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Benzoylation of substituted arenes using Zn-and Fe-exchanged zeolites as catalysts

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Abstract

The benzoylation of substituted arenes using benzoyl chloride has been investigated for Zn- and Fe- exchanged zeolites (H-ZSM-5, mordenite and zeolite Y). Toluene benzoylation preferentially gave 4-methylbenzophenone for all zeolites. The Zn-exchanged zeolites were more active than the proton forms of zeolites, but gave the same product selectivity, and it has been shown that extensive leaching of Zn^{2+} cations into solution occurs, particularly when zinc acetate is used to prepare the catalyst. For the Zn-exchanged zeolites it is concluded that a significant proportion of the reaction occurs in solution. However, Fe-exchanged zeolites gave only limited leaching of Fe cations into solution and in this case the cation-exchanged zeolite acts as a heterogeneous catalyst. The Fe-Na-Y has been shown to give high yields of substituted benzophenones for a range of substrates. The form of conversion/time curves is consistent with the existence of two types of catalytic site. One type appears to be inhibited by the product benzophenone and is responsible for the initial rapid rate of conversion. The other is not inhibited, giving rise to an approximately constant, slower reaction rate in the later stages.

Keywords: Benzoylation; Zeolites; Catalysts

1. Introduction

Acylation of arenes is a key step in the manufacture of aromatic ketones which are used as intermediates in the fine chemical and pharmaceutical industries. For example, they are components in the synthesis of ibrupofen, *S*-naproxen and the musk fragrance. These acylations are carried out industrially using conventional Lewis acid catalysts, such as $AlCl_3$, which is usually used in above stoichiometric amounts. These processes generate a high volume of waste material and with the current drive towards "green chemistry" it is recognised that there is a need to replace the conventional Lewis acid catalysts with re-usable, environmentally friendly catalysts that generate minimal waste by-products. In this respect, zeolites have received significant attention since Chiche and co-workers [1,2] showed that rare-earth-exchanged zeolite Y could catalyse the acylation of alkylbenzenes with carboxylic acids. This has prompted a number of studies using carboxylic acids [3–7] and acid anhydrides [7–10] as acylating agents. Although, acid chlorides can be considered the least environmentally friendly acylating agent, it has been shown that, in combination with a regenerable zeolite catalyst, acid chlorides can substantially decrease the chloride waste when compared with the $AlCl_3$ catalyst. Acylation

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of 1,3-dimethylbenzene using benzoyl chloride has been reported by Fang et al. [11] using dealuminated zeolited Y as catalyst. Singh and co-workers [12,13] have similarly reported the use of zeolite H-β for the acylation of benzene and toluene. The H-β has been found to exhibit shape selectivity for the acylation of naphthalene using benzoyl chloride [14] as 2- benzoylnaphthalene is the major product. van Bekkum and co-workers [5,10] have shown that Zn-exchanged zeolites are more active than the corresponding proton forms, but loss of Zn^{2+} into solution by leaching was observed. Similar findings have been reported by Spagnol and co-workers [15,16]. In this paper, we compare Zn- and Fe-exchanged zeolites as catalysts for the benzoylation of substituted arenes and demonstrate that Fe-exchanged zeolite Y is an active heterogeneous catalyst that gives minimal leaching of the cations into solution.

2. Experimental

2.1. Catalyst preparation

The proton form of the zeolites (H-ZSM-5, H-MOR, H-Y) were prepared by calcination (500°C, 24 h) of the corresponding ammonium-exchanged zeolite (NH_4-ZSM-5, Si/Al = 17.5, PQ Chemicals; NH_4-mordenite, Si/Al = 10, Laporte; NH_4-Y, Si/Al = 2.5, Union Carbide). The Na-Y (Si/Al = 2.6, Uniliver) was used as supplied.

Zinc-exchanged zeolites were prepared according to the following procedure. The dried H/Na-zeolites (200°C, 5 h) were stirred in aqueous zinc nitrate or acetate (0.1 M) at 100°C for 24 h. The zeolite was recovered by filtration, washed with de-ionised water and dried (200°C, 5 h). The iron-exchanged zeolites were prepared in a similar manner using an aqueous solution of iron nitrate (0.1 M) at 25°C for 24 h. The zinc and iron contents were determined using atomic absorption spectroscopy.

2.2. Benzoylation reactions

The arene substrate (0.25 mol) and benzoyl chloride (0.05 mol) were refluxed together under nitrogen (to minimise the formation of benzoic acid) with the zeolite catalyst (0.85 g, pre-dried, 200°C, 5 h). Following reaction the mixture was cooled to 25°C and analysed using gas chromatography following the addition of biphenyl (0.5 g) as an internal standard. In some reactions, samples (0.05 ml) were removed from the reaction mixture at specific times, added to a solution of biphenyl in toluene (0.1 ml; biphenyl (0.5 g) in toluene (25 ml)), and again analysed by gas chromatography.

