

Synthesis of jasminaldehyde using magnesium organo silicate as a solid base catalyst

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Abstract

Synthetic talc (magnesium organo silicates; MOS) was synthesized by sol–gel method under non-hydrothermal conditions and modified by introducing amine/diamine functionalities in the interlayer space. The applicability of amine/diamine functionalized MOS was studied as catalysts for the synthesis of jasminaldehyde or α -pentylcinnamaldehyde by condensation of 1-heptanal with benzaldehyde. The effect of amine/diamine functionality, amount of catalyst, benzaldehyde to 1-heptanal molar ratio and temperature on the selectivity of jasminaldehyde was studied in detail. The highest conversion of 1-heptanal (99%) with 82% selectivity of jasminaldehyde was achieved using MOS3 as a catalyst. The rate constant for condensation of 1-heptanal with benzaldehyde was calculated under optimized reaction conditions. This is the first report on application of MOS as a solid base catalyst for the condensation of 1-heptanal with benzaldehyde.

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1. Introduction

Magnesium organo silicates (MOS) possess lamellar structure similar to that of natural talc (NT, trioctahedral phyllosilicates) with general composition $\text{Si}_4\text{Mg}_3\text{O}_{10}(\text{OH})_2$, whereas, elementary sheet of MOS composed of a layer of magnesium-oxygen/hydroxyl octahedral, is sandwiched between two layers of silicon-oxygen tetrahedra, in which the components are linked by ionic and covalent bonds [1,2]. For MOS, similar inorganic matrix is formed with the organic groups covalently bonded within the interlayer space through the Si–C bonds derived from the trialkoxyorganosilane and the organic functionalities intercalated into the interlayer galleries [3]. Owing to the presence of organic functionalities, these hybrids materials could be used as sorbents, polymer fillers, chemical sensors and catalysts [4–6]. The work of Mann and Ozin [1] on magnesium silicates hybrids provided an impetus to research in this area and a number of hybrid materials using synthetic routes have been reported since then [7–10].

From economic and environmental point of view, new trend towards the application of synthetic inorganic–organic hybrids is undoubtedly increasing as heterogeneous catalysts for organic transformations [11–15]. The jasminaldehyde or α -pentylcinnamaldehyde is an important perfumery chemical which is synthesized by the condensation of 1-heptanal and benzaldehyde in the presence of sodium or potassium hydroxide as a homogeneous catalyst used in more than stoichiometric amounts [16]. The main drawbacks of homogeneous process for synthesis of jasminaldehyde include lack of reusability of the catalyst, production of liquid waste, use of hazardous liquid base like KOH, NaOH and post reaction work-up of spent liquid bases. To overcome such drawbacks, solid base catalysts such as hydrotalcites, MgO, alkali exchanged zeolites and alkali impregnated on neutral supports have been studied for numerous reactions such as self condensation of acetone [17], Knoevenagel condensation [18], synthesis of flavanones [19], condensation of citral and acetone [20]. Recently, Corma and co-workers reported synthesis of jasminaldehyde using large pore HY and Beta zeolites, mesoporous aluminosilicates (Al MCM-41) and amorphous aluminophosphate (ALPO) as solid acid catalysts [21–23]. However, this process involves two consecutive reactions; one is the acetalization of 1-heptanal with

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alcohol and second reaction is the reaction between the formed acetal and benzaldehyde. Abenhaem et al. reported 82% yield of jasminaldehyde at room temperature using solid–liquid phase transfer catalyst without solvent [24]. In the present study, we are reporting for the first time applicability of MOS as a solid base catalyst for the synthesis of jasminaldehyde by condensation of 1-heptanal with benzaldehyde in one step without any acetalization.

2. Experimental

2.1. Materials

Tetraethoxyorthosilicate (TEOS), 3-aminopropyltrimethoxysilane (APTMS), *N*-[3-(trimethoxysilyl) propyl] ethylenediamine (MSPEA, 80% solution), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) were obtained from Sigma–Aldrich and used as such. 1-Heptanal and benzaldehyde were purchased from Sigma–Aldrich and used as received. Methanol and sodium hydroxide were purchased from s.d. Fine Chemicals, India. Natural talc was gifted from Associated Soapstone Distribution Co. Pvt. Ltd., Rajasthan, India.

