Shape selective synthesis of long-chain linear alkyl benzene (LAB) with AlMCM-41/Beta zeolite composite catalyst

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Abstract

The liquid-phase alkylation of benzene with long-chain olefins such as 1-decene, 1-octene and 1-dodecene was carried out over AlMCM-41/Beta zeolite composite material as catalyst. The catalyst was prepared by seeding method and characterized by XRD, N_2 sorption, FTIR pyridine adsorption, NH_3-TPD and SEM. Powder XRD of AlMCM-41/Beta zeolite composite material showed the co-existence of well-structured microporous and mesophase of AlMCM-41. The typical textural characteristics of micro- and *meso*-structured phases were observed in the composite material. The effect of temperature, reactant molar ratios and catalyst weight on 1-dodecene conversion and products selectivity was studied. The composite catalyst was found to be the highly selective towards the formation 2-dodecylbenzene. Under the reaction conditions of 120 °C, benzene/1-dodecene molar ratio 10 and time 2 h, the catalyst gave 48% dodecene conversion with 76%, 2-dodecylbenzene selectivity. Significant improvement in catalytic activity has been achieved by composite material as compared to Al-MCM-41. Although zeolite beta and composite material gave similar conversion of dodecene, the composite material showed higher selectivity towards 2-dodecylbenzene, which could be due to higher diffusibility of 2-dodecylbenzene isomer in the composite material.
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Keywords: AlMCM-41/Beta zeolite composite; Benzene; Alkylation; Long-chain olefins

1. Introduction

The alkylation of aromatic hydrocarbons with olefins is applied on a large scale in the chemical industry. Alkylation of benzene with $C_{10–14}$ linear alkenes is used for the synthesis of linear alkyl benzenes (LABs), which are the primary raw material for the production of LAB sulfonates, a surfactant detergent intermediate [1]. Conventional method of this reaction is catalyzed by a homogeneous Lewis acid such as $AlCl_3$ or a strong Brønsted acid such as HF, which are highly toxic, generate a substantial amount of waste, and cause severe corrosion problems. At present, considerable efforts are being made to find efficient, sustainable, recyclable, and ecofriendly solid acid catalysts that can successfully catalyze [2,3] the above reaction. Various catalysts, such as zeolites, clays, heteropoly acids (HPAs), sulfated zirconia, and immobilized ionic liquids, were tested for this reaction [4–7]. The process developed by UOP uses solid acid catalysts for the alkylation of benzene with heavy olefins under liquid-phase conditions [1].

Microporous/mesoporous composite materials are actually molecular sieves with a bimodal pore size distribution, combining the advantages of both the microporous and the mesoporous materials. This two-fold molecular sieve might have potential applications in adsorption and catalysis [8]. For instance, these materials proved to be active solid acid catalysts for cracking of palm oil and alkylation of toluene with propylene [9]. From catalytic point of view it is interesting to investigate the efficiency of MCM-41 coating on H Beta in alkylation reactions for production of LABs.

The present work deals with the alkylation of benzene with 1-dodecene using AlMCM-41/Beta zeolite composite material as the catalyst. The reaction was carried out with an aim not only to maximize the olefin conversion but also increase the selectivity to alkyl benzene. The catalyst was used to study the effect of various reaction parameters such as temperature, molar ratio and catalyst weight on olefin conversion and product selectivity. The comparison of AlMCM-41/Beta zeolite composite material with AlMCM-41 and Beta zeolite in benzene alkylation with

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1-dodecene was investigated. Alkylation of benzene with other long-chain olefins like 1-octene and 1-decene were also studied using AlMCM-41/Beta zeolite composite material.

