DSC curve; first peak was observed at 80 to 130 ºC due to removal of water (humidity) and resulted in 8 % weight loss. Second endothermic peak between 320 °C and 400 ºC was due to evolution of CO$_2$ and decomposition of oxycarbonate corresponding to 12 % weight loss to get stable oxide forms. The overall analysis shows around 20 % weight loss and the catalyst was stable after 450 ºC up to 700 ºC.
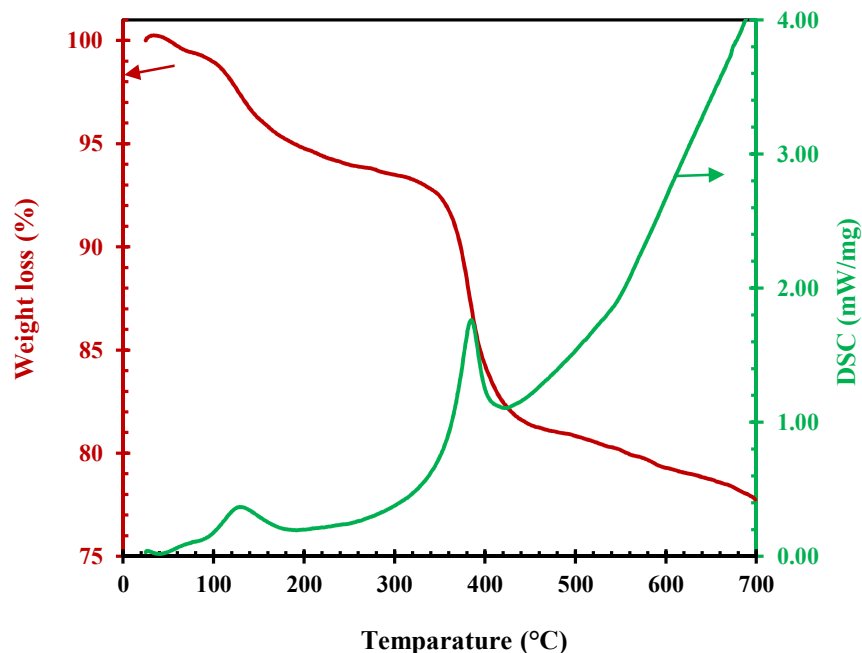
Figure 5. TGA-DSC analysis of 2 wt % K/ La_2O_3-MgO

SEM

The SEM images of La_2O_3-MgO, 2 wt % K/ La_2O_3-MgO catalysts are shown in Figure 6. La_2O_3-MgO catalyst forms a spherical and dendritic structure. There is no agglomeration takes place after the introduction of 2 wt % potassium on La_2O_3-MgO. Hence, it is assumed that with low loading of potassium, a high dispersion was obtained and the La_2O_3-MgO support intact its original structure.
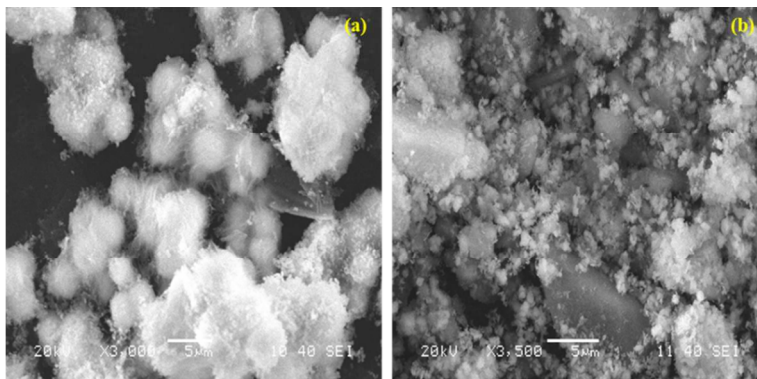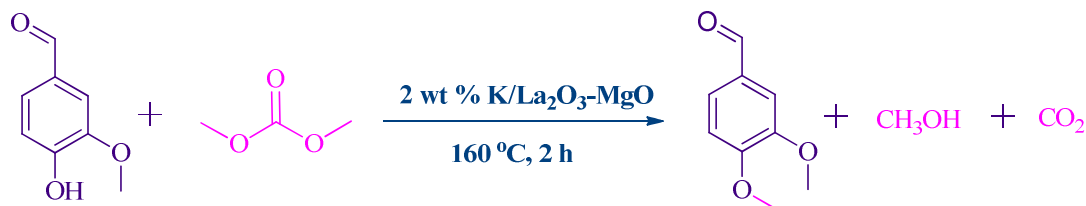

Figure 6. SEM images of (a) La_2O_3-MgO and (b) 2 wt % K/ La_2O_3-MgO

Catalytic reaction

The reaction of O-methylation of vanillin with DMC using 2 wt % K/ La_2O_3-MgO catalyst given in Scheme 1.


Scheme 1. O-methylation of vanillin with DMC

Efficacy of various catalysts.

