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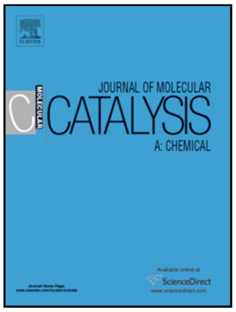

Title: *p*-Toluene sulfonic acid (PTSA)-MCM-41 as a green, efficient and reusable heterogeneous catalyst for the synthesis of jasminaldehyde under solvent-free condition

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p-Toluene sulfonic acid (PTSA)-MCM-41 as a green, efficient and reusable heterogeneous catalyst for the synthesis of jasminaldehyde under solvent-free condition

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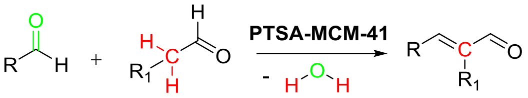
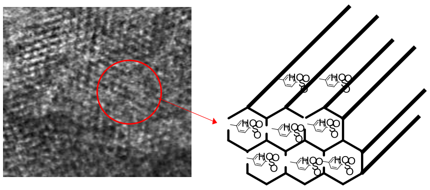
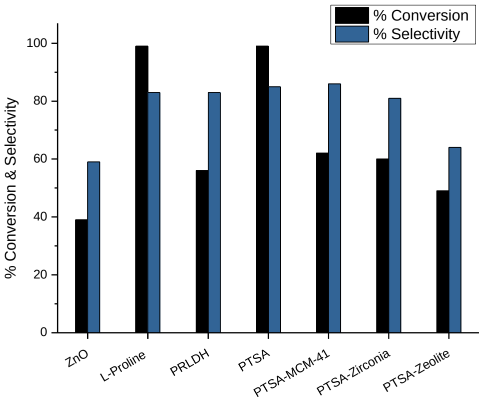
Graphical Abstract





PTSA-MCM-41

- Metal free
- Up to 91% yield
- 15 examples
- Recyclability
- Solvent free



Highlights:

- **PTSA** supported on **MCM-41** (**PTSA-MCM-41**) was synthesized and characterized by various analytical techniques such as XRD, FT-IR, TGA, N_2 adsorption–desorption isotherms, SEM, and TEM.
- As synthesized **PTSA-MCM-**41was used in cross-aldol condensation reaction for the synthesis of jasminaldehyde and its derivatives.
- The catalytic performance of **PTSA-MCM-41** was compared with other catalysts viz., ZnO, Proline, Proline-LDH, PTSA, PTSA-zirconia and PTSA-zeolite
- **PTSA-MCM-41** showed excellent catalytic performance (Conversion & Selectivity) in cross-aldol condensation reaction with a wide range of aromatic and aliphatic aldehydes as substrates.
- **PTSA-MCM-41** was recycled for 5 catalytic runs with no observable loss in its performance.

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Abstract

This paper reports the synthesis of *p*-Toluene sulfonic acid **(PTSA)-MCM-41** by impregnation method and its characterization XRD, FT-IR, TGA, N_2 adsorption–desorption isotherms, SEM, and TEM. The impregnated catalysts were used to catalyze cross-aldol condensation of active methylene bearing aliphatic aldehydes with aromatic aldehydes under solvent and metal-free condition particularly in the synthesis perfumery chemical-jasminaldehyde and related compounds. The as synthesized catalyst **PTSA-MCM-41** has displayed high efficiency (selectivity up to 91%) in catalyzing cross-aldol condensation reaction and was reusable (5 cycles) with no apparent loss in activity. The catalytic performance of **PTSA-MCM-41** was compared with other catalysts viz., ZnO, proline, proline-LDH, PTSA, PTSA-zirconia and PTSA-zeolite where **PTSA-MCM-41** showed better performance particularly in synthesis of jasminaldehyde.

Keywords. Jasminaldehyde • Heterogeneous catalysis • Cross-aldol condensation • Solvent free • 1-Heptanal.

1. Introduction

Jasminaldehyde, (α-amyl cinnamaldehyde), is a traditional perfumery product with a violet scent which can be obtained by the cross aldol condensation of 1-heptanal with benzaldehyde (Scheme 1) [1-5]. Its synthesis is traditionally carried out by using sodium or potassium hydroxide as base catalysts, where 1-heptanal is added slowly to the reaction mixture at moderate temperatures and is usually marred by the co-production of unwanted self-condensed products of 1-heptanal to form 2-n-pentyl- 2-n-nonenal [6]. The formation of self-condensation products can be inhibited, to some extent, by maintaining a very low concentration of 1-heptanal relative to benzaldehyde in the reaction mixture. This can be achieved by using a high benzaldehyde/1-heptanal molar ratio or/ and by adding slowly 1-heptanal into the reaction mixture [7]. Different solid base catalysts have also been reported [8-9] for the synthesis of jasminaldehyde. It is known in the literature that the condensation of 1-heptanal and benzaldehyde can also be carried out in the presence of solid acid catalysts [10-11] and acid-base catalysts [1, 2, 7, 12]. Moreover, for the aldol condensation mostly transition metal salts or their complexes have been used as catalyst under homogeneous reaction condition [13-14]. The use of strong acid or base catalyst at process level poses operational problems of corrosion

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and recycling/post-reaction handling of the spent catalyst. To this effect development of heterogeneous catalyst is relevant [15]. *p*-Toluene sulfonic acid (PTSA), has been found to be remarkably active to catalyse diverse organic transformations including aldol and other carbon-carbon bond forming reactions [16-23]. Heterogenization of PTSA in such a way that it retains its catalytic prowess of homogeneous condition while making its separation and reuse in post-catalytic run easy, is of great interest from practical point of view. To this effect MCM-41 presents significant advantage as a catalyst support due to its high specific surface area, large pore size and high thermal stability [24-25]. The **PTSA-MCM-41** has also received great attraction as an acid catalyst for several organic transformations [26-28].

