Acylation of anisole using acid clay catalyst

Vasanti G Yadav & S B Chandalia
Chemical Engineering Division, University Department of Chemical Technology, University of Mumbai, Matunga 400 019, India
Received 3 May 1999; accepted 18 March 2000

In this investigation para-methoxy acetophenone an important perfumery and flavouring chemical was synthesized by acylation of anisole with acetic anhydride as acylating agent in nitrobenzene as a solvent at 138°C by using 10% Lewis acids such as ferric chloride or zinc chloride impregnated on K-10 montmorillonite clay as a catalyst. This process could be a better alternative to the conventional Friedel-Crafts reaction using more than stoichiometric quantity of anhydrous aluminium chloride. The catalyst could be reused with no significant effect on the conversion if it was again impregnated with ferric chloride or zinc chloride.

Para-methoxy acetophenone having sweet, somewhat harsh, hay like floral animal note is extensively used in soap formulations, as it is relatively stable in mild alkaline conditions, and as a flavouring chemical 1. Para-methoxy acetophenone is commonly synthesized by Friedel Crafts acylation of anisole by using anhydrous aluminium chloride as a catalyst and an acylating agent such as acyl halide or acetic anhydride. Although aluminium chloride is widely used in industry for liquid phase alkylations and in massive amounts in acylation reactions, this is environmentally deleterious and corrosive. Recently, a major development based on solid supported catalysts has made it possible to dispense with the use of aluminium chloride 2,3.

In this investigation para-methoxy acetophenone was synthesized by using Lewis acid such as anhydrous ferric chloride or zinc chloride impregnated on K-10 montmorillonite clay as catalyst and acetic anhydride as an acylating agent. The advantage of using clay as a catalyst is its surface acidity and the Lewis acidic sites which could be further increased by cation exchange of the interstitial cation with transition metal ions such as Fe3+, Zn2+ etc.

Corma et al.4 have discussed the mechanism when zeolites are used as catalysts and phenyl acetyl chloride as the acylating agent which may be adapted to the present system.

Experimental Procedure

Materials — Anisole, K-10 montmorillonite clay, ferric chloride (anhydrous), zinc chloride, acetic anhydride and acetonitrile were commercial preparations and were used without further purification.

Preparation of the catalyst — Pre-determined quantity of Lewis acid was dissolved in minimum quantity of acetonitrile in a beaker. In another beaker pre-determined quantity of K-10 montmorillonite clay was taken. Lewis acid dissolved in acetonitrile was added dropwise to the clay with vigorous stirring by glass rod. A semi-solid mixture was obtained. The mixture was dried at 100°C in an oven for 3 h and the dried solid was used as a catalyst.

Experimental set-up — Acylation of anisole was carried out in a borosilicate glass reactor, provided with a stirrer, baffles, a reflux condensor. The reactor was maintained at the desired temperature by immersing it in a constant temperature bath.

Procedure — Pre-determined amount of catalyst, acetic anhydride, anisole and the solvent were taken into the reactor. The reactor and its contents were heated to the required temperature.

Analysis — Samples of 1-2 mL from the reaction mixture withdrawn at regular time interval were analyzed by gas chromatography (Model: Perkin Elmer). The details are: Column used, S.S. Column, 3.2 mm i.d. × 2 m length containing 10% OV-17 on Chromsorb — W; Carrier gas, Nitrogen; Flow rate, 30 L/min; Detector, F.I.D.; Oven temperature, 100°C for 1 min, 10°C/min ramp, 300°C; Injector temperature, 300°C; Detector temperature, 300°C.

Results and Discussion

The terms employed for the discussion of the results are
Effect

The amount of reactant consumed for the catalyst, however, better results were obtained when K-10 montmorillonite clay was impregnated with zinc chloride or ferric chloride. The results for both the catalysts are given below.

Overall conversion — The overall conversion is defined as the ratio of total moles of substrate reacted to the moles of the substrate initially taken.

Conversion to product — The conversion to any given product is defined as the ratio of moles of substrate consumed for the formation of that product to the moles of substrate taken in the reactor.

Yield — The amount of reactant consumed for the formation of a particular product divided by the total amount of reactant consumed is defined as yield.

Acylation may be carried using K-10 as such as a catalyst, however, better results were obtained when K-10 montmorillonite clay was impregnated with zinc chloride or ferric chloride. The results for both the catalysts are given below.

Table 1 — Effect of solvent nitrobenzene

<table>
<thead>
<tr>
<th>Without nitrobenzene as solvent</th>
<th>Anisole, 8g, 3.704 × 10^3 gmoI/cc; acetic anhydride, 12.66 mL; 5.902 × 10^3 gmoI/cc; catalyst loading, 2 g, 0.1 g/cc; temperature, 138 °C; speed of agitation, 1300 rpm, time, 3 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>K-10 montmorillonite clay</td>
</tr>
<tr>
<td>% Conversion of anisole</td>
<td>22</td>
</tr>
<tr>
<td>% Yield of 4-methoxy acetophenone</td>
<td>98</td>
</tr>
<tr>
<td>Using nitrobenzene as solvent</td>
<td>Anisole, 4 g, 0.037 gmoI; 9.25 × 10^3 gmoI/cc; acetic anhydride, 7.6 g, 0.074 gmoI; 1.85 × 10^3 gmoI/cc; catalyst loading, 4 g, 0.1 g/cc; nitrobenzene, 40 mL (total volume); temperature, 138 °C; time, 2 h; speed of agitation, 1300 rpm</td>
</tr>
<tr>
<td>Catalyst</td>
<td>K-10 montmorillonite</td>
</tr>
<tr>
<td>Time, min</td>
<td>% Conversion of anisole</td>
</tr>
<tr>
<td>30</td>
<td>40.6</td>
</tr>
<tr>
<td>120</td>
<td>54</td>
</tr>
<tr>
<td>PMA — para-methoxy acetophenone</td>
<td></td>
</tr>
</tbody>
</table>

