Synthesis and Characterization of Al-MCM-48 and Catalytic Performance for Ethylation of Tertiary Butylbenzene

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Abstract: The powder form the mesoporous materials Al-MCM-48 Al,Mg-MCM-48 was synthesized and extrudates into cylindrical form. Ethylation of tert-butylbenzene with ethanol was carried out over extrudated of Al-MCM-48(25), Al-MCM-48(50), Al-MCM-48(100), Al,Mg-MCM-48(25) Al,Mg- MCM-48(50) at 250 to 450 °C with the feed ratio of tertiary butyl benzene to ethanol, 1: 4 and WHSV 5.03h⁻¹. The products were m-ethyl tertiary butyl benzene (m-ETBB) and p-ethyl tertiary butyl benzene (p-ETBB). Bronsted acid sites chemisorbed ethanol and yielded ethyl cations which then reacted with TBB in the vapour phase to form p-ETBB and its isomerized product m-ETBB. The ortho ethylated product was not observed due to steric hindrance. Neither de-alkylation nor trans-alkylation of TBB was observed. Weak acid sites and competence of ethanol for chemisorption might be the cause for the absence of such reactions. There was no product complexity as the only direct product was p-ETBB. Only its isomerized product m-ETBB was obtained as the side product. Deactivation by coke formation was slow as the decrease in conversion was very slow during time on stream.

Keywords: Mesoporous, MCM-48, Extrudated, p-ETBB, m-ETBB

1. Introduction

Alkylation of aromatic hydrocarbons is a reaction of high commercial significance. Ethylbenzene, isopropylbenzene, isopropyltoluene and C₁₀-C₁₄ linear alkyl benzenes are a few of the many industrially important chemical intermediates obtained by acid catalysed alkylation of the appropriate aromatics [1]. In many commercial plants, alkylation of aromatics is still achieved with mineral acid catalysts such as HF and H₂SO₄. These catalysts pose problems such as difficulty in handling, safety, corrosion, waste disposal and difficulties in product separation. Even heterogeneous catalysts like kieselghur supported phosphoric acid, used for the production of cumene, are also felt to be undesirable owing to release of acid vapours. The first solid acid catalyst used for the alkylation of benzene with ethylene and propylene was amorphous silica–alumina gel in the year 1942 [2]. A wide variety of zeolites have been examined for alkylation since 1960. Zeolites X and Y were found to be more active catalysts for alkylation of benzene with olefins than amorphous silica–alumina gels [3,4]. Although zeolites and zeotype molecular sieves exhibit better catalytic performance than their corresponding amorphous catalysts, there are problems in the alkylation of alkyl aromatics and phenols with alcohols as the alkylation agents. Similarly, in the ethylation of toluene with ethanol in the vapour phase over NAP0-5 and ZAPO-5 molecular sieves, meta products predominated [5]. Formation of meta product in these reactions was attributed to aryl ring deactivation by adsorption on the Brønsted acid sites of the catalysts. Since these catalysts are microporous materials with more acidic sites, the chances of adsorption of aromatic substrates on the Brønsted acid sites during their diffusion through the pores are expected to be greater. Hence meta substitution increases and is unavoidable on alkylaromatic substrates in zeolites. These problems can be avoided if the recently discovered mesoporous MCM-41 molecular sieves are used as catalysts [6]. One of the members of this family Al-MCM-41 is attracted for catalytic applications owing to its high thermal stability, large straight pores of uniform size, high surface area, and mild acid sites [5,11]. Closely related to this material is MCM-48, which retains all the features of MCM-41 with additional advantage of cross-linked pores [12] that retard coke formation. It is also expected to give high conversion in catalytic alkylation as it possesses very scattered distribution of acid sites. Jun et al. [13] evaluated the catalytic activity of aluminium incorporated MCM-48 molecular sieves in the Friedel-Crafts alkylation of benzene, toluene, and m-xylene with benzyl alcohol. The catalytic activity depends on the preparation methods and the amount of aluminium content. It is also established that post-synthesis incorporation of aluminium is the most effective way to in-crease the catalytic activity. Dapurkar et al. [14] examined the catalytic activity of Al-MCM-48 catalysts in the tert-butylation of phenol and reported enhanced activity. This enhancement is attributed mainly due to its three-dimensional pore structure. Bhattacharyya et al. [15] reported methylation of phenol over Al-MCM-41. The high acidity favored C-alkylation whereas weak acidity favored O-alkylation. Shen et al. [16] reported selective alkylation of phenol with tert-butyl alcohol over [hmim]PF₆ and the products were 2,4-IBP, 4-IBP, and 1-IBP. Klerk and Nel [17] reported phenol alkylation with 1-octene over solid phosphoric acid, amorphous silica, aluminaes silica, zeolite , mordenite, and ZSM-5. Huang et al. [18] reported Al-MCM-48 as a potential hydrocrating catalyst support. The incorporation of aluminium into the framework facilitated enhanced adsorption of light-cycle oil (LCO). In the present
work, powder form of Al-MCM-48 was synthesized and extrudated into cylindrical form by compounding with bentonite as a binder, methylcellulose as a plasticizer (also as a macropore builder), TEOS as a cross-linking agent and water as a homogeneous mixer. In addition, MCM-48 can provide similar spatial environment for the reactants in the channels as that in the homogenous solution phase thus aiding the formation of products which are largely kinetic controlled. It is because of these features of MCM-48 that in the present study Ethylation of tert-butylbenzene with ethanol over Al-MCM-48 molecular sieves has been investigated, and the results obtained are discussed in the following sections. Hence, extruded mesoporous materials are convenient choices for the selective production of dialkyl aromatics with high conversion to monoalkyl aromatics which on polymerization produce polymers with enhanced plasticity over the parent polystyrene.

