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# FRIEDEL-CRAFTS ACYLATIONS WITH MODIFIED CLAYS AS CATALYSTS

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Friedel-Crafts acylations are very effectively catalyzed by clays modified through exchange of the interlamellar cations or through impregnation of metal chlorides. The acidic K10 montmorillonite exchanged with iron(III) gives outstanding results in quantitative (98–100%) acylation of anisole (15 min), mesitylene (15 min), and p-xylene (3 h) at 140–160 ° C. Clays impregnated with zinc chloride, such as the K10 montmorillonite, or Japanese acidic clay show near-equivalent catalytic performance.

## 1. Introduction

The recent appearance of a note on catalysis of the Friedel-Crafts alkylation of benzene by benzyl chloride using the K10 montmorillonite impregnated with zinc chloride ("clayzic") with a quantitative yield in 15 minutes at room temperature [1] prompts us to report on our continued [2] study of catalysis of the Friedel-Crafts reaction [3]. After the alkylations [2] came the acylations. The latter are notorious for their greater difficulty and often give rather unsatisfactory yields [4–7].

There will be two parts in this communication. Firstly, we shall give results in which modified clays as catalysts show comparable performances to sulfonated resins (Nafion) [5], at smaller cost and with easy regenerability. Secondly, we show on the selected examples of anisole, of p-xylene, and of mesitylene, that the optimized clay catalysts can give high yields and are regioselective.

## 2. Experimental

### A: EXPLORATORY EXPERIMENTS

The catalyst consists of K10-Fe(III), i.e. the K10 montmorillonite (Süd Chemie) exchanged with ferric ions according to our standard procedure [2]. The aromatic substrate to be acylated serves as its own solvent. A 1M solution of the acylating reagent in 100 mL of the aromatic is refluxed in the presence of 5 g of the catalyst. After the designated reaction time (see tables 1, 2), the catalyst is filtered and the solvent is removed on a rotary evaporator. The residue is recrystallized in ethanol.

### B: OPTIMIZED RESULTS

*Preparation of the catalysts*

The K10 montmorillonite is exchanged with various metallic cations according to our published standard procedure [2].

"Clayzic", "Kaozic", and "Japzic" are acronyms for clay(K10)-supported, kaolinite-supported, and Japanese acidic clay-supported zinc chloride, respectively. They are prepared by dissolving 10 g of zinc chloride in 100 mL of warm (60 ° C) acetonitrile in a 500 mL flask. To this vigourously stirred solution, 20 g of clay (K10 (Süd Chemie), kaolinite (Geogia kaolin CMS-KGa-1, Source Clay Minerals Repository), or Japanese acidic clay (Wako Pure Chemical Industries Ltd)) are added in small portions. Stirring is maintained for another 1/2 h after the end of addition of the clay. The solvent is then removed under reduced pressure in a rotary evaporator on a water bath at 50 ° C for 30 mn and at 95 ° C for another 30 mn. The resulting solid is powdered in a mortar and dried overnight under vacuum (5 mm Hg) in an oven at 180 ° C. Upon removal from the oven, the catalyst is, if necessary, ground again in a mortar and kept at 260 ° C under air at atmospheric pressure.

The catalyst designated as "clayzic" in the tables 5 and 6 has been prepared in the manner described, except for the drying under vacuum. The catalysts abbreviated as "clayzic-120" were stored as described but at a lower 120 ° C temperature.

Catalyst transfer from the drying oven to the reactor is performed in a dessicator under argon atmosphere. A light argon flow is systematically passed through the reaction vessels for few minutes before their use.

*General*

Anisole, mesitylene, p-xylene, and benzoyl chloride (Janssen Chimica, Beerse, Belgium) are distilled before use. Metallic chlorides, benzoic anhydride (Janssen Chimica), and hexadecane (Merck-Schuchardt) are used without purification. Solvents (Lab Chemistry, Ligney, Belgium) are distilled before use.