2.2. Catalyst synthesis

$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (8.36 g) was dissolved in three flasks having 200 ml of methanol in each, and the solutions were stirred at 25 °C. This was followed by the drop wise addition of solutions of 11.1 g TEOS (for synthesis of MOS1), 9.8 g APTMS (for synthesis of MOS2) and 15.3 g MSPEA (for synthesis of MOS3) in 50 ml of methanol into each flask. This gave mixtures with white suspensions in each flask. To each of the mixtures, 0.5 M NaOH solution was added slowly until pH reached to 10.5 and the solutions were vigorously stirred for 24 h at 25 °C. These suspensions were aged for 1 week at 25 °C. The gels formed were centrifuged, successively washed with double distilled deionized water until a neutral solution was detected, and dried at 65 °C. A white solid formed in each case was further ground to produce a powdered material, denoted as MOS1, MOS2 and MOS3. The Si/Mg molar ratio was maintained at 1.33 in the preparation of MOS, which is similar to molar ratio observed in NT.

2.3. Characterization of the catalysts

Powder X-ray diffraction (P-XRD) analysis of MOS was carried out with powder diffractometer (Philips X'Pert MPD system) using PW3123/00 curved Cu-filtered Cu K α ($\lambda = 1.54056 \text{ \AA}$) radiation with slow scan of 0.3° s^{-1} . Fourier transform infrared spectra (FT-IR) were measured with Perkin-Elmer, GX-FTIR using KBr pellet. CHN analysis of MOS was carried out with Perkin-Elmer CHNS/O analyzer (Series II, 2400). Thermogravimetric analysis (TGA) was done using Mettler Toledo TGA/SDTA 851e equipment in flowing nitrogen (flow rate, 50 ml/min), at a heating rate of 10°C/min . Surface area of MOS was determined from the N_2 adsorption data measured at 77.4 K using volumetric adsorption setup unit (ASAP

2010) from Micromeritics, USA. The samples were activated at 110 °C for 2 h under vacuum ($5 \times 10^{-2} \text{ mmHg}$) prior to N_2 adsorption measurements. The specific surface areas of the samples were calculated from the N_2 adsorption isotherms using the Brunauer, Emmett, Teller (BET) method.

2.4. Synthesis of jasminaldehyde

1-Heptanal and benzaldehyde (molar ratio = 1:5) were taken with 0.01 g of 1-decane as an internal standard in an oven dried double necked round bottom flask. One neck of the flask was fitted with 2.25 ft long refluxing condenser having spiral tube inside and another neck of the flask was blocked with silicon rubber septum. The top of the refluxing condenser was blocked by a standard cork. The water at 15 °C was circulated in refluxing condenser throughout the course of reaction from water chiller at flow rate of 6 l/min. The entire experimental setup was kept in an oil bath equipped with temperature and agitation speed controlling units. The calculated amount of MOS was added as a catalyst to the round bottomed flask at desired reaction temperature. The reaction was carried out at 125 °C for 8 h. The reaction mixture was cooled to room temperature on completion of reaction and was subsequently filtered. The silicon grease was used in all joints to prevent the vapor loss of reaction mixture and progress of reaction was monitored in terms of consumption of 1-heptanal. However, the weight of initial reaction mixture and product mixture after the reaction was compared to ensure the absence of vapor loss of reaction mixture. The analysis of product mixture was carried out by gas chromatography (GC) (Shimadzu 17A, Japan) and GC–MS (mass spectrometer, Shimadzu-QP2010, Japan). The GC has a 5% diphenyl and 95% dimethyl siloxane universal capillary column (60 m length and 0.25 mm diameter) and a flame ionization detector (FID). The initial column temperature was increased from 40 to 200 °C at the rate of 10°C/min . Nitrogen gas at a flow rate of 100 ml/min was used as the carrier gas. The temperatures of the injection port and FID were kept constant at 200 °C during product analysis. The retention times of different compounds were determined by injecting pure compounds under identical gas chromatography conditions. The conversion and selectivity were calculated by the following formula

$$\text{Conversion (\%)} = \frac{\text{moles of 1-heptanal reacted}}{\text{moles of 1-heptanal fed}} \times 100$$

$$\begin{aligned} \text{Selectivity of jasminaldehyde (\%)} \\ = \frac{\text{moles of jasminaldehyde}}{\text{moles of (jasminaldehyde + 2-pentyl-non-2-enal)}} \times 100 \end{aligned}$$

