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Vapour phase esterification of butyric acid with 1-pentanol over Al-MCM-41 mesoporous molecular sieves

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Al-MCM-41 molecular sieves with Si/Al ratios 25, 50, 75 & 100 were synthesized hydrothermally and characterized systematically by various analytical and spectroscopy techniques. Their catalytic activity was evaluated for the vapour phase reaction of butyric acid with 1-pentanol. Pentyl butyrate was obtained as the only product. Reaction parameters such as temperature, molar ratio and feed rate were optimized for higher butyric acid conversion. The time-on-stream study was carried out at optimum conditions resulting in gradual decrease in the activity of the catalyst.

KEY WORDS: esterification; Al-MCM-41 molecular sieves; 1-pentanol; butyric acid; pentyl butyrate.

1. Introduction

Esterification of carboxylic acid with alcohols is industrially carried out using homogeneous acid catalyst *viz*., mineral acids, metal hydroxides and metal chlorides [1]. Organic esters find extensive application in perfumery, solvents, flavours, pharmaceuticals, plasticizer and chiral auxiliaries [2]. The traditional industrial process of synthesizing esters using homogeneous acid catalyst is conveniently replaced by solid acid catalyst, ion exchange resins, clay etc [3–9]. Esterification reactions have been already reported over solid acid catalyst such as Nafion-H [10], zeolite Y [11, 12] and oxide catalyst [13–15]. In heterogeneous esterification, a per fluorinated resin sulponic acid gave high yields of various esters in the gas–solid system [10]. But these resins are expensive. It is well known that the esterification is a reversible reaction catalyzed by an acid environment and usually performed in the liquid phase. In order to drive the reaction towards the desired product, the excess amount of alcohol is used or the by-product water is removed continuously. Chen *et al*. [16] carried out the reaction between 3-methyl-1-butanol and butyric acid using sodium hydrogen sulfate as catalyst and toluene as solvent. Mao *et al*. [17] reported synthesis of pentyl butyrate using $ZnCl_2$ as the catalyst. It is a well-known fact that the reaction is thermodynamically favoured when performed in the vapour phase due to the higher values of equilibrium constants in comparison with those of the liquid phase [18]. Further advantages of the vapour phase esterification are to prevent corrosivity of equipment, to save energy and to reduce the cost of materials as well as to simplify technological process. When the reaction is carried out in vapour phase, there is no need to use a solvent. The MCM-41 materials have high thermal stability and large surface area, which lead to good adsorption capacity for organic molecules. Acid sites can be generated by the incorporation of aluminum in the framework. For these reasons, in our present study, we carried out esterification of butyric acid with 1-pentanol over Al-MCM-41 molecular sieves.

2. Experimental

2.1. Materials

All the reagents *viz*., sodium meta silicate, aluminium sulphate, cetyltrimethylammonium bromide (CTAB), sulfuric acid and butyric acid were purchased from Merck and used as such. 1-Pentanol (Merck) was distilled and used.

2.2. Synthesis of Al-MCM-41

Al-MCM-41 molecular sieves (Si/Al = 25, 50, 75 & 100) were synthesized hydrothermally as follows. Sodium meta silicate and Aluminium sulphate were used as the source for Si and Al respectively. These mesoporous materials were crystalised by autoclaving the gel composition SiO_2; x Al_2O_3; 0.2 CTAB; 0.89 H_2SO_4; 120 H_2O (x various with Si/Al ratios). The as synthesised sample was calcined at 550 °C in air for 6 h.

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Physico-chemical characterization of all the materials was carried out systematically.

2.3. Characterization

The powder X-ray diffraction (XRD) patterns of Al-MCM-41 materials were collected on Siemens D5005 diffracto meter using Cu Kα(λ = 1.54 nm) radiation. The diffractograms were recorded in the 2θ range of 0.8–10.0 with a step size of 0.1 with a count time of 10 seconds.

Nitrogen adsorption and desorption isotherms were carried out at 77 K on an ASAP-2010 volumetric adsorption analyzer manufactured by Micromeritics Corporation. Before nitrogen adsorption and desorption measurements, the samples were degassed at 523 K for 3 h ($p < 10^{-5}$ h Pa). The pore size distributions were obtained from the desorption branch of isotherm using the corrected form of the Kelvin equation by means of Barrett-Joyner-Halanda method.