Activity of different solid base catalysts towards synthesis of veratraldehyde was studied using vanillin and DMC. The reaction was carried out using vanillin to DMC mole ratio 1:15 at 800 rpm with catalyst loading of 0.03 g/cm^3 on the basis of total volume (30 mL). A variety of catalysts such as, MgO, La_2O_3, La_2O_3-MgO with different loadings (1 to 4 wt %) of potassium on La_2O_3-MgO like 1 wt % K/ La_2O_3-MgO, 2 wt % K/ La_2O_3-MgO, 3 wt % K/ La_2O_3-MgO and 4 wt % K/ La_2O_3-MgO catalysts were studied for O-methylation reaction (Figure 7). It was significant that no C-methylated by-products were identified and the selectivity to veratraldehyde was always 100 % regardless of type of catalysts. From Table 2 the basicity of different catalyst is in the following order: La_2O_3 (least) <MgO <La_2O_3-MgO <1 wt % K/ La_2O_3-MgO <4 wt % K/ La_2O_3-MgO <3 wt % K/ La_2O_3-MgO <2 wt % K/ La_2O_3-MgO (highest). The conversion and activity of the catalyst follow the same trend as La_2O_3 (least) <MgO <La_2O_3-MgO <1 wt % K/ La_2O_3-MgO <4 wt % K/ La_2O_3-MgO <3 wt % K/ La_2O_3-MgO <2 wt % K/ La_2O_3-MgO (highest). Thus, it is concluded that basicity of catalyst plays a major role in conversion and

selectivity. We have also plotted CO_2 uptake and conversion for different catalysts which further supports that basicity of catalysts is the governing parameter (Figure 7).

The obvious reason for excellent conversion of vanillin is the maximum basicity of catalyst observed at loading of 2 wt % potassium on La_2O_3-MgO. It is due to increase of moderate and strong basic sites. The further increase in the loading of potassium leads to decrease in the conversion possibly due to blocking of pores by excess amount of potassium. The activity of MgO, La_2O_3 catalysts was found to be less due to lack of strong basic sites. The optimum loading of potassium is 2 wt %, which is good agreement with the results of CO_2-TPD (Table 1) and BET surface area (Table 2). Hence, 2 wt % K/ La_2O_3-MgO was selected as superior catalyst for detailed kinetics.
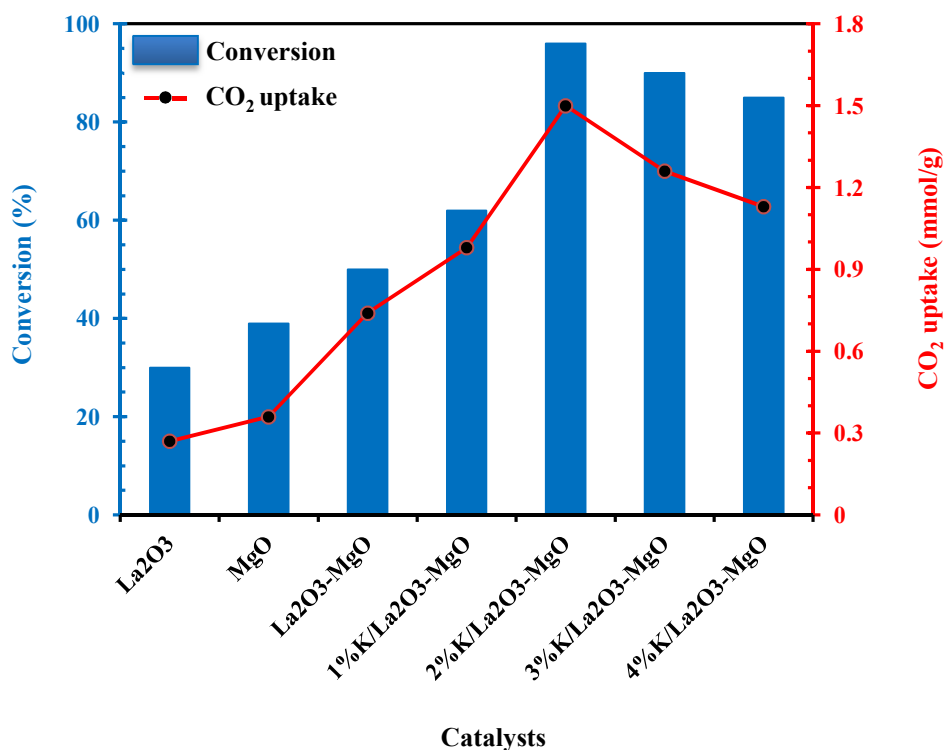
Figure 7. Effect of various catalysts and CO₂ uptake on conversion of vanillin: vanillin 0.02 mol, DMC 0.3 mol, speed of agitation 800 rpm, temperature 160 ºC, total volume 30 cm³, reaction time 2 h, catalyst loading 0.03 g/cm³

Effect of speed of agitation.

