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Mesoporous molecular sieves: alkylation of anisole using tert-butylalcohol

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Mesoporous aluninosilicate Al-MCM-41 molecular sieves with Si/Al ratios 25, 50, 75 and 100 have been synthesized under hydrothermal condition and these materials were characterized by XRD, FTIR, BET and pyridine adsorption techniques. The catalytic performance was examined in the vapor phase *tert*-butylation of anisole with *tert*-butanol at the temperatures between 150 and 250 °C under atmospheric pressure. The results indicate that Al-MCM-41 (25) was found to be more active than its relatives. The major products are found to be 4-*tert*-butyl anisole (4-TBA), 2-*tert*-butyl anisole (2-TBA) and 2,4 di-*tert*-butyl-anisole (2,4-DTBA). Maximum conversion of anisole is observed at 175 °C and decreased thereafter with increasing temperature. The influence of molar feed ratio, influence of temperature, WHSV and time on stream on the selectivity of products was investigated and the results are discussed.

KEY WORDS: *tert*-butylation; anisole; Al-MCM-41.

1. Introduction

Alkylation of aromatics is an important reaction in organic chemistry widely used in the synthesis of petrochemicals, fine chemicals, pharmaceuticals, fragrances, dyes, and agrochemicals [1]. Conventionally Friedel–Crafts reactions are performed in the liquid phase using homogeneous acid catalysts like $AlCl_3$, BF_3, and H_2SO_4, often lacking selectivity toward the targeted product [2] and the corresponding industrial processes present severe environmental problems [3]. Alkylation reactions over solid acid catalysts have generated a lot of interest as alternatives for the conventional catalysts and are also being employed in several industrial processes [4–6]. The use of solid catalysts such as zeolites [7–10], clays, [11,12], and ion exchange resins [13] for the alkylation of aromatic compounds has been studied. The use of zeolites as solid acid catalysts in various processes of refining, in production of petrochemicals and fine chemicals has grown over the last few decades because of their remarkable shape selectivity, durability and reusability [14,15]. However, the small size of their cages and pore apertures has become a drawback in the treatment of heavy feeds or in the diffusion of large reactant and product molecules. There has been an increasing demand for molecular sieves having pores sizes in the mesopore range in order to treat heavier feeds and produce (more bulky) fine chemicals [16–18]. Mesoporous Al-MCM-41 molecular sieves have become catalysts in widespread use in recent years in many reactions of industrial importance. Al-MCM-41 has already been proposed as an alkylation catalyst [19]. The combination of large pores and mild acidity in Al-MCM-41 has been exploited to carry out Friedel–Craft alkylation and acylation successfully [20–24]. The activity of MCM-41 in the transformation of small molecules is generally similarity that of amorphous silica–alumina their comparable acidities. However, MCM-41 gives much better results for the transformation of bulky molecules, e.g. cracking and hydro cracking of gas oil. Medinavaltierra *et al.* developed MCM-41/Al_2O_3 catalysts that contained mainly Lewis acid sites and reported successful para-selective alkylation of toluene with isopropanol [25]. The heteropoly-acid (HPA)-supported MCM-41 was found to be more active than the bulk HPA and H_2SO_4 in liquid phase alkylation of 4-*tert*-butylphenol with isobutene and styrene, which require strong acid sites [26–29]. Alkylation of methoxy benzene produces tertiary butylated methoxy benzene, which are used as anti oxidants, dye developers and stabilizers for fats, oils, plastic, etc., [30]. The alkylation of anisole to yield 4-*tert*-butyl anisole has been carried out in presence of $ZrCl_4$ [31], trifluroacetic acid [32], and *tert*-butyl acetate in presence H_2SO_4 [33] and Yadav *et al.* [34] reported alkylation of anisole over solid acid catalysts with MTBE. In the present study we have studied alkylation of anisole using *tert*-butanol

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under vapor phase condition over Al-MCM-41 mesoporous molecular sieves and results have been discussed.

