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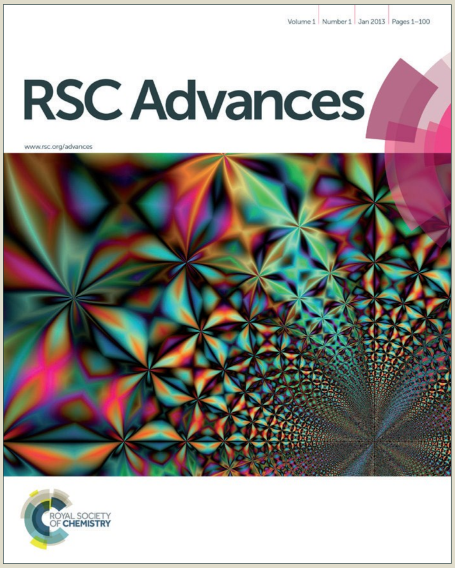

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Reaction control in heterogeneous catalysis using montmorillonite: Switching between acid-catalysed and red-ox processes

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The use of montmorillonite, modified with a super-acid (CF_3SO_3H), in the presence of hydroquinone as a radical scavenger and under a nitrogen atmosphere, induced the formation of tetrasubstituted furans as the major product from benzoins. In the absence of a radical scavenger, the only products obtained were 1,2-diketones.

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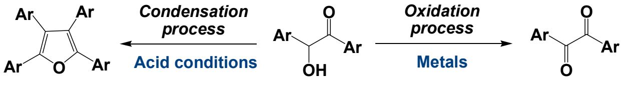
1. Introduction

Inspired by biocatalytic systems, artificial switchable[1] catalysts[2] have recently received increased attention because of their ability to perform specific and complex tasks as a consequence of external stimuli such as light irradiation,[3] pH variation,[4] the introduction of metal ions,[5] or modification of the reaction conditions (solvents, temperature, use of additives or agitation conditions).[6] Despite astonishing developments in the field of switching founded on changing reaction conditions, only one example has been reported on the switching of a heterogeneous catalyst such as montmorillonite (clay) achieved by the use of different solvents.[7] In that report, solvent induced selectivity was observed in the acid catalysed allylsilylation, arylsilylation and silylation of alkynes. To the best of our knowledge, the use of different reaction conditions to stimulate different non-interfering metals within a clay such as montmorillonite and to give rise to a switching process has not been explored.

Herein, we report our recent observation of the ability to tune the highly chemoselective condensation and oxidation of benzoins by altering the reaction conditions, which provides new protocols for the synthesis of tetrasubstituted furans[8] or 1,2-diketones,[9] depending on the conditions employed. Usually, the condensation of α-hydroxyl ketones in the presence of HCl,[10] *p*-toluensulfonic acid[11] or iodotrimethylsilane[12] gives a mixture of products, where tetraphenylfuran is typically the principal product (Scheme 1). Meanwhile, the oxidation of α-hydroxyl ketones into the corresponding 1,2-diketones can be carried out in the presence of a wide variety of metals,[13] including Fe[14] (Scheme 1). In this work, the general idea is based on the ability of montmorillonite to participate as a Lewis or Brønsted acid catalyst in organic reactions[15-16] and as a generator of free radical species in redox processes.[17] This dual functionality introduces an attractive possibility for the development of a switching process in presence of super-acid montmorillonite, that results from the amount and type of metals contained in this type of materials and makes studying these materials an interesting research topic.



Scheme 1. Synthesis of tetrasubstituted furans and 1,2-diketones

2. Results and discution

2.1. Material catalytic

Montmorillonite is a representative 2:1 clay mineral composed of units that consist of two tetrahedral silica sheets and an octahedral alumina sheet. It exhibits isomorphous substitution, which produces an excess negative charge. This excess negative charge is compensated for by the adsorption of exchangeable cations on the surface layer.[18] The treatment of these clays with acids and super-acids maximizes the number of Brønsted catalytic sites by replacing exchangeable cations with protons.[19] In the same way, the structural

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transformation brought about by super-acid treatment allows free aluminium ions to migrate from the alumina octahedral sheets into the interlayer region, where they displace sodium ions, maximizing the number of Lewis catalytic sites present.[20-21]

Table 1. Elements present in the clay samples was determined by EDS

Element	Elemental concentration weight (%)	
	Natural clay	Clay/CF_3SO_3H
Na_2O	2.60	0.13
K_2O	0.33	0.30
MgO	3.52	2.06
Al_2O_3	21.30	13.36
SiO_2	65.48	74.60
CaO	1.05	1.65
SO_3	-	2.30
TiO_2	0.33	0.27
MnO	0.31	0.03
FeO	5.08	5.30

