

The effects of solid acids as cocatalysts on the chelation-assisted hydroacylation of alkenes and alkynes

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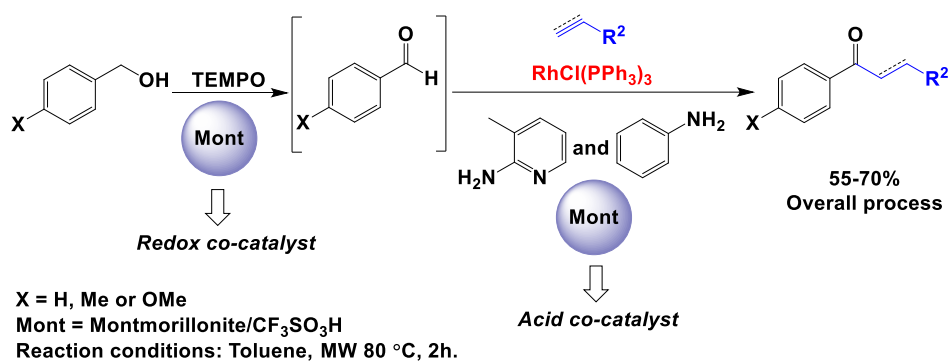
Abstract

The use of homogeneous Brønsted acid cocatalysts (such as benzoic acid) in hydroacylation reactions *via* imine intermediates has been extensively studied, but the use of heterogeneous cocatalysts has been limited to montmorillonite K10. Thus, we can use other solid acids to increase the efficiency of the reaction. Here, we described the effects of sulfated zirconia, Al-MCM-41 or superacid modified montmorillonite on the hydroacylation of alkenes and alkynes with aldehydes *via* imine intermediates and in the presence of the Wilkinson complex. Furthermore, we addressed the dual role of montmorillonite, a redox reagent in the presence of TEMPO and an acid solid, allowing the direct use of benzyl alcohols as substrates to generate saturated or α - β unsaturated ketones.

Keywords: Hydroacylation, solid acids, sulfated zirconia, Al-MCM-41, montmorillonite

Graphical Abstract

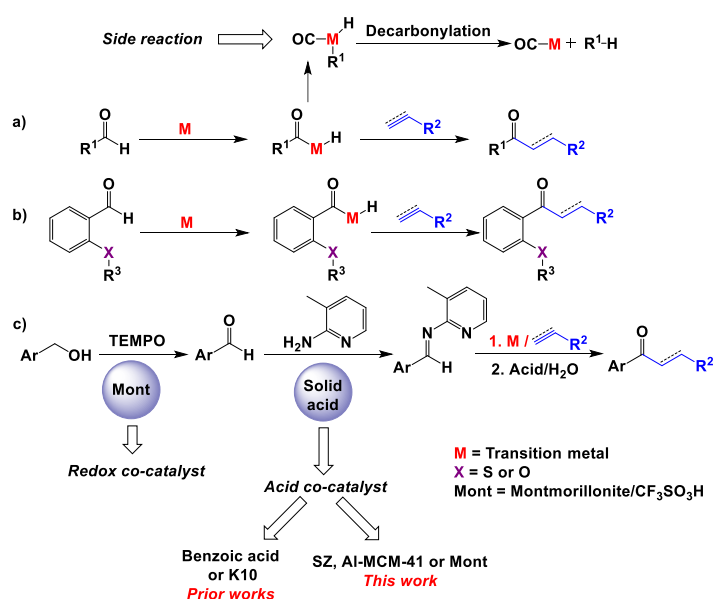
Hydroacylation of alkenes and alkynes in the presence of solid acids



1. Introduction

The transformation of an aldehyde into a saturated or α - β unsaturated ketone involves the hydroacylation of alkenes or alkynes.¹ This strategy of synthesis considers the aldehydic C-H bond as a functional group that can be activated to form a C-C bond in the presence of transition metal catalysis.² In the overall catalytic hydroacylation process, the principal drawback is the decarbonylation of aldehyde³, which results in the formation of carbonyl-metal complexes and alkanes (Scheme 1a). The following strategies have been used to avoid this problem: i) the use of a β -sulfide⁴ or β -OR⁵ group in the substrate² (Scheme 1b) and ii) the use of reversible imine formation with 2-aminopyridines⁶ (Scheme 1c). Both of these findings implicate the assistance of chelating groups to stabilise the intermediate that results in the formation of a ketone. In the last protocol, the *in situ* formation of imines from aldehydes is performed in the presence of aniline and benzoic acid as cocatalysts.⁷ This imine reacts with alkenes in the presence of Wilkinson's catalyst to generate ketimines, which are hydrolysed to saturated ketones (Scheme 1c).⁸

Alternatively, the use of montmorillonite K10⁹ as an efficient acidic solid and reusable cocatalyst to generate imines has been described. However, the study of other solid acids with different properties and structural characteristics has not been explored, even though the use of solid acids as cocatalysts in organic reactions is attractive due to the recyclability of solid materials.¹⁰



Scheme 1 Hydroacylation reaction: a) in the absence of chelating groups, b) with the use of a β -sulfide or β -OR chelating group and c) *via* an imine intermediate.