Therefore, for the present study we have synthesized **PTSA-MCM-41** and used it as a solid acid catalyst in the cross-aldol condensation reaction to synthesize jasminaldehyde and related compounds under solvent-free condition. The catalytic performance of **PTSA-MCM-41** was compared with other solid acid and base catalysts viz., ZnO, proline-LDH, PTSA-zirconia and PTSA-zeolite. **PTSA-MCM-41** was found to be efficient recyclable catalyst (5 cycles) in the synthesis of cross-aldol products particularly jasminaldehyde.

2. Experimental

2.1. Materials

The different aldehydes and reagents were used as received. Benzaldehyde, 1-heptanal and L-proline were procured from Sigma-Aldrich and used as received. All the solvents were purified before use. For the product purification flash chromatography was performed using silica gel 100-200 mesh.

2.2. Synthesis of MCM-41

Synthesis of MCM-41 silica was carried out at 35 °C by adding silicate solution to the surfactant solution as per the reported method [29]. In a typical synthesis, a solution of sodium silicate (SiO_2/Na_2O mole ratio 3.24) having 1 M SiO_2 concentration was added at a controlled rate with a peristaltic pump in 10 min to the 0.2 M solution of CTAB, followed by aging at room temperature for 20 min. This aged reaction mixture was partially neutralized under a controlled rate in 50 min with HCl to adjust the SiO_2/Na_2O mole ratio to 21 and subsequently aged for 1 h. The final composition of the gel was $SiO_2/Na_2O/CTAB/H_2O$ was 1:0.048:0.1:109. The final pH of the gel after completion of the reaction was 8.5 (0.1. The gel was collected by filtration, washed thoroughly with deionized water until Cl^- free, dried at 100 °C, and calcined in air at 600 °C for 6 h. CHNS data: C% (0.08), H% (0.777), S% (0.13).

*2.3. Synthesis of **PTSA-MCM-41***

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To a solution of PTSA (15 mL; 0.5 M in water) MCM-41 (1.0 g) was added and the resulting suspension was stirred for 24 h. Subsequently, water was evaporated at 80 °C under reduced pressure on a rotary evaporator and finally dried at 110 °C for 12 h to get **PTSA-MCM-41**. CHNS data: C% (21.18), H% (3.378), S% (7.92).

2.4. Characterization techniques

Powder X-ray diffraction patterns of the catalyst samples were recorded with Phillips X'Pert MPD system equipped with XRK 900 reaction chamber, using Ni-filtered Cu-Kα radiation (λ =1.54050 Å) over a 2θ range of 1-10°C at a step time of $0.05°s^{-1}$. The ^{1}H-NMR and ^{13}C (δ in ppm) spectra were recorded on Bruker 500 MHz spectrometer at operating frequencies of 500 MHz and 125 MHz, respectively, in $CDCl_3$ (δ = 77.33) using tetramethylsilane as an internal standard. The FT-IR spectra of the samples were recorded from 400 to 4000 cm^{-1} with a Perkin–Elmer Spectrum GX FT-IR system using KBr pellets. Thermo gravimetric analysis (TGA) was carried out on a Mettler TGA/DTA 851e, under nitrogen atmosphere with the flow rate of 50 ml/min. Surface morphology of samples were measured in a SEM instrument (Leo Series VP1430) equipped with EDX facility (Oxford instruments). SEM analysis was carried out at an accelerating voltage of 20 kV and probe current of 102 pA. The surface area analysis and pore size distribution of the samples were measured by nitrogen adsorption-desorption isotherm at -196 °C using a volumetric adsorption measurement system (Model: ASAP-2020, Micromeritics, Inc., USA). All the samples were degassed at 80 °C for 4 h prior to the measurements. The product was carried out using Gas Chromatography (GC) (Shimadzu 17A, Japan) using 5% diphenyl and 95% dimethyl siloxane universal capillary column and flame ionization detector (FID). The column temperature was programmed for 50 °C to 210 °C at a heating rate of 10 °C /min. N_2 gas was used as a carrier gas. The temperature of injection port and FID were kept constant at 250 °C during product analysis. The retention time for different compounds was determined by injecting pure compounds under identical conditions (GC-parameters).

2.5. Synthesis of Jasminaldehyde

In a three necked round bottom flask, benzaldehyde (39.5 mmol), n-decane (0.01g) as an internal standard and **PTSA-MCM-41** (100 mg) were taken under inter gas atmosphere to which 1-heptanal (7.9 mmol) was added at a rate of 1130 µL/h by using syringe pump, while keeping the reaction temperature at 125 °C. The controlled addition of 1-heptanal is important in order to minimize its self-condensation and maximize the yield of main product

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jasminaldehyde. The reaction was monitored on GC. All the reactions were done in triplicate to ensure the reproducibility of the reaction.