2. Experimental

All reagents *viz*., sodium metasilicate, aluminium sulfate, cetyltrimethyl ammonium bromide (CTAB), sulfuric acid, *tert*-butylalcohol, and anisole were purchased from Merck and used as such. Samples of Al-MCM-41 (25, 50, 75 and 100) were synthesized hydrothermally using a gel composition of SiO_2: xAl_2O_3: 0.2 CTAB: 0.89. H_2S0_4: $120H_20$ (x varies with Si/Al ratios) [35]. In a typical synthesis 10.6 g of sodium metasilicate in water was combined with an appropriate amount of aluminium sulfate in distilled water, and the pH of the solution was adjusted to 10.5 using 1 M sulfuric acid with stirring to form a gel. After 30 min, an aqueous solution of CTAB was added and the mixture was stirred for 1 h at room temperature. The resulting gel was then autoclaved at 170 °C for about 12 h. After crystallization, Al-MCM-41 material was recovered by filtration, washed with distilled water and dried at 80 °C for 8 h, Mesoporous Al-MCM-41 were obtained by removing the occluded surfactant, by calcining the sample at 550 °C in air for 6 h.

2.1. Characterization

The XRD powder diffraction patterns of the calcined mesoporous Al-MCM-41 (Si/Al ratio 25, 50, 75 and 100) molecular sieves were obtained from Sterescan diffraction using nickel-filtered Cu Kα radiation and a liquid nitrogen cooled germanium solid-state detector. The diffractrograms were recorded in the 2θ range of 0–10° in the steps of 0.02° with count time of 15 s at each point for MCM-41 molecular sieves. Mid-IR spectra of the mesoporous Al-MCM-41 molecular sieves were collected on Nicolet (Avatar 360) instrument using KBr pellet technique. About 10 mg of the sample was ground with about 200 mg of spectral grade KBr to form a pellet under hydraulic pressure. IR spectrum was recorded in the range of 4000–400 cm^{-1}. The acidity of the calcined materials was measured on a Nicolet (Avatar 360) FT-IR spectrometer equipped with a high-temperature vacuum chamber. Approximately 10 mg of the sample was taken in the sample holder and dehydrated at 500 °C for 6 h under vacuum (10^{-5} mbar). The sample was then cooled to room temperature. Then pyridine was adsorbed at room temperature. The physically adsorbed pyridine was removed by heating the sample at 150 °C under vacuum (10^{-5} mbar) for 30 min, the pyridine removed material was cooled to room temperature, and the spectrum was recorded. Surface area and pore volume were measured by nitrogen adsorption at 77 K using an SMARTSORB 92/93 from Smart Instruments Company, India. The sample was degassed at 473 K for 2 h under nitrogen atmosphere prior to the analysis. Surface area and pore volume of the catalyst was estimated by built-in software from Smart Instruments Company.

2.2. Catalytic performance

Tertiarybutylation of anisole was carried out in a fixed bed-vertical flow type reactor made up of a Borosil glass tube 40 cm in length and 2 cm in internal diameter. The catalyst (0.5 g), diluted with a fourfold amount of porcelain beads of equal size, was loaded at the center of the reactor and supported on either side with a thin layer of quartz wool. The reactor was heated to the requisite temperature with a help of a tubular furnace controlled by a digital temperature controller cum indicator. The catalyst was activated at 773 K for 5 h in a flow of dry air before the reaction were conducted. Reactants were introduced in to the reactor using a syringe pump. The bottom of the reactor was connected to a coiled condenser and a receiver to collect the products. The products were chilled, collected, and analyzed by GC (Perkin Elmer, Elite 5MS capillary column) and products were confirmed by GC-MS.

3. Results and discussion

3.1. Characterization

The XRD powder diffraction patterns of the calcined mesoporous Al-MCM-41 (25, 50, 75 and 100) molecular sieves are shown in the figure 1. As displayed in the figure 1, calcined samples exhibit an intense signal at 1.8 due to [100] plane and weak signals between 2 and 4°(2θ) due to [100], [200] and [210] planes. These peaks confirm the hexagonal mesophase of the material. The d_{100}

