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# Friedel–Crafts alkylation of sodium salicylate with 4-*tert* butylbenzyl chloride performed in aqueous dispersions of mesoporous oxides

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ABSTRACT

Reactant incompatibility is a common problem in organic chemistry. In this study we investigate the use of concentrated aqueous dispersions of mesoporous oxides to overcome incompatibility in the Friedel–Crafts reaction between sodium salicylate and 4-*tert*-butylbenzyl chloride. The mesoporous material was first impregnated with the water-soluble nucleophile, sodium salicylate, and the “loaded” particles were then dispersed in the apolar electrophile, 4-*tert*-butylbenzyl chloride. A range of different mesoporous oxides and one clay mineral, montmorillonite, were investigated as catalyst for the reaction. These were all characterised with small angle X-ray scattering (SAXS) and with nitrogen adsorption (BET and BJH methods). Their Lewis and Brønstedt acidities were determined by ammonia adsorption experiments using diffuse reflection infrared Fourier transform (DRIFT) spectroscopy as detection method. The reaction proceeded well and gave high yields provided proper stirring was maintained. Alumina, an aluminosilicate and montmorillonate were the most efficient catalysts. These were also the materials that showed the strongest Lewis acidity. In general, there was good correlation between Lewis acidity and efficiency of the material as catalyst for the Friedel–Crafts alkylation. Attempts to reuse the catalyst were not entirely successful. Deactivation occurred after the first run. ESCA indicated that the reduction in performance was due to adsorption of carbonaceous residues on the catalyst.

## 1. Introduction

Friedel–Crafts alkylation is one of the most useful types of reactions in synthetic organic chemistry and a common method for C—C bond formation to aromatic rings [1]. Typically, an alkyl halide is reacted with an arene using a strong Lewis acid, such as $AlCl_3$, $ZnCl_2$ or $BF_3$ [1]. The alkyl halide may be replaced by an alkene or some other species capable of generating a carbocation when exposed to strong acid [1]. The carbocation formed acts as the electrophile in an electrophilic aromatic substitution. Also strong Brønstedt acids, such as $H_2SO_4$ and HF, can be used as catalyst [2]. Liquid phase Friedel–Crafts alkylations performed in large industrial scale, employing Lewis or Brønstedt mineral acids, give rise to large volumes of corrosive waste streams [3,4].

Increased public awareness and more rigid environmental legislation have elevated the drive towards sustainable development and cleaner, less hazardous synthetic routes [5]. Environmentally benign synthesis routes sometimes suffer from increased cost and/or reduced process effectiveness and the use of water-soluble reactants may lead to problems with poor compatibility between reagents. Performing a Friedel–Crafts alkylation reaction with incompatible reactants in a two-phase system would require the use of a phase transfer catalyst (PTC). The PTC, usually a quaternary ammonium compound or a crown ether, is a relatively toxic species and needs to be completely removed from the product after completed reaction [6]. As an alternative to the PTC approach, a solvent capable of dissolving both hydrophobic and hydrophilic reactants may be used. Examples of such solvents are the polar aprotic liquids, such as dimethylsulfoxide, acetonitrile and tetrahydrofuran. These solvents are relatively expensive and have non-negligible toxicity [7–9]. It has previously been reported that a suspension of mesoporous oxide particles in an apolar medium is an environmentally attractive approach to the problem of reactant incompatibility [10–12]. The hydrophilic mesoporous particles are filled with an aqueous solution of the polar reactant and the surrounding apolar phase contains the apolar reactant. If the apolar reactant is a liquid, it may constitute the apolar phase, i.e., the reaction is then performed without any organic solvent. The environmental and safety advantages of such reaction systems are obvious.

Solid catalysts are attractive for industrial processes because they are normally relatively easy to separate from the product and

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they can often be reused. A number of solid, acidic catalysts, such as zeolites [13], clays [14] and metal oxides [15], have been used for the Friedel–Crafts alkylation reaction performed in conventional organic solvent systems [16]. Mesoporous oxides, such as mesoporous $SiO_2/Al_2O_3$, are particularly attractive since they combine a large and well-defined internal surface area with pore dimensions large enough not to be easily clogged by the reaction products. Clogging of the pores is a well-known problem with zeolites [17,18]. Clays are also useful but they have lower surface areas than mesoporous oxides and zeolites and they therefore expose fewer active sites per weight unit of catalyst.

We here report the use of a concentrated suspension of acidic mesoporous oxide particles as reaction system for a Friedel–Crafts reaction, alkylation of sodium salicylate with 4-*tert*-butylbenzyl chloride. A range of different mesoporous oxides is explored. Sodium salicylate, which is water-soluble, resides in the water-filled pores of the particles and 4-*tert*-butylbenzyl chloride constitutes the continuous phase. The catalytic sites are integrated into the pore walls. The suspension is kept under stirring and the reaction occurs at the interface between the two liquid phases, i.e., at the pore openings.

## 2. Experimental

### 2.1. Materials and reagents

Pluronic P123 (BASF), ethanol (Kemetyl, 99.5%), aluminium chloride (Aldrich, 98.0%), silicon tetrachloride (Aldrich, 99%), zinc chloride (Sigma–Aldrich 98%) aluminium isopropoxide (Aldrich, 98%), hexadecyltrimethylammonium bromide (CTAB; Sigma, 98%) and sodium hydroxide (Aldrich, 97% A.C.S.), were used as received for preparation of catalyst samples. 4-*tert*-Butylbenzyl chloride (99%, Aldrich) and sodium salicylate (99.5%, Aldrich) were the reactants used to perform the Friedel–Crafts alkylation reaction, montmorillonite (K30, Aldrich) was used as catalyst, and chloroform-d (ARMAR Chemicals, 99.8 atom % D) was used for the $^{13}C$- and $^{1}H$ NMR analyses.