3. Results and discussion

3.1. Characterization of the catalysts

The structural and textural properties of MOS are given in Table 1. The layered structure of MOS was confirmed by P-XRD patterns as shown in Fig. 1. The significant disorder in reflec-

Table 1
Structural and textural properties of MOS catalysts

Catalyst	MOS1	MOS2	MOS3
d_{001} -spacing (nm)	1.1	1.3	1.4
BET surface area (m^2/g)	189	3	2
Pore volume (cm^3/g)	0.1	0.006	0.002
Amine group content (mmol/g)	–	2.5	3.8
SiO_2 (%w/w)	54.3	44.9	35.7
MgO (%w/w)	17.9	14.8	11.8

tions of MOS as compared to NT was observed due to presence of organic functionalities in the interlayer space as well as non-hydrothermal synthetic conditions [2]. The presence of organic species present in the interlayer space of MOS was confirmed by an increase in the basal spacing of (001) plane. The basal spacing of (001) reflection was observed to be 1.1, 1.3 and 1.4 nm for MOS1, MOS2 and MOS3, respectively (Table 1). The reflections of (060) and (330) planes which are the characteristic of 2:1 trioctahedral phyllosilicate structure remain unchanged in MOS1, MOS2 and MOS3.

The BET surface area for MOS1, MOS2 and MOS3 was calculated as 189, 3 and $2 \text{ m}^2/\text{g}$, respectively (Table 1). The pore volume of MOS1, MOS2 and MOS3 was observed to 0.10, 0.006 and $0.002 \text{ cm}^3/\text{g}$, respectively. The decrease in surface area and

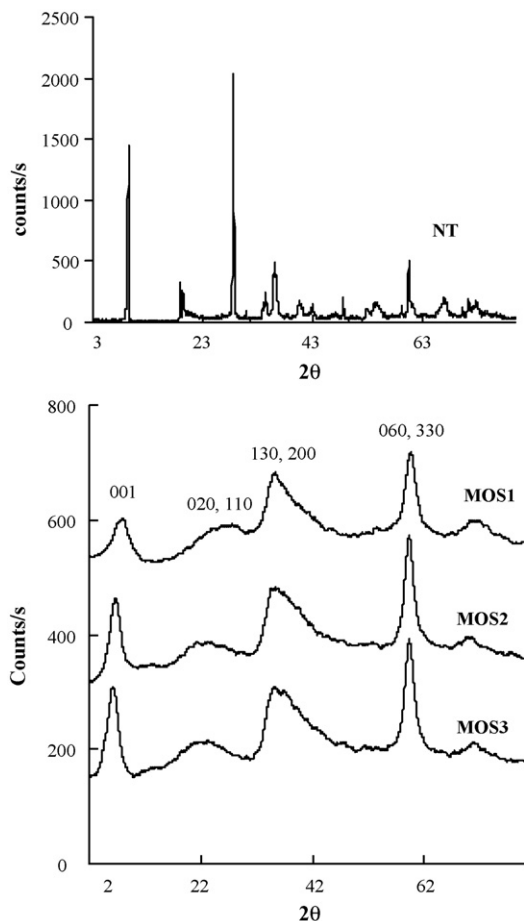


Fig. 1. P-XRD patterns of NT, MOS1, MOS2 and MOS3.

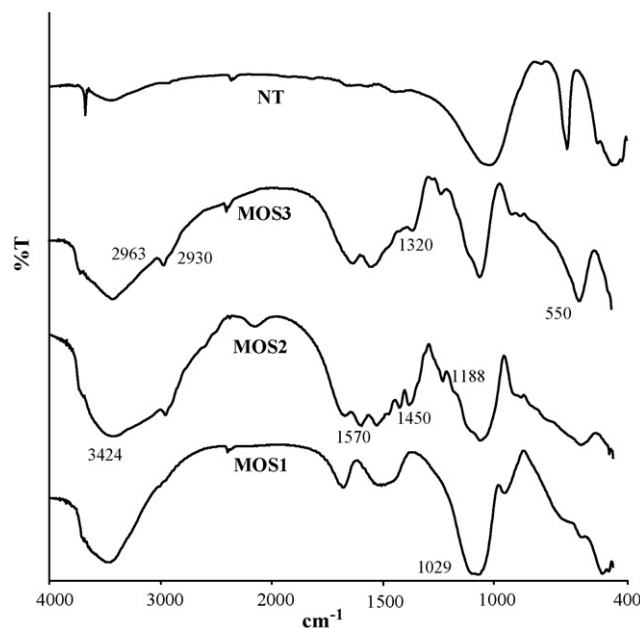


Fig. 2. FT-IR spectra of NT, MOS3, MOS2 and MOS1.