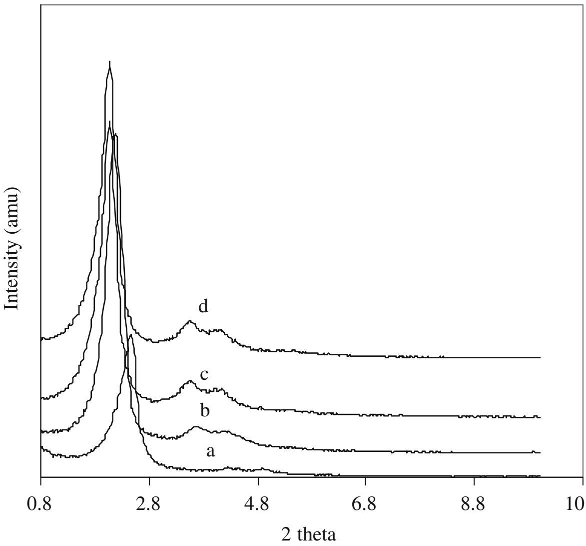


Figure 1. X-ray diffraction pattern of calcined (a) Al-MCM-41 (25), (b) Al-MCM-41 (50), (c) Al-MCM-41 (75) and (d) Al-MCM-41 (100).

spacing and lattice parameter (a_0) calculated as per the literature procedure are present in table 1. The calcined materials possess well-defined pore structure due to condensation of Si–OH groups. These XRD patterns coincide with the data already reported in the literature for mesoporous molecular sieves [36]. The infrared spectra of the as-synthesised and calcined Al-MCM-41 molecular sieves are presented in figure 2(A), (B). The broad envelope around 3500 cm^{-1} is due to O–H stretching of water, surface hydroxyl groups, and bridged hydroxyl groups. There are less intense peaks in the spectra of the as-synthesized samples just below 3000 cm^{-1} which are assigned to symmetric and asymmetric stretching modes of the $-CH_2$ group of the locked in template. Their corresponding bending mode is observed at 1400 cm^{-1}. The peaks between 500 and 1200 cm^{-1} are assigned to framework vibrations. The intense peak at 1123 cm^{-1} is attributed to the asymmetric stretching of T–O–T groups are observed around 800 cm^{-1}, and the peak at 460 cm^{-1} is due to the bending mode of T–O–T. The peak at 963 cm^{-1} is assigned to the presence of defective Si–OH groups. The symmetric and asymmetric stretching modes of the $-CH_2$ group of the template are absent in the spectra of calcined samples. These spectral features resemble those reported by previous workers [36]. The acidity of the calcined materials was measured by FT-IR spectroscopy using pyridine as probe (figure 3). The samples give the expected bands due to Lewis acid-bound (1450, 1575 and 1623 cm^{-1}) and both Lewis and Bronsted acid-bound (1490 cm^{-1}) pyridine. These data coincide with the reported literature [37]. Specific surface area, specific pore volume for calcined materials is presented in the table 1. The surface area and pore volume of the calcined materials are smaller than the already reported values. The smaller surface area of these materials may be due to their high wall thickness at all times [38,39].

3.2. *Influence of temperature*

The vapor phase *tert*-butylation of anisole over Al-MCM-41 molecular sieves was carried out at 150, 175, 200, 225 and 250 °C with molar feed ratio (Anisole: TBA) 1:3 and WHSV 3.3422 h^{-1}. The results are presented in table 2. The major product was 2-TBA, 4-TBA and 2,4-DTBA (Scheme 1). In addition 3-TBA, dimerised and oligomerised butenes [40] were also obtained, and they are given the last column of the table1