Gas phase analysis of product mixtures is carried out with a Varian 3300 gas chromatograph equipped with a flame ionisation detector, and a Varian 3400 integrator and a 30 m × 0.324 mm DB1 fused silica capillary column (J&W Scientific, 0.25 $\mu$m thickness). The various products are identified and their yield determined after calibration of the instrument using authentic samples and hexadecane as internal standard.

*Typical procedure*

A mixture of the aromatic substrate (5 mL) with benzoyl chloride or benzoic anhydride (10 mmol), the solid catalyst (0.5 g), and hexadecane (0.56 g, 2.5 mmol) is stirred at the desired temperature in a round-bottomed 50 mL flask equipped with a magnetic stirrer, an upright condenser and a $CaCl_2$ tube to guard against humidity. The reaction is followed by gas chromatography. After disappearance of the acylating reagent, the mixture is cooled, filtered, and the solid catalyst is washed with two or three 20 mL portions of diethylether or dichloromethane. Then, the solvent is removed under reduced pressure (20 mm Hg) from the gathered liquid phases.

*Preparation of p-methoxybenzophenone*

*a) With benzoyl chloride.* Anisole (5 mL ≈ 46 mmol) is reacted with benzoyl chloride (1.4 g, 10 mmol), using 0.5 g of catalyst, at the temperature and for the times indicated in table 6.

*b) With benzoic anhydride.* Anisole (5 mL ≈ 46 mmol) is reacted at 160 ° C with benzoic anhydride (1.4 g, 10 mmol or 0.7 g, 5 mmol), using various amounts of K10-Fe(III) catalyst (table 3).

*Preparation of 2,4,6-Trimethylbenzophenone*

Mesitylene (5 mL ≈ 35 mmol) is reacted at 70 ° C or at 160 ° C with benzoyl chloride (1.4 g, 10 mmol), using 0.5 g of the various catalysts for the times given in table 5.

*Preparation of 2,4-Dimethylbenzophenone*

Reaction of p-xylene (5 mL ≈ 41 mmol) with benzoyl chloride (1.4 g, 10 mmol), using 0.5 g of K10 exchanged with various metallic cations (table 4) is carried out at 140 ° C for 4 h.

## 3. Results and discussion

The results of exploratory experiments using K10-Fe(III) are given in tables 1 and 2. The reaction times are short, generally less than 30 mn. Acylation of

Table 1
Acylation of toluene by substituted benzoyl chlorides $RC_6H_4COCl$, with K10Fe(III) as the catalyst

| Substituent R | Yield (%) (Nafion) [5] | Products distribution [a] |
|---|---|---|
| p-$NO_2$ | 73 | 22 6 72 |
| p-$CH_3$ | 83 (83) | 26 5 69 |
| p-Cl | 68 | 20 5 75 |
| H | 52 (81) | 21 4 75 |
| m-$NO_2$ | 66 | 19 4 77 |
| o-Cl | 69 | 21 4 75 |

[a] :o/m/p.

Table 2
Acylations by p-nitrobenzoyl chloride, with K10-Fe(III) as the catalyst

| Substrate | Reaction time (mn) | Yield (%) (Nafion) [5] | Products distribution |
|---|---|---|---|
| Benzene | 600 | 50 (63) | |
| Chlorobenzene | 60 | 68 (73) | 13 2 85 [a] |
| Anisole | 30 | 100 | 20 0 80 [a] |
| o-xylene | 15 | 69 | 2 98 [b] |
| m-xylene | 15 | 87 (83) | 100 [c] |
| p-xylene | 15 | 81 | |

[a]: o/m/p, [b]: 2,3-dimethyl/3,4-dimethyl, [c]: 2,4-dimethyl.

toluene by p-nitrobenzoyl chloride is over in 1.6 mn as against 8 to 10 h using the Nafion acidic resin as a catalyst [5]. The catalyst can be recycled without any special treatment, up to four times; whereas the Nafion resin has to be regenerated after each use. The yields vary from good to very good and the product distributions which greatly favour *para* acylations are very close to those obtained when Nafion serves as the catalyst [5].

