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Acylation of anisole with long-chain carboxylic acids over wide pore zeolites

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Abstract

The acylation of anisole with long-chain carboxylic acids (hexanoic, octanoic and decanoic) has been studied over three large pore zeolites—beta (BEA), faujasite (FAU) and mordenite (MOR). The acylation of anisole with the long chain acids produced mainly the ketone (4-methoxy phenyl alkyl ketone) and small amounts of the ester (phenyl alkanoate). The results revealed the reaction to be influenced by the type of zeolite and its Si/Al ratio (acidity) besides the chain length (carbon number) of the carboxylic acid. In the acylation of anisole with hexanoic acid, the activity of the zeolites increased with dealumination as it led to the generation of mesopores that resulted in a decrease in diffusion resistance of the zeolites. The reactivity of the acids in the acylation reaction was found to decrease with increase in the carbon number. The experimental data have been fitted into a pseudo first order kinetic model.

Keywords: Acylation; Anisole; Hexanoic acid; Octanoic acid; Decanoic acid; Zeolites

1. Introduction

Friedel-Crafts acylation of aromatics with alkyl halides using mineral acid catalysts is widely practiced in the organic chemical industry. In view of the many disadvantages associated with mineral acids, efforts are on to find suitable recyclable and environment-friendly solid acid catalysts, which can successfully carry out acylation reactions with anhydrides and acids as acylating reagents. In this connection, many solid acid catalysts, including zeolites, have been reported to be suitable for carrying out the acylation of activated aromatic rings such as anisole with carboxylic acids [1–4]. Chiche et al. [5] studied the acylation of toluene and *p*-xylene with straight chain carboxylic acids catalyzed by CeNa–Y in the liquid phase. They observed a *para*-isomer yield of at least 94% with all the acids studied. The large positional selectivity was attributed by the authors to the shape selectivity of the zeolites. Gauthier et al. [6] investigated the activity of various cation exchanged zeolites in the acylation of toluene with octanoic acid and found the rare earth exchanged zeolites to be the most efficient catalysts.

Ma et al. [7] studied in detail the Friedel-Crafts acylation of anisole with alkanoic acids, anhydrides and substituted benzoic acids over zeolites. When carboxylic acids were used as acylating agents, the activity of the Y zeolite was related to its Lewis acidity. Freese et al. [8] have reported the Friedel-Crafts acylation of anisole by acetic anhydride and the Fries rearrangement of the ester (phenyl acetate) in the liquid phase over the H-form of various zeolites. Comparing the activities of NH_4–Y and H–Y, it appeared that the presence of Brönsted acid sites was a necessary prerequisite for catalytic activity. On the other hand, dealumination of H-beta (Si/Al = 90), i.e. a reduction of the number of Brönsted acid sites, increased the catalytic activity in the initial stages though the final conversion was similar to that of the parent BEA (Si/Al = 12). This behavior was attributed to different factors. Besides, the change in acidity, dealumination is accompanied by changes in pore distribution. The improved diffusion in the initial stages was suggested to lead to an initial higher activity until coking reactions became predominant. Consequently, the decrease in activity at longer run duration was attributed either to coke deposition or mass transfer limitations. Smith et al. have reported that H-beta can be recovered, regenerated and reused to give almost the same yield as that given by the fresh zeolite [9]. When Friedel-Crafts acylation of aromatics was performed

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with carboxylic acids over cation exchanged montmorillonite, the ketone yields were found to be dependent upon the nature of the interlayer cation and on the acid chain length [10]. The use of α,β-unsaturated organic acids such as acrylic, crotonic and methyl crotonic acids as acylating agents for the acylation of anisole over heteropoly acids (HPA) has been reported by Castro et al. [11].

The use of Fe or Zn salts impregnated on K-10 montmorillonite clays as acylation catalysts was studied by Yadav and Chandalia [12]. Studies on the benzoylation of toluene [13] over super acids have revealed that the yields of the products are higher when benzoyl chloride is used rather than the anhydride. Benzoylation of veratrole over large pore zeolites has been reported by Raja et al. [14]. Benzouhanova [15] studied the acylation of several substrates (benzene, naphthalene and aromatic heterocycles) over different zeolite catalysts using acid chlorides, anhydrides and carboxylic acids. The acylation of benzofuran and 2-methyl benzofuran in a fixed bed reactor over Y zeolite showed that 2-methyl benzofuran was twice as active as benzofuran [16]. An interesting study on catalyst deactivation during the acylation of anisole with acetic anhydride over zeolite beta has been reported by Rohan et al. [17]. The rapid catalyst deactivation that occurred was attributed, to a large extent, to the retention of di- and triacylated anisole in the large mesopore volume of the zeolite. A review of the acylation of several aromatic compounds has been presented by Jasra [18].