Following formula was used to report conversions and selectivity

$$\%\,\text{Selectivity of jasminaldehyde} = \frac{\text{Moles of jasminaldehyde}}{\text{Moles of jasminaldehyde+2-n-pentyl-2-nonenal}} \times 100$$

$$\%\,\text{Conversion} = \frac{\text{Moles of 1-heptanal reacted}}{\text{Moles of 1-heptanal fed}} \times 100$$

3. Results and discussion

3.1. Catalyst characterizations

3.1.1. Powder X-ray diffraction (P-XRD)

The PXRD patterns of MCM-41 and **PTSA-MCM-41** are shown in Fig. 1. The XRD pattern of MCM-41 showed a very broad peak, which does not change much on loading the PTSA indicating the loaded PTSA was highly dispersed on the surface of MCM-41.

3.1.2. FT-IR spectroscopy

The FT-IR spectra of PTSA, MCM-41, and **PTSA-MCM-41** are given in Fig 2. FT-IR spectrum of MCM-41 the band at 1080-1090 cm^{-1} due to Si-O stretching of Si-O-Si structure. The PTSA impregnation on MCM-41 in **PTSA-MCM-41** sample was confirmed by the presence of characteristic bands due to symmetric and asymmetric O=S=O stretching vibrations of the $-SO_3H$ in PTSA (1189 and 1124 cm^{-1}).

3.1.3. Thermo gravimetric analysis

The TGA of PTSA, MCM-41, and **PTSA-MCM-41** under nitrogen atmosphere are shown in Fig.3. All the samples were dried under vacuum at 110 °C for 4-6 h before the TGA measurements. In the case of **PTSA-MCM-41** first weight loss before 120 °C corresponds to the removal of water. The second stage of weight loss of 33.75 % at around 340 °C is associated to the decomposition of impregnated PTSA in the silica matrix.

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3.1.4. Surface area measurements

Textural characteristics of MCM-41 and **PTSA-MCM-41**:

The Nitrogen adsorption-desorption isotherms (at 77 K) of **PTSA-MCM-41** is shown in Fig. 4. The N_2 adsorption-desorption isotherms (at 77 K) of MCM-41 and **PTSA-MCM-41** falls in type-IV among the six types according to IUPAC nomenclature indicating the presence mesopores. Further the capillary condensation (hysteresis) was also observed, which further confirms the presence of mesopores. The nature of isotherms and hysteresis loop remained unchanged even after PTSA loadings, except that there was some reduction in N_2 adsorption capacity. The BET surface area and total pore of virgin/pure MCM-41 and **PTSA-MCM-41** are 734 m^2/g & 0.91 cm^3/g and 431 $m^{2/}g$ and 0.69 cm^3/g respectively, the reduction in surface area and total pore volume confirms the effective loading of PTSA on MCM-41. The catalytic activity of pure and PTSA loaded MCM-41 are discussed with the help of textural properties in section.

3.1.5. Scanning electron micrograph (SEM)

The SEM images of fresh (5a) and reused (5b) **PTSA-MCM-41**(Fig.5) show no change in its elliptical morphology. The TEM image of **PTSA-MCM-41**(5c) shows typical channel type structure of MCM-41. The EDX mapping image of **PTSA-MCM-41** in Fig. (5d) exhibited the presence of C, O and S elements, which proved that C,O and S particles were deposited on silica.

3.2. Catalytic activity for the synthesis of jasminaldehyde

3.2.1. Effect of catalysts

To begin with we have used the conventionally used reaction condition for the condensation of benzaldehyde (5 equivalents) with slow addition of 1-heptanal (1 equivalent) over a period of 120 min at 125 °C under nitrogen in the presence of 50 mg ZnO catalyst. Under this condition we got 39 % conversion (with respect to 1-heptanal) with jasminaldehyde selectivity of 59 % (Table 1; entry 1). At this juncture we thought of switching over to L-proline as catalyst

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instead of thus far used base catalysts. Although L-proline turned out to be excellent catalyst (Table 1; conversion, 99%; selectivity, 83%) but it required 40 mol% catalyst loading and faced catalyst recovery issues in post catalytic run. Supporting L-proline on LDH (PR-LDH) was not so helpful (Table 1; entry 3; conversion, 56%; selectivity, 83%). subsequently, we considered the use of an acid catalyst. Accordingly, we used PTSA as catalyst under homogeneous condition (Table 1; entry 4; conversion, 99%; selectivity, 85%) that provided excellent conversion and jasminaldehyde selectivity at relatively low catalyst loading (5 mol%). Excited by this result, we considered several inorganic supports for PTSA to prepare supported catalysts viz., **PTSA-MCM-41**(Table 1; entry 5), PTSA-zirconia (Table 1; entry 6) and PTSA-zeolite-A (Table 1; entry 7) so as to make the catalyst easily recyclable. Among these supported catalysts, **PTSA-MCM-41**(Table 1; entry 5; conversion 62 %; selectivity 86 %) was found to be the best, hence it was used as preferred catalyst for this reaction for further work on process optimization. Here it is to be noted that all the supports used here (without loading PTSA) were individually screened as catalyst for this reaction but they failed to show the formation of product jasminaldehyde under the reaction conditions used, although we noticed the formation of some unidentified side-products (data not included).

3.2.2. Effect of catalyst loading

The Effect of catalyst amount on the selectivity to jasminaldehyde was studied over a range of 25-300 mg with respect to 1-heptanal (7.9 mmol) and the data are given in Table 2 (Table 2; entries 1-5). It is evident from the results that 100 mg catalyst per 7.9 mmol of 1-heptanal is optimum for getting higher conversion and selectivity towards the formation of jasminaldehyde (Table 2; entry 3).