The agitation speed was studied at 400, 600, 800 and 1000 rpm at 160 °C in order to understand the effect of external mass transfer resistance on the rate of reaction (Figure 8). It is clear that beyond 800 rpm there is no effect on the conversion of vanillin signifying that the mass transfer resistance was absent. Thus, further experiments were carried out 800 rpm. Also, theoretical calculations were done as reported earlier to calculate mass transfer rate.[47,54] The calculated mass transfer rates were found to be very high in comparison of the reaction rate which confirms that there is no effect of external mass transfer resistance at and beyond 800 rpm.
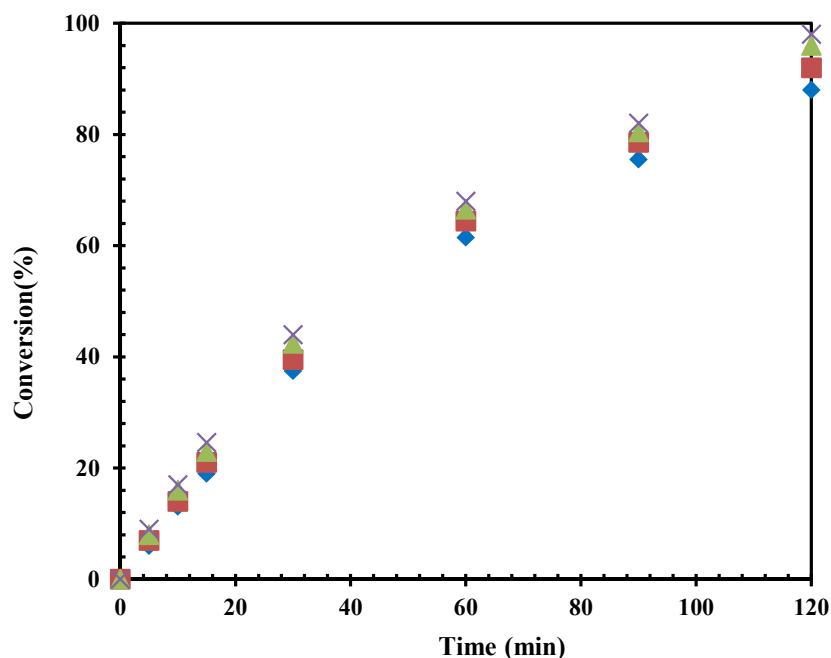
Figure 8. Effect of speed of agitation on conversion of vanillin: vanillin 0.020 mol, DMC 0.3 mol, catalyst 2 wt % K/ La₂O₃-MgO, temperature 160 ºC, total volume 30 cm³, reaction time 2 h, catalyst loading 0.03 g/cm³. (♦) 400 rpm, (■) 600 rpm, (▲) 800 rpm, (x) 1000 rpm

Effect of catalyst loading.

The influence of catalyst loading on conversion of vanillin was studied from 0.01 to 0.04 g/cm^3 (Figure 9). Vanillin conversion increases with the increase in catalyst loading which is due to proportional increase in number of active sites. Catalyst loading from 0.03-0.04 g/cm^3 there is no appreciable changes in the conversion of vanillin. It is due to surpassing the number of active sites available for reaction than the number of vanillin molecules actually present for the reaction. Therefore, further reaction was performed on 0.03 g/cm^3 catalyst loading. Figure10 shows initial rate of reaction increases linearly with the catalyst loading which confirms absence of mass transfer resistance. Wiesz-Prater criterion or modulus (C_{WP}) was also calculated at 0.03 g/cm^3 to find that the O-methylation of vanillin reaction was free from intra -particle diffusion limitation. The details related to these can be easily found in our earlier literature.[52] In this case, C_{WP} value was found to be 3.15×10^{-3} which is very less than unity and hence there is no role of intra-particle diffusion resistance on the overall rate of reaction.
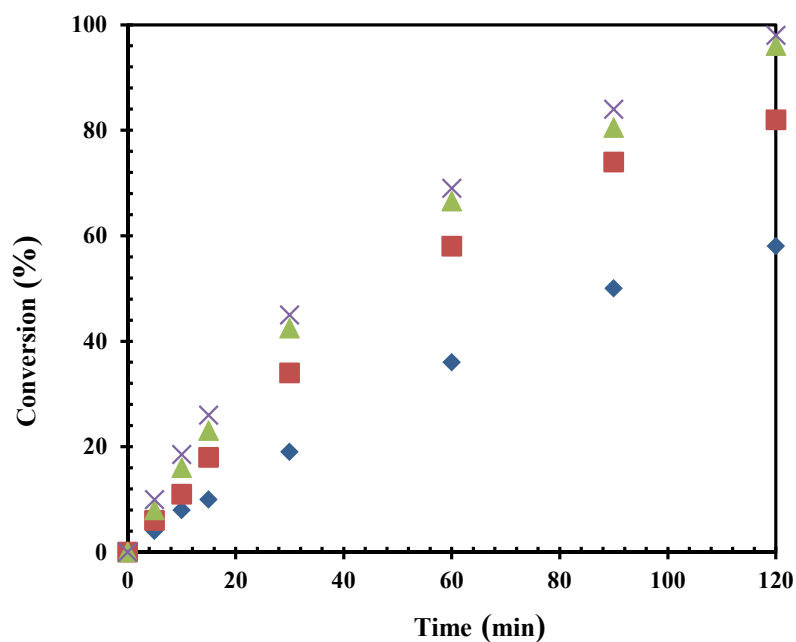
Figure 9. Effect of catalyst loading on conversion of vanillin: vanillin 0.020 mol, DMC 0.3 mol, catalyst 2 wt % K/La$_2$O$_3$-MgO, temperature 160 ºC, total volume 30 cm^3, reaction time 2 h, speed of agitation 800 rpm. (♦) 0.01 g/cm^3, (■) 0.02 g/cm^3, (▲) 0.03 g/cm^3, (x) 0.04 g/cm^3
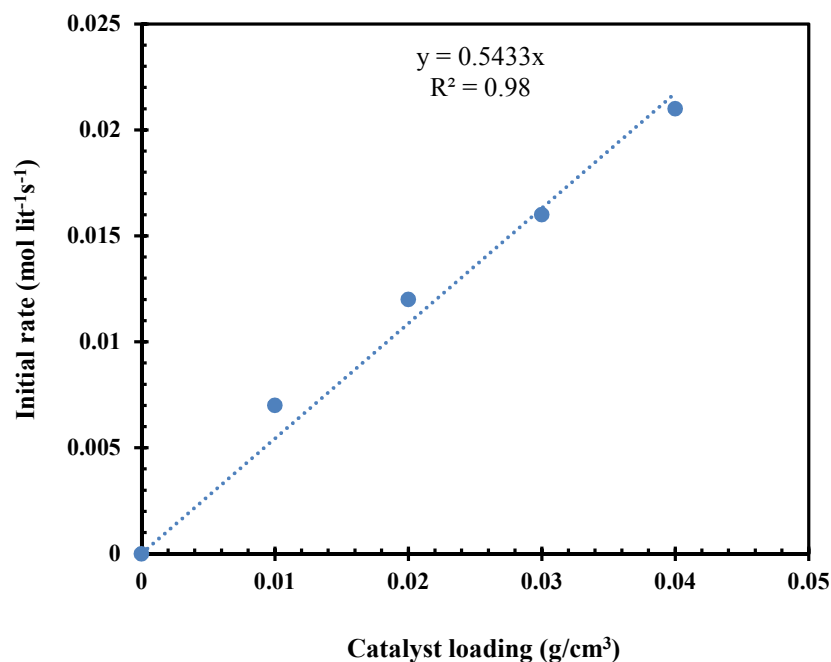
Figure 10. Plot of initial rate on conversion of vanillin: vanillin 0.020 mol, DMC 0.3 mol, catalyst 2 wt % K/ La$_2$O$_3$-MgO, temperature 160 ºC, total volume 30 cm^3, reaction time 2 h, speed of agitation 800 rpm.