2. Experimental

2.1 Preparation of the catalysts

In a typical synthesis of sodium form of Al-MCM-48, TEOS was added slowly to a solution of cetyltrimethylammonium bromide dissolved in distilled water. Sodium hydroxide (1M) was added to it and the pH was raised to 11.6. The gel was then stirred for 30 min at room temperature (solution 1). The required amount of aluminium hydroxide in 31.2 ml water was stirred for 2 h at 80 °C (solution 2). The aluminium hydroxide solution (2) was added slowly to solution (1) under constant stirring. The resulting mixture was then stirred for 1 h at room temperature. The mixture was transferred to a 500 ml autoclave and kept in an air oven at 100 °C for 72 h.[1] The samples were labelled as Al-MCM-48 (x) where x denotes Si/Al molar ratio. The solid product was obtained with washed with distilled water and dried at 100 °C. The dried material was calcined at 550 °C for 1 h in nitrogen atmosphere followed by 6 h in air to remove the organic template. The Na form of Al-MCM-48 was converted to H form by repeated ion exchange with 1M ammonium nitrate solution followed by calcination at 550 °C for 6 h in air. Al,Mg-MCM-48 with Si/(Al+Mg) ratios of 25 and 50 were synthesized by adopting the same procedure with magnesium acetate as the precursor for magnesium and finally extrudated into cylindrical form [19].

2.2 Characterization

The XRD patterns of the structure of Al-Mg-MCM-48 and Al-MCM-48 molecular sieves. All of them obtained the peak due to (100) but the peaks due to other planes are not clear. The intensity of the peaks due to (100) is also very weak. Presence of the binder is for the poor resolution of (110), (200) and (210) and less intensity of the peak due to (100). It arises as the binder can false scatter the differential beams for as the parent structure. Compared to the intensity of the binder were parent materials, here the intensity is very much less. The N₂ adsorption –desorption isotherms of the illustrates of AlMg-MCM-48 and Al-MCM-48 molecular sieves, all of them showed the behaviour of type IV adsorption isotherm. Presence of hysteresis loop in all of them. But capillary condensation occurs just below 3 (p/po). It is an evidence for microporous in all. The sharp increases in condensation N₂ in capillaries is the evidence uniform pore size. The FT-IR spectra the extrudates of Al,Mg-MCM-48 and Al-MCM-48 molecular sieves, the intense broad peaks between 2700 and 3700 cm⁻¹ due to O-H stretching vibration of water. The bending vibration water occurs close to 1620 cm⁻¹. The symmetric Si-O-Si vibrations occurs close to 940 cm⁻¹, and its asymmetric gives a broad band between 1000 and 1200 cm⁻¹. The Si-O-Al and Si-O-Mg stretching vibration occurs as a shows to the peak of Si-O-Si asymmetrical stretching vibration. The bending mode of Si-O-Si is very weaker close to 750 cm⁻¹. The TGA results of the extrudates of Al-MCM-48 obtained the desorption of water occurs below 120 °C due to decomposition of cellulose. The TGA results show similar features as that of the extrudates of other Al,Mg-MCM-48 and Al-MCM-48 molecular sieves.