The chemical compositions of montmorillonite and of montmorillonite modified with a super-acid (CF_3SO_3H) were determined by energy-dispersive X-ray spectroscopy (EDS). The montmorillonite was found to contain Na, K, Mg, Al, Si, Ca, Ti, Mn, Fe and S, the last of which was provided by the acid used while the other elements were found in the natural clays (Table 1). The use of CF_3SO_3H substantially enhanced the surface area, pore volume and pore diameter of the modified montmorillonite compared with the unmodified montmorillonite (Table 2). Ample discussion about the characterisation of this material has been provided in previous work.[17,20]

Table 2. Properties of montmorillonite clays[17,20]

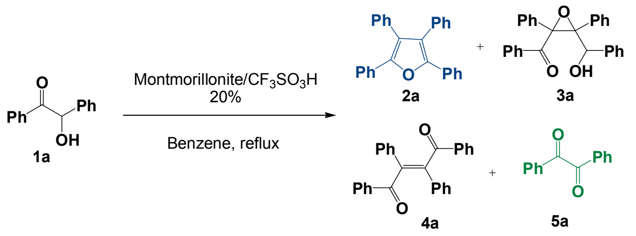
Parameters	Natural clay	Clay/CF_3SO_3H
Surface area (m^2/g)	23	185
Pore volume (cc/g)	0.140	0.603
Pore diameter (Å)	23.00	107.79

2.2. Catalytic activity

Once we characterised the material, we turned our focus to the study of the switching process. We found that the condensation of benzoin **1a** in the presence of modified montmorillonite, hydroquinone and using benzene or toluene as solvent afforded a 60% isolated yield of tetraphenylfuran **2a** product (Table 3, entry 1). Additionally, it was possible to isolate and identify three side products, **3a**, **4a** and **5a**, whose origin will be explained later (Table 3, entries 2 and 3). The heterogeneous reaction, when carried out in the absence of hydroquinone, produces 1,2-diketone **5a** as the only product (95%, Table 3, entry 4). It is noteworthy, that the modified montmorillonite can be recycled four times without significant losses in its catalytic activity in both processes, and that when the reactions were carried out in presence of natural clay the products **2a** and **5a** were obtained in low yield, 20 and 30% respectively, after three days of reaction. In absence of catalyst, the yield is 15% after the same time.

With these results in hand, we next investigated the scope of the condensation and oxidation processes with aromatic α-hydroxy-ketones **1b**-**1f** to demonstrate whether it is possible to selectively tune the reaction by controlling the reaction conditions. To do this, we first studied the reaction in the presence of hydroquinone under a nitrogen atmosphere. As shown in Table 4, tetrasubstituted furans **2b**-**2f** were obtained as major products in excellent yield. On the other hand, when the reaction was carried out in the absence of hydroquinone and under an open atmosphere, phenyl α-hydroxy-ketones **1b**-**1f** were easily converted to desired 1,2-diketones **5b**-**5f** with excellent yields (Table 4).

Table 3. Oxidation and condensation of benzoin



Entry	Product	Yield %[a]	
		With hydroquinone[b]	Without hydroquinone[c]
1	**2a**	60	0
2	**3a**	5	0
3	**4a**	5	0
4	**5a**	25	95

[a] Yield of isolated product after chromatographic purification. [b] Reagents and conditions for the reaction: benzoin **1** (1 mmol), clay (20%w), hydroquinone (50% mmol), benzene or toluene (50 mL), N_2 atmosphere, reflux, 12 h. [c]Benzoin **1** (1 mmol), clay (20%), benzene or toluene (50 mL), open atmosphere, reflux, 6.