Using this K10-Fe(III), an optimum ratio of catalyst to substrate was established for the benzoylation of anisole by benzoic anhydride (table 3). A quantitative yield of the p-methoxybenzophenone was obtained when the amount of catalyst was 0.1–0.25 g for 10 mM of the reagent and 5 mL of the aromatic substrate.

Our initial choice of K10-Fe(III) as catalyst for the exploratory experiments is vindicated by the relative efficiencies deduced from table 4. Using a given mass of K10 montmorillonite exchanged by various metallic cations (as the chloride salts) we observed the sequence $Zr^{4+} < Ti^{4+} < Al^{3+} < Cu^{2+} < Cr^{3+} < Co^{2+} < Zn^{2+} < Fe^{3+}$ for the efficiency in the acylation of p-xylene by benzoyl chloride. It differs totally from the normal sequence of catalytic activity of the metallic chlorides as Lewis acids for the Friedel-Crafts reaction [4], as we had already reported for alkylations [2]. The strong dependence upon the type of reaction and upon the

Table 3
Importance of the mutual adjustment of the amounts of reagent and K10-Fe(III) catalyst in the benzoylation of anisole (5 mL) by benzoic anhydride at 160 °C

| Amounts | | reaction time (mn) | Yield [a] (%) |
|---|---|---|---|
| catalyst (g) | $PhCO_2O$ (mM) | | |
| 0.50 | 10 | 6 | 81 |
| 0.25 | 10 | 10 | 100 |
| 0.10 | 10 | 30 | 100 |
| 0.50 | 5 | 6 | 50 |

[a]: The p-methoxybenzophenone is the sole observed product.

Table 4
Influence of the interstitial Lewis cations on the catalytic activity of the acidic K10 montmorillonite on the acylation of p-xylene (5 mL) by benzoyl chloride (1.4 g), with 0.5 g of catalyst

| Catalyst | Rn temperature (°C) | Rn time (h) | Rn yield (%) |
|---|---|---|---|
| K10-$Al^{3+}$ | 140 | 4 | 42 |
| K10-$Ti^{4+}$ | 140 | 4 | 32 |
| K10-$Cr^{3+}$ | 140 | 4 | 65 |
| K10-$Fe^{3+}$ | 140 | 3 | 100 |
| K10-$Co^{2+}$ | 140 | 4 | 78 |
| K10-$Cu^{2+}$ | 140 | 4 | 58 |
| K10-$Zn^{2+}$ | 140 | 4 | 80 |
| K10-$Zr^{4+}$ | 140 | 4 | 31 |

nature of the reactional partners excludes a simple effect from cation exchange and its extent. Such K10-Fe(III) catalysts have the added advantage of low cost and of low toxicity, since the metallic ions remain trapped in the electrical double layer next to the charged aluminosilicate sheets of the montmorillonite clay.

A comparison of the catalytic performances of exchanged versus impregnated clays is shown in tables 5 and 6 (benzoylation of mesitylene and of anisole by benzoyl chloride). Let us first consider the latter case. Use of the "zic" family of impregnated catalysts makes it possible to achieve in 5 minutes quantitative and regiospecific benzoylation at 160 °C (clayzic*-260), or to lower the reaction temperature to 70 °C but at the cost of longer reaction times, of somewhat lower yields, and of some loss of regioselectivity. By contrast, three exchanged K10