3. Catalytic Studies

Effect of temperature

Ethylation of tert-butylbenzene with ethanol was carried out over Al-MCM-48(25), Al-MCM-48(50), Al-MCM-48(75), Al-MCM-48(100), Al,Mg-MCM-48(25) Al,Mg- MCM-48(50) at 250, 300, 350, 400 and 450 °C with the feed ratio of TBB to EA 1: 4 and WHSV 5.03h⁻¹. The products were m-ETBB and p-ETBB. The conversion of tert-butylbenzene and selectivity of products are presented in fig 1. Bronsted acid sites chemisorbed ethanol and yielded ethyl cations which then reacted with TBB in the vapour phase to form p-ETBB and its isomerized product m-ETBB. The ortho ethylated product was not observed due to steric hindrance. Neither de-alkylation nor trans-alkylation of TBB was observed. Weak acid sites and competence of ethanol for chemisorptions might be the cause for the absence of such reactions. It is an advantage of mesoporous materials compared to zeolites which promote such reactions.

The conversion increased with the increase in temperature from 250 to 350 °C, but decreased above the later over Al-MCM-48(25). The decrease was due to coking formation which was verified physically. The coking formation was evident even from 250 to 350 °C but it was more above 350 °C. Similar results were also reported in the ethylation of benzene [20] ethylation of ethyl benzene and ethylation of toluene. At all the temperatures the selectivity of p-ETBB was higher than m-ETBB. Electrophilic ethylation occurs only at the para position and so p-ETBB is the direct product and m-ETBB is formed by the isomerization of the former. As isomerization is an activation energy demanding reaction, the selectivity of m-ETBB increased with the increase in temperature, and as a result the selectivity of p-ETBB decreased with the increase in temperature. Based on the formation of only one direct product, it is to be stated that higher the bulkiness of the alkyl group already present on the aromatic ring and the attacking electrophile, lesser is the products complexity. Again when the reactants themselves decide the selectivity of the products, selective features of catalysts such as zeolites are no longer important and in such reactions mesoporous materials are far better than any microporous counterparts. Free diffusion, easy accessibility of active sites and exclusive weak acid sites as the active sites are the important unique characteristics of
mesoporous materials for their better selection as catalysts to alkylation of alkyl aromatics than zeolites.

The conversion of TBB and selectivity to products over Al-MCM-48(50), Al-MCM-48(75) and Al-MCM-48(100) follow nearly similar trend as Al-MCM-48(25). But there is only a slight decrease in conversion with increase in the Si/Al ratio of them. Hence the inherent hydrophobic property of the silica framework of mesoporous materials and its slight tuning as a result of gradual increase in the Si/Al ratio of the catalysts is expected to have some influence on the catalytic activity. Since TBB is hydrophobic it can be better attracted by mesopores of materials of higher Si/Al ratios than those with lower ratios. Hence it might be the cause for the observed small decrease in conversion in the latter catalysts than Al-MCM-48(25).

