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Green synthetic route for perfumery compound (2-methoxyethyl) benzene using Li/MgO catalyst

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Abstract. Ethers are one of the most prominent compounds among perfumery chemicals. (2-Methoxyethyl) benzene commonly known as phenyl ethyl methyl ether (PEME) is widely used in flavour and fragrance industries. Conventionally, synthesis of PEME involves the use of hazardous and polluting chemicals, which in turn affects the purity of perfumery compound. Thus, developing a green route to synthesise PEME without any hazardous chemicals is desirable. In the current work, a new process is developed for the synthesis of PEME using solid base catalysts including MgO and Li/MgO (with different loadings of lithium) and dimethyl carbonate (DMC) as a methylating agent as well as a solvent. Different kinetic parameters were studied to achieve the optimum yield of the desired product. At optimum reaction conditions i.e., 1000 rpm of speed, 1.33×10^{-2} g/cm^3 of catalyst loading, 1:10.5 mole ratio (2-Phenyl ethanol: DMC), 180 °C, 95% conversion of 2-phenyl ethanol with 98% selectivity of PEME was achieved. A detailed kinetic model was also developed and apparent activation energy for the reaction was calculated as 11.93 kcal/mol.

Keywords. 2-Phenyl ethanol; (2-methoxyethyl)benzene; Li/MgO; perfumery compound; kinetics; solid base catalyst.

1. Introduction

Conventionally perfumery compounds are extracted from the natural sources but due to demanding trends in the market, the discovery of new synthetic pathways to prepare these compounds has received a lot of attention. Among a variety of organic compounds ethers, hemiacetals, etc., form an important group of compounds in perfumery and fragrance industry. Pandanus essential oil is a clear light yellow liquid highly soluble in water. The principal fragrance chemical constituent of the extract is phenyl ethyl methyl ether, which is responsible for the characteristic aroma of the flowers. Common pathways employed for the synthesis of phenyl ethyl methyl ether (PEME) are Williamson process using alkyl halides,[1] dimethyl sulphide,[2] dimethyl sulfoxide[3] and diazomethane[4] as methylating agents. These processes require toxic solvents like THF, benzene, hexane, etc., and the amount of strong base required to catalyse this reaction is over the stoichiometry thus producing

a large excess of dissolved inorganic salts and side-products. Though these processes are efficient the use of corrosive and toxic chemicals makes them environmentally hazardous. The industrial chemist, in his quest for aesthetic and creative solutions, must also take the cost and toxicity of the catalyst into account. Therefore, inventing a green catalytic route for the synthesis of PEME is desirable.

Dimethyl carbonate (DMC) has achieved a great attention as a methylating agent as it is an environmentally benign chemical[5,6] and a better substitute to the corrosive and toxic methylating agents like dimethyl sulfoxide,[7] methyl halides, etc. DMC favours the carboxymethylation with methanol as a co-product at a lower temperature, while at a higher temperature it favours the methylation reaction with methanol and carbon dioxide as co-products.[7,8] The methylation of alcohol with DMC involves two steps, namely, transesterification followed by decarboxylation in the presence base catalyst. Selva *et al.,* reported Y- and X-faujasites as base catalysts for the synthesis of methyl ethers from a variety of benzyl alcohols.[9] They achieved 100%

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conversion of benzyl alcohol with 100% selectivity of desired methyl ether. Tundo et. al reported basic alumina and hydrotalcite as a catalyst for methylation of benzyl alcohol with DMC. With hydrotalcite, they reported 100% conversion of benzyl alcohol with 96% selectivity for benzyl methyl ether in 3 h while with basic alumina they achieved 93% conversion of benzyl alcohol and 77% selectivity of benzyl methyl ether.[10]

Yadav and Bokade reported a liquid phase synthesis of PEME using methanol as a methylating agent and heteropoly acid supported on K-10 (clay) as a catalyst.[11] But there are no reports on the synthesis of PEME using DMC as a methylating agent. Thus, the aim of current work deals with the development of a new catalyst for synthesis of PEME using 2-phenyl ethanol (2-PE) and DMC.

Alkali promoted alkaline earth metal oxides are one of the well-known solid super-base catalysts and have been widely used as catalysts for a variety of reactions such as condensation, oxidative coupling, oxidative dehydrogenation, etc.[12–17] These catalysts are prepared by different methods like co-precipitation, decomposition of carbonates, sol gel[18] and incipient wetness technique. Conventionally synthesized Li promoted on magnesium oxides requires high-temperature treatment which results in sintering and lower surface area of the resultant catalyst. To employ the sol-gel method, magnesium alkoxides are used as precursors and is affected by the problems as these chemicals are quite expensive as well as moisture sensitive and unstable. Also, gelation process is quite time-consuming. Thus, catalyst synthesis route is needed with advantages of simplicity, ease of preparation, shorter time and cost-effective.[17,19,20] Therefore, combustion method was employed to synthesize Li/MgO catalyst with different Li loadings by a process developed in our lab.[21] The structural properties of the catalyst were studied by different analytical techniques like BET surface area, TPD with 10% CO_2, SEM and XRD.