3.2.3. Effect of temperature

Temperature has great influence in the selectivity as well as the conversion of jasminaldehyde. So, the effect of reaction temperature on selectivity of jasminaldehyde was studied in the temperature range of 40-170 °C at constant 1-heptanal: benzaldehyde molar ratio 1:5 and 100 mg of **PTSA-MCM-41** as catalyst and the data are given in Table 3. It is evident from the data that as we increase the temperature of reaction from 40 °C, the conversion as well as the selectivity of the jasminaldehyde increase till 125 °C (Table 3; entries 1-5), thereafter a further increase in the temperature loss in jasminaldehyde selectivity was observed particularly above

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140 °C (Table 3; entry 7). Therefore, 125 °C was taken as optimum temperature for this reaction.

In order to highlight the utility of our methodology, the reaction was also performed on a relatively larger scale (50g of 1-heptanal, Table 3; entry 8) under the optimized reaction as per Table 3; entry 5 of this Table, and found no change in the outcome of the reaction. This shows that the present protocol for the preparation of jasminaldehyde is scalable and may find application in industry.

Having established the utility of **PTSA-MCM-41** as catalyst in cross aldol-condensation of benzaldehyde with 1-heptanal to form jasminaldehyde, we next explored its capability to accommodate various aromatic aldehydes as well as aliphatic aldehydes using the above optimized reaction conditions.

3.2.4. Expansion of substrate scope (aromatic aldehyde)

To expand the substrate scope, we first varied aromatic aldehydes by keeping 1-heptanal as common aliphatic substrate as constant and the results are given in Table 4 (Table 4; entries 1-11). In majority of the cases aromatic aldehydes produces the desired cross-condensation products with selectivity at par with benzaldehyde. However, for 3-methoxy benzaldehyde (Table 4 , entry 11) both conversion (85 %) and selectivity (60 %) were remarkably less, possibly due to the strong electron donating nature of methoxy group causing carboxy carbon poorer electrophile; consequently formation of self-condensation product of heptanal was more (40 %) in this case.

3.2.5. Effect of substrate variation (aliphatic aldehyde)

Next, we kept benzaldehyde as common aromatic aldehyde and varied aliphatic aldehyde with variable alkyl chain and results are given in Table 5 (entries 1-5). It is evident from the results that on increasing chain length (as compared to heptanal, Table 5, entry 1) conversions (99 %) and cross-aldol product selectivity (89 %) remained good (Table 5, entries 2 and 3). Whereas, shorter chain length aldehydes like butanal (Table 5, entry 4) though the conversion remained 99 %, gave relatively more self-condensation product (12 %) and the self-condensation product was even more (entry 5; 14 %) with branched aldehyde viz. 3-methyl butanal.

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*3.2.6. Recycling of the catalysts **PTSA-MCM-41** in the cross-aldol condensation reaction*

The study on the reusability (5 times at 125 °C) of the catalyst **PTSA-MCM-41** in the cross-aldol condensation reaction was performed and corresponding results are depicted in Fig 6. The catalyst was reused under identical conditions of the cross-aldol condensation reaction. The catalyst showed high stability under reaction environment and showed no significant change in its ability in imparting selectivity and conversion. The catalyst recyclability was checked by retrieving the catalyst by centrifugation of reaction mass in the post-catalysis unit operation. The recovered catalyst was washed sequentially with DCM, acetone and dried at 60 °C. The recovered catalyst showed characteristics peaks in IR (see Fig 2) as observed in fresh catalyst. The recovered catalyst was used as fresh catalyst in subsequent catalytic runs that showed no sign of deactivation over 5 cycles used.

4. Conclusions

In conclusion, we have developed a simple and green method for the synthesis of fine chemical jasminaldehyde catalysed by **PTSA-MCM-41** under solvent-free condition at 125 °C. The major advantages of the method lies in its easy catalyst preparation using inexpensive raw materials, thereby making the catalytic protocol attractive for commercial exploitation. This cross-aldol protocol was found to be equally competent in accommodating other substrates as well.

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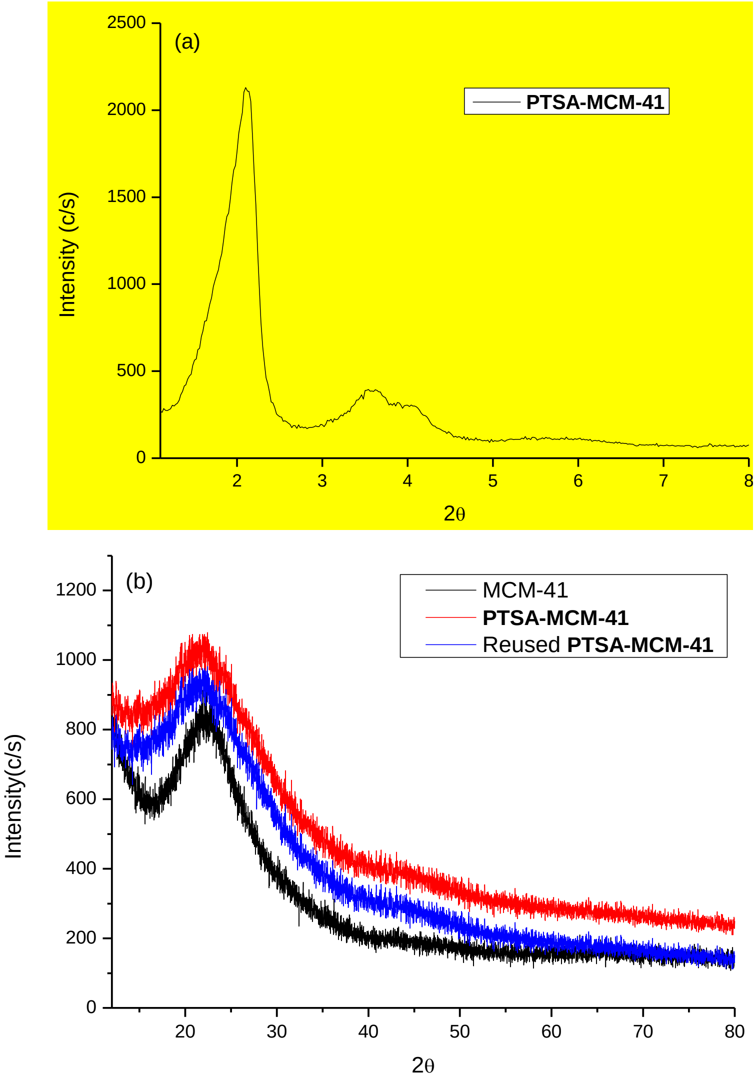