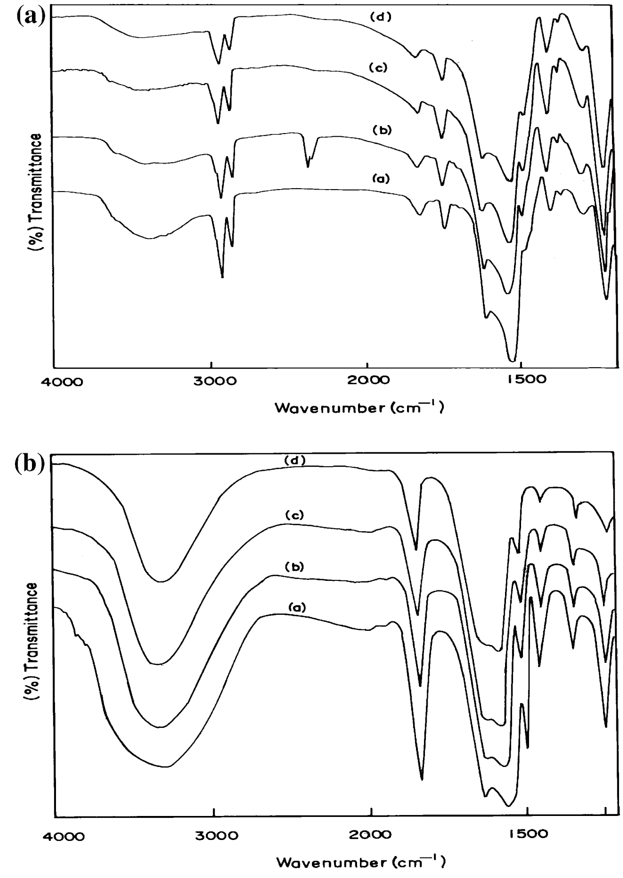
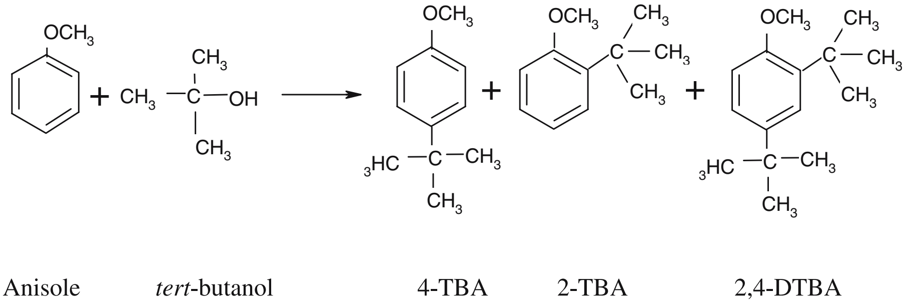


Figure 2. (A) FT-IR spectra of as-synthesized mesoporous materials. (a) Al-MCM-41 (25), (b) Al-MCM-41 (50), (c) Al-MCM-41 (75), (d) Al-MCM-41 (100). (B) FT-IR spectra of calcined mesoporous materials (a) Al-MCM-41 (25), (b) Al-MCM-41 (50), (c) Al-MCM-41 (75), (d) Al-MCM-41 (100).

The conversion increases from 150 to 175 °C, but decreases thereafter for all the catalysts. The decrease in conversion is due to oligomerisation of butenes that block the active sites of coke. The spent catalyst also appeared black at the end of the reaction. Although the same trend in conversion is observed over all the cata-



Anisole *tert*-butanol 4-TBA 2-TBA 2,4-DTBA

Scheme 1. Scheme 1 for alkylation of anisole with *tert*-butanol.

Table 1
Textural properties of catalysts

Catalysts	*d*-spacing value (Å)	Unit cell parameter (Å)	BET surface area (m^2/g)	Pore volume (cm^3/g)
Al-MCM-41 (25)	35.38	40.8	897.5	0.724
Al-MCM-41 (50)	40.60	46.9	950.2	0.916
Al-MCM-41 (75)	42.50	49.0	1038	0.931
Al-MCM-41 (100)	42.50	49.1	1045	0.933