Table 5
Benzoylation of mesitylene (5 mL) by benzoyl chloride (1.4 g) in the presence of various catalysts

| Catalyst | Rn temperature (°C) | Rn time (mn) | Yield (%) |
|---|---|---|---|
| Kaozic-260 | 70 | 1,800 | 85 |
| Japzic-260 | 70 | 1,800 | 72 |
| Kaozic-260 | 160 | 60 | 74 |
| Japzic-260 | 160 | 60 | 100 |
| Japzic-400 [a] | 160 | 15 | 100 |
| Clayzic*-260 | 160 | 10 | 100 |
| K10-$Al^{3+}$ | 160 | 15 | 98 |
| K10-$Ti^{4+}$ | 160 | 15 | 100 |
| K10-$Cr^{3+}$ | 160 | 15 | 94 |
| K10-$Fe^{3+}$ | 160 | 15 | 98 |
| K10-$Co^{2+}$ | 160 | 15 | 100 |
| K10-$Cu^{2+}$ | 160 | 15 | 84 |
| K10-$Zn^{2+}$ | 160 | 15 | 85 |

[a]: Activated by storage at 400 °C.

Table 6
Benzoylation of anisole (5 mL) by benzoyl chloride (1.4 g) in the presence of various catalysts (0.5 g)

| Catalyst | reaction temp. (°C) | reaction time | Yield (%) | products distr. [a] | |
|---|---|---|---|---|---|
| Clayzic*-120 | 18 | 5 d | 22 | 99 | 1 |
| Clayzic-260 | 18 | 5 d | 46 | 99 | 1 |
| Clayzic-120 | 70 | 2 h | 96 | 83 | 17 |
| Clayzic-260 [b] | 70 | 2 h | 66 | 82 | 18 |
| Clayzic-120 | 70 | 100 mn | 60 | 82 | 18 |
| Clayzic-260 | 110 | 30 mn | 89 | 94 | 6 |
| Clayzic*-120 | 110 | 15 mn | 89 | 93 | 7 |
| Clayzic*-260 | 160 | 5 mn | 100 | 100 | |
| Kaozic-260 | 70 | 2 h | 69 | 68 | 32 |
| Japzic-260 | 70 | 2 h | 54 | 81 | 19 |
| K10-Al$^{3+}$ | 160 | 15 mn | 80 | 78 | 22 |
| K10-Ti$^{4+}$ | 160 | 15 mn | 70 | 83 | 17 |
| K10-Cr$^{3+}$ | 160 | 30 mn | 97 | 90 | 10 |
| K10-Fe$^{3+}$ | 160 | 5 mn | 100 | 91 | 9 |
| K10-Co$^{2+}$ | 160 | 15 mn | 89 | 76 | 24 |
| K10-Cu$^{2+}$ | 160 | 10 mn | 72 | 90 | 10 |
| K10-Zn$^{2+}$ | 160 | 15 mn | 96 | 75 | 25 |

[a]: p/o.
[b]: Exposed to atmosphere at room temperature for 2 days before activation at 260 °C.

catalysts, with iron(III), chromium(III), and zinc(II), gave quantitative or nearly quantitative yields in 15–30 mn. For preparation of 2,4,6-trimethylbenzophenone by acylation of mesitylene with benzoyl chloride (table 5), while nearly all the catalysts experimented gave outstanding results, at 160 °C the "japzic-260" and "400", the "clayzic*-260" and K10 exchanged with titanium(IV), or cobalt(II) are the best.

## 4. Conclusions

We have shown that efficient acylations are possible with catalysis by modified clays. While we anticipated greater catalytic performance from impregnated as compared to merely exchanged catalysts, due to easier accessibility by the reactants of the Lewis acidic centers on the surface of the former, we did not find such an effect to be truly significant. The benzoic acid formed as a by-product from the reaction of benzoic anhydride is inactive. It is important that the amounts of catalyst and of the reaction partners be matched. The dry state is essential to maintenance of the catalytic activity. The procedures thus devised for acylations commend themselves by their ease of implementation, by the reduced amount of catalyst necessary as compared to the use of standard Lewis acids, and by their recourse to highly innocuous substances such as ferric chloride trapped between the layers of a commercial and inexpensive clay catalyst.

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