Fig. 1. Small angle PXRD of **PTSA-MCM-41 (a)** and Wide angle PXRD of MCM-41, **PTSA-MCM-41(b).**

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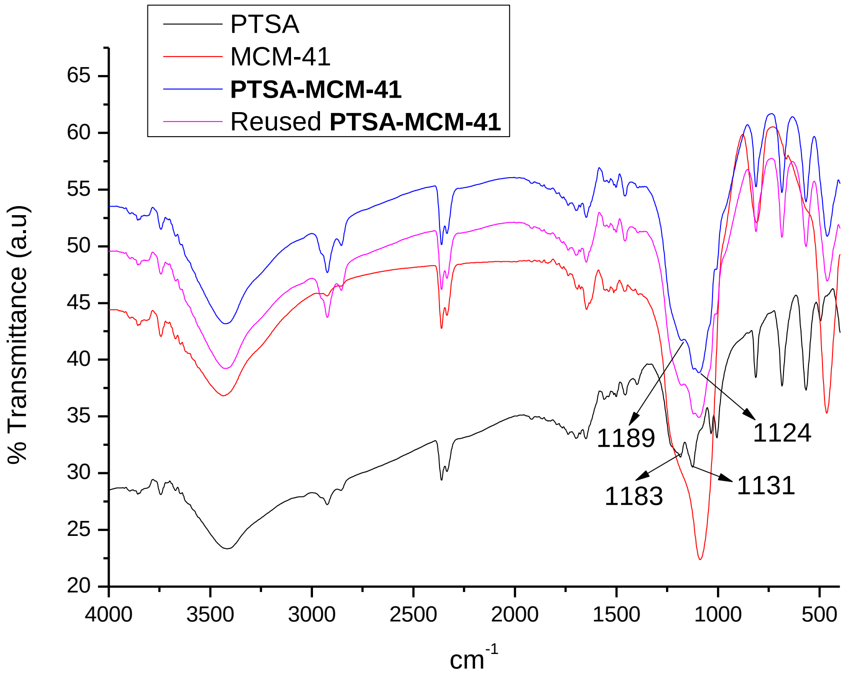

Fig. 2. FT-IR of PTSA, MCM-41, **PTSA-MCM-41.**

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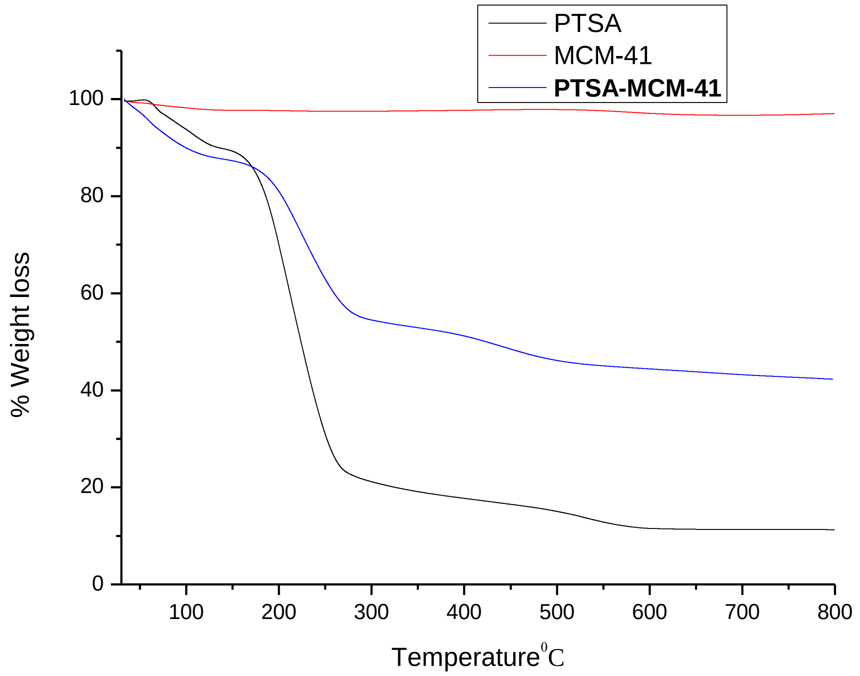