The main objective of the current work is to develop a solid base catalyst for synthesis of phenyl ethyl methyl ether selectively from 2-phenyl ethanol and to optimize the reaction parameters like the speed of agitation, catalyst loading, concentration and temperature, etc. and to develop a detailed mechanism and kinetic model for the process.

2. Experimental

2.1 *Chemicals*

All chemicals were purchased from reputed companies and used as received: Lithium nitrate, magnesium nitrate, glycine,
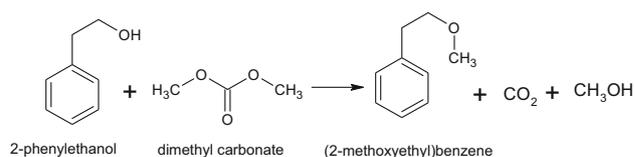
Scheme 1. *o*-Alkylation of 2-PE with dimethyl carbonate.

n-decane from M/s. S.D. Fine Chemicals Pvt. Ltd., Mumbai, India. Dimethyl carbonate was purchased from Alfa Aesar, Mumbai. Gift sample of 2-phenyl ethanol was received from U. K. Aromatics, Boisar, India.

2.2 *Preparation of Li/MgO*

All catalysts were synthesized by combustion method. Initially, 0.1% Li/MgO was synthesized as per the process reported by Yadav and Surve[21] and described in SI section 1. Using the same method pure MgO and 0.3% Li/MgO were also synthesized.

A typical reaction was carried out in an autoclave (Amar Equipments, Mumbai) of 100 mL capacity fitted with four blade stirrer, and a temperature controller. The reaction scheme is represented as Scheme 1. 2-Phenyl ethanol (0.0299 mol) was dissolved in DMC (0.314 mol) with a mole ratio of 2-PE to DMC as 1:10.05 and final volume of the reaction as 31 mL. This was followed by addition of 0.2 g of catalyst to the reaction mixture. The reactor was heated to attain a temperature of 170 °C and speed of agitation maintained at 1000 rpm. Samples were regularly withdrawn starting with zero minute. Samples were analysed by GC using BP-1 (30 cm × 0.03 μm) capillary column.

The product confirmation was done by Perkin Elmer GC-MS (DB-5ht column).

3. Results and Discussion

3.1 *Catalyst characterization*

The catalysts were characterized by various techniques[22,23] and the details are given in the SI Section 2.

3.1a *BET surface area analysis*: The surface area analysis of MgO, Li/MgO with different loadings (0.1% and 0.3%) and reused catalysts were recorded by nitrogen adsorption-desorption technique by BJH and multipoint BET method (Figure 1). It was found that the BET surface area of the MgO was higher than that of alkali-promoted MgO (Table 1). As the loading of alkali on MgO is increased there was a decrease in the BET surface area which could be due to deposition of excess Li_2O in a few junctions of pore network thus blocking the pores. The catalyst had mesoporous nature as it showed Type IV adsorption desorption isotherm with
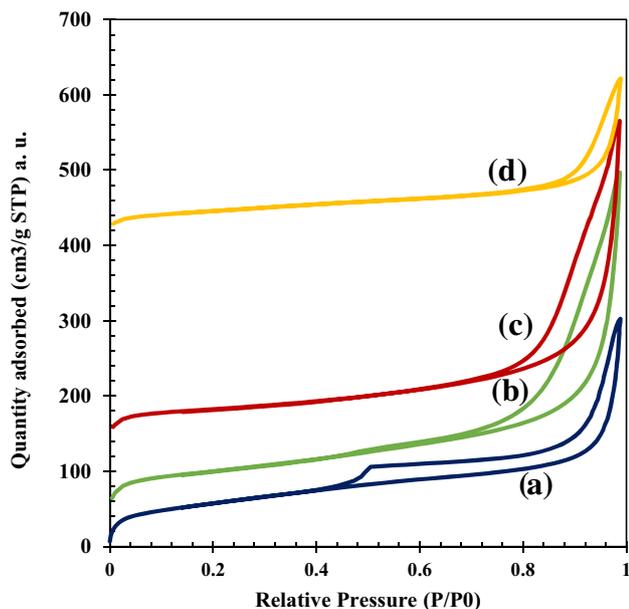
Figure 1. BET surface area analysis (a) MgO, (b) 0.1% Li/MgO, (c) reused 0.1% Li/MgO and (d) 0.3% Li/MgO.

Figure 2. TPD Analysis with 10% CO_2 (a) MgO, (b) 0.1% Li/MgO, (c) 0.3% Li/MgO and (d) reused 0.1% Li/MgO.

Table 1. Textural properties of catalysts.