Effect of mole ratio

Mole ratio of vanillin to DMC was studied at 1:5, 1:10, 1:15 and 1:20 to know its effect on the rate of reaction by keeping the total reaction volume constant (Figure 11). The conversion of vanillin increases with increase in mole ratio. The conversion of vanillin at 1:5 mole ratio is 50 % which increased to 96 % at 1:15 mole ratio. There was no significant change in conversion in between 1:15 to 1:20 mole ratio. Therefore it is concluded that 1:15 mole ratio is ideal parameter for this reaction and used for further reactions.

Figure 11. Effect of mole ratio on conversion of vanillin: vanillin 0.02 mol, catalyst 2 wt % K/ La$_2$O$_3$-MgO, temperature 160 ºC, total volume 30 cm^3, reaction time 2 h, speed of agitation 800 rpm. (♦) 1:05, (■) 1:10, (▲) 1:15, (x) 1:20.

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Effect of temperature
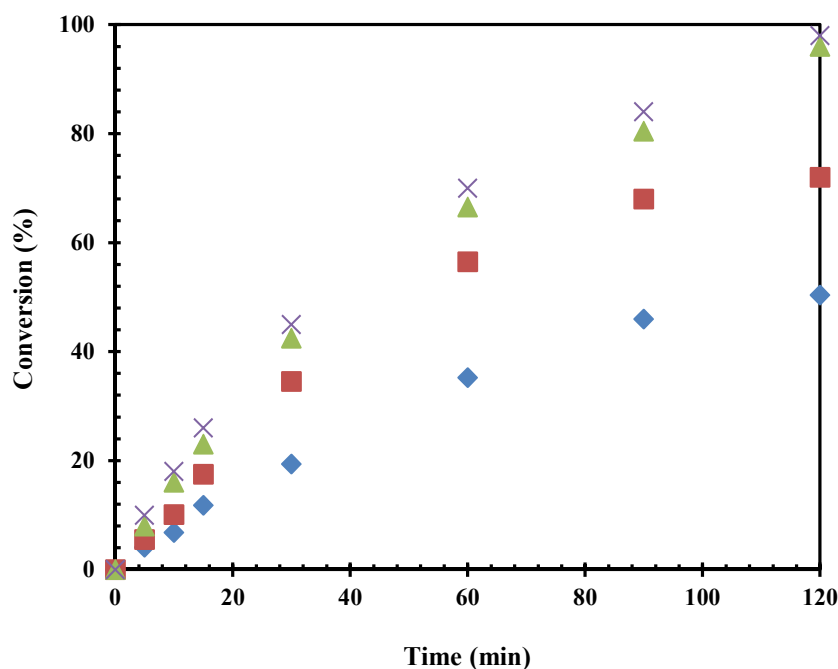
The effect of temperature was studied at 140, 150, 160 and 170 °C (Figure 12) to see its effect

and to prove that the reaction is only kinetically controlled and all other resistance have been

successfully avoided. The increase in temperature resulted in increase in the initial rate of

