

Editor Choice paper

# Friedel-Crafts acylation reactions using heterogeneous catalysts stimulated by conventional and microwave heating

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## Abstract

The acylation of anisole with decanoic acid over a range of solid-acid catalysts has been studied under conventional heating and microwave stimulation. The microwave-irradiated experiments exhibited increased reaction rates, the extent of which was dependent upon the nature of the catalyst. The origin of this microwave enhancement has been attributed to the selective desorption of water from the surface of the catalyst.

Pyridine adsorption has been used to quantify the number of acid sites present on the catalyst. The nature of the acid sites in terms of their Brønsted/Lewis acidity has been determined using infrared analysis of the adsorbed pyridine. The strength of the acid sites has been characterised by differential thermal analysis (DTA) of the pyridine desorption. This indicated that the sulphated zirconia and supported heteropoly acids contained significantly more strong acid sites than the cerium exchanged zeolite.

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## 1. Introduction

Acylation of aromatic compounds is a widely used reaction for the production of fine chemicals [1]. The classic methodology for Friedel-Crafts acylation uses stoichiometric amounts of Lewis acids, such as metal halides ( $\text{AlCl}_3$ ), or Brønsted acids, such as polyphosphoric or sulphuric acid [2]. Moreover, the reaction is carried out homogeneously and the Lewis acid complex must be hydrolysed to obtain the final products, thus generating a substantial amount of corrosive and toxic waste. This has prompted considerable research into the use of solid-acids to catalyse these reactions [3–10]. The choice of the acylating agent is also important from an environmental perspective, carboxylic acids being highly preferable to the more active acyl chlorides [11,12]. Unfortunately, these reactions have tended to be relatively slow with high yields only being obtained within acceptable timescales when activated aromatic compounds have been used or when less environmentally acceptable acyl chlorides are used as the acylating agent [13,14].

Since 1986, when Gedye et al. [15] published the first pioneering report concerning the use of microwave heating for chemical synthesis, the utilisation of microwave radiation in this area has increased dramatically, which is reflected in the number of reviews relating to this topic [16–22]. Microwaves have also been used successfully to stimulate catalytic reaction, with much of the work focusing on gas/solid reactions. There has been much debate in the literature concerning the origin of the observed rate enhancements and this has been reviewed by Zhang and Hayward [23]. Catalytic reactions involving solid/liquid systems have been studied to a lesser extent; the work to date is covered in the review articles by Kappe and Stadler [24] and Loupy [25]. Within these systems, due to more efficient heat transfer between solid catalyst and liquid reactants, effects such as temperature differences between the catalyst and reactant and spatial hot spots will be minimized.

The aim of this study was to determine if microwave stimulation could be used to enhance the rate of solid-acid catalysed acylation reactions. The work focuses on the acylation of anisole with carboxylic acids, comparative experiments have been carried out under conditions of microwave and conventional heating.

Pyridine adsorption has been used to quantify the number of acid sites present on the catalyst. The nature of the acid sites

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in terms of their Brønsted/Lewis acidity has been determined using infrared analysis of the adsorbed pyridine. The strength of the acid sites has been characterised by differential thermal analysis (DTA) of the pyridine desorption. The loss tangent of the catalysts has also been determined. This provides a measure of the catalysts ability to adsorb microwave energy and convert it to heat.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Silica supported heteropoly acids

The catalysts were prepared using an incipient wetness method, whereby the appropriate amount of phospho-12-tungstic acid (Aldrich) was dissolved in deionised water and slurried with sufficient silica (Aerosil 380, Degussa), to give a supported catalyst with a loading of 30 wt.% (HPW30). Previous studies [26] have shown that this loading is optimal for this type of catalyst.

#### 2.1.2. Lanthanum exchanged zeolite-Y

The ion-exchanged zeolites were prepared using the method described by Carvajal et al. [27].

Initially, powdered type Y zeolite (10 g) in the sodium form (Strem Chemicals) was ion-exchanged with ammonium nitrate solution (3 L, 1 M), at 70 °C for a period of 24 h, filtered and washed with deionised water prior to being lanthanum exchanged by stirring with lanthanum nitrate solution (3 L, 1 M) for 24 h. The zeolite in the lanthanum form was filtered and washed with deionised water and dried at 120 °C (24 h) prior to calcination in air at 300 °C for a further 24 h.