The literature cited above reveals that though data is available on the acylation of long-chain acids over FAU and BEA, direct comparisons of the activities of the large pore zeolites with different Si/Al ratios under similar reaction conditions is not available. Such data should enable in identifying the most suitable zeolite and Si/Al ratio for the acylation reaction. We now compare the activity of three large pore zeolites, BEA, FAU and MOR in the acylation of anisole with three long-chain carboxylic acids, hexanoic, octanoic and decanoic acids. The influence of various factors, such as the chain-length of the carboxylic acid, and the nature of the zeolite (its structure, Si/Al ratio and acidity) on the conversion of anisole is reported. A kinetic analysis of the reaction assuming a pseudo first order is also presented.

2. Experimental

2.1. Materials

H-beta (BEA(15); Si/Al = 15) and H-mordenite (MOR(11); Si/Al = 11) were obtained from PQ Zeolites. Dealuminated samples of BEA and MOR were prepared from these parent zeolites. Zeolite beta was dealuminated by heating at 358 K with 55 wt.% HNO_3 (60 g acid per g of zeolite) for 12 h. The dealuminated zeolite was repeatedly washed with deionised water and dried at 373 K. The procedure was repeated to obtain samples dealuminated to different extents. Mordenite samples with different Si/Al ratios were prepared by acid leaching (358 K) with 6 M hydrochloric acid for different time periods. The dealuminated samples were washed repeatedly with distilled water followed by dilute ammonia solution (1% solution) to remove residual acid and free aluminium species, and dried at 373 K for two hours. Samples of dealuminated faujasite (FAU) with Si/Al ratios of 6, 15 and 40 were procured from Zeolyst, Holland. All the catalysts were calcined in air at 723 K for 6 h prior to use in the reactions.

Hexanoic, octanoic and decanoic acids used in the experiments were obtained from s.d. Fine Chemicals (India), Merck (India) and Aldrich (USA), respectively.

2.2. Characterization

The parent zeolites and the dealuminated samples were characterized by different techniques. Compositional analyses of the zeolites were carried out by X-ray fluorescence (XRF) using a Rigaku 3070 X-ray wavelength dispersive spectrometer. The phase purity and crystallinity of the zeolites were examined by XRD (Rigaku, Miniflex) in the 2θ range of 5–50°. The total surface area of the samples was obtained from N_2 adsorption at liquid N_2 temperature by the BET method (Quantachrome, Nova 1200). As the BET method is not necessarily applicable in the case of zeolites, values for monolayer volume (V_m) were extracted from the initial section of the adsorption isotherms using the point-B method normally used in the case of Type-II isotherms [19]. The external area of the samples was obtained by the t-plot method. Acidity of the zeolite samples was characterized by the TPD of adsorbed NH_3 (Micromeritics, Autochem Z910). The standard procedure for TPD measurements involved the activation of the zeolite in flowing He at 873 K (3 h), cooling to 298 K and adsorbing NH_3 from a stream of He–NH_3 (10%), removing the physically adsorbed NH_3 by desorbing in He at 373 K for 1 h and finally carrying out the TPD experiment by raising the temperature of the catalyst in a programmed manner (10 K min^{-1}). The acidity of the samples was estimated from the area under the TPD plots based on injection of known volumes of the He–NH_3 mixture at similar conditions.

2.3. Acylation of anisole

The reactions were carried out in a two-necked RB flask using anisole (0.02 mol) and carboxylic acid (0.005 mol) with 0.15 g of freshly calcined H-forms of the zeolites as catalysts, in N_2 atmosphere. An excess of anisole was used in the studies to prevent diacylation reactions. Besides, anisole itself acted as the solvent. The reaction mixture was stirred with a magnetic stirrer and heated by immersion in a silicon oil bath. Aliquots of the reaction were collected at different time intervals and analyzed by gas chromatography (Varian Star 3400 C_X; capillary column: CP Sil 5CB, 30 m and i.d. 0.05 mm). The reaction products were identified by GC-MS and GC-IR. The conversions were calculated based on the acid.

2.4. Kinetics

Acylation reactions were carried out using hexanoic, octanoic and decanoic acids. As anisole was used in excess (mole ratio of anisole to acid = 4:1) in all the experiments, these were considered as pseudo first order reactions with respect to the acid. So the standard first order reaction rate expression

$$-\ln(1 - X_A) = kt$$

was used for the kinetic analysis of the reaction and the activation energy of the reaction was estimated using the Arrhenius expression

$$k = k_0\,e^{(-E/RT)}$$

where k_0 is the frequency factor, E the activation energy, R the universal gas constant and T is the reaction temperature.