Catalyst	BET surface area (m²/g)	Pore size (nm)	Pore volume (cm³/g)
MgO	204.20	13.25	0.62
0.1% Li/MgO	185.24	12.96	0.58
0.3% Li/MgO	117.21	11.79	0.49
Reused 0.1% Li/MgO	154.50	12.52	0.51

Table 2. The concentration of different basic sites

Catalyst	Weak	Basicity (mmol/g) Medium	Strong	Total
MgO	0.13	0.40	0.08	0.61
0.1% Li/MgO	0.12	0.53	0.11	0.76
0.3% Li/MgO	0.12	0.46	0.07	0.65
Reused 0.1% Li/MgO	0.11	0.51	0.09	0.71

H3 type hysteresis. There was no substantial difference in the BET surface area of the reused catalyst compared well to the virgin catalyst. This validates that the catalyst retains the mesoporosity even after reuse.

3.1b *CO_2 – temperature programmed desorption (TPD)*: The CO_2 TPD analysis is given for MgO, Li/MgO with different loadings (0.1% and 0.3%) and reused catalyst 0.1% Li/MgO (Figure 2). The basicity trend is: MgO (least) < 0.3% Li/MgO < 0.1% Li/MgO (highest) based on the strength (concentration of weak, medium and strong basic sites in mmol/g) and total basicity of catalyst (Table 2). This confirms that there is an increase in total basicity of MgO with the incorporation of Li in its lattice structure. With loading of Li of 0.3% the pore size and pore volume of MgO is decreased resulting in a decrease in total surface basicity due to Li_2O trapped inside the pores of MgO as was mentioned above. Depending upon temperature, there are three regions to signify the strength of basicity, namely,
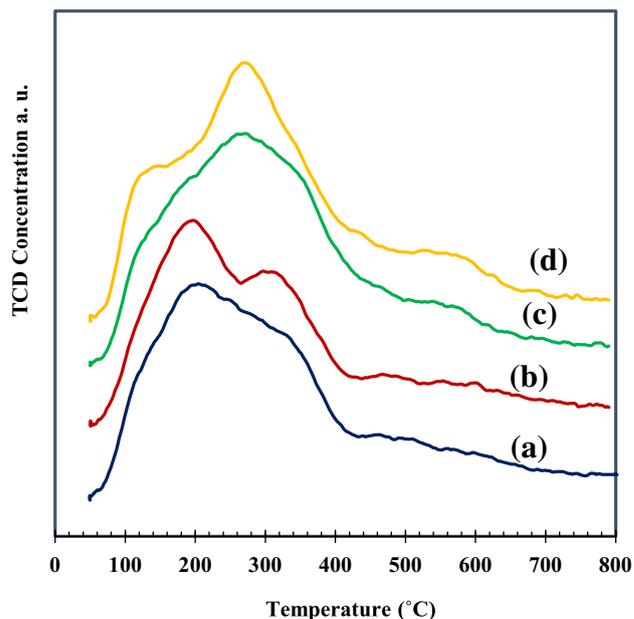
$100 - 150\,°C$ as weak basic, $150 - 450\,°C$ as moderate basic and finally $450 - 750\,°C$ as strong basic sites. MgO, Li/MgO with different loadings (0.1% and 0.3%) and reused catalyst 0.1% Li/MgO showed peaks in the region of $100 - 150\,°C$, $150 - 450\,°C$ and $450 - 750\,°C$ signifying weak, moderate and a few strong basic sites are present.

3.2 *Scanning electron microscopy (SEM)*

SEM images for fresh and reused catalyst were obtained (Figure 3). Irregular morphology was observed for all synthesized catalysts which is a characteristic of the combustion synthesized catalyst due to the evolution of gases (CO_2 and N_2) during the combustion process. Despite irregular morphology, the catalyst showed uniform particle size in the range of 20–100 nm. No significant change in the morphology and particle size for reused catalyst was observed (Figure 3b). This confirms the retention of catalytic activity of catalyst even after the reuse.
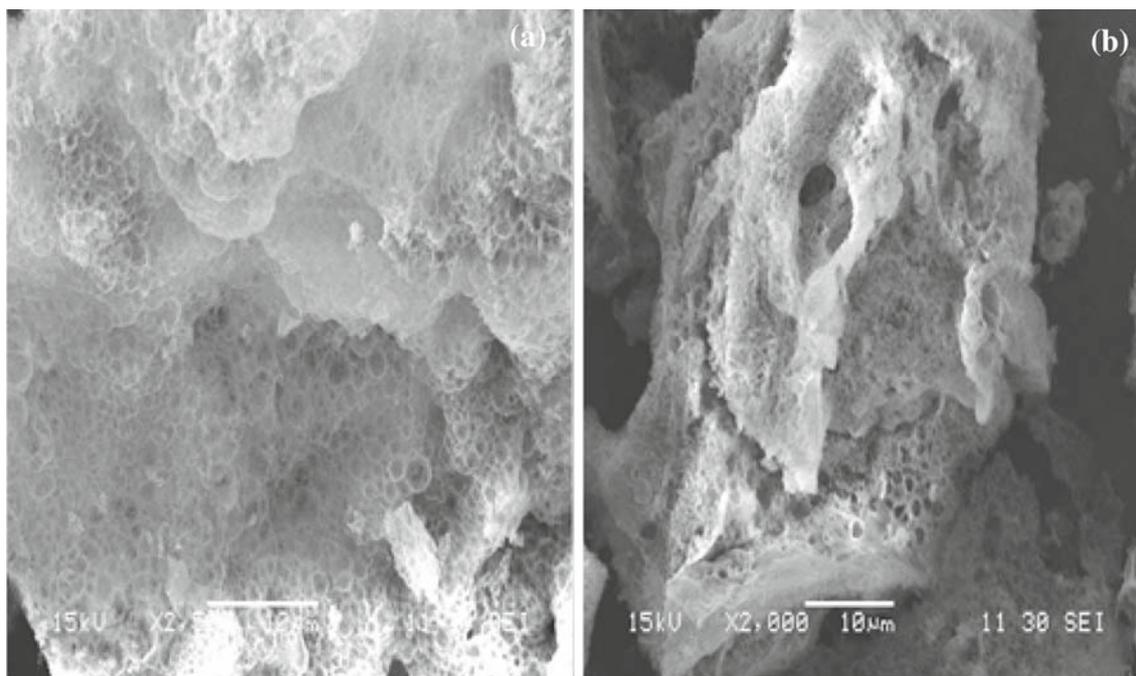
Figure 3. SEM analysis (a) 0.1 % Li/MgO, (b) reused 0.1% Li/MgO.