lysts, the activity of the catalyst followed the order Al-MCM-41 (25) > Al-MCM-41 (50) > Al-MCM-41 (75) > Al-MCM-41 (100). Hence it is suggested that density of acid sites on the catalyst surface is an important factor for *tert*-butylation. If we compare the magnitude of conversion for all the catalysts at 175 °C, the difference in conversion from one catalyst to another does not correlate with the density of acid sites. For example, when Al-MCM-41 (25) and Al-MCM-41 (50) is compared there must be 50% decrease in conversion (i.e. 41.5 % for Al-MCM-41 (50)). But the actual conversion obtained over Al-MCM-41 (50) is just 5% less. Hence in addition to density of acid sites the strength of acid sites might also play an important role in deciding catalytic activity. Yet another factor to be considered is hydrophobic and hydrophilic properties of the catalysts [41,42]. Since Al-MCM-41 with high Si/Al ratio is more hydrophobic than those with less Si/Al ratios, the former catalysts can exhibit high activity with reactants, which are hydrophobic. Therefore in reaction with Al-MCM-41, acid strength, hydrophilic and hydrophobic properties are also important in addition to density of acid sites in accounting for the activity of the catalyst. The selectivity to 4-TBA increases with increase in temperature over all the catalysts. Here again Al-MCM-41 (25) gives higher selectivity than other catalysts. The selectivity to 2-TBA decreases with increase in temperature, at 150 °C the selectivity is high, because anisole can acquire a stable conformation with *o*-methyl grouping coplanar with respect to benzene ring. This conformation facilitates enhanced resonance interaction between oxygen lone pair and aromatic ring. At this conformation, the ortho position remote methyl grouping will be freely available for electrophilic reaction with *tert*-butyl cation. But with increase in temperature the *o*-methyl grouping can acquire more and more free rotation offering more and more steric hindrance for substitution at ortho position. Hence the selectivity becomes less at and above 175 °C. So this observation becomes an evidence to support free rotation about the phenyl and oxygen bond that reduces resonance interaction between phenyl and *o*-methyl groupings. Similarly, the decrease in selectivity with increase in temperature for 2-TBA is also observed over other catalyst. The selectivity to 2,4-DTBA exhibits similar trend as that of 2-TBA supporting again steric hindrance for substitution at the ortho position with respect to *o*-methyl grouping of 4-TBA. Based on the decrease in selectivity of 2,4-DTBA with increase in temperature it can be said that the precursor of 2,4-DTBA might be 4-TBA rather than 2-TBA. If 2-TBA is the precursor of 2,4-DTBA then increases in temperature will might not reduce the selectivity to 2,4-DTBA, as the 4th position of 2-TBA is steric free. The selectivity to 2,4-DTBA also follows similar trend for Al-MCM-41 with Si/Al = 50, 75, 100 as that of Al-MCM-41 (25). From this study it is concluded that optimum temperature is found to be 175 °C as it provides high conversion and selectivity in comparison to higher temprature.

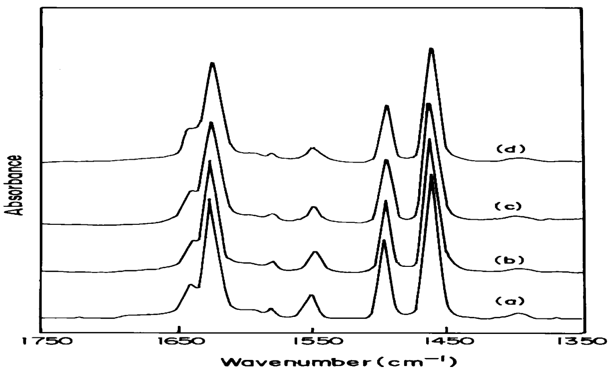


Figure 3. Pyridine adsorbed FT-IR spectrum of MCM-41 has been recorded at the room temperature (a) Al-MCM-41 (25), (b) Al-MCM-41 (50), (c) Al-MCM-41 (75) and (d) Al-MCM-41 (100).

3.3. *Effect of WHSV*

The effect of WHSV on the conversion of anisole of selectivity of the products was studied at 175 °C, at 3.3422 h^{-1}, 4.177 h^{-1} and 5.0125 h^{-1} with molar feed ratio 1:3 and shown in figure 4. The conversion decreases with increase in WHSV. Decreased adsorption of TBA on the Bronsted acid sites of the catalyst with increase in WHSV might be cause for the decrease in conversion. About 13% decrease in conversion when WHSV is changed from 3.3422 to 5.0125 h^{-1} observed. Such a high decrease in conversion therefore suggests much reluctance for TBA for chemisorptions on the bronsted acid sites of the catalyst. The low angle conversion at high space velocities could be accounted in terms of the shorter contact time: i.e., the less adsorption of TBA on the bronsted acid sites, which could be attributed to the side reaction (oligomerisation) of TBA [40]. The selectivity 2-TBA is not much varied irrespective of the magnitude of increase in WHSV. The selectivity to 4-TBA increases with increase WHSV due