Solid state ^{27}Al-MAS-NMR experiments were performed at room temperature on a BRUKER MSL 500 NMR spectrometer with resonance frequency of 104.22 MHz, spinning rate of 8 KHz with a pulse length of 1.0 s, a delay time of 0.2 s and spectral width of 330 ppm. The total scans were 150 and the line broadening was 50Hz. ^{27}Al-MAS-NMR chemical shifts were reported with reference to the liquid solution of aluminium nitrate.

The acidity of the calcined material was recorded on a Nicolet Avatar 360 FT-IR spectrometer equipped with a high temperature vacuum chamber. About 100 mg of the material was evacuated for 3 h at 523 K under vacuum ($p < 10^{-5}$ h Pa). Then the material was collected at room temperature followed by exposure of pyridine. Subsequently, physisorbed pyridine was removed by heating the sample at 150 °C under vacuum ($p < 10^{-5}$ h Pa) for 30 min. The removed material was then collected to room temperature and the spectrum was recorded. The acidity was calculated using the extinction co-efficient of the bands of Bronsted and Lewis acid sites adsorbed pyridine.

The SEM pictures were recorded on a Leoscan Scanning Electron Microscope (JEOL 640). All the samples were suspended in methanol and the specimen stub was dipped into the liquid and removed. The powder got evenly deposited onto the surface of the stub when methanol evaporated. This specimen was coated with gold for 2/, min using an ion sputter coater (Scientific Instrument PS-2 coating unit). The SEM pictures were developed on thin photographic paper.

2.4. Experimental for synthesis of pentyl butyrate

Esterification of butyric acid with 1-pentanol was carried out in a fixed-bed, vertical-flow type reactor made up of a glass tube of 40 cm in length and 2 cm in internal diameter. About 0.5 g of the catalyst was placed in the middle of the reactor and supported on either side with a thin layer of quartz wool and ceramic beads. The glass reactor was heated to the requisite temperature with the help of a tubular furnace controlled by a digital temperature controller cum indicator. The reactants were fed into the reactor using a syringe infusion pump (SAGE instruments) that could be operated at different flow rates. The reaction was carried out at atmospheric pressure. The bottom of the reactor was connected to a coiled condenser and a receiver to collect the products. The products collected in the first 10 min were discarded, and the products collected after 1 h was analyzed for identification. After each catalytic run, the catalyst was regenerated by passing moisture and carbon dioxide free air through the reactor for 6 h at 500 °C.

The percent conversion of butyric acid was analyzed in a gas chromatograph (Shimadzu GC-17A) with FID detector equipped with a 25 m capillary column (cross-linked 5% phenyl methyl polysiloxane) using the formula given below.

Conversion of butyric acid

$$= 100 - 100 \times \frac{[\text{butyric acid}]}{[\text{butyric acid}] + [\text{pentyl butyrate}]}$$

2.5. Mass balance studies for coke formation

The formation of coke in the catalyst on time-on-stream was studied by a mass balance technique. The studies were carried out using 0.5 g of Al-MCM-41 (100) at a feed molar ratio of butyric acid: 1-pentanol = 1:2 at 250 °C. The reactant was left on stream for 1 h to study the effect of temperature, whereas the reactant was on stream for 5 h to determine the effect of time-on-stream. In both the cases, the catalyst and the reactant were weighed before and after the experiment. The difference between the weight of the reactant and the weight of the mixture obtained at the product end gave the net weight loss. The weighed catalyst was subjected to calcination at 500 °C for a period of 5 h. After attaining room temperature, the catalyst was weighed again. The difference in weight of the catalyst, before and after calcination is the weight of the coke. The difference between the net weight loss and weight of the coke is probably the weight of olefin.

3. Results and discussion

3.1. Charcterization

The XRD powder diffraction patterns of the as-synthesized and calcined materials are shown in the figure1 and they are well matched with those reported earlier [19–22]. The d_{100} values are given in table 1 along with the corresponding unit cell parameter (a_0) of the catalysts calculated from the peak with hkl = 100 using the equation $a_0 = 2d_{100}/\sqrt{3}$.