3.2a *X-ray diffraction (XRD)*: XRD patterns were recorded for pure MgO, Li/MgO with different loadings (0.1% and 0.3%) to understand the effect of Li loading on the crystal structure of MgO (Figure 4). The diffraction peaks are observed for all samples at 2θ values of 37.1, 42.8 and 62.4° which are characteristics peaks representing a single phase of MgO periclase. In the case of 0.1% and 0.3% Li/MgO we observed a peak at 2θ of 33° which confirmed the presence of Li in the form of Li_2O (JCPD 12-0254). Pure Li_2CO_3 shows peaks at 2θ of 21, 23.8, 29.7, 30.5, 31.6, 34, 36, 37, 39.6 and 48.5°. These peaks were absent in MgO and Li/MgO with different loadings (0.1% and 0.3%) confirms that the Li is present in the Li_2O form and not in the carbonate form. The shift in the peak at 2θ of 37.1° for 0.3% Li/MgO may be due to deposition of Li as Li_2CO_3 as the characteristic peaks for Li_2CO_3 are $2\theta = 21$, 23.8, 29.7, 30.5, 31.6, 34, 36, 37, 39.6 and 48.5° from which it is inferred that Li might be deposited as Li_2CO_3 after 0.1 % loading of Li.

Figure 4. XRD Analysis (a) MgO, (b) 0.1% Li/MgO and (c) 0.3% Li/MgO.

3.3 *Optimization of reaction parameters*

3.3a *Catalyst screening*: A variety of base catalysts were screened for the synthesis of PEME from 2-PE and DMC like pure MgO, 0.1% Li/MgO, 0.3% Li/MgO and 0.1% K/MgO (Figure 5). Among all the screened catalysts 0.1% Li/MgO was found to be a better catalyst in terms of conversion of 2-PE and selectivity of PEME.
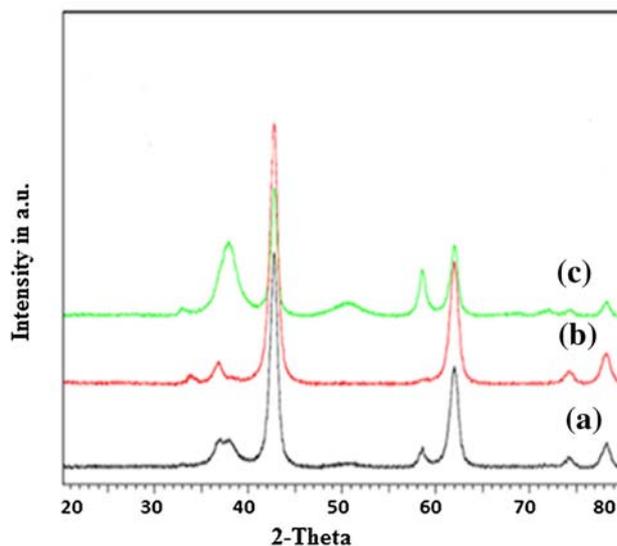
The surface basicity of MgO is increased with the incorporation of Li on MgO. Thus, using unsupported MgO as a catalyst we got only 65% conversion. Even though the basicity increases in the order of MgO (least) < 0.3% Li/MgO < 0.1% Li/MgO < 0.1% K/MgO (highest), the acidic sites required for successive methylation are present only in 0.1% Li/MgO.[21]