Fig. 3. TGA of PTSA, MCM-41, **PTSA-MCM-41.**

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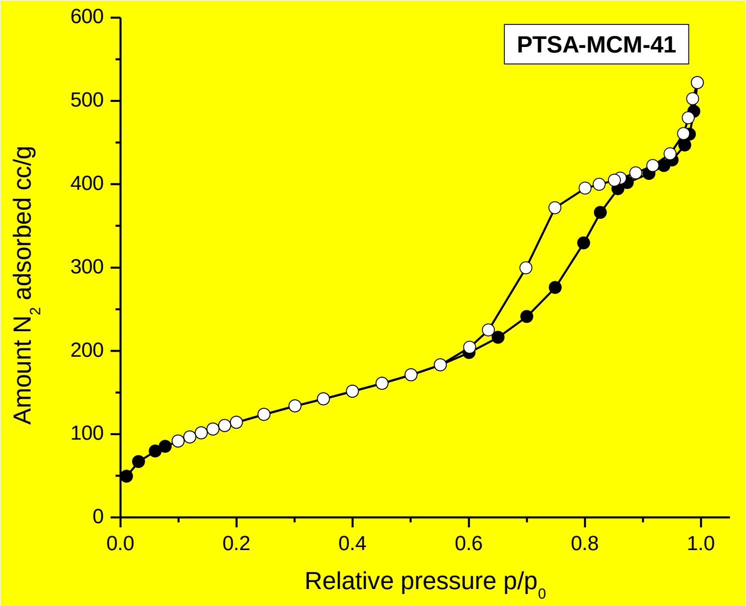

Fig. 4. Nitrogen adsorption-desorption isotherms (at 77 K) of **PTSA-MCM-41.**

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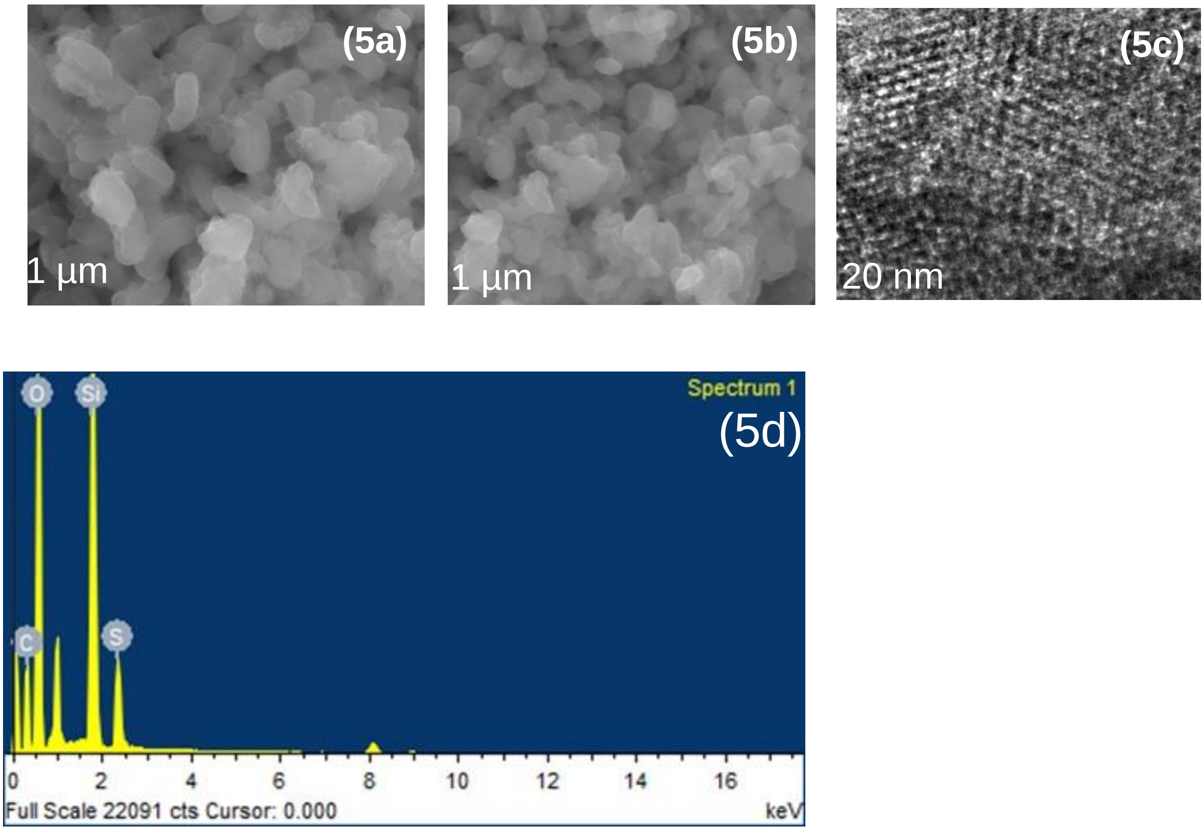