### 2.2. Preparation of mesoporous materials

#### 2.2.1. Mesoporous silica, alumina, and mixed alumina/silica

The materials were prepared following the method described by Yang et al. [19]. The template, EO-PO-EO triblock copolymer P123 (10.0 g), was dissolved in ethanol (100 g) under stirring at room temperature. After 30 min the chloride precursor was stepwise added and the stirring was continued for 30 min. The solution was transferred to an open petri dish and gelled by standing for an appropriate time in the oven. The thin film obtained was directly calcined; see Table 1 for conditions, amounts and reagents.

#### 2.2.2. Mesoporous alumina/silica

The material was synthesised essentially following the preparation method described by Wang et al. [20]. Aluminium isopropoxide was added to a water solution (90 g) containing sodium hydroxide (7.8 g) under stirring at room temperature. Additional water was added (910 g) and the solution was stirred for 30 min. The template was added and the temperature was fixed at 25 °C. When the template had completely dissolved, tetraethyl orthosilicate was added and the resulting gel was stirred for 2 h. Hydrochloric acid (37 wt%) was drop-wise added until the pH had been adjusted to 12. After 4 h under stirring at pH 12 the pH was lowered to 11 and the stirring was continued for another 12 h. The solid was vacuum filtered, washed with water and calcined. See Table 1 for conditions, amounts and reagents.

### 2.3. Friedel–Crafts alkylation in mesoporous slurry

Mesoporous material (0.60 g), aqueous sodium salicylate solution (1.50 g, 4.68 mmol), and 4-*tert*-butylbenzyl chloride (0.90 g, 4.93 mmol) were added in that order into a round bottomed flask fitted with a magnetic stirrer. The slurry was heated in an oil bath under a condenser at 90 °C. Aliquots were taken at various intervals during 24 h and analysed with $^{1}H$ NMR and $^{13}C$ NMR for the reaction products. Sodium 3-(4-*tert*-butylbenzyl)-2-hydroxybenzoate was characterized by the following NMR pattern: $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 1.35 (s, 3H), 3.96 (s, 2H), 6.96–7.04 (d/t, H), 7.15 (d, H), 7.34 (d, H), 7.40 (d, H), 7.75–7.85 (d, H). $^{13}C$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 31.3, 34.2, 35.1, 120.9, 123.3, 125.5, 128.8, 130.0, 132.2, 135.3, 138.4, 148.8, 162.5, 171.0. Sodium 5-(4-*tert*-butylbenzyl)-2-hydroxybenzoate was characterized by the following NMR pattern: $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 1.35 (s, 3H), 3.96 (s, 2H), 6.96–7.04 (d/t, H), 7.15 (d, H), 7.34 (d, H), 7.40 (d, H), 7.75–7.85 (s, H). $^{13}C$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 31.3, 34.2, 41.3, 119.7, 123.3, 125.5, 128.8, 132.2, 133.8, 134.2, 148.8, 162.7, 171.0.

### 2.4. Recycling of mesoporous oxides

Mesoporous material, obtained after reaction at 90 °C and a stirring rate of 800 rpm, was recovered by vacuum filtration and washed with $CH_2Cl_2$. The material was air dried at room temperature and was then transferred to a reaction flask and used for a new 24 h reaction under the same experimental conditions. The mesoporous material was stored at room temperature in air atmosphere between the experiments. To validate the washing procedure the mesoporous material was impregnated with the reactants, 4-*tert*-butylbenzyl chloride and sodium salicylate, and $^{1}H$ NMR was used to confirm that no product resided in the mesoporous material after the washing procedures.

### 2.5. Analysis techniques

$^{1}H$ NMR spectra were recorded at 400 MHz using a JEOL, model Eclipse FT-NMR Oxford instrument. The consumption of 4-*tert*-butylbenzyl chloride was determined by monitoring the decrease in the signal from the $-CH_2Cl$ group in 4-*tert*-butylbenzyl chloride, which appears at $\delta$ (ppm) = 4.6–4.7. The yield of the alkylation product, two isomers of sodium 4-*tert*-butylbenzylsalicylate, was estimated by monitoring the increase in the signal of the $Ar-CH_2-Ar$ group, which appears at $\delta$ (ppm) = 3.9–4.0. The yield was calculated from the ratio between the appearing and the disappearing peaks. The $^{1}H$ NMR experiments were made at 25 °C using $CDCl_3$ as solvent.

$^{13}C$ NMR spectra were recorded using the same instrument. The products; sodium 3-(4-*tert*-butylbenzyl)-2-hydroxybenzoate and sodium 5-(4-*tert*-butylbenzyl)-2-hydroxybenzoate, could be identified by the position of the signal from the $Ar-CH_2-Ar$ group, which appears at $\delta$ (ppm) = 35.1 and 41.3, respectively. The $^{13}C$ NMR experiments were made at 25 °C using $CDCl_3$ as solvent and run for 14 h. $^{13}C$ NMR was only used for analysing the product composition for reactions with the three best performing catalytic materials; $Al_2O_3$, $Al_2O_3/SiO_2$-5 and montmorillonite.

Gas chromatography (GC) was performed on a Varian 3400 GC fitted with a SUPELCO Chromosorb WHP 80-100 Mesh, SS 1.8 m × 1/8 mm × 2.0 mm diatomite column, and a flame ionization detector (FID). The injected sample in $CHCl_3$ was run using a 30 min program with a temperature ramp ranging from 40 to 300 °C. The program is capable of eluting $C_5$–$C_{30}$ aliphatic hydrocarbons, as proved by the calibration run.

Electron spectroscopy for chemical analysis (ESCA or XPS) was performed on a Quantum 2000 scanning ESCA microprobe