#### 2.1.3. Sulphated zirconia

Sulphate doped zirconium hydroxide (MEL<sup>®</sup> Chemicals), was calcined at 550 °C in air prior to use. This calcination temperature was chosen, as previous studies have shown that this results in the most active catalyst [28].

### 2.2. Catalyst characterisation

#### 2.2.1. Total surface area determination

The total surface area of the catalysts was determined using nitrogen adsorption at 77 K, using the BET method. The experiments were performed using a Micrometrics 2010 gas adsorption analyser.

#### 2.2.2. Surface acidity

The total numbers of acid sites were probed via pyridine adsorption using a purpose built vacuum microbalance. The catalyst was placed in the microbalance and degassed under vacuum for 1 h at 100 °C, prior to being exposed to pyridine vapour. The vapour pressure of the pyridine was increased in incremental steps until it reached saturated vapour pressure. The catalyst was then evacuated at 25 °C for 90 min in order to remove the physisorbed pyridine. The sample was then removed and the

infrared spectrum recorded using a spectrometer (Jasco 410) fitted with a “Golden gate” ATR accessory (Specac Ltd.).

Determination of the concentration of the chemisorbed pyridine bonded to the Brønsted and Lewis acid sites was achieved by measuring the intensity of the infrared frequencies of the characteristic bands at 1545 cm<sup>-1</sup> and 1445 cm<sup>-1</sup>, respectively. Using the methodology and extinction coefficients given by Emeis [29], the numbers of Brønsted and Lewis acid sites present on the catalysts were calculated.

#### 2.2.3. Analysis of the strength of the acid sites

Information concerning the strength of the acid sites on the individual catalysts was obtained from pyridine desorption experiments performed using a differential thermal analyser (Shimadzu, DTA50). All desorption experiments were performed in an atmosphere of flowing nitrogen (20 ml min<sup>-1</sup>) over the temperature range 50–600 °C and a temperature rate of 15 °C min<sup>-1</sup>. A nullifying procedure, as described by Aboul-Gheit [30], was adopted, in which the sample pan was loaded with an equivalent amount of catalyst which had not had pyridine pre-adsorbed.

#### 2.2.4. Determination of dielectric properties

Both the real and imaginary parts of the complex dielectric permittivity of the catalysts were determined using the cavity perturbation method [31]. The measurements were made on powdered catalysts that had been activated previously as described above and stored in a desiccator.

### 2.3. Catalyst testing

All the catalysts were tested in a batch reactor operating under reflux conditions (154 °C) for a period of 3 h. The reactions were stirred continuously using a magnetic stirrer. The reactor was charged with, 0.57 mol of anisole and  $1.8 \times 10^{-2}$  mol of decanoic acid. The reaction mixture was then heated until reflux commenced, at which point the catalyst was added and timing of the reaction commenced. This approach was adopted such that any differences in initial heating rates resulting from the different heating techniques would not influence the rates of reaction. A blank experiment in which no catalyst was added was performed in order to confirm that the reaction did not proceed in the absence of the catalyst. All experiments were carried out in triplicate. The reaction mixture was sampled periodically and analysed using gas liquid chromatography. The gas chromatograph (Varian CP-3380) was fitted with a flame ionisation detector. Separation of the products was achieved using a 25 m BP5 (5% phenylpolysiloxane) column. The isomer selectivity was confirmed by isolation of the product and subsequent analysis using NMR spectroscopy (Bruker DPX250).

Comparative experiments were performed under microwave irradiation. The experiments were again performed in an open batch reactor operating under reflux. Identical quantities of catalyst and reactant were loaded into the reactor as in the conventionally heated reactions. The reaction was placed in the microwave cavity of a Discover (CEM) focused microwave system. This instrument was fitted with a 300 W microwave gen-

Table 1

Total surface area determined by nitrogen adsorption (77 K), surface acidity determined by pyridine adsorption and infra red spectroscopy and  $\tan \delta$  as determined by cavity perturbation for the catalysts HPW30, SZ and LaY

Catalyst	Total surface area ( $\text{m}^2 \text{g}^{-1}$ )	Pyridine adsorbed ( $\text{mg g}_{\text{cat}}^{-1}$ )	Brønsted sites (%)	Lewis sites (%)	Tan $\delta$
HPW30	176	139	58	42	0.039
SZ	99	31	72	28	0.007
LaY	471	270	49	51	0.005

erator and has a unique cavity design that allows the sample to be irradiated through  $360^\circ\text{C}$ . The reaction temperature was monitored by an infrared pyrometer and a feedback loop provided the required variations in microwave power necessary to maintain the predetermined temperature. The reaction mixture was again agitated using a magnetic stirrer. The progress of the reaction was monitored as with the conventionally heated reactions.