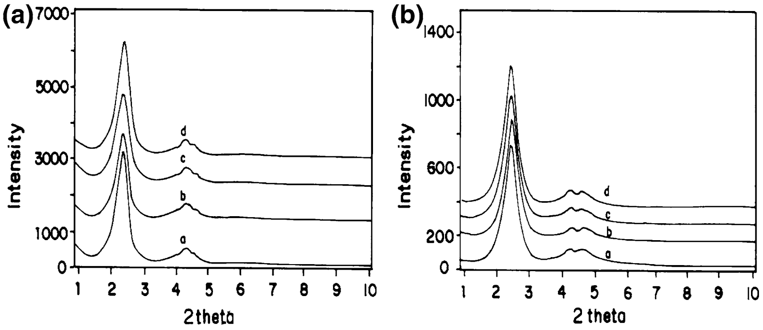

Figure 1. X-ray diffraction pattern of Al-MCM-41 molecular sieves before (A) and after (B) calcination. (a) Al-MCM-41 (25), (b) Al-MCM-41 (50), (c) Al-MCM-41 (75), (d) Al-MCM-41 (100).

The specific BET surface area, average pore diameters (BJH method) and specific pore volume for the calcined materials are presented in table 1. The ^{27}Al-MAS-NMR spectra of the samples are shown in figure 2. The peak around 53.7 ppm is attributed to the presence of aluminium in tetrahedral coordination [23]. There is a broad signal at 0.6 ppm. Generally materials with high aluminium content are susceptible to framework leaching of aluminium during calcinations [24]. The peak at 53.7 ppm in all the spectra is assigned to tetrahedrally coordinated framework aluminium and the peak at 0.6 ppm is assigned to octahedral non-framework aluminium species.

The acidity of the catalysts was measured by IR spectroscopy using pyridine as probe (figure 3) confirmed Bronsted acid character of the catalysts. The spectra showed the expected bands due to Lewis acid bound (1450 and 1623 cm^{-1}), Bronsted acid bound (1545 and 1640 cm^{-1}) and both Lewis and Bronsted acid bound pyridine (1490 cm^{-1}). These data coincide with those reported by Climent *et al.* [25] and Shanmugapriya *et al.* [26].

The size and morphology of Al-MCM-41 (Si/Al = 25, 50, 75 & 100) catalysts were investigated with SEM and the pictures are presented in figure 4. The SEM micrographs revealed the rough measure of the particle size at different magnifications. As depicted in the SEM image, it can be seen that as metal incorporation increases, the samples shows irregular morphology.

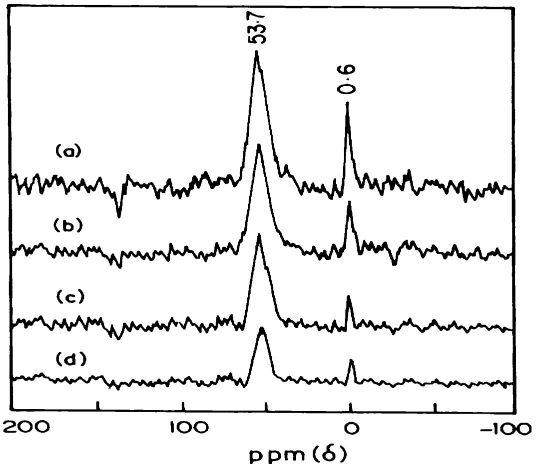

Figure 2. FT-IR spectrum of (a) Al-MCM-41 (25), (b) Al-MCM-41 (50), (c) Al-MCM-41 (75), (d) Al-MCM-41 (100) catalysts containing adsorbed pyridine.

3.2. Catalytic reaction

Vapour phase esterification of butyric acid with 1-pentanol was studied at 175, 200, 225, 250 & 300 °C over Al-MCM-41 (Si/Al = 25, 50, 75 & 100) catalyst with the feed molar ratio (butyric acid: 1-pentanol = 1:1) and feed rate 2 ml/h. The reaction results are presented in the figure 5. Conversion is increased linearly up to 250 °C but at 300 °C there is a decrease in conversion that is observed for all the catalysts. The increase up to

Table 1
Physical characteristics of Al-MCM-41 (25), Al-MCM-41 (50), Al-MCM-41 (75), Al-MCM-41 (100)

Catalysts	Calcined		Uncalcined		Surface area (m^2/g)	Pore size (A°)	Pore volume (cm^3/g)
	d_{100} (A°)	Unit cell (A°)	d_{100}(A°)	Unit cell (A°)			
Al-MCM-41 (25)	37.51	43.3	37.83	43.7	898.7	26.11	0.749
Al-MCM-41 (50)	37.65	43.5	38.21	44.1	958.2	25.18	0.936
Al-MCM-41 (75)	36.87	42.6	38.42	44.4	1027	26.32	0.945
Al-MCM-41 (100)	37.34	43.1	38.16	44.1	1043	26.51	0.957