pore volume of MOS2 and MOS3 as compared to MOS1 is attributed to the intercalation of amine/diamine molecules in the interlayer space of MOS.

The presence of organic groups covalently attached to the inorganic matrix was confirmed by the FT-IR spectra of synthetic talc (Fig. 2). The bands at 1029 and 550 cm^{-1} in the FT-IR spectra of NT and MOS1 were attributed to Si–O and Mg–O stretching vibrations respectively, which remained present in inorganic structure of amine/diamine functionalized MOS2 and MOS3. The IR vibrations of the inorganic framework remain unchanged after intercalation of amine/diamine molecules. For MOS2 and MOS3, the methyl and methylene units were represented by the appearance of bands at 2963, 2930 and 1450 cm^{-1} . Another prominent band was also observed at 1188 cm^{-1} due to Si–C stretching. The N–H and N–C vibration bands were observed at 1570 and 1320 cm^{-1} , respectively. The IR band at about 3424 cm^{-1} is attributed to hydroxyl groups present in MOS1, MOS2 and MOS3 samples.

The %C, %H and %N were calculated from CHN analysis and found as: for MOS2 11.4 (%C), 4.6 (%H) and 3.6 (%N); for MOS3 was 14.8, 5.6 and 5.3. Theoretically, for complete hydrolysis of methoxy groups, C/N ratio for MOS2 and MOS3 needs to be 3.0 and 2.5, respectively. The C/N ratio of MOS2 and MOS3 was calculated as 3.1 and 2.8, respectively, confirming the complete hydrolysis of all methoxy groups in MOS2 and MOS3 samples [3,4,6].

The first weight loss up to 250°C in TGA of MOS1, MOS2 and MOS3 samples was observed due to elimination of adsorbed water, strongly bound water on the surface and rearrangement of grafted silanol groups (Fig. 3). The weight loss in the temperature range of $300\text{--}700^\circ\text{C}$ is attributed to decomposition of amines present in the interlayer of MOS2 and MOS3 samples. For MOS3, two step weight losses were observed in $350\text{--}600^\circ\text{C}$ temperature range which is due to presence of ethylenediamine

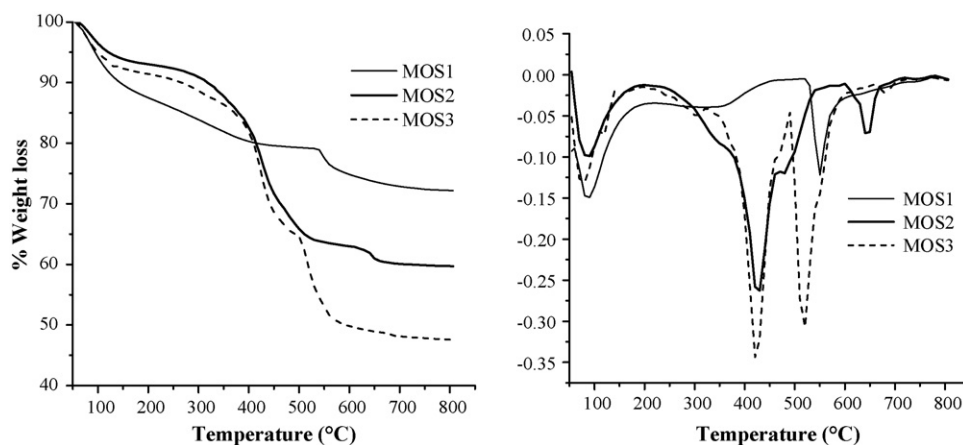


Fig. 3. TGA patterns of MOS1, MOS2 and MOS3.

molecules in the sample. The structural hydroxyl groups present in MOS samples, i.e., Si–OH and Mg–OH escape in the temperature range of 550–700 °C. From TGA study, it could be concluded that the MOS samples are thermally stable up to 200 °C in an inert atmosphere.