Thus, better conversion of 2-PE, as well as better selectivity of PEME, was achieved with 0.1% Li/MgO
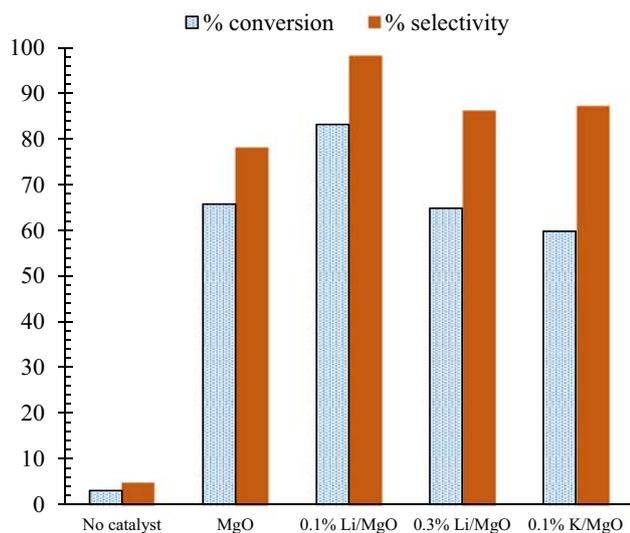
Figure 5. Efficacy of different catalyst on conversion of 2-PE and selectivity of PEME, Catalyst: 0.1% Li/MgO, catalyst concentration: 1.13×10^{-2} g/cm^3, temperature 170 °C, 2-PE: DMC = 1 : 10.5, speed of agitation: 800 rpm, time 3 h.

as a catalyst. And hence it was used as the best catalyst in the further experiments.

3.3b *Speed of agitation*: The effect of external mass transfer resistance was studied by varying the speed of agitation in the range of 800–12000 rpm (Figure 6). It was observed that rate of reaction increased with speed agitation from 800 to 1000 rpm indicating the presence of external mass transfer resistance of reactants to the surface of the catalyst. But beyond 1000 rpm the rate of reaction did not change significantly which implied that the reaction is free from mass transfer resistance and thus further experiments were carried out at 1000 rpm. The details for the absence of external mass transfer resistance are provided in earlier work[24,25] and explained in SI section 5.

3.3c *Catalyst loading*: Once the reaction is free from external mass transfer resistance, the reaction rate is dependent on catalyst loading. Thus, to study the effect of catalyst loading on reaction rate the catalyst concentration was varied from 6.6×10^{-3} to 2×10^{-2} g/cm^3 (Figure 7). It was observed that there was a liner increase in the reaction rate with a catalyst loading. But beyond, 1.3×10^{-2} g/cm^3 of catalyst loading the total active sites available were more than those required for adsorption and therefore no change was observed in reaction rate. For further studies, the catalyst concentration was optimised at to 1.3×10^{-2} g/cm^3. The details to prove the absence of intra-particle resistance are explained in some of earlier work[25,26] and given in SI section 6.
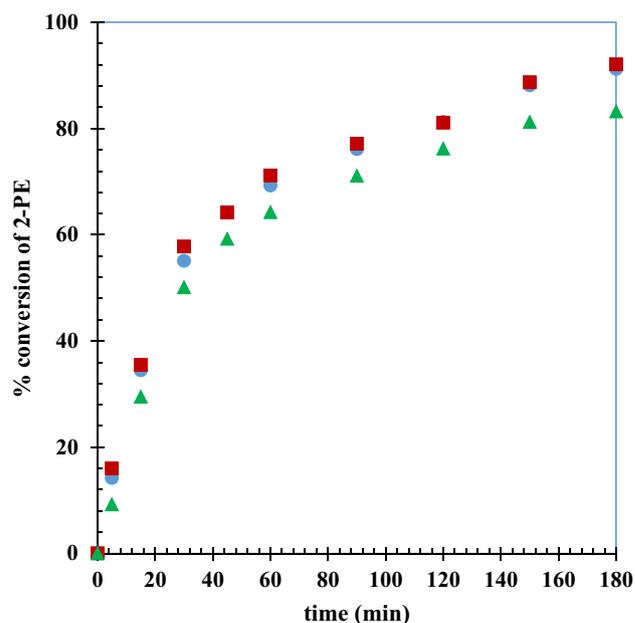

Figure 6. Effect of speed of agitation on conversion of 2-PE, Catalyst: 0.1% Li/MgO, catalyst concentration: 1.13×10^{-2} g/cm^3, temperature 170 °C, 2-PE: DMC = 1:10.5, (■) 1200 rpm (●) 1000 rpm (▲) 800 rpm.
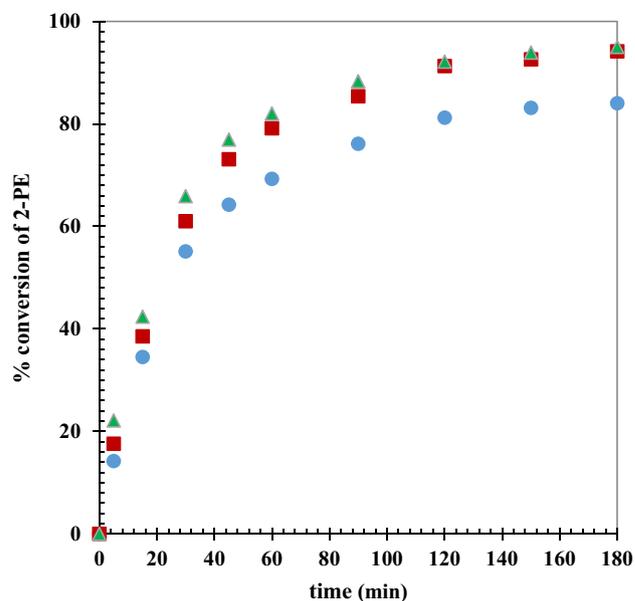