2. Experimental

2.1. Chemicals

Cetyltrimethylammonium bromide (CTMABr) and ammonium nitrate were procured from Loba Chemie, Mumbai. Sulphuric acid and Benzene were obtained from Merck (India) Ltd. Mumbai. Sodium silicate (27 wt.% SiO_2, 8 wt.% Na_2O) and sodium aluminate (53 wt.% Al_2O_3, 43 wt.% Na_2O) were procured from Riedel-de Haen (Sigma–Aldrich). Silica sol (40 wt.% SiO_2) and tetraethylammonium hydroxide (TEAOH, aq. 30% solution) were procured from V.P. Chemicals, India. 1-Dodecene, 1-decene and 1-octene were purchased from Aldrich. Zeolites HY ($SiO_2/Al_2O_3 = 4.8$) and USY ($SiO_2/Al_2O_3 = 80$) were collected from Union Carbide and Zeolyst, respectively. All the chemicals were used in as received form without further purification.

2.2. Synthesis

2.2.1. Synthesis of zeolite Beta

Zeolite Beta was prepared by following the procedure similar to the one described elsewhere [10].

2.2.2. Synthesis of AlMCM-41

The AlMCM41 was synthesized by a method as follow: 8.67 g of CTMABr and 29 g of water were mixed and stirred for 30 min. Thereafter, 9.31 g of sodium silicate solution was added drop wise to the surfactant solution with vigorous stirring. After stirring for 30 min, 0.12 g of sodium aluminate dissolved in 2 g of water was added to the synthesis mixture and the resulting gel was stirred for another 15 min. Then, 0.6 g of conc. H_2SO_4 in 2.5 g of water was added to the above mixture to reduce the pH to ~11.5 and stirred for 1 h. The homogeneous gel having composition $10SiO_2:5.4CTMABr:0.0125Al_2O_3:4.25Na_2O:3H_2SO_4:480H_2O$ was then transferred to a 150 cm^3 Teflon-lined stainless steel autoclave and heated for 24 h at 110 °C. The solid was filtered and thoroughly washed with deionized water, dried at 90 °C and then calcined in continuous flow of nitrogen at 540 °C for 10 h. The calcined product is finally ion-exchanged by stirring for 6 h (three times) in an ethanol solution of 1 M NH_4NO_3 (50 ml/g) at 50 °C and subsequently washed and dried at 90 °C. This was further calcined at 450 °C for 6 h and used for experiments.

2.2.3. Synthesis of composite material

The AlMCM-41/Beta zeolite composite material was prepared via. seeding method [11] using Beta zeolite as a seed. About 8.67 g of CTMABr and 29 g of water were mixed and stirred for 30 min. Thereafter, 9.31 g of sodium silicate solution was added drop wise to the surfactant solution with vigorous stirring. After stirring for 30 min, 0.12 g of sodium aluminate dissolved in 2 g of water was added to the synthesis mixture and

the resulting gel was stirred for another 15 min. Then, 0.6 g of conc. H_2SO_4 in 2.5 g of water was added to the above mixture to reduce the pH to ~11.5 and stirring was continued for another 30 min. To this, a slurry containing 2 g of zeolite Beta and 10 g of 7.5% aqueous solution of CTMABr was added after refluxing it at 40 °C for 12 h with constant stirring and stirring was continued for further 1 h. The homogenous gel thus obtained was then transferred to a 150 cm^3 Teflon-lined stainless steel autoclave and heated for 24 h at 110 °C. The solid was filtered and thoroughly washed with deionized water, dried at 90 °C and then calcined in continuous flow of nitrogen at 540 °C for 10 h. The calcined product is finally ion-exchanged by stirring for 6 h (three times) in an ethanol solution of 1 M NH_4NO_3 (50 ml/g) at 50 °C and subsequently washed and dried at 90 °C. This was further calcined at 450 °C for 6 h and used for experiments.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns of samples were recorded using Rigaku Geigerflex diffractometer equipped with Ni filtered Cu Kα radiation (λ = 1.5418 Å). The XRD profile was obtained by keeping scan rate as 1° min^{-1} in the 2θ range of 1.5–10°.

Nitrogen adsorption and desorption isotherms were obtained at 77 K using Quantachrome Nova-1200. Prior to the experiments, the samples were degassed under vacuum at 300 °C for 2 h. The specific surface area of the sample was calculated using BET method. The pore size distribution was calculated using desorption branches of nitrogen isotherms and Barrett–Joyner–Halenda (BJH) method.