### 3. Results and discussion

#### 3.1. Catalyst characterisation

##### 3.1.1. Investigation into the nature of the acid sites

The surface areas determined from nitrogen adsorption at 77 K are contained in Table 1. As anticipated, the LaY zeolite catalyst has by far the greatest surface area.

The number of acid sites as measured by pyridine adsorption using a vacuum microbalance is expressed as milligrams of pyridine adsorbed per gram of catalyst.

The fraction of Brønsted and Lewis sites has been determined from the infrared spectra of adsorbed pyridine. The spectra for pyridine adsorbed on LaY zeolite, sulphated zirconia and HPW30 displays three bands at  $1445 \text{ cm}^{-1}$ ,  $1490 \text{ cm}^{-1}$  and  $1545 \text{ cm}^{-1}$ . The bands at  $1545 \text{ cm}^{-1}$  and  $1445 \text{ cm}^{-1}$  indicate the presence of Brønsted and Lewis acid sites, respectively. The third strong band at wave number  $1490 \text{ cm}^{-1}$  has been attributed to the pyridine associated with both Lewis and Brønsted acid sites [32]. There is unfortunately some degree of uncertainty in quantifying the numbers of adsorbed acid sites from the infrared spectra due to uncertainty regarding the molar extinction coefficients.

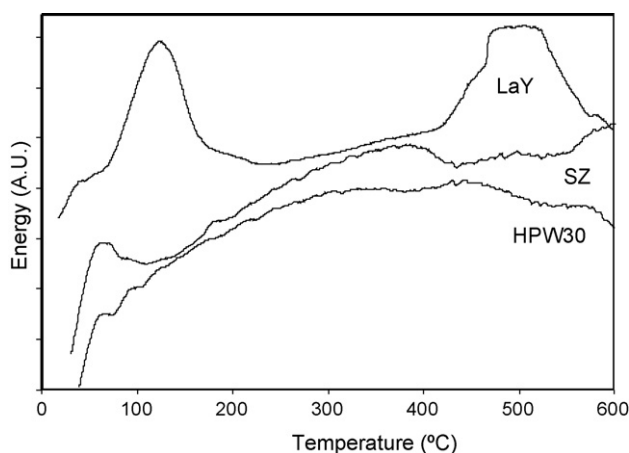


Fig. 1. DTA traces for the desorption of pyridine from LaY zeolite, sulphated zirconia and HPW30 catalysts.

##### 3.1.2. Investigation into the strength of the acid sites

The relative strengths of the acid sites have been assessed from the temperature programmed desorption of pyridine, the thermograms produced are shown in Fig. 1. All the catalysts tested exhibit, to varying extents, attributes associated with pyridine desorption over the temperature range  $50\text{--}200^\circ\text{C}$ . Desorption at these relatively low temperatures can be ascribed to the remnants of any physically adsorbed pyridine and also that associated with weak acid sites on the surface of the catalyst. Aboul-Gheit [33] have described the adsorption of pyridine on these weak acid sites as resulting from hydrogen bonding, where a hydrogen atom serves as a bridge between two pyridine nitrogen atoms. Pyridine desorption at low temperatures can also be assigned to desorption of vertically bound pyridine, which occurs when bonding is predominantly through the lone pair of electrons on the nitrogen atom [30]. Adsorption of pyridine can also occur in a nearly planar orientation where bonding takes place through a combination of both the lone pair and the  $\pi$  electrons from the aromatic ring [35]. Bonding to the surface of the catalyst in this conformation is much stronger and results in desorption of pyridine in the temperature range  $400\text{--}575^\circ\text{C}$  (Fig. 1).