3.2. Catalytic activity

The catalytic activity of NT, MOS1, MOS2 and MOS3 samples was investigated for condensation of 1-heptanal with benzaldehyde. Natural talc sample showed 58% conversion of 1-heptanal with 56% selectivity of jasminaldehyde (Table 2). In the present study, only jasminaldehyde and 2-pentyl-non-2-enal were observed as the reaction products. GC–MS fragmentation data of jasminaldehyde and 2-pentyl-non-2-enal are given in Fig. 4. The mass data showed standard fragmentation pattern corresponding to jasminaldehyde (m/z : 202, 145, 129, 117, 91) and 2-pentyl-non-2-enal (m/z : 210, 153, 125, 97, 81, 55, 41, 29). The conversion of 1-heptanal was observed to increase on introducing the amine functionalization in the synthetic talc. The conversion of 1-heptanal was found to be 55% with 49% selectivity of jasminaldehyde using MOS1 as a catalyst synthesized

Table 2

Effect of amine functionalization on selectivity of jasminaldehyde

Run	Catalyst	Conversion (%)	Selectivity (%)	
			Jasminaldehyde	2-Pentyl-non-2-enal
1	NT	58	56	44
2	MOS1	55	49	51
3	MOS2	99	80	20
4	MOS3	99	82	18

Reaction conditions: Benzaldehyde = 39.6 mmol, heptanal = 7.9 mmol, catalyst = 75 mg, temperature = 125 °C, reaction time = 8 h.

without amine functionalization and conversion increased up to 99% with 80% selectivity of jasminaldehyde on functionalization with the amine (MOS1). The selectivity of jasminaldehyde further increased up to 82% using diamine functionalized MOS as a catalyst (MOS3), without increase in conversion which remained at 99%. The intercalation of amine/diamine molecules into the interlayer space of MOS leads to increase in basicity of the catalyst which results into an increase in the conversion of 1-heptanal. The increase in basicity of MOS was supported by CO₂ adsorption–desorption data measured at 30 °C. The CO₂ adsorption capacities for MOS1, MOS2 and MOS3 samples

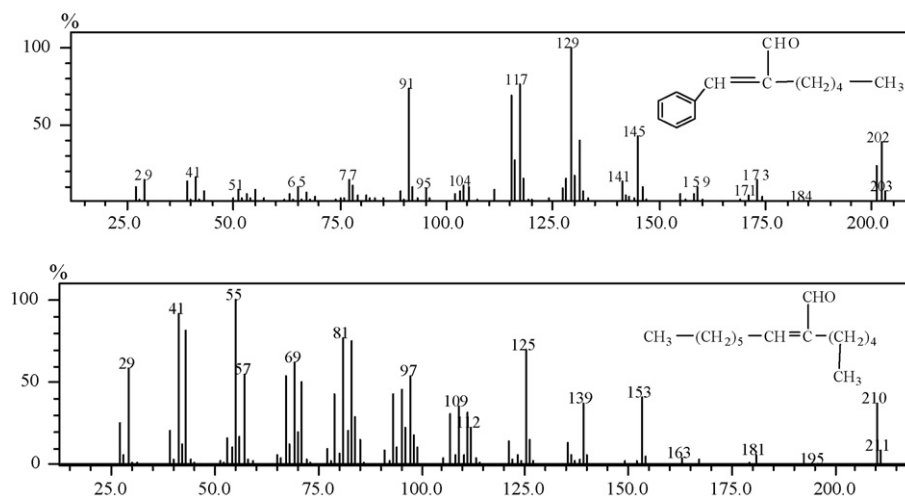


Fig. 4. GC–MS fragmentation patterns of jasminaldehyde and 2-pentyl-non-2-enal.