3. Results and discussion

The results for the benzoylation of toluene using zeolite catalysts are given in Table 1. The proton forms of the zeolite show a small amount of activity and the predominant product for all zeolites was 4- methylbenzophenone. The Zn-exchanged zeolites all showed much higher conversion levels similar to these shown by the use of zinc nitrate and zinc acetate as homogeneous catalysts. However, it is apparent that on use the zinc-exchanged zeolites leach considerable quantities of Zn^{2+} into solution. This is particularly the case when zinc acetate is used as the source of Zn^{2+} when compared with the nitrate-prepared Zn-zeolites. The catalytic results obtained with the zinc-exchanged zeolites are all consistent with the reaction occurring wholly in solution, catalysed by the leached Zn^{2+} acting homogeneously. This is consistent with previous studies [10,15] and confirms that zinc-exchanged zeolites are not stable as heterogeneous acylation catalysts.

In contrast, Fe-exchanged zeolites exhibit considerably higher stability and relatively low levels of iron are leached into solution (Table 1). The conversions observed with the Fe-exchanged zeolites are significantly higher than those that would have been expected if it was solely the solution iron species that was acting as the homogeneous catalyst. This is particularly exemplified by the Fe-Na-Y catalyst (containing 1.34×10^{-3} mol Fe) which gives a higher yield of benzophenone than that observed when $FeCl_3$ (1.52×10^{-3} mol Fe) is used as a homogeneous catalyst. The Fe-Na-Y catalyst gives a very high yield of the methylbenzophenone as the exclusive products, with 4-methyl benzophenone being produced in 77% yield. To achieve these high yields it is essential that the reactions are carried out under nitrogen, since in the absence of nitrogen by-product formation decreases the yield to ca. 40%. To demonstrate that the Fe-exchanged Fe-Na-Y

Table 1
Benzoylation of toluene with benzoyl chloride using metal-exchanged zeolites[a]

Catalyst	[M][b]/mol 10^{-4}		[M][c]	Conversion[d] (%)	Product Selectivity (%)		
	Before	After			2-	3-	4-
None	–	–	–	<1	–	–	–
H-ZSM-5	–	–	–	3	12	13	75
H-MOR	–	–	–	4	14	4	82
H-Y	–	–	–	4	19	6	75
Na-Y	–	–	–	1	–	–	–
$Zn(OAc)_2$	4.40	4.40	9049	31	25	3	73
$Zn(NO_3)_2$	4.40	4.40	9042	10	20	3	77
Zn-H-ZSM-5[e]	15.4	8.35	15000	43	21	2	77
Zn-H-MOR[e]	12.8	8.90	8300	22	21	3	76
Zn-H-MOR[f]	3.39	3.14	530	10	14	3	83
Zn-Na-Y[e]	16.7	11.6	10850	45	22	3	75
$FeCl_3$[g]	15.2	15.2	2843	91	15	3	82
Fe-H-ZSM-5	1.19	0.89	56	13	15	5	80
Fe-H-MOR	0.74	0.74	tr[h]	5	11	2	87
Fe-H-Y	8.0	7.2	148	51	17	2	81
Fe-Na-Y	13.4	13.0	74	96	17	3	80

[a] Toluene (0.25 mol), benzoyl chloride (0.05 mol), zeolite (0.85 g), 110°C, 24 h.
[b] The mol metal cation in reaction mixture. For zeolite catalyst: (before) total mol cation added with zeolite; (after) total present in zeolite at end of reaction. For homogeneously catalysed reaction: before and after signify solution concentration.
[c] The ppm metal cation present at end of reaction in solution.
[d] Conversion of benzoyl chloride.
[e] Prepared from acetate.
[f] Prepared from nitrate.
[g] 6 h reaction.
[h] tr: trace levels <10 ppm.

catalyst was acting heterogeneously, the following experiment was carried out. Toluene (25 ml) was refluxed at 110°C under nitrogen with benzoyl chloride (5 ml) and Fe-Na-Y catalyst (0.7 g, dried: 200°C, 20 h) for 30 h and the conversion of benzoyl chloride was monitored (Fig. 1). After the reaction, the zeolite was recovered by filtration and the filtrate was diluted with toluene to give a total volume of 25 ml, benzoyl chloride (5 ml) was added and mixture was refluxed under nitrogen for a further 30 h and the benzoyl chloride conversion was monitored (Fig. 1). The low conversion (ca. 3%) obtained from the filtrate confirms that the catalytic activity originates from Fe-Na-Y acting as a heterogeneous catalyst.

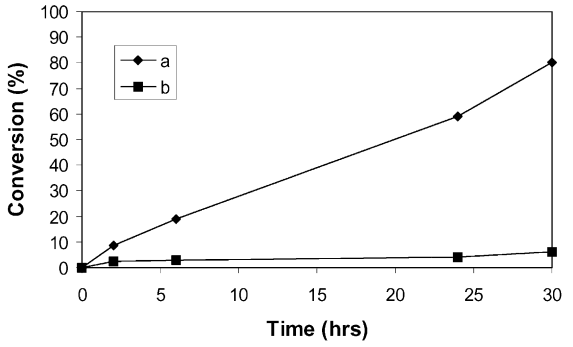

Fig. 1. Benzoylation of toluene at 110°C (a) Fe-Na-Y, (b) filtrate.