Table 2
Products distribution of *tert*- butylation of anisole over Al-MCM-41 at different reaction temperatures, molar feed ratio = 1:3, WHSV = 3.3422 h^{-1}

Catalyst	Temperature °C	Conversion %	2-TBA	4-TBA	2,4-DTBA	Others
Si/Al = 25	150	72.64	11.81	61.60	20.17	6.42
	175	78.29	9.97	68.03	15.86	6.14
	200	70.63	8.52	72.70	12.0	6.78
	225	63.12	6.52	73.60	11.0	8.88
	250	55.44	4.52	78.10	9.0	8.48
Si/Al = 50	150	64.52	10.5	60.6	15.20	13.70
	175	70.27	8.45	66.2	13.34	12.01
	200	64.25	6.40	69.4	12.44	11.76
	225	48.75	5.81	72.2	10.60	11.39
	250	39.23	3.40	74.3	7.10	15.20
Si/Al = 100	150	51.16	9.84	58.40	14.70	17.06
	175	55.93	8.74	64.08	12.12	15.06
	200	38.82	8.14	67.50	11.01	13.35
	225	31.50	7.50	69.50	9.09	14.0
	250	25.72	6.50	70.10	8.20	15.2
Si/Al = 75	150	47.49	9.86	57.50	15.05	17.59
	175	53.54	8.13	59.18	14.67	18.02
	200	43.78	7.98	62.18	13.17	16.67
	225	35.64	6.35	64.27	12.0	17.38
	250	27.60	5.10	67.64	12.0	15.26

to reduced conversion of it to 2,4-DTBA. If the selectivity to 2-TBA, 4-TBA and 2, 4-DTBA is carefully analyzed, it will be evident that 2-TBA might not be making significant contribution of 2,4-DTBA as the selectivity of it is very less.

3.4. *Effect of mole ratio*

The conversion of anisole was studied at 175 °C over Al-MCM-41 (25) with the molar feed ratio 1:1, 1:2, 1:3 and WHSV 3.3422 h^{-1}. The results are illustrated in figure 5. Since the reaction requires formation of *tert*-butyl cation on the catalyst surface the conversion increases with increase in the tertiary butyl alcohol in the feed. If the difference in conversion between 1:1 and 1:2, and 1:2 and 1:3 is compared the former gives more increase in conversion than the later. Hence even at the molar feed ratio 1:2 almost all the bridged hydroxyls might be put to chemisorptions of TBA to give tertiary butyl cation. But at the molar feed ratio 1:3, there must be formation of nearly same number of *tert*-butyl cations even at molar feed ratio 1:3. So there must be slight excess unreacted TBA, which might be presumed to be not sufficient enough to dilute anisole by preventing electrophilic reaction with *tert*-butyl cation. Hence the conversion at molar feed ratio 1: 3 is not very high compared to 1:2. The selectivity to 2-TBA decrea-

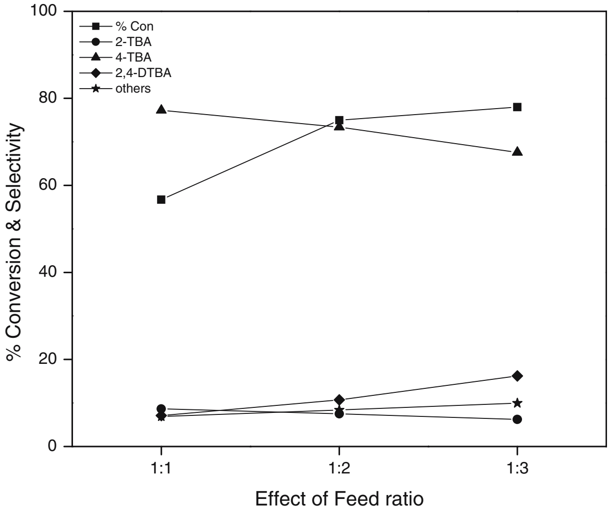


Figure 4. Effect of molar ratio on over *tert*-butylation of anisole Al-MCM-41 (25), Temperature = 175 °C, WHSV = 3.3422 h^{-1}.