The lanthanum exchanged zeolite catalyst displays a broad peak in the temperature region  $400\text{--}575^\circ\text{C}$ . Desorption in this region has previously been attributed to the adsorption of TEA at Brønsted acid sites with the formation of pyridinium ions [32]. Although, there is some discrepancy in the literature as this is contradicted by Aboul-Gheit who claims pyridine desorption from H-Mordenite at approximately  $200^\circ\text{C}$  [34]. The high temperature peak in the thermogram for the desorption of pyridine from the catalyst LaY produced in this study is likely

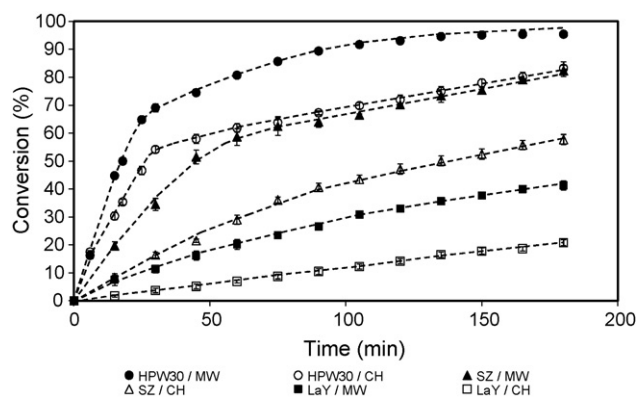


Fig. 2. Comparisons of use microwave and conventional heating on percentage conversions of the decanoic acid as a function of time, using various catalysts (1.0 g).

to be a combination of near planar adsorbed pyridine adsorbed at Lewis acid sites and also the pyridinium ion adsorbed at the Brønsted sites. This may account for the event occurring over a large temperature range. Interestingly, neither the sulphated zirconia nor the heteropoly acid catalyst displays any significant features in the higher temperature region. This observation is consistent with that of Stevens et al. [35] who also observed that desorption of pyridine from sulphated zirconia was devoid of features. They combined their study with *in situ* infrared spectroscopy and mass spectrometry and concluded that the strong acid sites resulted in decomposition of the pyridine rather than desorption.

As a result of this study it is possible to differentiate the catalysts in terms of the strength of their acid sites; the LaY catalyst has a large number of weak acid sites while the SZ and HPW30 catalysts have acid sites that are much stronger.

### 3.1.3. Acylation of anisole

The catalysts tested in this study show differing initial rates of reaction for the acylation of anisole when activation is provided by conventional heating (Fig. 2). The rate of reaction for acylation reactions has been shown previously to be related to the number, and also the strength, of the Brønsted sites [12]. This accounts for the relative activities of the catalysts tested in this study.

When the reactions are stimulated via microwave radiation the catalysts consistently display some enhancement in performance compared to when the reaction was performed using an oil bath. In an attempt to quantify the microwave enhancement the ratio of initial rate under microwave heating/initial rate under conventional heating was determined (Table 2).

Undoubtedly, the microwaves are affecting the performance of the catalyst and an attempt must be made to explain how this might arise.

Differences in heating rate can be excluded as a potential explanation of the observed phenomenon, due to the catalyst only being added once the system had started to reflux. Microwave heating of solutions has been shown to result in the super heating of solvents even at atmospheric pressure [36,37], however, once the systems start to reflux superheating cannot be maintained and the normal boiling temperature of the solvent is established. Also, agitation of microwave-heated solutions has been shown to prevent super heating from occurring [38,39].

As all reactions performed during this study were agitated and performed under refluxing conditions it is highly unlikely that super heating can account for the increases in reaction rates that have been observed.

There are several reports in the literature of non-uniform heating of heterogeneous systems by microwaves [40]. Heterogeneous catalysts operating in the gas phase have been shown to operate with enhanced activity when irradiated using microwaves and this has been explained in terms of non-uniformity of heating [41–45]. This has been dismissed as being the origin of the observed rate enhancements in this study on two accounts. First, a significant temperature gradient between the catalyst particle and the liquid phase is less likely than in gas phase catalysis due to the more efficient heat transfer by the liquid. Secondly, if this were the case then it would be expected that the catalysts with the highest values of  $\tan \delta$  to display the greatest microwave enhancement. The measured values of  $\tan \delta$  for the catalyst are all low (Table 1), as would be expected for these types of material, but display an inverse relation with the microwave enhancement. Therefore preferential heating of the catalyst by the microwaves can be disregarded as being plausible for accounting for the microwave enhancement.