The nature of the acid sites (Brönsted and Lewis) of catalyst sample was characterized by ex-situ FTIR spectroscopy with chemisorbed pyridine. A freshly activated catalyst powder sample was saturated with pyridine vapors placed in a desiccator containing pyridine. The pyridine-absorbed sample was then activated at 300 °C for 2 h in continuous N_2 flow and the FTIR spectra of the samples was recorded on a Shimadzu (Model-820 PC) spectrophotometer under DRIFT (diffuse reflectance infrared Fourier transform) mode.

The acidity of the catalyst was measured by temperature programmed desorption of NH_3 (NH_3-TPD) using a micromeritics AutoChem-2910 instrument. It was carried out after of the catalyst sample was dehydrated at 500 °C in He (30 cm^3 min^{-1}) for 1 h. The temperature was decreased to 100 °C and NH_3 was adsorbed by exposing sample treated in this manner to a stream containing 10% NH_3 in He for 1 h at 100 °C. It was then flushed with He for another 1 h to remove physisorbed NH_3. The desorption of NH_3 was carried out in He flow (30 cm^3 min^{-1}) by increasing the temperature to 450 °C at 10 °C min^{-1} heating rate measuring NH_3 desorption using TCD detector.

2.4. Catalytic activity

The liquid-phase alkylation of benzene with long-chain alkene was carried out under atmospheric pressure in a Parr autoclave. The catalyst was activated at 400 °C for 2 h in flow of dry air and cooled to the reaction temperature prior to its use in
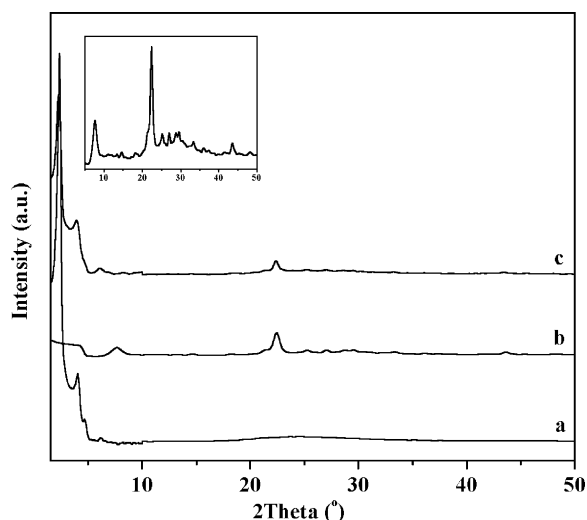
Fig. 1. Powder XRD patterns of (a) AlMCM-41, (b) Zeolite Beta, (c) AlMCM-41/Beta zeolite composite (inset XRD pattern of Zeolite Beta).

the reaction. In a typical run, 25 g of the reaction mixture (benzene/dodecene molar ratio = 10) was taken in the Parr autoclave and the 2.5 g of the catalyst was added and the reaction mixture was heated to the desired temperature under constant stirring. The clear solution of the reaction mixture was withdrawn periodically, centrifuged and analyzed by Shimadzu 14B gas chromatograph, equipped with a FID detector using HP-5 capillary column (cross linked 5% ME silicone, 30 m × 0.53 μm × 1.5 μm film thickness). The products were confirmed by GC–MS.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. X-ray diffraction