reaction and conversion substantially which suggested that reaction was kinetically controlled.
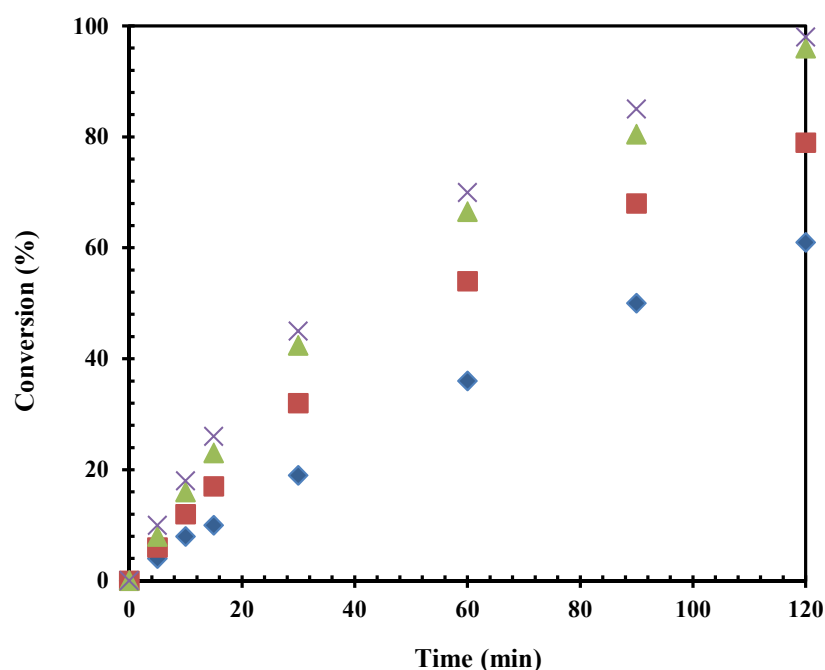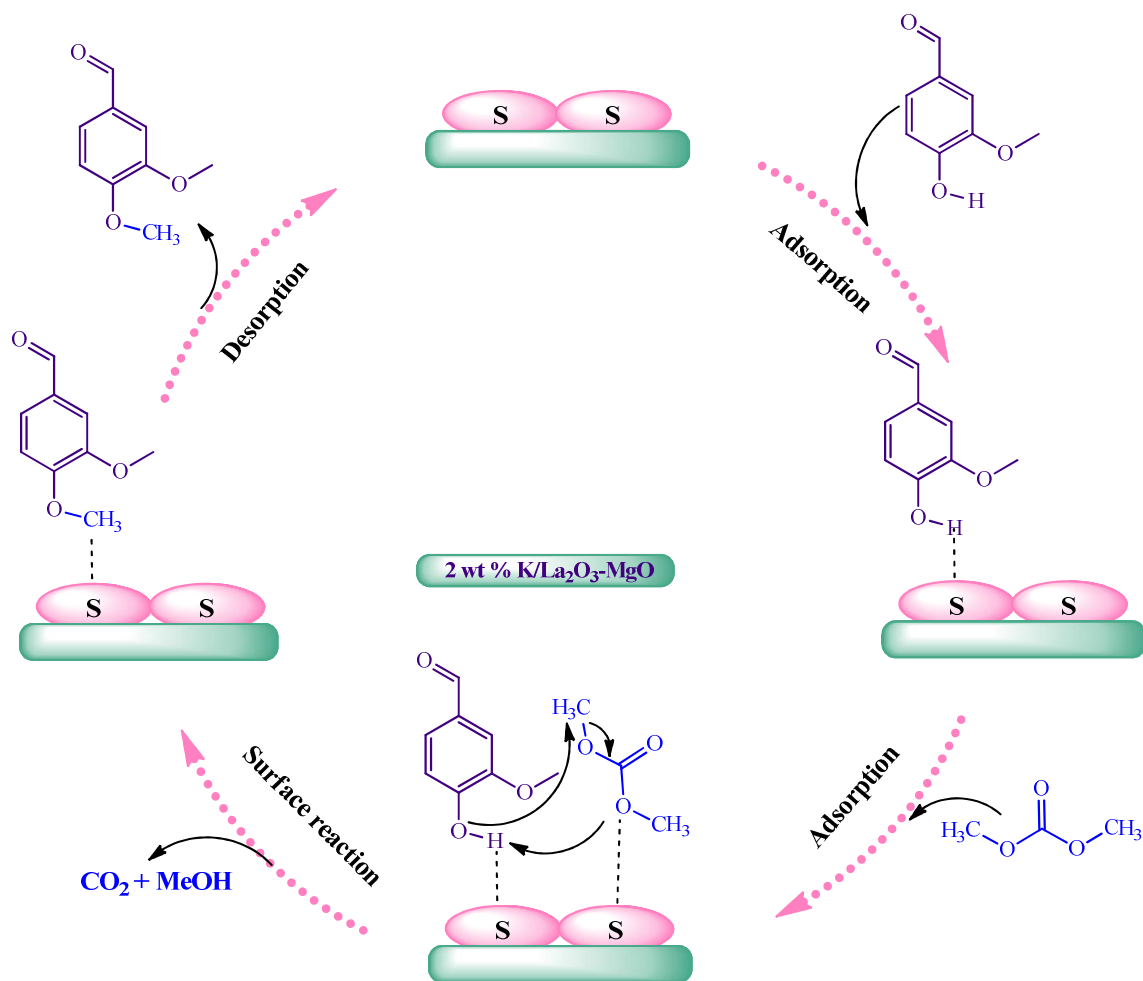

Figure 12. Effect of temperature on conversion of vanillin: vanillin 0.02 mol, DMC 0.3 mol,

catalyst 2 wt % K La$_2$O$_3$-MgO, speed of agitation 800 rpm, total volume 30 cm^3, reaction time 2

h, catalyst loading 0.03 g/cm^3. (♦) 140 ºC, (■) 150 ºC, (▲) 160 ºC, (x) 170 ºC

Reaction mechanism and mathematical model.