Acylation reactions with carboxylic acids are reversible and consequently are affected by the concentration of water. High-localised concentrations of water at the active site of a catalyst can reduce the activity of the catalyst significantly. Corma et al. [46] have shown that by using supports that are hydrophobic, concentrations of water at the surface of the catalyst can be reduced resulting in enhanced activity. Microwaves are well known to be highly effective at dehydrating materials such as zeolites [47,48], therefore, the microwave enhancement could be explained in terms of the microwaves removing water from the surface of the working catalyst, making the hydrolysis reaction less likely to occur, as in the case with the hydrophobic materials used by Corma and co-workers. This hypothesis, would appear to be supported by data contained within in this paper. The LaY catalyst which has mainly weak acid sites and consequently should adsorb water at the active sites relatively weakly might be expected to display only moderate rate enhancement as a result of microwave stimulation. However, although the water may not be adsorbed strongly at the acid site; removal of water from the zeolite cages presents an additional problem which may also be assisted by microwave radiation as this has been

Table 2  
Initial rates of reaction for the solid-acid catalysts (HPW30, SZ and LaY) stimulated by conventional and microwave heating using masses of catalyst varying between 0.5 g and 1.5 g

Catalyst	Mass of catalyst (g)	Reaction rate MW (mol s <sup>-1</sup> )	Reaction rate CH (mol s <sup>-1</sup> )	Ratio of reaction rates MW/CH
HPW30	0.5	6.93(±0.12) × 10 <sup>-6</sup>	4.91 (±0.10) × 10 <sup>-6</sup>	1.4(±0.03)
SZ	0.5	2.42(±0.08) × 10 <sup>-6</sup>	0.72(±0.13) × 10 <sup>-6</sup>	3.4(±0.51)
LaY	0.5	1.10(±0.09) × 10 <sup>-6</sup>	2.32(±0.28) × 10 <sup>-7</sup>	4.8(±0.76)
HPW30	1.0	8.79(±0.07) × 10 <sup>-6</sup>	6.42(±0.37) × 10 <sup>-6</sup>	1.4(±0.05)
SZ	1.0	3.93(±0.14) × 10 <sup>-6</sup>	1.66(±0.09) × 10 <sup>-6</sup>	2.3(±0.15)
LaY	1.0	1.51(±0.20) × 10 <sup>-6</sup>	3.48(±0.39) × 10 <sup>-7</sup>	4.3(±0.75)
HPW30	1.5	11.12(±0.39) × 10 <sup>-6</sup>	9.14(±0.31) × 10 <sup>-6</sup>	1.2(±0.06)
SZ	1.5	6.21(±0.19) × 10 <sup>-6</sup>	2.91(±0.09) × 10 <sup>-6</sup>	2.1(±0.01)
LaY	1.5	2.12(±0.1) × 10 <sup>-6</sup>	6.04(±0.57) × 10 <sup>-7</sup>	3.5(±0.39)

Table 3

Isomer percent selectivity using conventional and microwave heating for the catalysts HPW30, SZ and LaY

Catalyst	Isomer selectivity (%)					
	Conventional heating			Microwave heating		
	<i>Para</i>	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>	<i>Ortho</i>	<i>Meta</i>
HPW30	97	2	1	98	1	1
SZ	98	1	1	98	1	1
LaY	96	2	2	96	2	2

shown to increase that rate of diffusion in certain circumstances [49]. Consequently, microwave stimulation of the reaction over this zeolite-based catalyst exhibited an enhancement in initial reaction rate by a factor of approximately 4.8 compared to the conventionally heated reaction. It would then follow that the second greatest enhancement in rate should have been observed for the HPW30 catalyst. However, in terms of initial rate of reaction there is only a minor difference in initial rates between the two heating regimes. Assessing the performance in terms of initial rates may be flawed, as this highly active catalyst may have been operating under conditions of diffusion control. This is borne out by experiments in which the mass of catalyst has been varied. A non-linear variation of catalyst mass and reaction rate was observed indicating that this catalyst was operating under diffusion control in the initial stages of the reaction. Once the reaction rate declined a significant enhancement in conversion was observed in the microwave-irradiated experiments. While the SZ catalyst has a relatively low surface area and hence capacity to adsorb water however, this catalyst contains relatively few acid sites, but those which are present are strong and hence adsorb water strongly. This catalyst may be expected to be deactivated quickly due to strongly adsorbed water when operating under conventional heating, but under microwave irradiation preferential desorption of water would give rise to a significant rate enhancement and indeed a enhancement of factor of approximately 2 was observed.

There was no observed difference in the isomer selectivity between the two heating regimes (Table 3). All catalysts were highly selective towards production of the para-isomer

#### 4. Conclusions

This paper demonstrates that microwave irradiation of catalytic systems may induce more subtle effects than merely selective heating. The ability to desorb products selectively from the surface of a heterogeneous catalyst may have beneficial results in systems in which the product poisons the active sites. This may have more far reaching implications for preventing the deactivation of heterogeneous catalysts.

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