3. Results and discussion

3.1. Physicochemical characterization

The XRD patterns of all the dealuminated samples were similar to the parent sample. The crystallinity of the samples was not significantly affected by dealumination, the intensities of the prominent lines being within 10% of those of the parent sample. The total surface area, external surface area (by the t-plot method) and the pore volume of zeolites with different Si/Al ratios are given in Table 1 [20]. Surface areas of the samples were obtained by the BET and the point-B methods. The values obtained by the point-B method were slightly larger than those from the BET method, the difference being about 3.8% for BEA(15), 5.5% for MOR(11) and 5.1% for FAU(6). The external surface areas are derived from the external surface of the crystallites, mesopores in the crystallites and amorphous material. The external area of the beta samples is large, being ~17 to 25% of the total area. The external area of the other zeolite samples is lower, contributing to about 7–13% of the total area. The small decrease in the external area on dealumination observed in the case of BEA may be due to the leaching out of amorphous material by the nitric acid. In the case of the other zeolites, the external area generally increased due to the formation of intracrystalline mesopores and crystal damage during dealumination. The acidity of the different samples based on the area of the TPD peaks (converted into mequiv./g) is also reported in Table 1. The acidity of the three zeolites (BEA, FAU and MOR) is related to their Al-content. The characteristics of the zeolite samples have already been described in greater detail by us in earlier publications [20,21].

Table 1
Physicochemical properties of the zeolite catalysts

Sample	Si/Al	Pore volume (cc/g)	Surface area (m^2/g) S_{BET}[a]	Surface area (m^2/g) S_B[b]	Surface area (m^2/g) External	Acidity (mequiv./g)[c]
Zeolite beta						
BEA(15)	15	0.32	656	681	166	1.22
BEA(34)	34	0.36	754	800	150	0.51
BEA(48)	48	0.35	760	795	128	0.39
Mordenite						
MOR(11)	11	0.24	562	593	52	1.87
MOR(29)	29	0.23	550	566	53	1.45
MOR(57)	57	0.24	564	580	57	0.99
Faujasite (Y zeolite)						
FAU(6)	6	0.32	749	787	53	1.31
FAU(15)	15	0.31	697	728	93	0.58
FAU(40)	40	0.34	747	782	77	0.26

[a] Obtained by BET method.
[b] Obtained by point-B method.
[c] Based on total area under TPD plots.

3.2. Acylation of anisole

The acylation of anisole was carried out with three different long chain acids, hexanoic, octanoic and decanoic, in the temperature range of 403–428 K and different mole ratios of anisole to acid (2–8) over FAU, BEA and MOR with different Si/Al ratios. The reactions were generally conducted over a period of 6 h. The acylation was found to occur predominantly at the *p*-position and 4-methoxy phenyl alkyl ketone was the major product along with very small amounts (less than 1% in most experiments) of the *o*-isomer (2-methoxy phenyl alkyl ketone) and small amounts (less than 5%) of the ester (phenyl alkanoate). The formation of the *m*-isomer was not noticed at the experimental conditions. Some workers have reported the formation of small amounts (a few percent) of the *o*- and *m*-isomers [7,8] while others [5,9] have not reported their formation. It appears that the formation of *o*- and *m*-isomers is favored when anhydrides are used as the acylating agents [8]. The ester product was formed in small amounts (a few percent) in all our experiments. The formation of the ester is a result of the demethylation of anisole and esterification of the phenol formed as the anisole used in our experiments did not contain any detectable amount of phenol as impurity. It is also possible that the formation of phenol occurred by bimolecular disproportionation of anisole on the acid sites. However, as methyl anisoles were not noticed in the products, this reaction is not the likely source of phenol. Diacylation products were not detected, as the acid was the limiting reactant in the experiments.

FAU has a three-dimensional (3D) intersecting pore system made up of interlinked α-cages (diameter ~12 Å) through 12MR (12-membered ring) windows of diameter 7.4 Å. Essentially, FAU has 3D intersecting pores with 7.4 Å openings. BEA has a 3D intersecting pore system with pore openings (12MR) of 6.6 Å × 6.7 Å in two directions and 5.6 Å × 5.6 Å in the third direction. MOR has 12MR pores with dimensions 6.5 Å × 7.0 Å in one direction only with 8MR pores (3.4 Å × 4.8 Å) intersecting the 12MR pores [22]. Generally, commercially available FAU in the as-synthesized form has a Si/Al ratio typically between 2.2 and 2.6, while BEA and MOR are usually synthesized with Si/Al ratios between 8 and 20 and 5 and 15, respectively. All the zeolites can be dealuminated by steaming (typically for FAU) or acid extraction (for BEA and MOR) to give products with higher Si/Al ratios than the parent zeolites; the severity of the steaming and extraction procedures will determine the final Si/Al ratios of the product. During the steaming and extraction procedures slight destruction of the framework structure occurs creating mesopores in the zeolite crystallites enabling faster diffusion of

