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 NH₄–Y and H–Y, it appeared that the presence of Brønsted 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 Brønsted 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...
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 dealoylation 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. Benzylation 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 benzo furan and 2-methyl benzo furan in a fixed bed reactor over Y zeolite showed that 2-methyl benzo furan was twice as active as benzo furan [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.% HNO₃ (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 N₂ adsorption at liquid N₂ 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 (Vₒ) 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 NH₃ (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 NH₃ from a stream of He–NH₃ (10%), removing the physically adsorbed NH₃ 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–NH₃ 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 N₂ 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 Cx; 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
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