Figure 7. Effect of catalyst loading (g/cm^3) on conversion of 2-PE, Catalyst: 0.1% Li/MgO, temperature 170 °C, 2-PE: DMC = 1:10.5, (●) 6.6×10^{-3} (■) 1.13×10^{-2} (▲) 2.0×10^{-2} g/cm^3.

3.3d *Mole ratio of 2-PE to DMC*: The effect of mole ratio of 2-PE to DMC on the reaction rate was studied at 1:4.9, 1:10.5 and 1:20.06 (Figure 8) by keeping all other reaction conditions constant. A linear increase in initial rate of reaction of 2-PE was observed with increase in mole ratio of 2-PE: DMC. For further experiments 1:
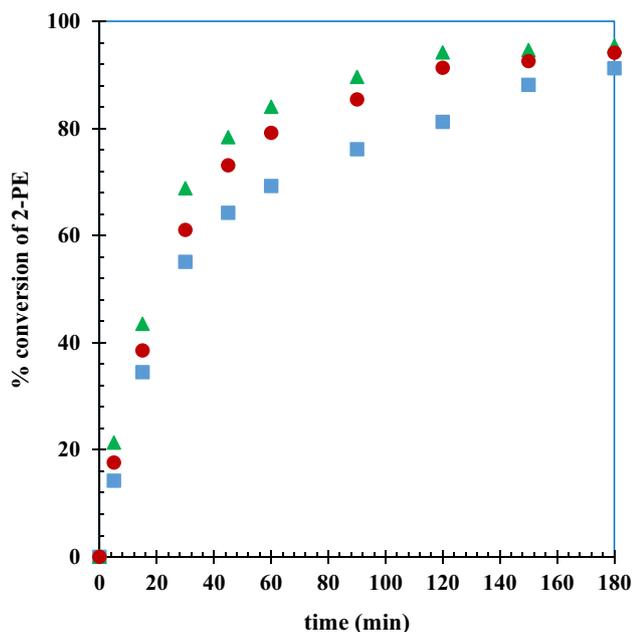
Figure 8. Effect of mole ratio of 2-PE: DMC, Catalyst: 0.1% Li/MgO, catalyst concentration: 1.13×10^{-2} g/cm^3, temperature 170 °C, speed of agitation 1000 rpm, (■) 1:4.9 (●) 1:10.5 (▲) 1:20.06.
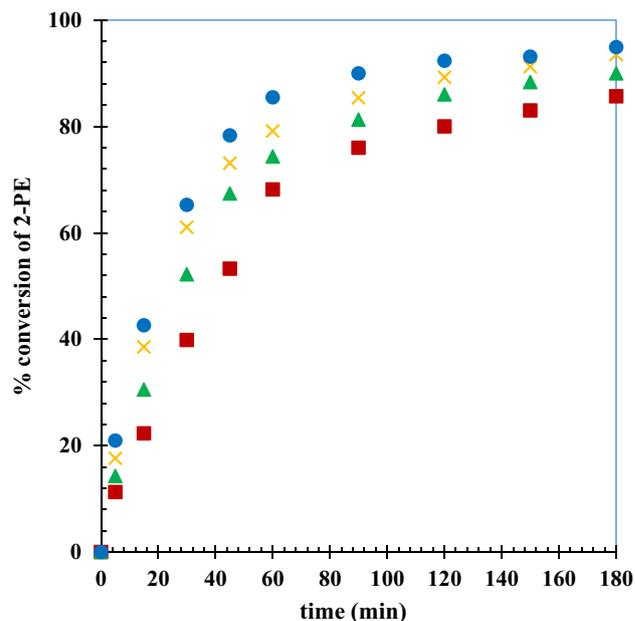

Figure 9. Effect of Temperature on conversion of OPDA, Catalyst: 0.1% Li/MgO catalyst concentration: 0.0133 g/cm^3, speed of agitation 1000 rpm, (■) 150 °C (▲) 160 °C (X) 170 °C; (●) 180° C.

10.5 mole ratio of 2-PE: DMC was taken as optimum mole ratio as good conversion and selectivity for PEME were achieved at this mole ratio.

3.3e *Temperature*: Under the same reaction conditions, the reaction temperature was varied from 160 − 190 °C to study its effect on reaction rate (Figure 9). The reaction rate increased substantially with temperature which suggested that the reaction was kinetically controlled.