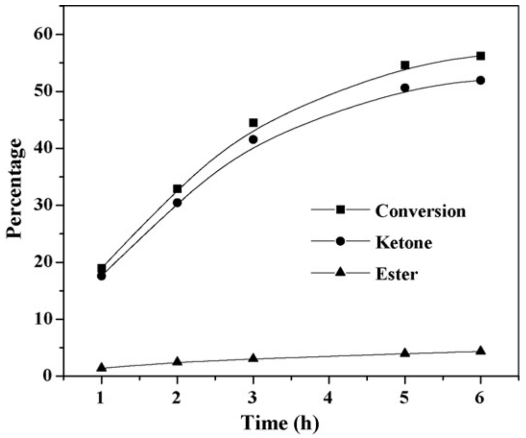

Fig. 1. Influence of run duration on the conversion of the acid, and yields (based on acid) of ketone and ester in the acylation of anisole with hexanoic acid, expressed as mol% (reaction temperature: 428 K, catalyst: BEA(15), 30 g/mol acid; anisole:hexanoic acid (mol) = 4:1).

the reactant molecules in the dealuminated samples than the parent ones [23]. Similarly, small amounts of extra-framework aluminum ions may also be formed in the dealuminated products [23].

3.2.1. Hexanoic acid

The influence of run duration on the acylation of anisole (at 428 K) with hexanoic acid over BEA(15) is presented in Fig. 1. The reaction proceeds rapidly in the beginning and slows down after about 4 h, and produces predominantly 4-methoxyphenyl hexyl ketone along with small amounts of the ester (phenyl hexanoate). As the ester formation is noticed from the beginning, it is also, apparently, a primary product formed from anisole. The influence of catalyst (BEA(15)) amount on the reaction is presented in Fig. 2. A three-fold increase in catalyst amount from 10 to 30 g catalyst/mol acid increases conversion by only about 1.3 times. Such limited increase with catalyst loading is often noticed in liquid phase reactions and could be a result of thermodynamic or diffusion limitations [8]. All further experiments in this study were carried out using 30 g of catalyst per mol of the acid. The influence of anisole:hexanoic acid mole ratio on conversion and product yields over BEA(15) is presented in Fig. 3. A general increase in the conversion of the acid and ketone yield is noticed with increase in the amount of anisole, the increase being small beyond an anisole:acid mole ratio of 4. However, the increase in the ester yield is small suggesting a small and nearly constant demethylation of anisole over the catalyst. All further studies were carried out at a mole ratio (anisole:acid) of 4.

The influence of temperature on the reaction over BEA(15) is presented in Fig. 4. A rapid increase in conversion, along with increase in the yields of both the ketone and the ester, is noticed with increase in temperature. A kinetic analysis of the reaction was carried out assuming a pseudo-first order reaction and the activation energy (E_a) for the reaction was calculated from the k values at the different temperatures. The E_a values are 22.4, 22.5 and 15.8 kcal mol^{-1} for the overall reaction, for the formation of the ketone and the ester, respectively.

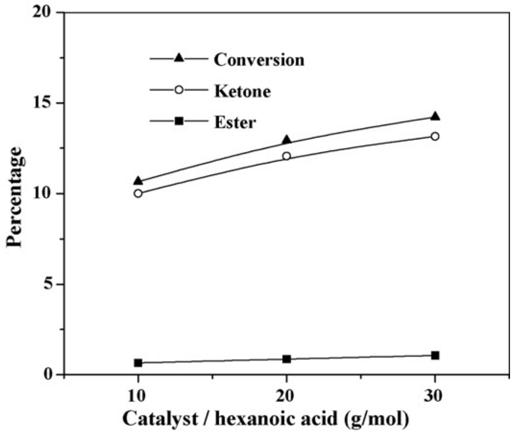

Fig. 2. Influence of catalyst/substrate (hexanoic acid) ratio (g/mol) on conversion of the acid, and yields (based on acid) of ketone and ester in the acylation of anisole with hexanoic acid, expressed as mol% (catalyst: BEA(15), temperature: 413 K, anisole:hexanoic acid (mol) = 4:1).

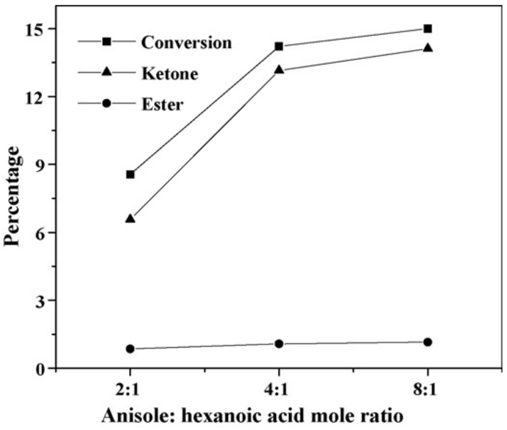

Fig. 3. Influence of anisole to hexanoic acid mole ratio on conversion of the acid, and yields (based on acid) of ketone and ester in the acylation of anisole with hexanoic acid, expressed as mol% (catalyst: BEA(15), 30 g/mol acid; temperature: 413 K; run duration: 3 h).