Powder XRD patterns of AlMCM-41, AlMCM-41/Beta composite and are depicted in Fig. 1. The XRD patterns of individual Beta and AlMCM-41 materials have shown characteristic peaks of these phases without any contribution of other phase/s. The XRD pattern of the composite material has shown presence of mixed phase containing the characteristic peaks of both beta and Al-MCM-41 phases. Moreover, it is evident from the XRD profile of this sample that it does not contain any other phase or amorphous matter. The appearance of the (1 0 0), (1 1 0) and (2 0 0) reflections in lower 2θ region demonstrates the well-ordered nature of MCM-41 phase in the composite material. Similarly, the characteristics peaks of beta structure can be clearly seen in the zeolite Beta and the composite material.
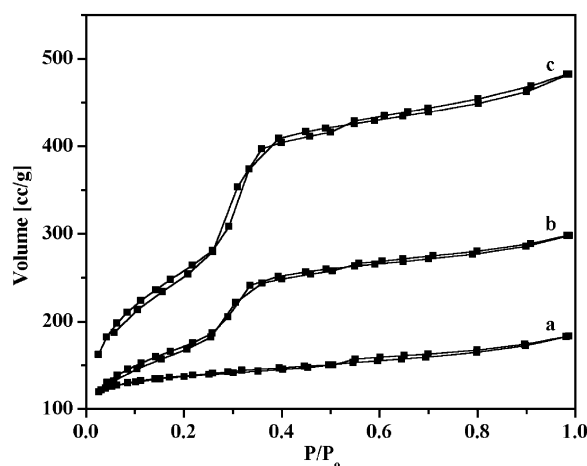

Fig. 2. N_2 adsorption–desorption isotherms of (a) Zeolite Beta, (b) AlMCM-41/Beta zeolite composite and (c) AlMCM-41.

Furthermore, it is evident from the XRD pattern of composite material that the crystalline nature has not damaged even it has undergone the hydrothermal treatment while synthesizing the AlMCM-41/Beta zeolite composite material.

3.1.2. N_2 sorption

The N_2 adsorption-desorption isotherms for the, AlMCM-41/Beta zeolite composite and AlMCM-41 are shown in Fig. 2. The type IV isotherms of AlMCM-41/Beta zeolite composite material and AlMCM-41 have indicated the confined mesoporous framework [9]. A steep rise was observed in the P/Po range from 0.2 to 0.4. An isotherm of Beta zeolite indicated a typical profile of crystalline microporous material. The BJH pore size distribution curves for the, AlMCM-41/Beta zeolite composite and AlMCM-41 is shown in Fig. 3. The composite material and Al-MCM-41 has exhibited narrow mesopore size distribution. However, the pore volume and average pore diameter of composite material was found to be lower as compared to Al-MCM-41. The textural characteristics such as BET surface area, pore size distribution and pore volume are summarized in Table 1 for comparison purpose. The BET surface area of composite material was found to be lower than Al-MCM-41 but higher than zeolite Beta. From the above results we can conclude that AlMCM-41/Beta zeolite composite contains a microporous–mesoporous system.

3.1.3. FTIR pyridine adsorption

Adsorption of pyridine as a base on the surface of solid acid is one of the most frequently applied method for the characterization of surface acidity. The use of IR spectroscopy to detect

Table 1
Physicochemical properties of different catalysts

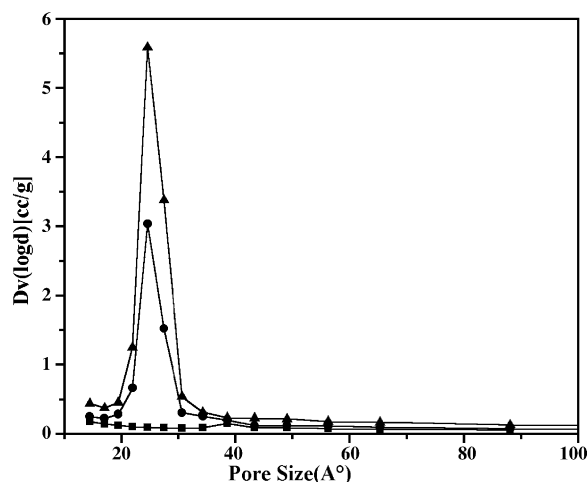| Catalyst	Surface area (m²/g)	Pore volume (cm³/g)	BJH average mesopore diameter (nm)	Total acidity (in terms of mmol NH_3/g cat)
Zeolite Beta	518	0.28	–	0.58
Composite	618	0.46	2.98	0.29
AlMCM-41	933	0.75	3.2	0.20

Fig. 3. Pore size distribution of (■) zeolite Beta, (●) AlMCM-41/Beta zeolite composite and (▲) AlMCM-41.