Table 3
Effect of catalyst amount on selectivity of jasminaldehyde

Run	Catalyst (mg)	Conversion (%)	Selectivity (%)	
			Jasminaldehyde	2-Pentyl-non-2-enal
1	25	77	80	20
2	50	98	79	21
3	75	99	80	20
4	100	100	79	21
5	125	100	77	23
6	150	100	74	26
7	250	100	73	27
8	500	100	69	31

Reaction conditions: Benzaldehyde = 39.6 mmol, heptanal = 7.9 mmol, temperature = 125 °C, reaction time = 8 h.

were calculated as 34.4, 5.1 and 6.0 cm³/g, respectively. CO₂ desorption values (14.9 cm³/g for MOS1, 0.28 cm³/g for MOS2, 0.17 cm³/g for MOS3) indicate that 43% of CO₂ is desorbed from MOS1, while only 5.5 and 2.8% of CO₂ gets desorbed from MOS2 and MOS3 at 30 °C, clearly indicating that chemisorbed CO₂ is higher in MOS2 (94.5%) and MOS3 (97.2%) as compared to MOS1 (57%). As CO₂ chemisorption occurs on basic sites of the catalyst, CO₂ desorption data clearly show that the basicity of catalysts increases on introducing amines functionalities in the synthetic talc. From CO₂ desorption data, basicity was observed in the order of MOS1 < MOS2 < MOS3. Higher conversion of 1-heptanal in case of natural talc as compared to pristine synthetic talc as a catalyst is attributed to the presence of basic oxides and hydroxyl groups in natural talc. The effect of reaction parameters such as amount of catalyst, benzaldehyde to 1-heptanal molar ratio and reaction temperature on selectivity of jasminaldehyde was studied in detail using MOS2 as a catalyst.

3.3. Effect of catalyst amount

The effect of catalyst amount on conversion and selectivity of jasminaldehyde was studied by varying the amount of catalyst from 25 to 500 mg at constant concentration of 1-heptanal and benzaldehyde (Table 3). The conversion of 1-heptanal was found to be 77% with 80% selectivity of jasminaldehyde at 25 mg catalyst. On increasing the amount of catalyst up to 75 mg, 98% conversion of 1-heptanal with 80% selectivity of jasminaldehyde was observed. On further increase in the amount of catalyst

to 500 mg, the conversion did not change significantly. However, the selectivity of jasminaldehyde was observed to decrease from 80 to 74% on increasing the amount of catalyst from 75 to 150 mg under identical reaction conditions. The selectivity of jasminaldehyde was observed to decrease to 69% on increasing the amount of catalyst to 500 mg. The decrease in the selectivity of jasminaldehyde at higher catalyst amount is due to the self condensation of 1-heptanal to 2-pentyl-non-2-enal under studied experimental conditions. The self condensation of 1-heptanal is catalyzed by the active basic sites available on the surface of catalyst. On increasing the amount of catalyst, the number of the active basic sites increase significantly. The rate of self condensation of 1-heptanal was observed to be higher than the condensation of 1-heptanal with benzaldehyde at higher amount of catalyst. Further optimization studies were carried out by taking 75 mg catalyst as higher selectivity of jasminaldehyde and conversion of 1-heptanal was obtained with this amount of catalyst.

3.4. Effect of benzaldehyde to 1-heptanal molar ratio

Benzaldehyde to 1-heptanal molar ratio plays a significant role for the selectivity of jasminaldehyde. The conversion of 1-heptanal was observed to remain constant on varying benzaldehyde to 1-heptanal molar ratio from 1 to 10 (Table 4). At lower ratio, selectivity of jasminaldehyde was observed to decrease and increased on increasing the benzaldehyde to 1-heptanal molar ratio. For example, 54% selectivity of jasminaldehyde was found at benzaldehyde to 1-heptanal molar ratio of 1 which increased to 80% at molar ratio of 5. However, on further increase in this ratio to 10, no significant change in the selectivity of jasminaldehyde was observed. The lower selectivity of the jasminaldehyde at lower benzaldehyde to 1-heptanal molar ratio is due to the self condensation of 1-heptanal. The selectivity of 2-pentyl-non-2-enal, which is a self condensation product of 1-heptanal, was observed to decrease on increasing the benzaldehyde to 1-heptanal molar ratio. This indicates that the self condensation of 1-heptanal is faster than the condensation of 1-heptanal with benzaldehyde at higher concentration of 1-heptanal (lower benzaldehyde to 1-heptanal molar ratio). As the concentration of 1-heptanal was decreased on increasing the benzaldehyde to 1-heptanal molar ratio, the self condensation of 1-heptanal seems to get suppressed significantly.