Fig. 5. SEM (**5a**), TEM (**5c**) and EDX (**5d**) image of **PTSA-MCM-41.**

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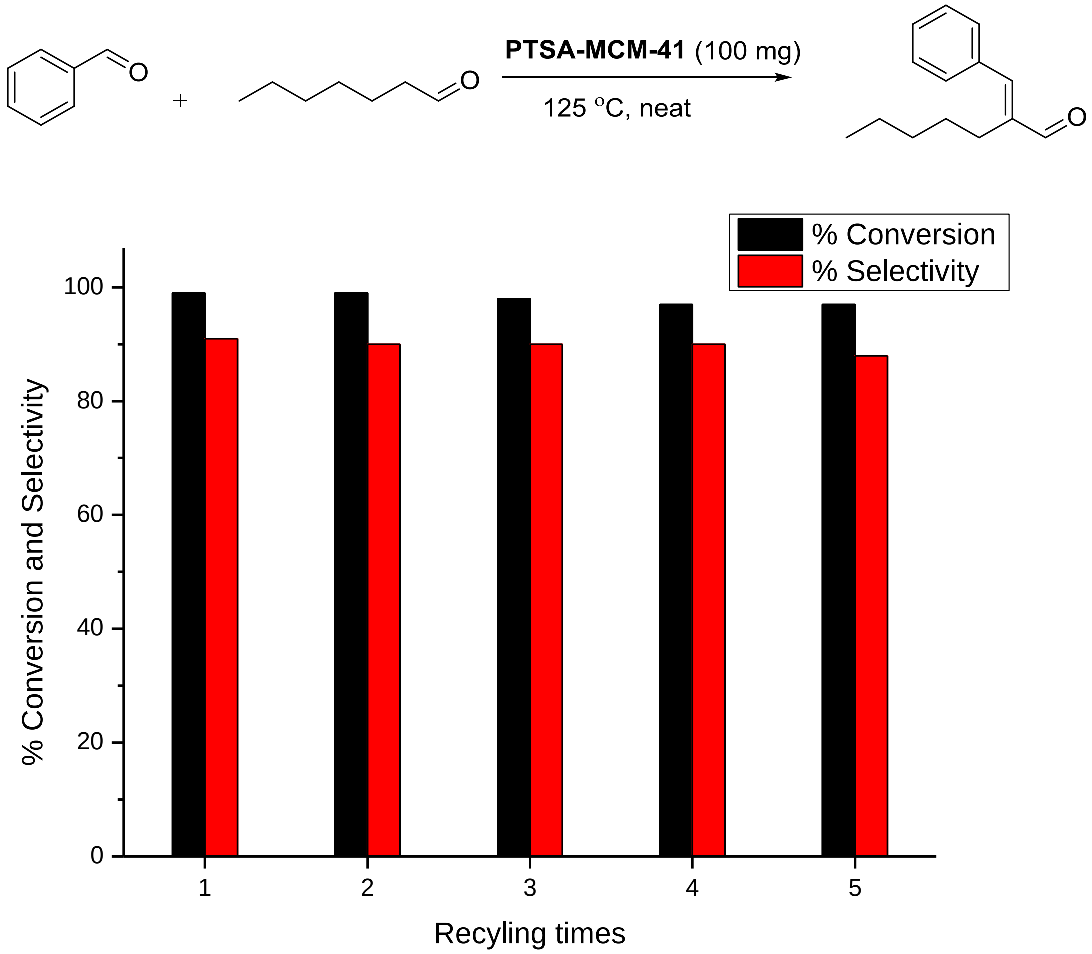

Reaction conditions: heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol, Time 13 h, 100 mg of catalyst. Selectivity and conversion is determined by GC analysis.

Fig. 6. Reusability of the catalyst (**PTSA-MCM-41**).

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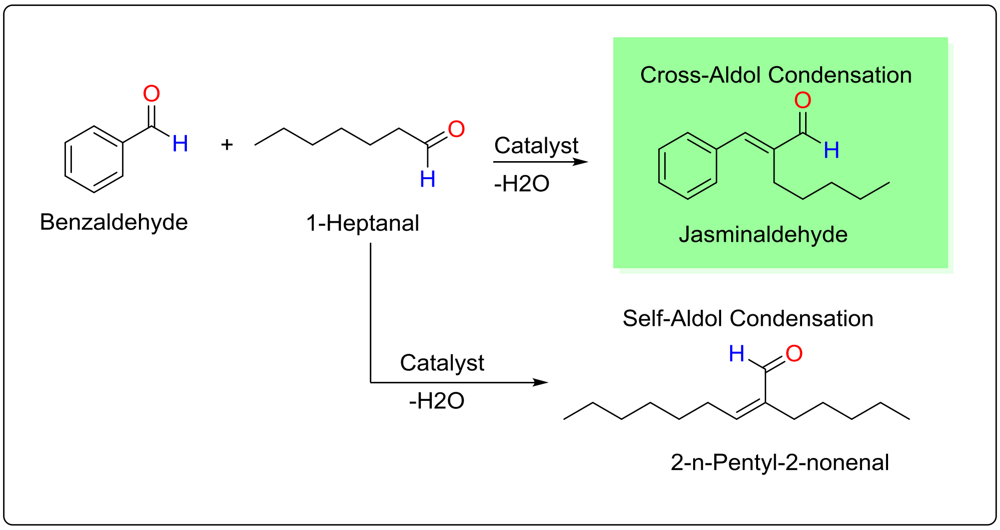

Scheme 1. Condensation of benzaldehyde with 1-heptanal.

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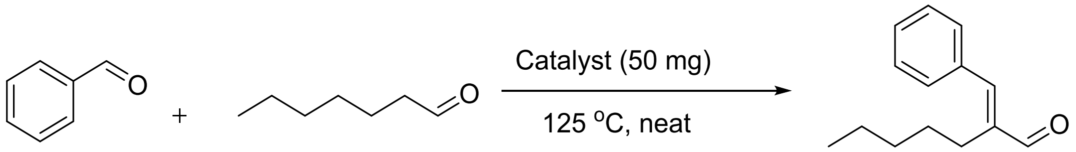
Table 1 Screening of catalyst[a]



Entry	Catalyst (loading)	Time (h)	Conversion (%)[b]	Selectivity (%)[c]	
				jasminaldehyde	2-pentyl non-2-enal
1	ZnO	5	39	59	41
2	*L-proline	1	99	83	17
3	PR-LDH	5	56	83	17
4	#PTSA	1	99	85	15
5	**PTSA-MCM-41**	5	62	86	14
6	PTSA-zirconia	5	60	81	19
7	PTSA-Zeolite	5	49	64	36

[a] Reaction conditions: heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol, temperature = 125 °C, 50 mg of catalyst. [b, c] Determined by GC analysis. *Catalyst loading 40 mol%, #Catalyst loading 5%.