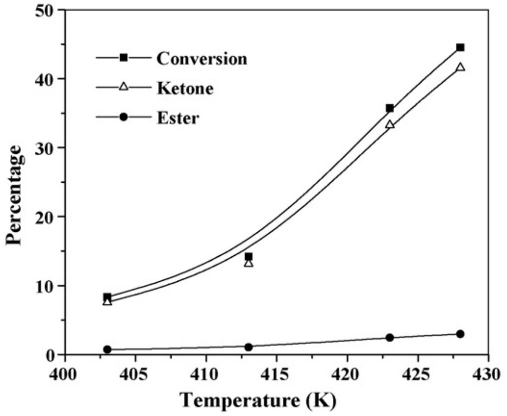

Fig. 4. Influence of temperature on conversion of the acid, and yields (based on acid) of ketone and ester in the acylation of anisole with hexanoic acid, expressed as mol% (catalyst: BEA(15), 30 g/mol acid; anisole:hexanoic acid (mol) = 4:1; TOS: 3 h).

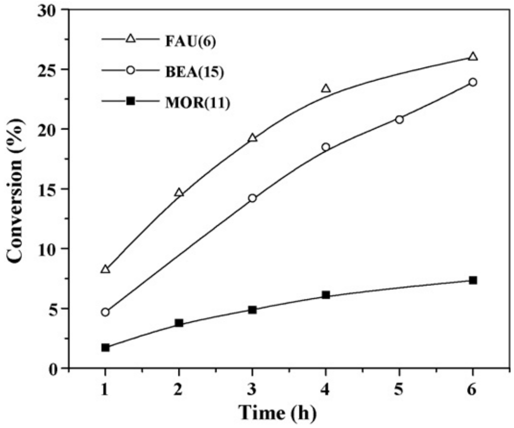

Fig. 5. Influence of run duration on conversion of hexanoic acid over FAU(6), MOR(11) and BEA(15) (catalyst amount = 30 g/mol acid, temperature: 413 K; anisole:hexanoic acid (mol) = 4:1).

The reaction was also investigated over MOR, FAU and BEA with similar Si/Al ratios. A plot of the activity of the three zeolites (at 413 K) is presented as a function of run duration in Fig. 5. At this temperature, the activity of the zeolites is in the order, FAU(6) > BEA(15) > MOR(11). This observed order is due to the effects of both zeolite structure and Al-content. The influence of Al content of the three zeolites on conversion and overall reaction rate constant is presented in Fig. 6a and b, respectively. In the case of BEA, a rapid increase in conversion (or k) is noticed with decrease in Al content, i.e. increasing dealumination. A similar, but less pronounced, trend is found in the case of FAU. The performance of MOR is not much influenced by the Al content, though its low activity (less than 5%) makes accurate comparisons between the three dealuminated MOR samples difficult. Corresponding plots of k values as a function of the acidity of the three zeolites are presented in Fig. 6c. These plots also show similar trends as the conversion and rate data. The increase in activity with Si/Al ratio (or decreasing acidity) in the case of all the three zeolites is surprising as one would expect the activity to decrease with decreasing acidity (increase in Si/Al ratio). We reported similar inverse trends in the Claisen rearrangement of allyl phenyl ether [20] and attributed this trend to the creation of mesopores in the dealuminated samples and the ease of diffusion of the reactants and products. Ma et al. have reported a similar trend during the acylation of anisole with propionic acid in a batch reactor in the absence of a solvent [7] over FAU samples with different Si/Al ratios. They have attributed the increase in activity on dealumination to the creation of Lewis acid centers. Freese et al. also reported an increase in the initial activity of BEA (Si/Al = 12) on dealumination (to Si/Al = 90) and attributed it to the creation of mesopores and increased mass transfer in the dealuminated sample [8]. Though both the above reasons are likely, as the NMR data did not show an increase in extra frame work Al-species (that are generally attributed to the creation of Lewis acidity) in our dealuminated samples [20], it is likely that the increase in the activity of the zeolites on dealumination is due primarily to the creation of mesorpores that cause an increase in mass transfer.