Scheme 2. Reaction mechanism of O-methylation of vanillin with DMC

The plausible O-methylation mechanism of vanillin with DMC on basic sites of 2 wt % K/La$_2$O$_3$-MgO catalyst is depicted in Scheme 2. O-methylation of vanillin (A) with DMC (B) occurs by strong adsorption of vanillin on basic sites leading to the formation of veratraldehyde.

The detail mathematical model was developed using LHHW mechanism as same reported in recent literature.[45,52] The detail derivation steps are provided in supplementary. The rate of reaction of vanillin can be given as:

$$-r_A = -\frac{dC_A}{dt} = C_{A_0}\frac{dX_A}{dt} = k_{R_2}wC_{A_0}\left(1-X_A\right)C_{B_0} \qquad (1)$$

DMC was taken in molar excess over vanillin ($C_{B_0} > C_{A_0}$), it becomes a pseudo-first order equation which can be integrated as follows:

$$-\ln(1-X_A) = k_1 wt \qquad (2)$$

Where $k_1 = C_{Bo}k_{R_2}$ is the pseudo-first order constant.

A plot of -ln (1-X_A) against time was made at a various temperature to get excellent fit, there by supporting the model. This is an overall pseudo first order reaction (Figure 13). Energy of activation was calculated by plotting Arrhenius plot of ln k against time (Figure 14) and energy of activation was found to be 13.5 kcal/mol, which supports the fact that reaction is intrinsically kinetically controlled.
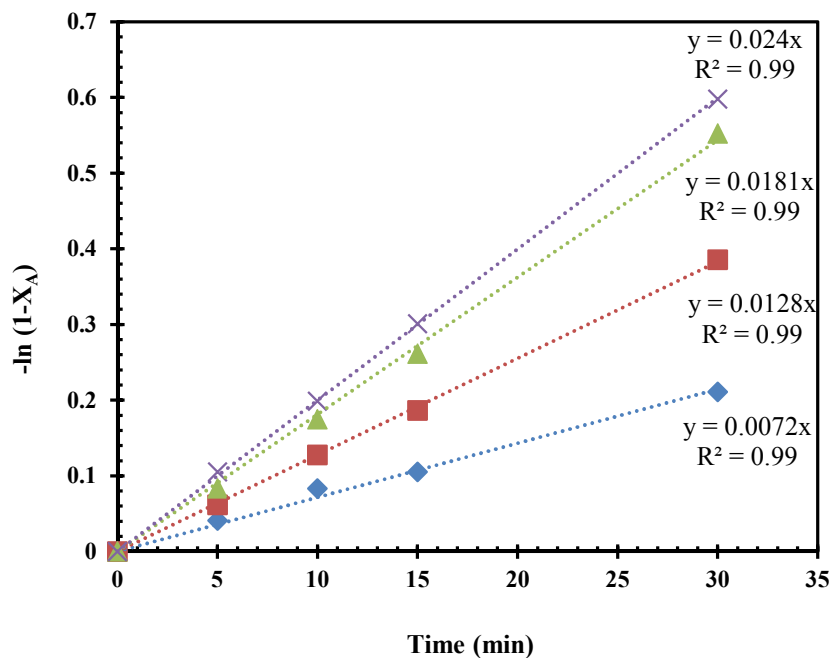

Figure 13. Kinetics plots for various temperatures: vanillin 0.02 mol, DMC 0.3 mol, catalyst 2 wt % K/ La$_2$O$_3$-MgO, speed of agitation 800 rpm, total volume 30 cm^3, reaction time 2 h, catalyst loading 0.03 g/cm^3. (♦) 140 ºC, (■) 150 ºC, (▲) 160 ºC, (x) 170 ºC

The chart shows an Arrhenius plot with x-axis "1/T (K^{-1})" ranging from 0.0023 to 0.0025, and y-axis "ln (k$_1$)" ranging from -5.5 to -3. Data with trend line: $y = -6929.5x + 12.331$, $R^2 = 0.98$.
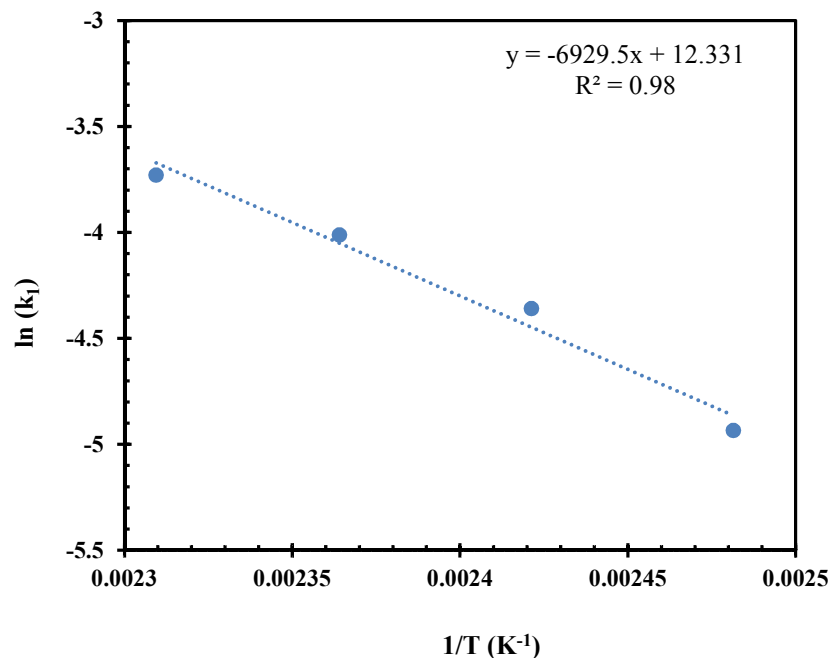
Figure 14. Arrhenius plot