adsorbed pyridine enables us to distinguish among different acid sites. FTIR pyridine adsorption spectra of Beta zeolite, AlMCM-41/Beta zeolite composite and AlMCM-41 are shown in Fig. 4. The catalysts showed Brønsted (B) and Lewis (L) acidity at 1543 and 1492 cm^{-1}, respectively and the B/L ratios calculated from the IR absorbance intensities are given in Table 2. The showed the highest Brønsted acidity, while AlMCM-41 showed negligible acidity. The Brønsted acidity of composite material is lower than that of Beta zeolite due to its lower amount in the composite. However, the Brønsted acidity of composite compared to AlMCM-41 is higher because of the presence of both Beta zeolite and AlMCM-41 in it.

3.1.4. TPD of NH₃

This adsorption–desorption technique permits the determination of the strength of acid sites present on the catalyst surface, together with total acidity. The NH₃-TPD profiles of different catalysts are shown in Fig. 5. The amount of NH₃ desorbed in the interval 100–450 °C corresponds to the total number of
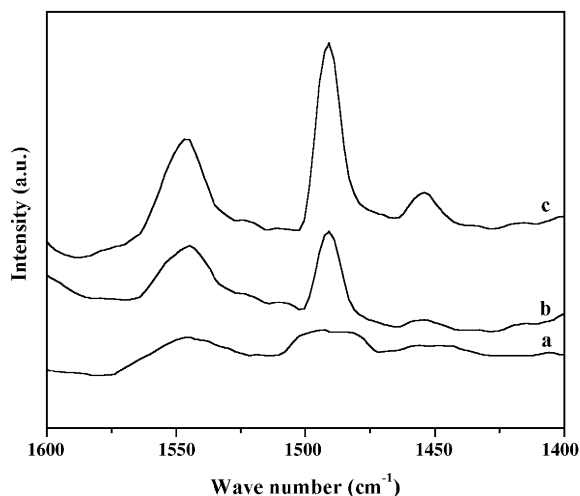

Fig. 4. FTIR pyridine adsorption spectra on (a) AlMCM-41, (b) AlMCM-41/Beta zeolite composite and (c) zeolite Beta after ex-situ activation at 300 °C.
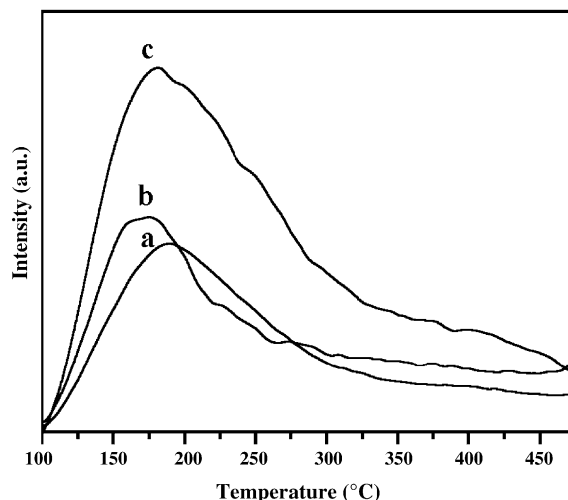

Fig. 5. NH₃-TPD profiles of (a) AlMCM-41, (b) AlMCM-41/Beta zeolite composite and (c) Zeolite Beta.

acid centers in the samples studied. According to these results (Table 2), composite material is having acidity between zeolite Beta and AlMCM-41. The number of acid sites in each of the components seems to be preserved during the preparation procedure and constitutes the overall acidity of the final material. The sharpness of the peak of the zeolite Beta (Fig. 5) is lost in case of the composite material, which is an indication of the presence of a wider acidic spectrum and different distribution of the acid sites in it (Table 2).

3.2. Catalytic activity

1-Dodecene undergoes double bond shift isomerization and benzene alkylation in presence of catalyst. The different isomers of dodecene react with benzene to form different dodecylbenzene isomers. The formation of dialkylated and olefin olegomerized products was not observed in the reaction. The conversion was expressed as the percentage of alkene converted into alkylated products.