On the basis of the above results, which are consistent with previous mechanistic proposals in which an acid catalyses the condensation reaction,[10,11] a putative reaction mechanism is shown in Scheme 2. Modified montmorillonite clays are known for their acidic properties and have been used as efficient solid acid catalysts in a number of organic reactions that require Brønsted and/or Lewis acid sites.[15-16] Here, we hypothesize that the protons and aluminium ions present in the interlayer region as a consequence of the treatment with CF_3SO_3H are responsible for catalysing the condensation reaction. The first step of this reaction is the self-condensation of benzoin **1a** to **A**, which is a precursor of **B** and **5a**. The intermediate **B** loses H_2O, furnishing deoxybenzoin **C**, which has been proposed in the past as a key intermediate in this condensation reaction. Deoxybenzoin **C** condenses with other molecule of benzoin **1a**, forming a carbon-carbon bond and resulting in intermediate **D**. After the elimination of two molecules of H_2O, tetrasubstituted furan **2a** is obtained from **D**. Finally, the formation of compounds **3a** and **4a** can be rationalized from intermediate **A** (Scheme 2). However, neither of these products (**3a** and **4a**), nor 1,2-diketone **5a**,[22] are precursors of

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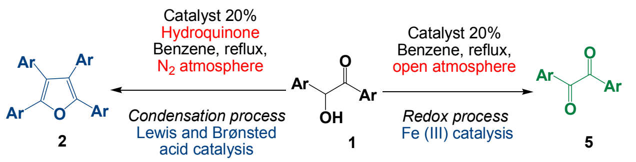
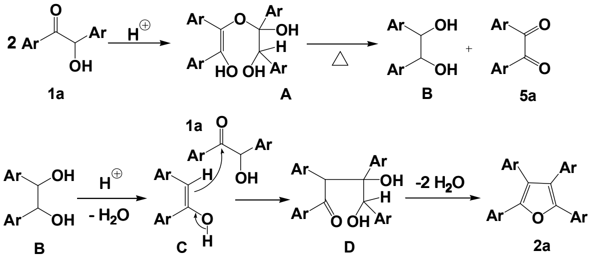
tetrasubstituted furan **2a**, because they were subject to reaction conditions studied in this work, tetrasubstituted furan **2a** was not obtained. It is important to remark that the origin of **5a** in condensation process is different than its proposed origin in the oxidation reaction. In this case **5a** is a disproportionation product that occurs as a consequence of a thermal process. Conversely, in the oxidation reaction, **5a** is produced by a free radical process as discussed below.

Table 4. Switching between acid-catalysed and redox processes

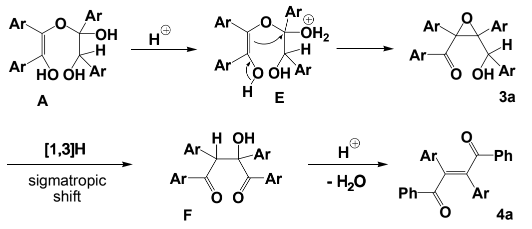


Entry	Ar	Product (Yield %)[a] With hydroquinone[b]	Without hydroquinone[c]
1	4-MeC$_6$H$_4$ **1b**	**2b** (62)	-
		5b (33)	**5b** (95)
2	4-MeOC$_6$H$_4$ **1c**	**2c** (65)	-
		5c (33)	**5c** (95)
3	4-EtC$_6$H$_4$ **1d**	**2d** (65)	-
		5d (31)	**5d** (95)
4	4-BrC$_6$H$_4$ **1e**	**2e** (60)	-
		5e (28)	**5e** (90)
5	3-MeC$_6$H$_4$ **1f**	**2f** (60)	-
		5f (32)	**5f** (95)

[a] Yield of isolated product after chromatographic purification. [b] Reagents and conditions for the reaction: benzoin **1** (1 mmol), clay (20%w), hydroquinone (50% mmol), benzene (50 mL), N_2 atmosphere, reflux, 12 h. [c]Benzoin **1** (1 mmol), clay (20%), benzene (50 mL), open atmosphere, reflux, 6 h.



Scheme 2. Proposed mechanism of condensation process



Scheme 3. Proposed mechanism for side products

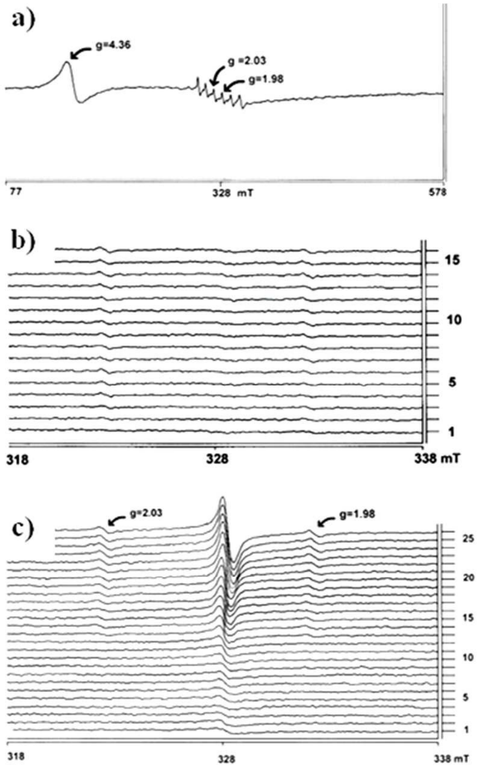


Figure 1. EPR spectra of: a) super-acid montmorillonite without solvent, b) super-acid montmorillonite in benzene at 70 °C scanned every 5 minutes and c) benzoin **1a** in benzene at 70 °C in the presence of super-acid montmorillonite scanned every 5 minutes.