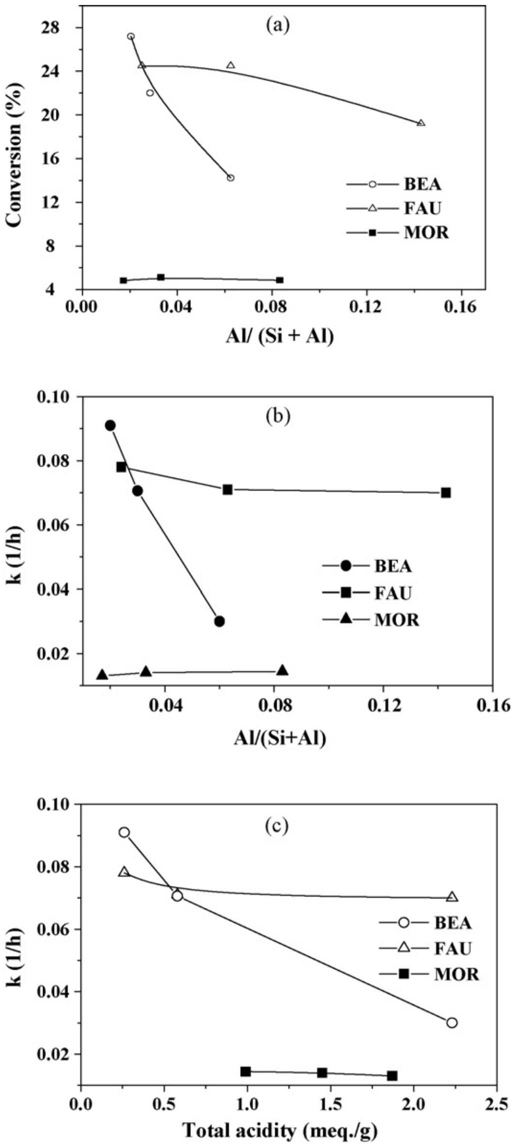

Fig. 6. Acylation of anisole with hexanoic acid: influence of Al content of zeolites BEA, FAU and MOR on conversion at TOS = 3 h (a) and on overall reaction rate constant (b); influence of acidity on overall reaction rate constants (c) (catalyst amount = 30 g/mol acid; temperature: 413 K; anisole:hexanoic acid (mol) = 4:1).

Based on the kinetic data obtained at different Si/Al ratios of the zeolites (Fig. 6b), the activity of the three zeolites at two constant Al contents (Al/(Si+ Al) ratio of 0.06 and 0.02; Si/Al = 16 and 49, respectively) is reported in terms of the rate constants in Table 2. As the highest Si/Al ratios of FAU and BEA samples were only 40 and 48, a small amount of extrapolation of the data of Fig. 6b was carried out to get relative activity data at Si/Al = 49 (Al/(Si + Al) = 0.02). This slight extrapolation shows that at very high Si/Al ratios (Si/Al > 40) BEA overtakes FAU in activity and that highly dealuminated BEA is a better catalyst than FAU. The order of activity is FAU > BEA > MOR at a Si/Al of 16 and BEA > FAU > MOR at a Si/Al of 49. At the same Al/(Si + Al) ratio of 0.06, FAU is about 2.2 times more active than BEA, while it is about five times more active than MOR. However, at

Table 2
Comparison of the activity of BEA, FAU and MOR at constant Al contents

Zeolite	Al/(Si + Al)[a]	Rate constant, *k* (1/h)		
		Ester	Ketone	Overall
BEA	0.06	0.002	0.030	0.032
FAU	0.06	0.002	0.069	0.071
MOR	0.06	0.001	0.014	0.014
BEA	0.02	0.006	0.083	0.091
FAU	0.02	0.001	0.076	0.078
MOR	0.02	0.0004	0.013	0.013

[a] Based on data of Fig. 6b. In the case of BEA and FAU, slight extrapolation of the data of Fig. 6b has been done to get rate constants at Al/(Si + Al) = 0.02. Reaction conditions: given in Fig. 6.

the Al/(Si + Al) ratio of 0.02, BEA and FAU possess nearly similar activities, BEA being slightly more active (by about 17%) than FAU. However, they are six to seven times more active than MOR. The large activities of BEA and FAU are attributed to their large 3D channels; the low activity observed over MOR is due to the diffusion effects in its narrow one-dimensional channels. The larger activity of FAU compared to BEA at Si/Al = 16 is due to the fact that the FAU (Si/Al = 16) is a dealuminated sample (Si/Al of a typical as synthesized Y zeolite is ~2.6) with large number of mesopores that enable easy access of the active centers to the reactant molecules, while the BEA sample is an as synthesized material (Si/Al ~15) with few mesopores. At Si/Al ~49, both FAU and BEA possess substantial mesopores (due to dealumination) and exhibit nearly similar activity, BEA being superior to FAU.