In this study, alkylation of benzene with 1-dodecene was studied over different zeolites like HY, Zeolite Beta and USY and the results are presented in (Table 3). The zeolites USY and HY showed higher activity and it could be due their higher acidities. The zeolite Zeolite Beta showed lower activity compared to USY and HY zeolites, but better selectivity towards 2-dodecylbenzene and hence it is chosen for the synthesis of composite material.

The comparison of the catalytic activity of composite material with Beta zeolite and AlMCM-41 showed negligible conversion of dodecene by AlMCM-41 (Table 4). H Beta and composite

Table 2
Pyridine adsorption data for different catalysts

Catalyst	B acidity, $I(B)$	L acidity, $I(L)$	B/L ratio, $I(B)/I(L)$
Zeolite Beta	0.37	0.14	2.64
Composite	0.13	0.05	2.6
AlMCM-41	0.08	0.04	2.0

Table 3
Activity of different zeolites in alkylation of benzene with 1-dodecene

Catalyst	Dodecene conversion (wt.%)	2-Dodecylbenzene selectivity (%)
Zeolite Beta	45	55
HY	94	28
USY	99	25

Reaction conditions: temperature, 120 °C; total weight of the reaction mixture, 25 g; catalyst weight, 1.25 g; time, 2 h.

Table 4
Activities of Beta, composite and AlMCM-41 in alkylation of benzene with 1-dodecene

Catalyst	Dodecene conversion (wt.%)	2-Dodecylbenzene selectivity (%)
Zeolite Beta	45	55
AlMCM 41	2	67
Composite material	48	76

material showed similar conversions of dodecene but composite material shows higher selectivity towards 2-dodecylbenzene. It is to be noted that in order to keep weight of Beta zeolite similar, the weight of composite material used in the reaction is twice the amount of Zeolite Beta zeolite. The higher 2-dodecylbenzene selectivity with the composite material could be due to higher diffusibility of 2-dodecylbenzene isomer in the composite material. The higher conversion of dodecene in case of Beta zeolite compared to AlMCM-41 is due to its higher Brønsted acidity. A reaction was also conducted with a mechanical mixture of Beta zeolite and AlMCM-41 with identical ratio of composite, which had lower activity and selectivity to 2-dodecylbenzene compared to AlMCM-41/Beta zeolite composite. The lower activity of the

mechanically mixed catalyst could be due to either poor homogeneity or dispersability of Zeolite Beta in AlMCM-41.

The reaction was studied in the range of temperatures from 80 to 140 °C for 2 h using the composite material catalyst (Fig. 6A). At 80 °C, dodecene conversion was 39% and increased to 48% at 120 °C. Further increase in reaction temperature to 140 °C had no appreciable effect on dodecene conversion. The selectivity to 2-dodecylbenzene decreased from 84% at 80 °C to 76% at 140 °C.

The effect of molar ratio on dodecene conversion and product selectivities was studied at 120 °C with benzene/dodecene molar ratio 6, 8 and 10 (Fig. 6B). As the benzene/1-dodecene molar ratio decreased from 10 to 6, dodecene conversion decreased from 48% to 43% and the selectivity to 2-dodecylbenzene increased from 76% to 81%.

The effect of catalyst weight was studied at 120 °C using benzene/1-dodecene molar ratio of 10 (Fig. 6C). The conversion of dodecene was 41% with 8 wt.% catalyst weight, which increased to 48% with 10 wt.% catalyst. Further increase in catalyst weight had no appreciable effect on conversion. 2-Dodecylbenzene selectivity was not changed appreciably with an increase in catalyst weight.

The effect of time on stream was studied at 120 °C using benzene/1-dodecene molar ratio of 10 up to 4 h (Fig. 6D). The conversion of dodecene increased from 43% at 1 h to 53% at 4 h. Additionally, alkylation of benzene with other olefins like 1-decene and 1-octene were also carried out and conversions were 51% and 57%, respectively (Table 5) under identical conditions.

