

## Regioselective Acylation of Anisole with Carboxylic Acids over HZSM-5 Catalyst

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Over a HZSM-5 catalyst, the liquid-phase acylation of anisole with carboxylic acid gave the phenyl carboxylic ester at lower temperatures (< 403 K) while at higher temperatures (> 423 K) 4-acyl anisole was the predominant product.

Friedel–Crafts acylation of aromatic rings has proved of great importance in fine chemical synthesis.<sup>1</sup> In order to avoid the disadvantages of using soluble Lewis acids (*e.g.* AlCl<sub>3</sub>) as ‘catalysts’ and acyl halides as the acylating agents, the use of acid zeolite (*e.g.* 1000 g per mole of reactant) as the catalyst has been studied over the past decade.<sup>2–4</sup> Here we report our preliminary results concerning the acylation of anisole with carboxylic acids over HZSM-5 zeolite.

The catalyst HZSM-5 (Si/Al = 30) was synthesised according to the Mobil method<sup>5</sup> and calcined in air at 773 K for 3 h immediately before use. The reaction was carried out in a batch reactor equipped with condenser, stirrer and water-segregator. Carboxylic acid (0.10 mol), anisole (0.12 mol) and HZSM-5 (3.0 g) were mixed in the reactor and heated to reflux. The resulting suspension was stirred under reflux for 48 h. The catalyst was then filtered and the solution analysed by GC and by titration with a KOH–EtOH solution (0.1 mol dm<sup>-3</sup>) to determine the conversion. The products were identified by GC-MS. The solution was then distilled and the structure of the pure product confirmed by <sup>1</sup>H NMR.

The results are listed in Table 1. HZSM-5 was the active catalyst for the reaction studied. From propanoic acid to stearic acid the conversion decreased from 92 to 0%. This order of activity of HZSM-5 was due to its small micropore size in which the formation of the larger product molecules was difficult (in the case of pentanoic to octanoic acid) or impossible (in the case of higher carboxylic acids). On the other hand, the poor conversion of acetic acid is explained by the low reflux temperature.

The acylation of anisole over HZSM-5 gave only two products: 4-acyl anisole and the phenyl carboxylic ester. Neither *ortho*- nor *meta*-acyl anisole were formed. Acylation could therefore occur at the oxygen atom of anisole as well as at the *para*-position of aromatic ring (*e.g.* the reaction of anisole with acetic acid lead almost completely to phenyl acetate, the *O*-acylation product;† the yield of 4-acetyl anisole was negligible). The selectivity of HZSM-5 for 4-acyl anisole increased from

0.5% with acetic acid to 60% with propanoic acid and finally reached 80% with butanoic or higher acids.

The above selectivity results hints that the ‘regioselective’ acylation of anisole over HZSM-5 might be performed by optimizing the reaction conditions. Thus the reaction of anisole (0.40 mol) with acetic, propanoic or butanoic acid (0.10 mol) over HZSM-5 (10 g) was carried out at different temperatures. The results are shown in Table 2. At lower temperature (393 K) the reaction gave the phenyl carboxylic ester with a selectivity higher than 70%. When the temperature increased from 393 to 423 K, the selectivity decreased to 37, 33 and 17% for acetate, propionate and butyrate respectively. Inversely the selectivity for 4-acyl anisole increased to a value higher than 60% at 423 K. Therefore at lower temperatures the *O*-acylation of anisole over HZSM-5 was predominant over the Friedel–Crafts acylation of the aromatic ring and *vice versa*. The activation energy of the *O*-acylation reaction was consequently lower than that of the

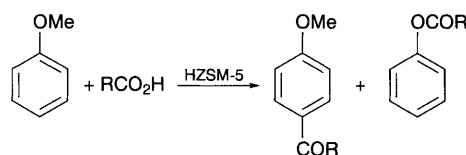
**Table 2** Results of the reaction of anisole (0.40 mol) with RCO<sub>2</sub>H (0.10 mol) over HZSM-5 (10 g) at various temperatures for 48 h

R	T/K	Conversion (mol%)	Product distribution (mol%)	
			<i>p</i> -RCOC <sub>6</sub> H <sub>4</sub> OMe	RCO <sub>2</sub> Ph
Me	393	29.2	1.1	98.9
	423 <sup>a</sup>	90.4	63.3	36.7
Et	393	32.6	26.9	73.1
	403	65.0	40.4	59.6
	418	98.2	58.0	42.0
	423	100 <sup>b</sup>	66.5	33.5
Pr	393	25.3	30.4	69.6
	418	64.2	66.8	33.2
	423	87.6	83.0	17.0

<sup>a</sup> Reaction carried out in autoclave (0.5 dm<sup>3</sup>). <sup>b</sup> 100% Conversion reached in only 29 h.

**Table 1** Results of the reaction of anisole (0.12 mol) with carboxylic acids (0.10 mol) over HZSM-5 (3.0 g) with a reaction time of 48 h

R	T/K	Conversion (mol%)	Product distribution (mol%)	
			<i>p</i> -RCOC <sub>6</sub> H <sub>4</sub> OMe	RCO <sub>2</sub> Ph
Me	393	5	0.5	99.5
Et	420	92	60.0	40.0
Pr	423	73	83.6	16.4
Bu	423	38	82.1	18.0
C <sub>5</sub> H <sub>11</sub>	423	24	83.0	17.0
C <sub>6</sub> H <sub>13</sub>	423	9.0	81.2	18.8
C <sub>7</sub> H <sub>15</sub>	423	5	80	20
C <sub>11</sub> H <sub>23</sub>	423	0.6	—	—
C <sub>17</sub> H <sub>35</sub>	423	0.8	—	—
Ph	423	0	—	—



Friedel–Crafts acylation reaction in the presence of HZSM-5 catalyst.

At the same temperature, the selectivity of HZSM-5 for 4-acyl anisole increased with the length of the carboxylic acid carbon chain. This implies that the attack of electrophilic species at the oxygen atom of anisole would lead to a more branched and large intermediate than that formed through attack at the *para*-position of the aromatic ring. The production of the phenyl carboxylic ester would therefore be more limited by the size of the micropores of HZSM-5 than the production of 4-acyl anisole. This type of 'shape selectivity' was due to the inherent pore structure of zeolite.

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#### Footnote

† Methyl acetate was also produced but in very small amounts compared to phenyl acetate. This was probably due to the low boiling point of methyl acetate.

#### References

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