Reusability of catalyst

The reusability of the 2 wt % K/ La$_2$O$_3$-MgO catalyst was tested four times in case of O-methylation of vanillin. After each reaction, the catalyst was separated by filtration and washed with methanol and then dried at 120 ºC. We have make up the catalyst during reaction. It was observed that 2 wt % K/ La$_2$O$_3$-MgO shows the very small difference in activity after third time use. In case of fourth time reuse there is a 6 % conversion difference compare to fresh catalyst (Figure 15). These results clearly show the stability of 2 wt % K/ La$_2$O$_3$-MgO catalyst. Further, we also characterized the used catalyst by different techniques and discussed above. The morphology and the surface area analysis confirmed that there was no much difference in fresh and used catalyst and hence the prepared catalyst was stable and reusable in the reaction.

Further, the hot filtration test was also conducted to study leaching of active sites, if any. Reaction was stopped after 30 min and the catalyst filtered. The reactor was washed to get rid of any traces of catalyst. The reaction was continued further for 2 h. The slight increase in conversion was noticed from 41 to 43 % conversion which was an experimental error. This confirmed the strong interaction between K_2O and support i. e. La_2O_3-MgO. As reported by Noiroj et al.[47] who claimed that nature or type of support plays an important role to prevent a leaching of active species. In the current work La_2O_3-MgO not only plays a role of base catalyst but also acts as a good support to prevent leaching of potassium.
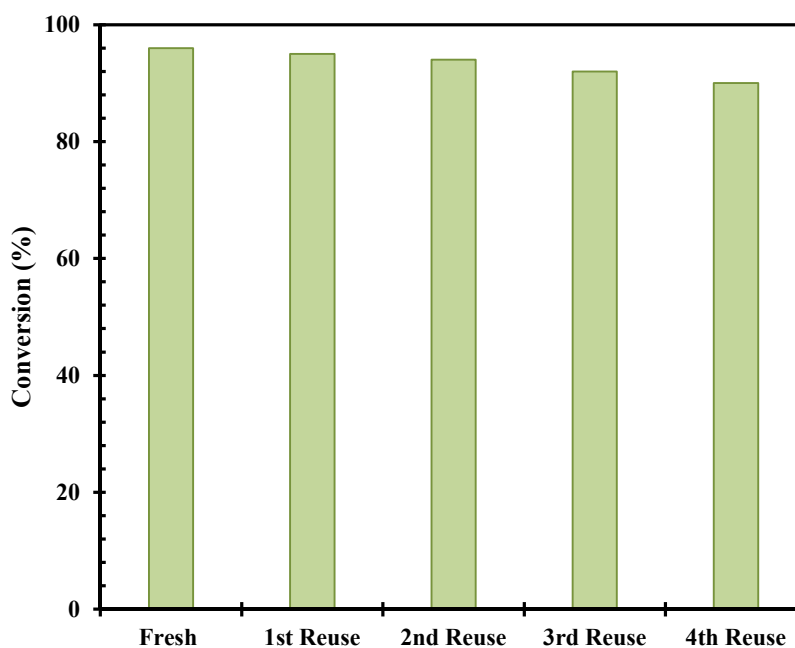

Figure 15. Catalyst reusability: vanillin 0.02 mol, DMC 0.3 mol, catalyst 2 wt % K/ La_2O_3-MgO, speed of agitation 800 rpm, temperature 160 ºC, total volume 30 cm^3, reaction time 2 h, catalyst loading 0.03 g/cm^3

Large-scale synthesis

From equation (2), the fractional conversion is theoretically given as follows:

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$$X_A = 1 - e^{-k_1 wt} \quad (3)$$