The high selectivity of the oxidation processes in the heterogeneous conditions studied herein cannot be explained in terms of a Lewis or Brønsted acid catalysed mechanism, but rather as a result of performing the reactions in the presence of super-acid treated montmorillonite. The treatment with acid could dissolve structural iron in the clay, allowing the now free iron cations to reach the interlayer or surface of the clay,[17,20] where the oxidation of benzoin **1a** to benzil **5a** may be catalysed. To obtain more insight on this point, the EPR spectrum of modified montmorillonite was recorded without solvent and is shown in Figure **1a**. The six peaks with a hyperfine coupling resonance signal centred at g=2.01 are assigned to MnO$_2$ and MnO species, which possess S=5/2 and S=1/2 electron spin states, respectively. Meanwhile, the singlet signal at approximately 165 mT and g=4.36 corresponds to high-spin Fe(III), which is also present in the clay. These signals disappeared when the spectrum was recorded at 70 °C and used benzene as solvent (Figure **1b**). To our delight, when benzoin **1a** was added to the EPR tube and the experiment was recorded at 70 °C, the presence of a free radical centred on carbon was observed at approximately 328 mT g = 2.003, after a half hour of reacting (Figure 3c). Once the oxidation was completed, that signal disappeared. Additionally, this signal was not observed when the same experiment was carried out in presence of hydroquinone. Based on these results, we propose that benzoin **1a** donates an electron to Fe(III) to form

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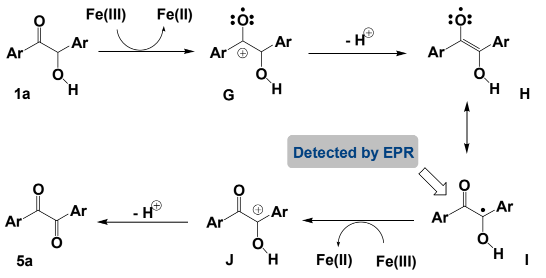
benzoin radical cation **G**. Next, **G** loses a proton to produce radical structure **H**,[23] which isomerises to **I** (detectable in EPR, Figure **1c**). The donation of an electron from **I** to Fe(III) furnishes **J**, which loses a proton produce the 1,2-diketone **2**. Finally, Fe(II) may be reoxidised to Fe(III) by oxygen in the atmosphere (Scheme 4).

With the idea to support the proposed mechanism of the oxidation process, the reactions was carried out in presence of silica and MCM-41, which are material free of Fe(III). In both case the benzyl **5a** was obtained in 15% of yield after three days of reaction. Thus, we assume that Fe(III) is responsible for oxidation reaction. The heterogeneous redox processes was demonstrated by an analysis post-reaction to identify Fe(III) dissolved in toluene. In this case was not possible to identified Fe(III) species by EPR. Finally, analysis of material after reaction by EDS, showed the same elemental composition and concentration weigh.



Scheme 4. Proposed mechanism of oxidation process

3. Conclusions

In conclusion, we have shown that for a montmorillonite clay modified with a super-acid, two different modes of behaviour can take place simply by a judicious choice of reaction conditions. The introduction of free radicals favours the oxidation of benzoins, while the presence of a free radical scavenger triggers the condensation of the same benzoins. EPR experiments provide significant support in determining the radical mechanism involved in the oxidation reaction. Several side products were isolated and characterised to shed light on the acid-base mechanism related to the synthesis of tetrasubstituted furans through the condensation reaction. This finding enriches the understanding of the behaviour of such materials in organic reactions. Further application in different organic reactions and synthesis studies to further investigate the material properties reported here are currently underway in our laboratory.

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Reaction control in heterogeneous catalysis using montmorillonite: Switching between acid-catalysed and red-ox processes

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For a montmorillonite clay modified with a super-acid (CF_3SO_3H)., two different modes of behaviour can take place simply by a judicious choice of reaction conditions.