3.2.2. Octanoic and decanoic acids

The influence of temperature on conversion and product yields in the acylation of anisole with octanoic and decanoic acids is presented in Fig. 7a and b. A general increase in conversion and product yields with increase in temperature is observed. A comparison of the activity of the three zeolites (BEA(15), FAU(6) and MOR(11)) for the acylation of anisole with octanoic and decanoic acids is presented in Fig. 8a and b. The detailed product distribution obtained over the three zeolites for all the three substrates is presented in Table 3. An activity order similar to that noticed in the case of hexanoic acid is found in the case of octanoic acid: FAU(6) > BEA(15) > MOR(11). For decanoic acid, it is slightly different, being BEA(15) > FAU(6) > MOR(11). The exact reason for the difference in the case of decanoic acid is not clear, though it could be related to differences in the diffusivity of the longer decanoic acid in the

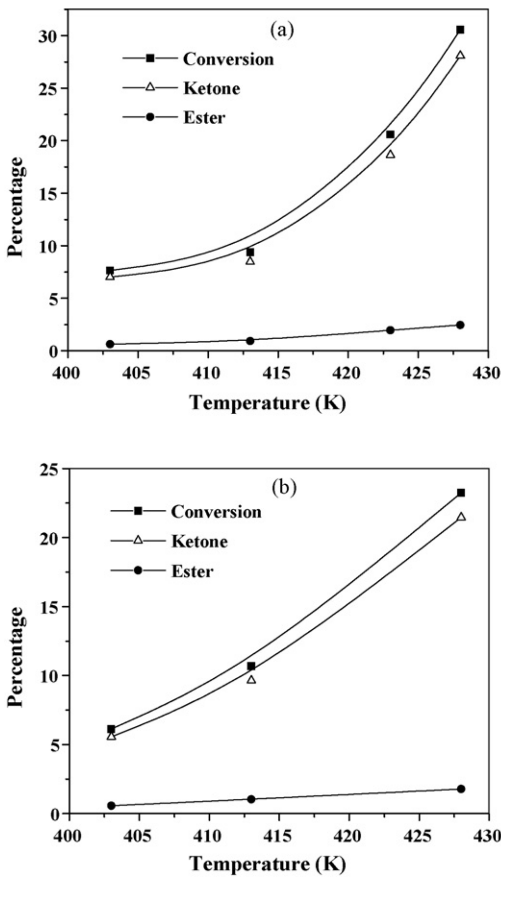

Fig. 7. Influence of temperature on conversion and product yields in the acylation of anisole with (a) octanoic acid and (b) decanoic acid (catalyst = -BEA(15), 30 g/mol acid; temperature: 413 K; anisole:acid (mol) = 4:1, TOS = 3 h).

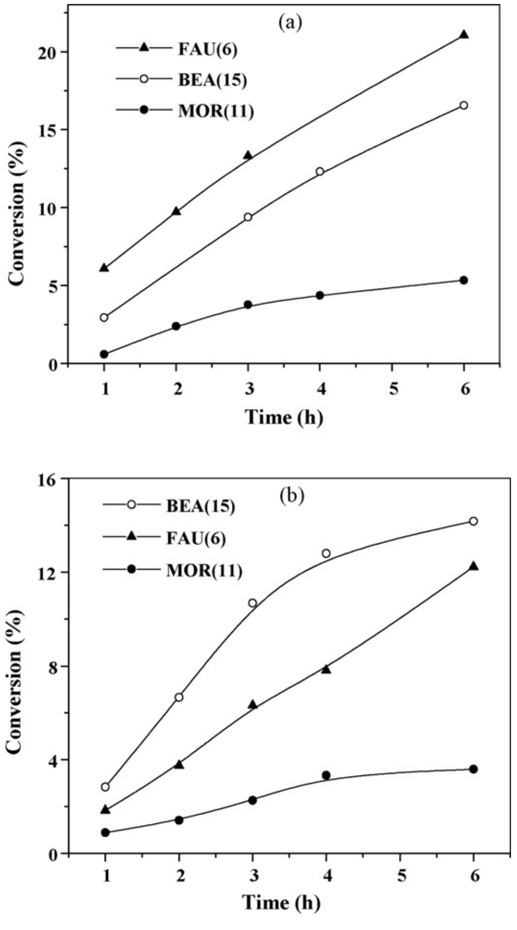

Fig. 8. Comparison of the activity of the three zeolites (BEA(15), FAU(15) and MOR(11)) in the acylation of anisole with (a) octanoic acid and (b) decanoic acid (catalyst amount = 30 g/mol acid; temperature: 413 K; anisole:acid (mol) = 4:1).

Table 3
Comparison of zeolites BEA(15), MOR(11) and FAU(6) in the acylation of anisole with long chain acids (catalyst amount = 30 g/mol acid; temperature = 413 K; anisole:acid = 4:1; TOS = 6 h)

Catalyst	Hexanoic acid				Octanoic acid				Decanoic acid			
	Conversion (mol%)	Product distribution (mol%)			Conversion (mol%)	Product distribution (mol%)			Conversion (mol%)	Product distribution (mol%)		
		o-[a]	*p*-[b]	Ester		*o*-[a]	*p*-[b]	Ester		*o*-[a]	*p*-[b]	Ester
BEA(15)	23.9	0.5	21.5	1.9	16.5	0.5	14.4	1.6	14.2	0.4	12.4	1.4
MOR(11)	7.4	0	7.0	0.4	5.3	0	4.9	0.4	3.6	0	2.9	0.7
FAU(6)	26.0	0.6	24.0	1.4	21.1	0.5	18.7	1.9	12.2	0.6	10.1	1.5

[a] 2-Methoxy phenyl alkyl ketone.
[b] 4-Methoxy phenyl alkyl ketone.