The viability of the present method was also studied for a somewhat scaled-up experiment with vanillin (21 g; 0.14 mol), DMC (176 g; 2.1 mol) and 1.4 mL of n-decane as an internal standard with optimized catalyst loading of 0.03g/cm^3 (6.3 g)against a total volume (210 cm^3) of the liquid. The reaction mass heated at 160 °C with speed of agitation 800 rpm for 2 h. The reaction was monitored. The conversion was 92 % in 2 h and the isolated yield 88 %. Also the fractional conversion $X_{A-experimental}$ was plotted against $X_{A-predicted}$ value as given in Figure 16. The parity plot shows that there is an excellent match. This experiment demonstrated the efficiency of the 2 wt % K/La$_2$O$_3$-MgO for the large-scale production as well.
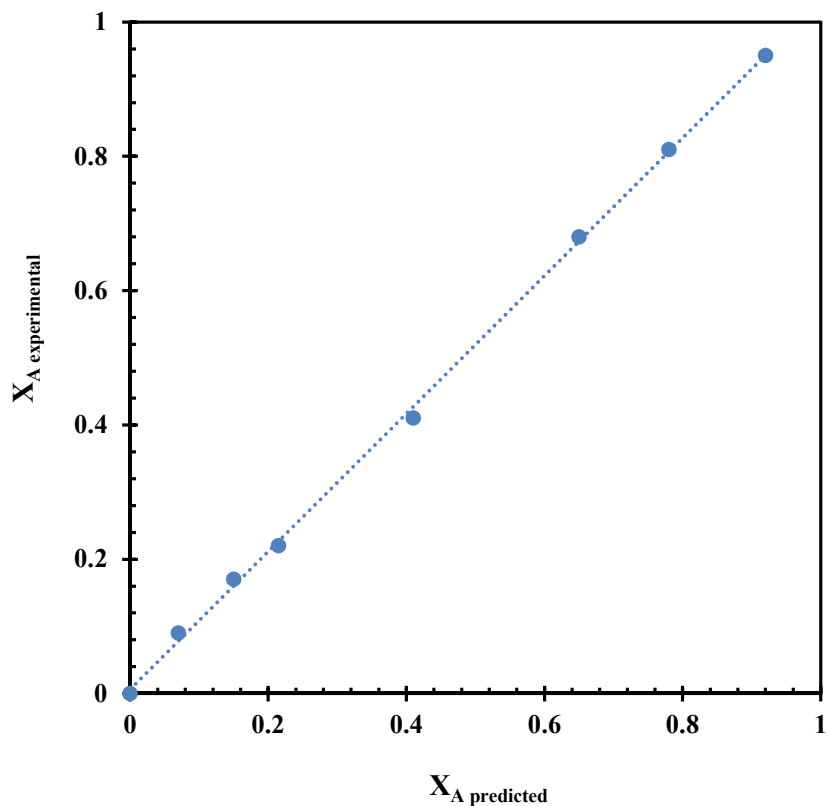

Figure 16: Parity plot of experimental values against predicted values for a large scale experiment.

CONCLUSION

Synthesis of veratraldehyde using a catalytic green process is desirable in today's environmentally conscious world. Therefore a new process was devised in this work using a novel catalyst using mixed metal oxides. Different loadings of potassium promoted on La_2O_3-MgO (1-4 wt %) catalysts were synthesized and characterized by various techniques. The activity of catalyst was studied in the reaction of vanillin with DMC for the synthesis of veratraldehyde in comparison with several other catalysts such as MgO, La_2O_3, La_2O_3-MgO, 1 wt % K/ La_2O_3-MgO, 2 wt % K/ La_2O_3-MgO, 3 wt % K/ La_2O_3-MgO and 4 wt % K/ La_2O_3-MgO. Potassium promoted mixed oxides showed much higher catalytic activity than the corresponding pure La_2O_3-MgO mixed oxide, due to increase in moderate, strong, super basic sites. Moreover, loading of potassium on La_2O_3-MgO changes the structural properties like pore volume and surface area, and it gives higher conversion towards the desired product. 2 wt % K/ La_2O_3-MgO is the best and gives 96 % of conversion at mole ratio of 1:15 of vanillin to DMC and 0.03 g/cm^3 catalyst loading at 160 °C. By using this catalyst, we studied various parameters systematically to establish kinetics. The catalyst is reusable up to four cycles. The energy of activation for O-methylation of vanillin was found to be 13.5 kcal/mol. A scale up was also attempted. Experimental and theoretical values matched very well. The process is green and clean.

ASSOCIATED CONTENTS

Supporting Information

Supporting information for this article contains catalyst characterization methodology and development of kinetic model.

AUTHOR INFORMATION

Corresponding Author

*Ganapati D. Yadav. E-mail: gd.yadav@ictmumbai.edu.in, Phone: +91-22-3361-1001, Fax: +91-22-3361-1020; +91-22-3361-1002

NOTES

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

NOMENCLATURE

A	reactant species, vanillin
B	reactant species, DMC
A_S	chemisorbed vanillin
B_S	chemisorbed DMC
C	product species C, veratraldehyde
S	vacant site
C_A	concentration of vanillin in mol/cm^3

C_B concentration of DMC, mol/ cm^3

C_{Ao} initial concentration of vanillin in bulk liquid phase, (mol/ cm^3)

C_{Bo} initial concentration of DMC in bulk liquid phase, mol/ cm^3

C_{BS} concentration of DMC at solid surface, mol/ cm^3

Cc concentration of veratraldehyde, mol/ cm^3

C_{CS} concentration of veratraldehyde at solid surface, mol/ cm^3

C_S concentration of vacant sites, mol/ cm^3

C_T total concentration of sites, mol/ cm^3

k_{R_2} reaction rate constant, cm^6 g-cat mol^{-1}s^{-1}

k_1 pseudo-first order rate constant, s^{-1}

K_i adsorption equilibrium constant for species i, cm^3/mol

W product species, methanol

w catalyst loading g/cm^3 of the liquid volume

X_A fractional conversion of A

$-r_A$ rate of reaction of A, mol cm^{-3} s^{-1}

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