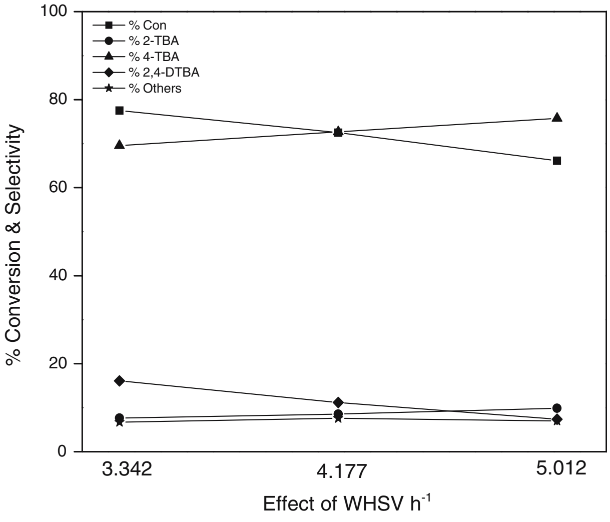


Figure 5. Effect of WHSV on conversion and product selectivity over Al-MCM-41 (25), molar feed ratio = 1:3, Temperature = 175 °C.

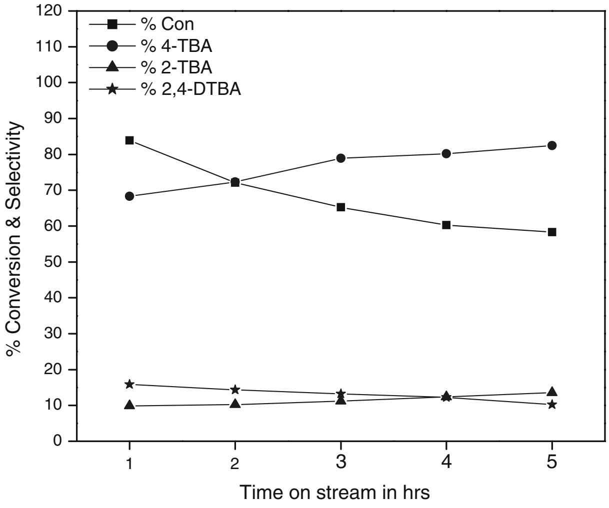


Figure 6. Effect of time on stream in *tert*-butylation of anisole over Al-MCM-41 (25), molar feed ratio = 1:3, WHSV = 3.3422 h^{-1}, Temperature = 175 °C.

ses but that of 2,4-DTBA increase with increases in the *tert*-butanol content in the feed. Hence 2-TBA might also be converted to 2,4-DTBA, as discussed in the effect of WHSV. The selectivity to 4-TBA decreases with the increase in the *tert*-butanol content in the feed. Hence for the increase in selectivity of 2,4-DTBA, 4-TBA might be the major contributor.

3.5. *Time on stream*

The effect of time on stream and the activity of catalyst Al-MCM-41 (25) was studied 175 °C with molar feed ratio 1:3 and WHSV 3.3422 h^{-1}. The results are illustrated in figure 6. The conversion of anisole decreases with increase in time on stream. It is due to coke formation. The catalyst appeared slightly black after 5 h of time on stream. But the decrease in anisole conversion is equal to 20%. This value appears to be not high as the materials are mesoporous by which coke formation is much discouraged. The selectivity of 4-TBA increases it is due to gradual decrease in its conversion to 2,4-DTBA. As expected, the selectivity of 2,4-DTBA also decreases with increase in time on stream. The selectivity of 2-TBA shows high increment with time on stream. It is also due to gradual decrease in its conversion to 2,4-DTBA with increase in time on stream. The enhanced *p*-selectivity with time can be accounted in terms of coke induced *p*-selectivity. During time on stream, the coke formed over the catalysts block the pores and the narrow the pore size, which favors para products.

4. Conclusion

From this study it is concluded that running the reaction at 175 °C can enhance the selectivity of 4-TBA. High temperature around 300 °C may not be advised, as anisole is converted into phenol. The selectivity of 2-TBA can be suppressed by running the reaction at high temperature. In addition, partial blocking of active sites can be more beneficial in getting 4-TBA with high selectivity.

Acknowledgments

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