Table 4
Comparison of the reactivity of hexanoic, octanoic and decanoic acids, at different temperatures in the acylation of anisole (catalyst = BEA(15), 30 g/mol acid; anisole:acid (mol) = 4:1; TOS = 6 h)

Temperature (K)	Hexanoic acid				Octanoic acid				Decanoic acid			
	Conversion (mol%)	Product distribution (mol%)			Conversion (mol%)	Product distribution (mol%)			Conversion (mol%)	Product distribution (mol%)		
		o-[a]	*p*-[b]	Ester		*o*-[a]	*p*-[b]	Ester		*o*-[a]	*p*-[b]	Ester
403	17.0	0.3	15.2	1.5	12.3	0.3	11.0	1.0	10.8	0.3	9.5	1.0
413	23.9	0.5	21.5	1.9	16.5	0.5	14.4	1.6	14.2	0.4	12.4	1.4
423	44.2	0.8	40.6	2.8	35.2	0.8	31.0	3.4	22.5	1.0	20.0	1.5
428	56.3	1.0	51.0	4.3	42.6	1.0	38.0	3.6	31.1	1.2	27.7	2.2

[a] 2-Methoxy phenyl alkyl ketone.
[b] 4-Methoxy phenyl alkyl ketone.

two zeolites or differences in the hydrophilicity of the two zeolites leading to differences in the adsorption of the more hydrophobic decanoic acid.

A comparison of the reactivity of the three acids, hexanoic, octanoic and decanoic over BEA(15), at different temperatures is presented in Table 4. The *p*-isomer is the major product in all the cases along with a small amount of the *o*-isomer (Table 4). The reactivity of the acid is found to decrease with its C-number at all the temperatures. The decrease is probably due to a decrease in diffusivity with increase in the molecular size of the acid. Based on the data obtained at different temperatures and at different run durations, the reaction rate constants (k) were calculated. The k-values and the conversion decrease generally with increasing C-number. The activation energy values (E_a) calculated from the k-values are presented in Fig. 9 as a function of the C-number of the acid. It is noticed that the E_a values decrease with increasing C-number for ketone formation and for the overall reaction, indicating the increasing influence of mass transfer on the reaction. However, E_a for ester formation is not significantly dependent on the C-number of the acid.

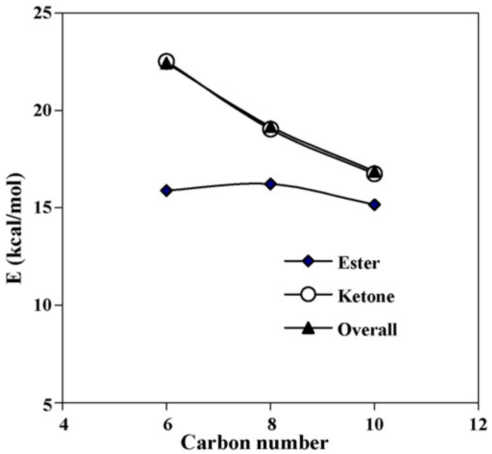

Fig. 9. The variation of the activation energy with the number of carbon atoms in the carboxylic acid in the acylation of anisole (catalyst = BEA(15), 30 g/mol acid; temperature: 413 K; anisole:acid (mol) = 4:1).

4. Conclusions

The acylation of anisole with long chain carboxylic acids (hexanoic, octanoic and decanoic) has been investigated over the large pore zeolites BEA, FAU and MOR. The products of the reaction are the ketone (major) and the ester (minor). Acylation occurs predominantly at the 4-(*p*-) position with small amounts of the *o*-isomer also being formed. The activity of BEA increases with dealumination during acylation with hexanoic acid. This is attributed to the generation of mesopores during dealumination and the corresponding ease of diffusion of the reactants and products. The reactivity of the acid decreases with carbon number due (presumably) to increasing diffusion resistance with C-number. The orders of the activity of the three zeolites are similar for hexanoic acid and octanoic acid (FAU(6) > BEA(15) > MOR(11)) but different for decanoic acid (BEA(15) > (FAU(6) > MOR(11)). A comparison of the activities (reaction rate constants) of the zeolites at the same Si/Al ratio of 49 reveals that BEA is about seven times more active than MOR and about 17% more active than FAU in the acylation of anisole with hexanoic acid. But at a Si/Al ratio of 16, FAU is about 2.2 and five times more active than BEA and MOR, respectively, for the same reaction.

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