Table 4
Effect of benzaldehyde to heptanal molar ratio on selectivity of jasminaldehyde

Run	Benzaldehyde/heptanal molar ratio	Conversion (%)	Selectivity (%)	
			Jasminaldehyde	2-Pentyl-non-2-enal
1	1	98	54	46
2	2	98	66	44
3	3	98	74	26
4	5	99	80	20
5	7	99	79	21
6	10	99	80	20

Reaction conditions: Catalyst = 75 mg, temperature = 125 °C, reaction time = 8 h.

Table 5
Effect of reaction temperature on selectivity of jasminaldehyde

Run	Temperature	Conversion (%)	Selectivity (%)	
			Jasminaldehyde	2-Pentyl-non-2-enal
1	60	40	87	13
2	80	62	87	13
3	100	78	84	16
4	125	99	80	20
5	140	99	78	22
6	160	99	77	23

Reaction conditions: Benzaldehyde = 39.6 mmol, heptanal = 7.9 mmol, catalyst = 75 mg, reaction time = 8 h.

3.5. Effect of reaction temperature

The increase in conversion of 1-heptanal accompanied by decrease in selectivity of jasminaldehyde was observed on increasing reaction temperature (Table 5). For example, 40% conversion of 1-heptanal with 87% selectivity of jasminaldehyde was observed at 60 °C that increased to 78% with decrease in selectivity to 84% at 100 °C. At 125 °C, the conversion of 1-heptanal was observed to be 99% and with selectivity of jasminaldehyde decreasing to 80%. On further increase in the reaction temperature to 160 °C, the conversion value of 1-heptanal did not change. However, the selectivity of the jasminaldehyde was observed to decrease to 77%. The selectivity of self condensation

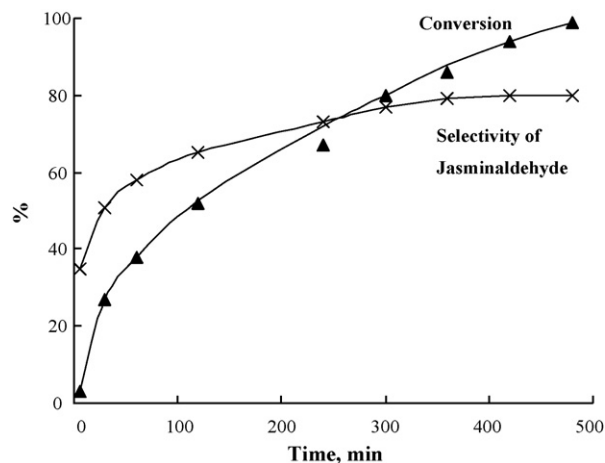
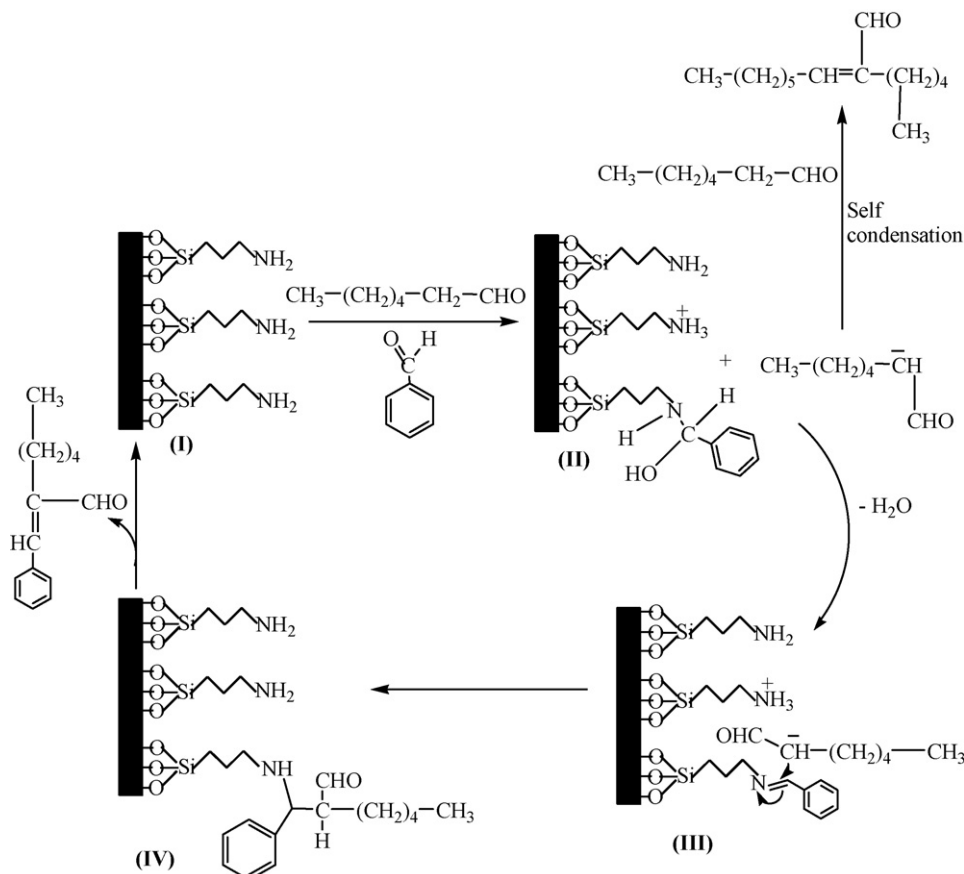