In order to study the recyclability of the catalyst, the reaction was studied at 120 °C with 10 wt.% catalysts using benzene/1-dodecene molar ratio 10 for 2 h. Fresh catalyst showed 48% dodecene conversion. For recycling, after first use, the catalyst was separated by filtration, washed with methanol and dried at
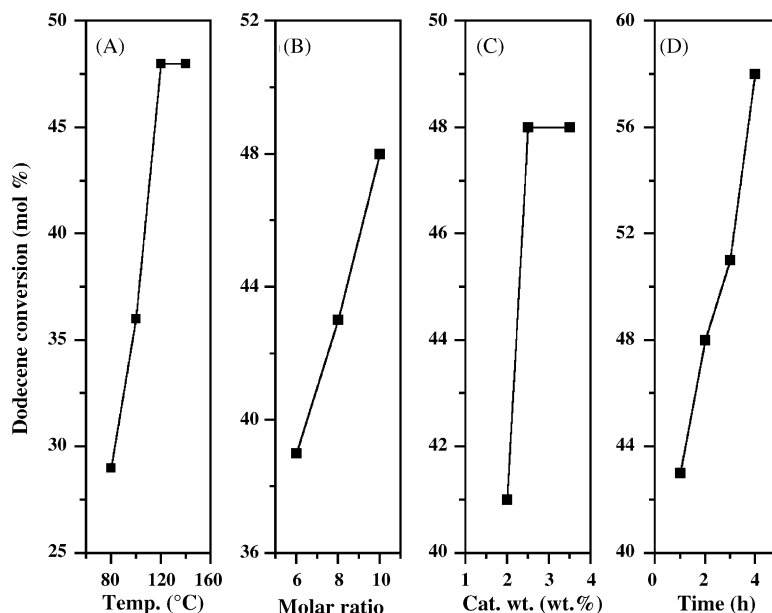

Fig. 6. (A) Effect of temperature (conditions: total weight of the reaction mixture, 25 g; benzene/1-dodecene (molar ratio) = 10; catalyst weight, 2.5 g; time, 2 h). (B) Effect of molar ratio (conditions: temperature, 120 °C; total weight of the reaction mixture, 25 g; catalyst weight, 2.5 g; time, 2 h). (C) Effect of catalyst weight (conditions: temperature = 120 °C; total weight of the reaction mixture = 25 g; benzene/1-dodecene (molar ratio) = 10; time = 2 h). (D) Effect of time on dodecene conversion (conditions: total weight of the reaction mixture = 25 g; benzene/1-dodecene (molar ratio) = 10; temperature, 120 °C; catalyst weight, 2.5 g).

Table 5
Activity of the composite material in alkylation of benzene with different olefins

Alkenes	Alkene conversion (wt.%)	2-Alkyl benzene selectivity (%)
1-Dodecene	48	76
1-Decene	51	73
1-Octene	57	69

Reaction conditions: temperature, 120 °C; total weight of the reaction mixture, 25 g; catalyst weight, 2.5 g; time, 2 h.

100 °C for 3 h and used with fresh reaction mixture in the second run. The methanol washed catalyst showed 39% dodecene conversion and the decease in conversion with the used catalyst could be due to the blockage of active sites of the catalyst by heavy aromatics and oligomerised dodecene [12]. However, after regeneration of the catalyst by calcination at 450 °C for 6 h, dodecene conversion increased to 43%. The small activity loss observed with the regenerated catalyst could be due to partial loss of acid sites of the catalyst during regeneration.

4. Conclusions

The liquid-phase alkylation of benzene with 1-dodecene has been studied using AlMCM-41/Beta zeolite composite material catalysts and the catalytic activity has been compared with AlMCM-41 and Zeolite Beta. The catalyst composite material was found to be active and under the reaction conditions of 120 °C, benzene/1-dodecene molar ratio 10 and time 2 h, dodecene conversion was 48% with 76% 2-dodecylbenzene selectivity. The catalyst AlMCM-41/Beta zeolite composite material is also an active catalyst for alkylation of benzene with other long-chain olefins.

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