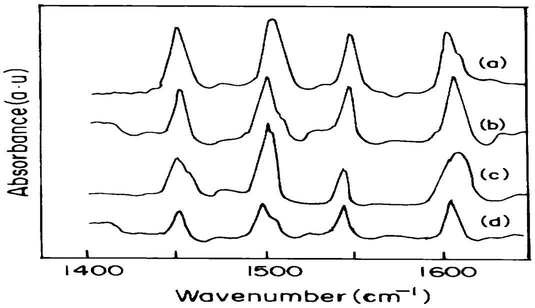

Figure 3. ^{27}Al-MAS-NMR spectrum of Al-MCM-41 molecular sieves after calcination. (a) Al-MCM-41 (25), (b) Al-MCM-41 (50), (c) Al-MCM-41 (75), (b) (d) Al-MCM-41 (100).

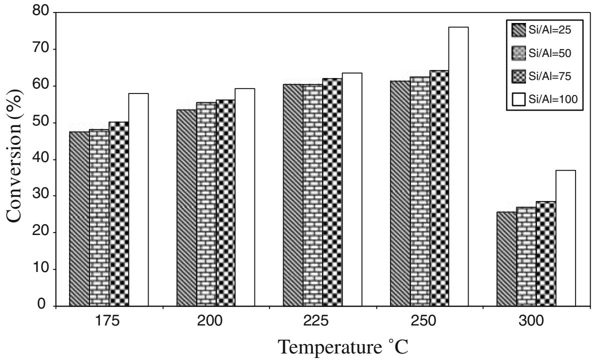

Figure 5. Effect of temperature in butyric acid esterification with 1-pentanol over Al-MCM-41 with various Si/Al ratios (25, 50, 75 & 100).

Table 2
Comparison with various solid acid catalysts

Catalysts	Conversion of butyric acid (%)
Al-MCM-41 (Si/Al = 100)	96.6
Si-MCM-41	11.63
Hβ (Si/Al = 10)	75.02
ZSM-5 (Si/Al = 17)	29.42

Feed molar ratio 1:2 (butyric acid: 1-pentanol), flow rate 2 mL/h, temperature 250 °C and selectivity to pentyl butyrate 100%.

250 °C clearly demonstrates the requirement of more energy demanding for this reaction. The requirement of high energy is due to aggregation of 1-pentanol to form alcohol clusters. The long chain alcohol clusters formed around the Bronsted acid sites through H-bonding at lower temperatures [27]. At higher temperatures the decrease in conversion is attributed to coke deposition due to oligomerization of olefin (yellow mass). There is similar level of activity at 225 and 250 °C for all the catalyst except Al-MCM-41 (100). Al-MCM-41 (100) has more hydrophobic property than other catalyst and more conversion of butyric acid is registered. The hydrophobicity of the catalyst plays an important role since expulsion of water out of the pores during esterification in liquid phase and vapour phase reaction necessarily leads to higher conversion.

The reaction was also studied over Si-MCM-41, Hβ and ZSM-5 zeolites at 250 °C with flow rate of 2 ml/h and molar ratio 1:2 (butyric acid: 1-pentanol). The reaction results are presented in the table 2. The conversion over silica was 85% less than that of MCM-41, although silica possesses defective sites, the acid strength may not be sufficient to activate esterification. The conversion over Hβ is higher than ZSM-5. This difference is attributed to large pore diameter of Hβ com-