Acylation using K-10 as such as a catalyst

Effect of solvent — In the initial runs K-10 montmorillonite clay was used as such without supporting any Lewis acid on it, at refluxing temperature of acetic anhydride. Initially a few runs were carried out without nitrobenzene as solvent. The overall conversion in 3 h was only 22%. When nitrobenzene was used as a solvent there was a considerable improvement in the overall conversion of anisole. In both the cases the selectivity towards the para-isomer was around 98%. With nitrobenzene as a solvent 50% conversion was obtained in 2 h. Beyond 2 h, there was no appreciable increase in the overall conversion of anisole (Table 1).

Effect of speed of agitation — The speed of agitation was varied from 500-1300 rpm, at the highest temperature used in the investigation (Fig. 1). Above a speed of 980 rpm there was no effect of the speed of agitation on the overall conversion of anisole thereby, indicating that external mass transfer effects were eliminated.

Effect of the moles of acetic anhydride — The ratio of the moles of acetic anhydride to the moles of anisole was varied from 1:1 to 3.2:1 using K-10 montmorillonite as a catalyst (Fig. 2). There was an increase in the overall conversion when the ratio was increased from 1:1 to 2:1 under otherwise similar conditions. Beyond the ratio of 2:1 there was no effect on the overall conversion (Fig. 2). Hence, the mole...
ratio of acetic anhydride to anisole was kept at 2:1 in the subsequent work.

**Effect of temperature**—The temperature was varied in the range 60-138\(^\circ\) C using K-10 montmorillonite clay as catalyst. At 60\(^\circ\) C the overall conversion was as low as 8.2\% in 2 h whereas at 138\(^\circ\) C an overall conversion of 40.6\% was obtained in 30 min. (Fig. 3). When acylation was carried out using Filtrol as catalyst and acetyl chloride as acylating agent at temperature 40\(^\circ\) C a very low level of conversion was observed. By using 10\% ferric chloride or zinc chloride supported on K-10 montmorillonite clay as catalyst at 138\(^\circ\) C and nitrobenzene as solvent, the level of conversion was 85\% in 15 min with 98\% selectivity towards the p-isomer (Fig. 4). The energy of activation was found to be 11.9 kcal / gmol.

**Acylation using K-10 impregnated with Lewis acid**—Using nitrobenzene as a solvent it was possible to realize as high as 90\% conversion with catalyst containing zinc chloride and ferric chloride impregnated on K-10 montmorillonite under otherwise similar conditions (Fig. 4). Catalysts impregnated with zinc chloride gave significantly lower conversion compared to that deposited with ferric chloride particularly when the reaction period up to 30 min was considered.

**Effect of substrate concentration using K-10% ferric chloride supported on K-10 montmorillonite as catalyst**—When montmorillonite impregnated with ferric chloride or zinc chloride was used, kinetic run were obtained mainly with acetic anhydride in large excess while the anisole concentration was varied. For the reaction conditions employed, the initial rate was found to be first order with respect to anisole. The values of specific reaction rates obtained from initial rate data calculated for different runs, starting with different initial concentrations, were essentially constant, indicating that the above assumption is valid (Table 2).

**Reusability of catalyst**—In the case of 10\% ferric chloride on K-10 montmorillonite clay as catalyst there was an appreciable decrease in the activity of the catalyst when reused for the second run, the conversion decreased from 73.6\% to 39\%. When fresh ferric chloride was reimpregnated on used catalyst it was almost as active as the fresh catalyst used in the first run and gave comparable results. During the reaction the Lewis acid supported on clay may be getting leached out in the reaction mixture.

**Separation and purification of product**—As discussed earlier the main advantage of clay catalyst is that it can be easily separated from the reaction mixture by filtration after carrying out the reaction. In
the conventional method the reaction mixture is transferred to relatively large amount of aqueous hydrochloride acid solution to break the complex of ketone with aluminium chloride. It may be that such a procedure is not required in the present case. The product mixture consisting of para-methoxy acetophenone, small amount of unreacted anisole, nitrobenzene acetic anhydride and acetic acid formed in the reaction could be separated by fractional distillation.

**Conclusion**

Acylation carried out using 10% Lewis acids such as ferric chloride or zinc chloride supported on K-10 montmorillonite clay using acetic anhydride as acylating agent and nitrobenzene as solvent at 138\(^\circ\) C gave very interesting results and this process could be a substitute for the conventional Friedel-Crafts reaction using more than stoichiometric quantity of anhydrous aluminium chloride. The catalyst could be reused with no significant effect on the conversion if it was again impregnated with ferric chloride or zinc chloride. Under suitable reaction condition [anisole, 9.25 \times 10^{-4} \text{ g mol/cc}; acetic anhydride, 1.85 \times 10^{-4} \text{ g mol/cc}; catalyst, 10\% ferric chloride on K-10 montmorillonite clay; catalyst loading, 0.1 g/cc reaction volume; solvent, nitrobenzene, 40 ml (total reaction volume); temperature, 138\(^\circ\) C] an overall conversion of 87\% with 98\% yield towards para-methoxy acetophenone was obtained in 15 min.

**Acknowledgements**

VGY thanks the University’s Grant Commission for the award of scholarship during the course of this research work.

**References**