3.3f *Reusability and stability of Catalyst*: After the completion of the reaction the catalyst was filtered from the reaction. It was refluxed with methanol for 1 h to remove any adsorbed materials. The catalyst was filtered again and dried at 120 °C and calcined at 500 °C for 4 h. This catalyst was used in the further reusability experiments. The loss in the weight of the reused catalyst was recovered by adding fresh catalyst (approx. 5% of total weight) and experiments were done under the same reaction conditions. There was no significant decrease in the conversion of 2-PE and selectivity of product for three catalytic cycles (Figure 10). This confirmed that the catalyst retained its activity over three cycles.

Leaching test of catalyst in the liquid phase was done by stopping the reaction after 30 min and immediately quenching the reaction mixture to arrest the reaction
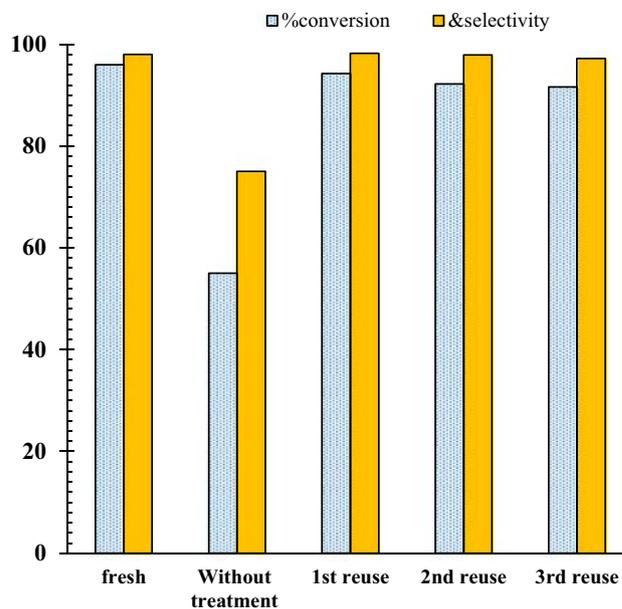

Figure 10. Reusability of catalyst.

progress followed by centrifuging the reaction mixture. The separated clear supernatant reaction mixture was then charged into the reactor and continued reaction under the same condition without any traces of catalyst. There was practically no conversion during next two hours which suggests that catalyst is stable and there is no leaching of alkali metal into the reaction mass.
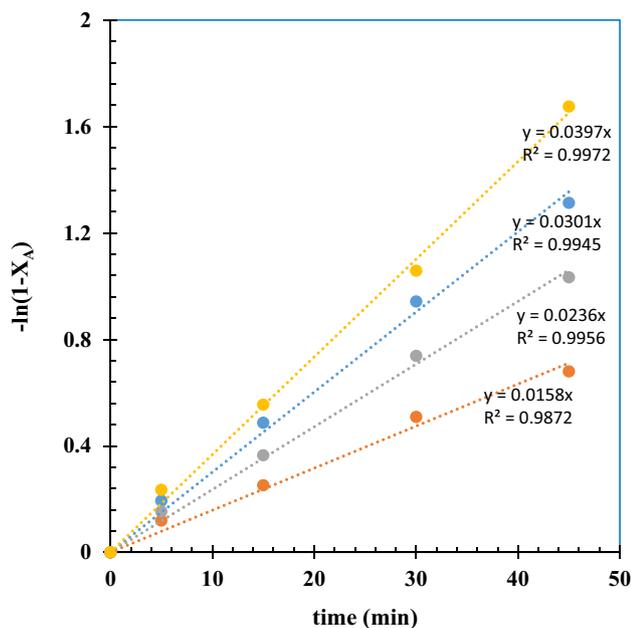
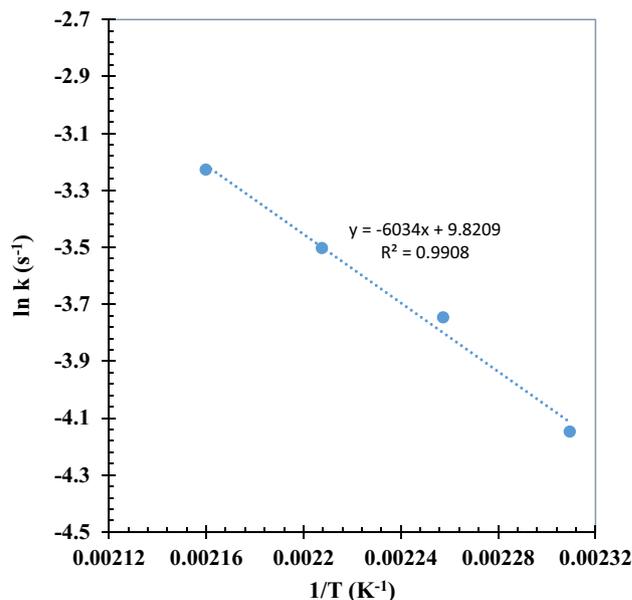**Figure 11.** Plot of –ln $(1 - X_A)$ vs time for different temperatures.