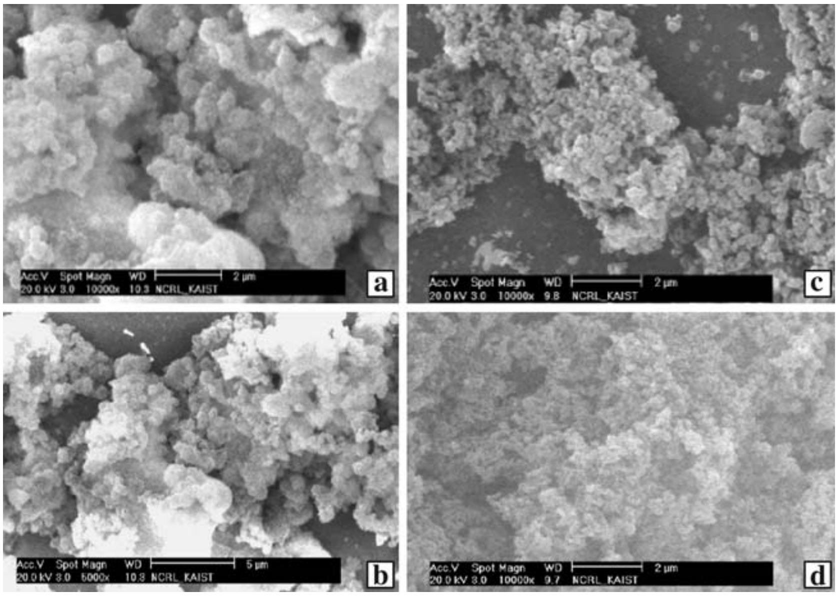

Figure 4. SEM images of mesoporous Al-MCM-41 (Si/Al = 25, 50, 75 & 100) molecular sieves. a = Al-MCM-41(25), b = Al-MCM-41(50), c = Al-MCM-41(75), d = Al-MCM-41(100).

pared to ZSM-5, which could permit easy diffusion of the reactant into the pores. Although the acid strength of ZSM-5 is higher than that of Hβ, the less conversion over ZSM-5 clearly illustrates that the strength of acid alone is sufficient for esterification and that the free diffusion of reactants into pores is also important.

3.3. *Influence of feed molar ratio*

The influence of feed molar ratio on butyric acid conversion was studied at 250 °C over Al-MCM-41 (100) catalyst. The feed rate was maintained at 2 ml/h for the feed molar ratios. The results are presented in the figure 6. The data indicates that conversion is increased with increase in the alcohol content in the feed up to the feed molar ratio 1:1 to 1:2. Since acidic catalyst is used in this study, the reaction may occur either by protonation of acid or alcohol. The reaction is bimolecular up to the feed molar ratio 1:2. Hence, it becomes difficult to decide whether the acid or alcohol is protonated. But there is a report in the literature [28] stating that acid is protonated in preference to alcohol. Although the bimolecularity of the reaction is retained with the feed molar ratio 1:2.5 & 1:3, there is nearly about 25% conversion is decreased. This decrease in conversion is due to preventing of butyric acid for chemisorption on the catalyst surface. This is felt to be appropriate because the catalyst is hydrophobic and hence it will have more preference for 1-pentanol to bring it close to the catalyst surface. Thus, it is concluded that the feed molar ratio 1:2 is optimum for maximum conversion.

3.4. *Effect of flow rate*

To study the influence of flow rate and conversion the feed molar ratio 1: 2 was used, the flow rates were varied as 1, 2, 3, 4 & 5 ml/h. The reaction results are presented in figure 7. There is 96.6% conversion at the flow rate 2 ml/h, which is higher than other flow rates. There is a step decrease in conversion, when the flow rate change is from 2 to 3 ml/h. Then after 3 ml/h, there is gradual decrease in conversion due to gradual increase in diffusion rate. As a result, the flow rate 2 ml/h is found to be optimum for maximum conversion.

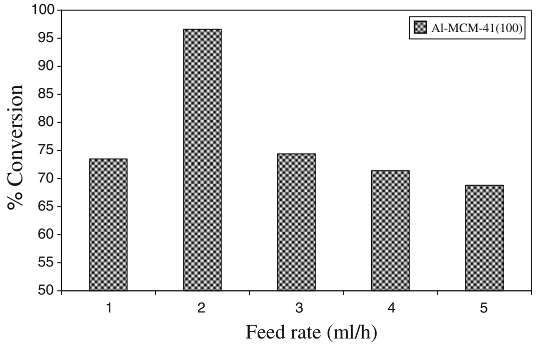

Figure 7. Effect of feed rate in butyric acid esterification with 1-pentanol over Al-MCM-41 (100) at 250 °C.

3.5. *Time-on-stream*

The effect of time-on-stream on conversion over Al-MCM-41 (100) was studied at 250 °C with the feed molar ratio 1: 2 and flow rate 2 ml/h. The results are presented in the figure 8. The conversion decreases with stream but decrease is not much rapid. Even for 5 h of stream only about 14% decrease in conversion is observed. So, this observation clearly illustrated not much rapid blocking of the active sites by the above said yellow mass. For the feed molar ratio 1:1 shown in the figure 9, only 64.5% conversion is obtained. But with the feed molar ratio 1:2, there is more than 14% conversion even at the end of 5 h of stream. Hence, increase in the alcohol content in the feed is suggested to have favourable influence on conversion.