In a further set of experiments for the benzoylation of toluene, the conversion of benzoyl chloride was monitored over a 30 h reaction period under standard reaction conditions as specified in Table 1. The results, shown in Fig. 2 indicate that the reaction consists of two distinct stages: (a) an initial fast formation of methylbenzophenone, with the corresponding removal of benzoyl chloride, which accounts for ca. 20% of the total reaction and this occurs within the first 1–2 h of reaction time, and (b) a much slower reaction over the period 2–30 h which appears to follow zero order kinetics. Similar two stage reaction profiles

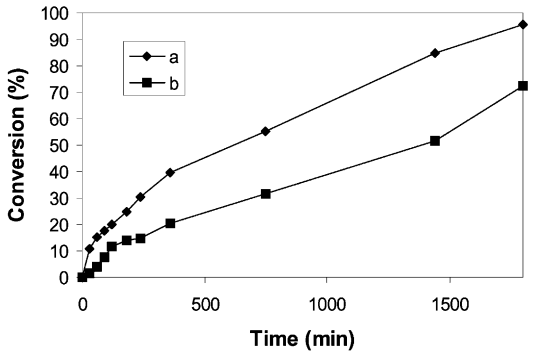

Fig. 2. Benzoylation of toluene at 110°C using Fe-Na-Y as catalyst: (a) without addition of 4-methylbenzophenone (b) with and.

with an initial rapid phase have also been observed by Singh and co-workers [12,14] for the benzoylation of benzene with benzoyl chloride using zeolite H-β as catalyst, and by Rohan et al. [17] for the acylation of anisole using acetyl chloride with zeolite La-Y as catalyst. Such phenomena could be indicative of product inhibition, especially since in the benzoylation of toluene the methylbenzophenone products are larger than either of the reactants and will be expected to exhibit a higher heat of adsorption; consequently the products will be preferentially adsorbed. To determine if the slower reaction rate observed after 2 h reaction time could be attributed to product inhibition, the reaction was repeated with 4-methylbenzophenone (in an amount equivalent to 20% conversion of benzoyl chloride) added to the mixture containing the zeolite at the beginning of the reaction. The mixture was stirred for 30 min prior to heating to the reaction temperature of 110°C. The results (Fig. 2) show that the initial fast reaction is not so pronounced and the reaction proceeds at a much slower rate, similar to that observed for stage (b) when no methylbenzophenone was added. We conclude that preferential adsorption of the product is the reason for this decrease in reaction rate. Indeed, the pattern of behaviour can be modelled on the basis that reaction takes place by two distinct pathways: (i) an initial, rapid reaction at catalytic sites where acylation is progressively inhibited by the product benzophenone; plus (ii) benzoylation involving catalytic sites that activate benzoyl chloride but are not subject to competitive adsorption by the product, leading to a roughly constant rate throughout the course of reaction. Stage (a) of the reactions corresponds to reaction through both pathways, while in stage (b) the faster pathway is completely inhibited and only reaction by the second pathway is observed. Recently, Derouane et al. [18] have shown a similar product-inhibiting effect as suggested for stage (a) in the acetylation of anisole using zeolite H-β as catalyst; addition of the product 4-methoxyacetophenone significantly decreased the initial rate of reaction. Derouane et al. [18] attribute this to a confinement effect in which the zeolites act as solid solvents with preference for the adsorption of the bulky products from these reactions.

Table 2
Benzoylation of arenes with benzoyl chloride using Fe-Na-Y[a]

Catalyst[b]	Substrate	Conversion[c] (%)	Product selectivity (%)		
			2-/2,3-	3-/3,4-	4-
$FeCl_3$[d]	Toluene	91	15	3	82
Fe-Na-Y	Toluene	96	17	3	80
$FeCl_3$[e]	Ethylbenzene	81	10	4	86
Fe-Na-Y	Ethylbenzene	92	11	4	85
$FeCl_3$[d]	*t*-butylbenzene	74	–	9	91
Fe-Na-Y	*t*-butylbenzene	64	–	9	91
$FeCl_3$[e]	1,2-dimethylbenzene	99	8	92	–
Fe-Na-Y	1,2-dimethylbenzene	93	8	92	–

[a] Substrate (0.25 mol), benzoyl chloride (0.05 mol), Fe-Na-Y (1.34×10^{-3} mol Fe), 110°C, 24 h.
[b] $FeCl_3 = 1.52 \times 10^{-3}$ mol Fe.
[c] Conversion of benzoyl chloride.
[d] 6 h reaction.
[e] 2.5 h reaction.

The benzoylation of a range of substituted benzenes was investigated with the Fe-Na-Y zeolite catalyst and the results are given in Table 2. Comparison with the homogeneous $FeCl_3$ catalyst shows that the heterogeneous catalyst gives very similar product yields and selectivities but at much longer reaction times.

The results of this study demonstrate that Fe-exchanged zeolites can act as effective heterogeneous benzoylation catalysts. Recently, He et al. [19] and Choudhary et al. [20] have shown that iron-containing zeolites are effective catalysts for the benzylation of benzene, and it is therefore clear that iron-exchanged zeolites may be able to play a more general role as heterogeneous Friedel–Crafts catalysts.

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