Figure 12. Arrhenius plot.

3.4 *Kinetic model and mechanism*

A plausible mechanism for the reaction is given in Scheme 2. The kinetic model for this reaction can be explained by LHHW model[24,26] where 2-PE (A) is adsorbed on the basic sites of the catalyst while DMC (B) was adsorbed on the acidic sites to form an intermediate. This intermediate rearranges to give PEME with carbon dioxide and methanol as co-products. During analysis, it was observed that all the reactants were weakly adsorbed on the catalytic sites. Thus, the power law was applied to get the rate of reaction as,

$$-\frac{dC_A}{dt} = k_1 K_A K_B w C_A C_B \qquad (1)$$

$$\frac{-dC_A}{d_t} = k_2 C_A C_B \qquad (2)$$

Where, $k_2 = k_1 K_A K_B w$

Let $C_{B_0}/C_{A_0} = M$ be the molar ratio of 2-PE to DMC at time t = 0. Equation (2) can be written in terms of fractional conversion as:
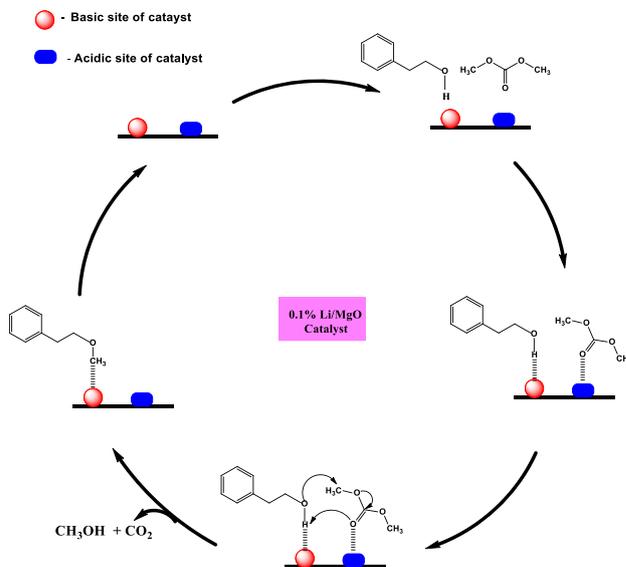
$$\frac{dX_A}{d_t} = k_2 C_{A_0}(1 - X_A)(M - X_A) \qquad (3)$$

Above equation on integration gives:

$$\ln\frac{(M - X_A)}{M(1 - X_A)} = k_2 C_{A_0}(M - 1)t \qquad (4)$$

When M >> 1, equation (4) can be written for pseudo-first order as:

$$-\ln(1 - X_A) = kt$$

Scheme 2. Mechanism of *o*-methylation of 2-PE.

Thus, plots of -ln $(1 - X_A)$ vs time (Figure 11) were drawn for different temperatures to prove a linear relation, where X_A is the fractional conversion of 2-PE. The reaction followed the pseudo first order kinetics. The model was validated by plotting it for different temperature and the slopes of these lines are used to plot the Arrhenius plot (Figure 12). The apparent activation energy was calculated as 11.93 kcal/mol, signifying that the reaction is kinetically controlled.

3.5 *Mechanism*

0.1% Li/MgO provides both acidic and basic sites. There is adsorption of 2-PE on basic sites provided by catalyst through hydrogen atom while dimethyl carbonate is adsorbed on acidic sites of the catalyst. The carboxymethylation takes place at a lower temperature (T ≤ 120 °C) while methylation is favoured at a higher temperature (T >> 120 °C).[8] Thus, the reaction proceeds with an attack of a lone pair of electrons on methyl group, to give an unstable intermediate. This intermediate rearranges to PEME as a product with methanol and carbon dioxide as co-products. PEME is desorbed from catalyst surface into the solution and leaves the catalytic sites vacant for the next adsorption.

4. Conclusion

The green catalytic route to synthesise phenyl ethyl methyl ether from 2-PE and DMC was invented using 0.1% Li/MgO as a catalyst which holds wide applications as a perfumery compound. The prepared catalyst as well as reused catalyst, were well-characterised by different analytical techniques to understand its surface properties like surface area, total basicity, pore size, pore volume, etc. A detailed kinetic model was developed for etherification of 2-PE by studying different reaction parameters. At optimum conditions i.e., 1000 rpm, 1.33×10^{-2} g/cm^3 catalyst loading, 1:10.5 mole ration (2-PE: DMC), 180 °C, 95% conversion of 2-phenyl ethanol and 98% selectivity of PEME was achieved. The reaction follows the LHHW model with weak adsorption of all species leading to second order kinetics and apparent activation energy for the reaction was calculated as 11.93 kcal/mol.

Supplementary Information (SI)

The detailed method for synthesis of Li/MgO with different loadings and MgO is given in the supplementary. Catalysts were characterized by various techniques and details are provided in the supplementary information. The details of the absence of mass transfer resistance and intra-particle resistance are also given in the supplementary.

Acknowledgements

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