The same reaction was also run over Al,Mg-MCM-48(25) and Al,Mg-MCM-48(50) under the same conditions and the results are presented in fig 2. The conversion of TBB and the selectivity to products were nearly same as the corresponding magnesium free catalysts. Actually these catalysts were tested to establish whether the reaction followed Langmuir Hinshelwood or Eley Riedel mechanism. The former requires closely adsorbed TBB and ethyl cation for electrophilic reaction and this requirement can be met with catalysts of high density of acid sites. But adsorption of TBB can lead to its deactivation to electrophilic reaction and hence Langmuir Hinshelwood mechanism cannot operate. Since every magnesium site can plant two Bronsted acid sites closer it is suggested to be better than aluminium to catalyze reactions that follow this mechanism. On the other hand if the reaction follows the Eley Riedel mechanism only one reactant particularly ethyl cation is to be in the adsorbed state. Since the decrease in conversion with the increase in the Si/Al ratios of the catalysts is not much high, the mechanism that actually followed is the latter one.

Effect of WHSV

In order to suppress isomerization of p-ETBB to m-ETBB the WHSV was increased gradually from 5.03 to 10.04h⁻¹ over Al-MCM-48(25), and the results are presented in fig 3. As expected the selectivity to isomerization decreased, but the conversion rapidly decreased. The results over Al,Mg-MCM-48(25), given in fig also indicated similar trend. Hence the WHSV 5.03h⁻¹ was chosen as the optimum for both the catalysts.

Effect of time on stream

The effect of time on stream on conversion and products selectivity was studied over Al-NMCM-48(25) and Al,Mg-MCM-48(25) at 350 °C with the feed ratio 1:4 and WHSV 5.03h⁻¹, and the results are presented in fig 4. There was decrease in conversion with the increase in stream over both the catalysts. But the decrease was not high. Hence, there might
Figure 1: Effect of temperature extrudates of a) Al-MCM-48 (25), b) Al-MCM-48 (50), C) Al-MCM-48 (75), d) Al-MCM-48 (100), e) Al,Mg-MCM-48 (25), f) Al,Mg-MCM-48 (50) Reaction condition: Catalyst amount 0.5g; Feed ratio 1:4 (TBB(tert-butyl benzene): ethyl alcohol); WHSV 5.03 h⁻¹

Figure 2: Effect of feed ratio extrudates of a) Al-MCM-48 (25), b) Al, Mg-MCM-48 (25) Reaction condition: Catalyst amount 0.5g; Temperature 350 °C; (TBB: ethyl alcohol); WHSV 5.03 h⁻¹

Figure 3: Effect of WHSV extrudates of a) Al-MCM-48 (25), b) Al, Mg-MCM-48 (25) Reaction condition: Catalyst amount 0.5g; Temperature 350 °C; Feed ratio 1:4 (TBB: ethyl alcohol)
Figure 4: Effect of time on stream extrudates of a). Al-MCM-48 (25), b) Al, Mg-MCM-48 (25)

Reaction condition: Catalyst amount 0.5g; Temperature 350 °C; Feed ratio 1:4 (TBB: ethyl alcohol); WHSV 5.03 h⁻¹ be reduced rate of blocking of active sites by coke. High WHSV and constraint free diffusion through mesopors might be the cause for low rate of coke formation. The isomerization of p-ETBB to m-ETBB also slow thus supporting low rate of coke formation. The catalyst was also not much dark after 6h of stream. Extruded catalysts were shown to be better recyclable than the parent catalyst [19]. In order to verify it, in this study to the time on stream was repeated once over both the catalysts. The results are presented in the same fig 4. The data indicated no appreciable change in conversion.

4. Conclusion

This study showed that the mesoporous Al-MCM-48 and Al,Mg-MCM-48 catalysts extruded using methyl cellulose and pentonite clay binders were better than the unmodified catalysts for the vapour phase alkylation of alkyl aromatics. They resisted degradation due to binders. Extra wall thickness added by the binders might be the cause for their stability and recyclability. There was no product complexity as the only direct product was p-ETBB. Only its isomerized product m-ETBB was obtained as the side product. Deactivation by coke formation was slow as the decrease in conversion was very slow during time on stream. Hence, extruded mesoporous materials are convenient choices for the selective production of dialkyl aromatics with high conversion to monoalkyl aromatics.

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References