The formation of coke on the catalyst surface in time-on-stream study was calculated by taking (Optimum conditions: feed molar ratio = 1:2; Feed rate = 2ml/h, temperature = 250 °C) 8.5400 g of reactant which was fed into 0.5 g of the Al-MCM-41 (100) catalyst, and this was left on stream for 5 h. Results showed that 7.7862g (91.17%) of reactant was

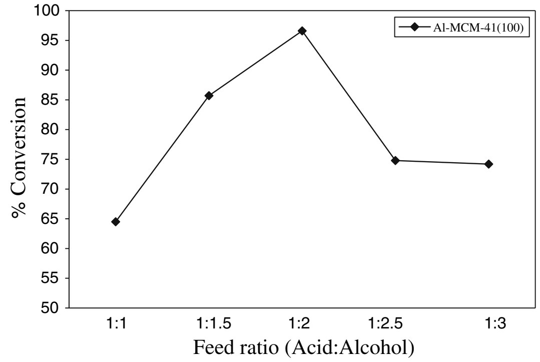

Figure 6. Effect of feed molar ratio in butyric acid esterification with 1-pentanol over Al-MCM-41 (100) at 250 °C.

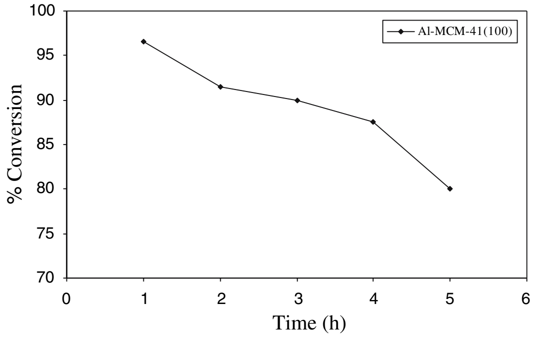

Figure 8. Effect of time on stream in butyric acid esterification with 1-pentanol over Al-MCM-41 (100) at 250 °C.

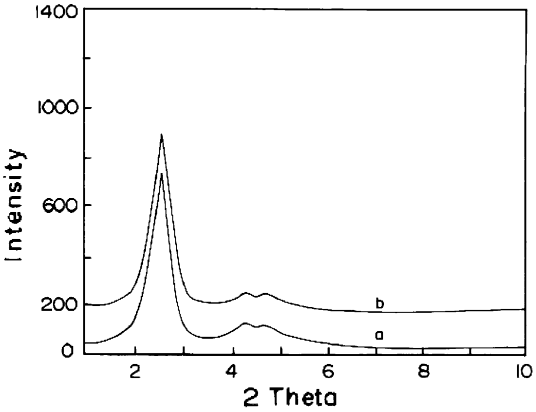

Figure 9. X-ray diffraction patterns of calcined (a) and spent (b) catalyst of Al-MCM-41 (100) molecular sieves.

converted into product at the end of 5 h on stream. Out of the remaining 0.7538g (8.83%) of reactant, an amount of 0.0593 g (0.69%) of the reactant transformed itself into coke. The weight loss of 0.6945 g (8.13%) of reactant will be probably due to olefine formation. This study illustrates that the vapour phase esterification butyric acid can easily be carried out over Al-MCM-41 (100) with minimum problem of catalyst deactivation. The spent catalyst was subjected to XRD and surface area measurements (figure 9). There is no significant change in the crystalline nature of the catalyst observed from XRD analysis. The BET measurement showed a little decrease in surface area from 1043 to 1038 m^2/g.

4. Conclusion

To conclude butyric acid esterification with 1-pentanol can very well be carried out over Al-MCM-41 catalyst. These catalysts are eco-friendly and convenient alternatives to the existing hazardous homogenous catalysts. The temperature at 250 °C, flow rate 2 ml/h and feed molar ratio 1:2 are found to be the optimum parameters for 95% conversion over Al-MCM-41 (100). The reaction is bimolecular and temperature above 250 °C is not preferable. The catalyst deactivation was found to be very slow even at end of 5 h of the stream. It is an interesting observation from the commercial point of view. The study of mass balance also suggests that the vapour phase esterification may be convenient as the mass balance is well maintained.

Acknowledgments

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