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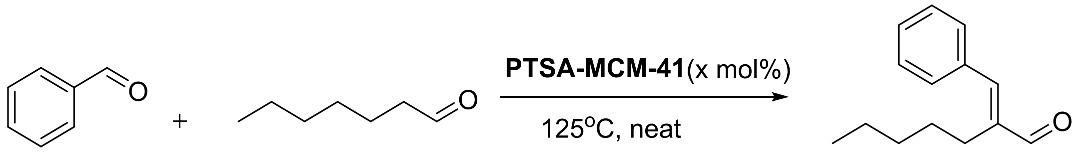
Table 2 Variation of Catalyst amount[a]



Entry	Catalyst Loading (mg)	Conversion (%)[b]	Selectivity (%)[c]	
			Jasminaldehyde	2-pentyl non-2-enal
1	25	39	55	45
2	50	76	79	21
3	100	99	91	09
4	200	99	90	10
5	300	99	88	12

[a] Reaction conditions: heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol, temperature =125°C, Time 13 h. [b, c] Determined by GC analysis.

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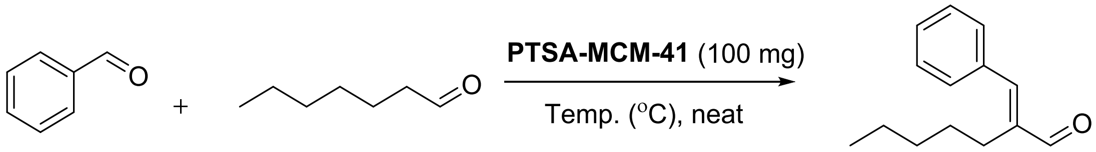
Table 3 Effect of reaction temperature[a]



Entry	Temperature (°C)	Conversion (%)[b]	Selectivity (%)[c]	
			Jasminaldehyde	2-pentyl non-2-enal
1	40	52	53	47
2	60	67	59	41
3	80	71	67	33
4	100	89	73	27
5	125	99	91	09
6	140	99	91	09
7	170	99	88	12
8*	125	98	90	10

[a]Reaction conditions: heptanal = 7.9 mmol, benzaldehyde = 39.5 mmol, Time 13 h, 100 mg of catalyst. [b, c] Determined by GC analysis.*Bulk scale.

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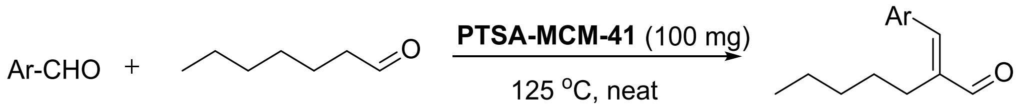
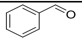
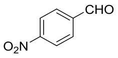
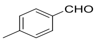
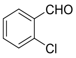
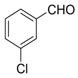
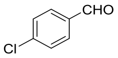
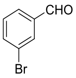
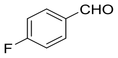
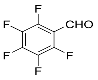
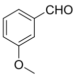
Table 4 Cross-aldol condensation between heptanal and various aromatic aldehydes **PTSA-MCM-41** as a catalyst[a]



Entry	Ar-CHO	Conversion (%)[b]	Selectivity (%)[c]	
			CA	SA
1		99	91	09
2		99	91	09
3		99	89	11
4		99	91	09
5		99	91	09
6		99	91	09
7		99	90	10
8		99	91	09
9		99	89	11
10		99	91	09
11		85	61	39

[a]Reaction conditions: heptanal = 7.9 mmol, aromatic aldehyde = 39.5 mmol, temperature = 125 °C, Time 13 h, 100 mg of catalyst. [b,c]Determined by GC analysis. CA= cross-aldol condensed product of aromatic aldehyde and 1-aliphatic aldehyde. SA= self aldol condensed product of 1-aliphatic aldehyde.

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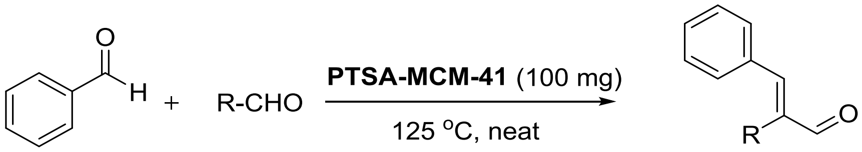
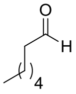
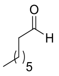
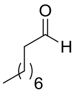
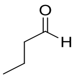
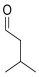
Table 5 Cross aldol condensation between benzaldehyde and various aliphatic aldehydes **PTSA-MCM-41** as a catalyst[a]



Entry	R-CHO	Conversion (%)[b]	Selectivity (%)[c]	
			CA	SA
1		99	91	09
2		99	89	11
3		99	89	11
4		99	88	12
5		99	86	14

[a] Reaction conditions: Aliphatic aldehyde = 7.9 mmol, benzaldehyde = 39.5 mmol, temperature = 125°C, Time 13 h, 100 mg of catalyst. [b, c] Determined by GC analysis. CA= cross-aldol condensed product of aromatic aldehyde and 1-aliphatic aldehyde. SA= self aldol condensed product of 1-aliphatic aldehyde.