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Hydrothermal alkylation of phenols with alcohols in diluted acids

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ABSTRACT

Diluted acids (typically 0.05 M HCl) are shown to be very effective media to promote the alkylation of phenols with activated alcohols under hydrothermal conditions (from 150 to 200 °C). These results are an elegant alternative to “usual” Friedel-Crafts alkylations avoiding the use of alkylchlorides as alkylating agents and the use of Lewis acidic promoters or concentrated acids but also shade some light on the processes occurring during the hydrothermal carbonisation (HTC) of biomass.

RÉSUMÉ

Dans ce manuscrit nous montrons que les acides faiblement concentrés (concentration de l’ordre de 0,05 M) se trouvent être de très bons milieux pour réaliser l’alkylation de composés phénoliques par des alcools en conditions hydrothermales (entre 150 et 200 °C). Cette approche constitue non seulement une alternative élégante aux autres méthodes d’alkylation des phénols mais elle permet aussi de mieux comprendre les mécanismes à l’œuvre lors de la carbonisation hydrothermale de la biomasse (HTC).

1. Introduction

Over the last few decades, environmental awareness found its way into chemical process engineering and much effort has been devoted to make the production of chemical commodities greener [1]. To achieve green(er) organic syntheses, it is necessary, among other requirements, to employ nontoxic starting compounds and to obtain high conversion rates while avoiding the formation waste and by-products [1]. In a landmark paper of 1999, James Clark selected Friedel-Crafts reactions as a textbook example of a process, which is (or was) both very important from an industrial point of view and extremely “ungreen” [2]. Indeed, in its initial form, the reaction was conducted by adding an, at least, equimolar amount of aluminium chloride to a solution of an alkyl chloride in a large excess of the desired aromatic compound at room temperature [3]. This resulted in the formation of more than 80 mass-% of waste products [2]. Therefore numerous ways have been investigated to reduce the amount of waste produced in this type of alkylation reactions.

Among these attempts, one can cite the use of various (true) homogeneous (based either on transition metals [3–7], on Lewis acids [8–10] or on Brönsted acids [11]) and heterogeneous catalysts (be they acidic resins [12] or molecular sieves [13]).

Some of the above mentioned works and numerous others also aim at using alcohols as alkylation agents. Indeed, alcohols are easier to synthesise than chlorides and when they are employed as alkylation agents, only water is eliminated. [14–19].

In an effort to both avoid the use of any catalyst and favour the use of alcohols as alkylation agents; Sato et al. investigated the use supercritical water as solvent for the

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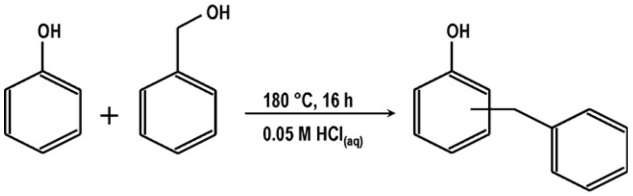

Scheme 1. A typical example of diluted acid promoted alkylation of phenol with benzyl alcohol.

alkylation of phenol [20–23]. Unfortunately, processes involving supercritical water impose strong requirements on the used reactors in terms of mechanical and corrosion resistance. However, water at temperatures below the critical point can also be employed, but at the expense of the yield of the reaction [24].

As the concentration, respectively the activity, of hydronium ions seems to be the main factor impacting the curse of Friedel-Crafts' reactions in water [22], we anticipated that the use of diluted acids under hydrothermal conditions (between 150 °C and 180 °C) could allow one to overcome the technical problems caused by the use of concentrated acids on the one side and supercritical water on the other. We show here that it is possible to perform the alkylation of phenol (Scheme 1) successfully with activated alcohols under hydrothermal conditions in diluted acids at 180 °C.

2. Experimental

2.1. Experimentation

All experiments were run in stainless steel autoclaves fitted with 21 mL PTFE inlets. The inlets were cleaned with water at 180 °C for 16 h before usage.

In standard tests, 0.5 mmoL of alcohol and 15 mmoL of phenolic derivatives were mixed with 10 mL of solvent (pure water or the acidic solutions) and heated up to the wanted temperature for 16 h. The concentration and nature of the acids, the reaction temperature and the nature of the reagents were varied to gain insights into the versatility of this reaction.

2.2. Characterisation

After the reaction, the autoclaves were cooled down to room temperature; the products of the reaction were extracted with 3 mL of EtOAc. The organic phase was prepared for GC-FID and GC-MS by addition of a standard solution of toluene in EtOAc. The results of the GC-FID were quantified using the procedure described by Jorgensen et al. [25].

3. Results and discussion

3.1. Optimization of the reaction conditions for the system phenol–benzyl alcohol

In a first step we selected HCl as a reference (inorganic) acid to promote the alkylation of phenol with benzyl alcohol, which is known to be very electrophilic. The impact of the reaction temperature on the formed products for three HCl concentrations (0, 0.5 M and 1 M, respectively) was investigated. Table 1 summarizes the obtained results.

As can be seen, the use of pure water is not sufficient (at such moderate temperatures) to yield high amounts of the expected alkylation products, which is compatible with the results reported by Katritzky et al. [24]. In presence of HCl however, high conversion rates are observed at any temperatures and the yields of mono alkylated products range from about 60 up to 90%. By-products of the reaction are mainly diakylation products.

Actually, our initial aim was to use the lowest possible concentration of acid in order to ease corrosion constrains on possible reactors for such alkylations. We, thus, decided to perform our following test at 180 °C and to try decreasing the concentration of acid or to employ weaker acids. Figs. 1–3 report the results we obtained for the alkylation of phenol with benzyl alcohol at 180 °C for 16 h for increasing acid concentrations with HCl, acetic acid and formic acid.

As can be seen on Fig. 1, with HCl being the acid, it was already possible to achieve high yields of the expected alkylation products at very low acid concentrations (60% at

Table 1
Alkylation of phenol with benzyl alcohol in aqueous media[a].

Solvent	Temperature (°C)	Conversion (%)[b]	Yield of mono-substituted Friedel-Crafts product (%)[c]	o/p-ratio
Water	125	0	0	–
	150	0	0	–
	180	1	1	–
	200	7	7	61:39
	220	14	14	59:41
0.5 M HCl	125	100	89	50:50
	150	99	72	52:48
	180	100	66	53:47
	200	100	67	53:47
	220	100	63	53: 47
1 M HCl	125	84	71	48:52
	150	100	75	50:50
	180	100	69	51:49
	200	94	65	51:49
	220	100	62	52:48

[a] Reaction conditions: 0.5 mmoL of benzyl alcohol, 15 mmoL of phenol, 10 mL of solvent heated up to the wanted temperature for 16 h.

[b] Conversion rates were determined as the ratio between the initial and final amount of benzyl alcohol.

[c] Yields were determined as the ratio between the amount of mono alkylation products and the initial amount of benzyl alcohol.