Fig. 5. Kinetics profile with respect to time.

product of 1-heptanal was observed to increase on increasing temperature as higher reaction temperature favors to the self condensation of 1-heptanal in the studied reaction conditions.

3.6. Reaction kinetics

The effect of reaction time on conversion of 1-heptanal and selectivity of jasminaldehyde was studied at optimum reaction conditions, i.e., 75 mg catalyst, benzaldehyde/1-heptanal molar



Scheme 1. Proposed reaction mechanism for the synthesis of jasminaldehyde from condensation of 1-heptanal with benzaldehyde using MOS₂ as a catalyst.

ratio = 5 and reaction temperature = 125 °C. As seen from Fig. 5, the conversion of 1-heptanal was observed to increase linearly up to 7 h. The selectivity of jasminaldehyde was observed to increase from 35 to 66% within 2 h reaction time, however on increasing the reaction time up to 8 h the selectivity of jasminaldehyde increased from 66 to 80%. The value of rate constant was calculated as $0.82 \text{ M}^{-1} \text{ h}^{-1}$ at optimum reaction conditions. The order of reaction was calculated from kinetic data and found to be second order reaction with respect to reactants.

3.7. Reaction mechanism

The proposed reaction mechanism for condensation of 1-heptanal with benzaldehyde is shown in Scheme 1. The reaction is proposed to initiate on the Bronsted basic sites (amine groups) present on the surface of catalyst (I). Imine species (II) are formed by the adsorption of benzaldehyde molecule on the active basic sites of the catalyst in first step. The resulting intermediate active species (II) reacts with carbanion of 1-heptanal to produce corresponding C=N imines species (III) in second step. The proton transfer from the C=N imine species takes place in third step for the formation of an unstable intermediate called as carbino-lamine (IV). Desorption of jasminaldehyde from intermediate species (IV) takes place in fourth step and active sites of the catalyst are reused for further catalytic cycles. The pathway for the self condensation of 1-heptanal is also shown in the Scheme 1. The reaction of carbanion of 1-heptanal with another 1-heptanal molecule takes place on the active basic sites of catalyst to form 2-pentyl-non-2-enal as a product.

4. Conclusions

The amine and diamine functionalized MOS samples were synthesized and used as catalysts for synthesis of jasminaldehyde by condensation of 1-heptanal with benzaldehyde. The conversion of 1-heptanal was observed to increase with increase in basic character of the studied catalysts. Amine functionalized synthetic talc (MOS2) showed 99% conversion with 80% selectivity of jasminaldehyde. Selectivity of jasminaldehyde was observed to be strongly influenced by benzaldehyde to 1-heptanal molar ratio, with higher value favoring higher jasminaldehyde selectivity. Reaction temperature of 125 °C was found to show higher 1-heptanal conversion with 80% selectivity of jasminaldehyde. The value of rate constant was found to be $0.8 \text{ M}^{-1} \text{ h}^{-1}$ at optimum reaction conditions.

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