Thus, in this work, we chose to use three structurally different solid acids, namely, sulfated zirconia (SZ),¹¹ Al-MCM-41¹² and montmorillonite¹³ modified with a superacid ($\text{CF}_3\text{SO}_3\text{H}$), to develop a cooperative system through which hydroiminoacylation of the corresponding aldimines generates ketones (Scheme 1c). Additionally, we considered extending this study to a process in which a simple alcohol is used as the aldehyde precursor in the presence of modified montmorillonite and TEMPO to generate the ketone. To the best of our knowledge, montmorillonite has not been used in similar dual processes (redox and acid catalysis).

2. Results and discussion

2.1. Materials

The SZ investigated in the present study was synthesised by the sol-gel technique and characterised by X-ray powder diffraction (XRD).¹⁴ Fig. 1a shows the diffractogram for SZ, in which the characteristic pattern of the crystalline tetragonal phase can be observed, given by the reflections at $2\theta = 30.21^\circ$, 35.35° , 50.207° , 59.23° , 60.17° , 62.84° , 74.78° and 81.78° . These values are congruent with what is described in the literature¹⁴ for the crystalline tetragonal structure of a super acid material.

The mesoporous material Al-MCM-41 was synthesised by an ultrasound-assisted technique.¹⁵ The structure of the mesoporous material was confirmed by XRD. Fig. 1b shows the diffractograms for Al-MCM-41, in which reflections can be observed at $2\theta = 2.2^\circ$ and 4.0° . These values are identical to those described in the literature for these kinds of materials.

On the other hand, natural montmorillonite was treated with concentrated $\text{CF}_3\text{SO}_3\text{H}$ acid to generate the modified material. Fig. 1c shows the diffractogram with the characteristic reflections to a montmorillonite clay at $2\theta = 7.0^\circ$, 20.0° , 35.0° and $61.8.0^\circ$.¹⁶

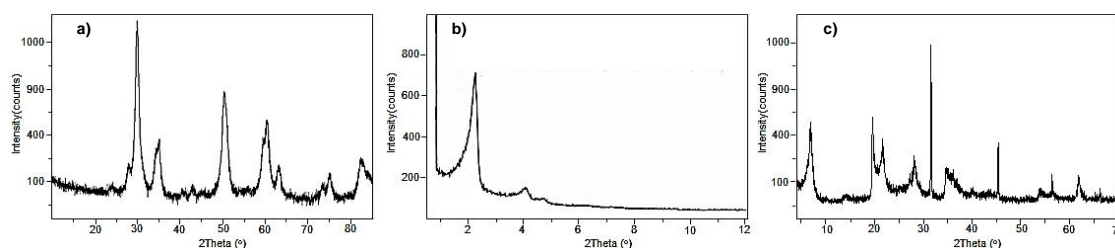


Fig. 1 Diffractogram of a) SZ, b) Al-MCM-41 and c) Montmorillonite modified with $\text{CF}_3\text{SO}_3\text{H}$.

The textural properties of the synthesised materials were determined by nitrogen adsorption-desorption (BET) methods, allowing us to compare the surface area, pore volume and pore size of the catalysts. Compared with the SZ and Al-MCM-41 materials, the modified montmorillonite had a larger surface area and larger pore size (Table 1).

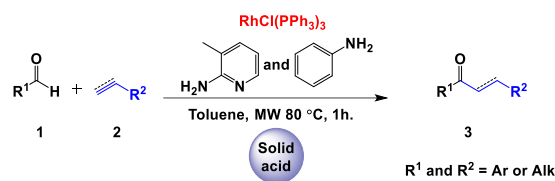
Table 1. Textural properties of acid materials

Properties	Material		
	SZ	Al-MCM-41	Modified montmorillonite
BET area (m ² /g)	90.35	1221.79	185.00
Pore volume (cm ³ /g)	0.12	0.85	0.60
Pore size (Å)	52.01	26.49	107.79

2.2. Catalytic activity of solid acids in direct hydroacylation

Initially, we optimised typical reaction parameters, including the catalytic reagents, solvent, temperature, and time, for the hydroacylation of 1-butene with benzaldehyde (Table S10, S1). Subsequently, and based on the results previously obtained, we focused on studying the reaction trend with different substrates and the following different solid acids: modified montmorillonite, SZ or Al-MCM-41. As shown in Table 2, the hydroacylation of alkenes in the presence of 2-amino-3-picoline, aniline, Wilkinson's complex, and toluene as the solvent at 80 °C afforded saturated ketones **3a-3e** in very good yields (80-92%). Similar yields were observed when the reaction was carried out with alkynes to generate α - β unsaturated ketones **3f-3j**. In contrast, the yields of the reaction decrease considerably when the aldehyde is aliphatic (acetaldehyde), as demonstrated by the yields obtained for ketones **3k** and **3l**.

We think that the difference between the yields obtained with the three materials may be explained by their acidic properties and direct influence on the formation of picolyl imines. The SZ has $H_0 \leq -14$,¹⁷ Al-MCM-41 $H_0 \leq 6.80$ ¹⁸ and modified montmorillonite has $H_0 \leq -12.75$,¹⁹. Therefore, materials with major acidity properties catalyse the formation of imines more efficiently.

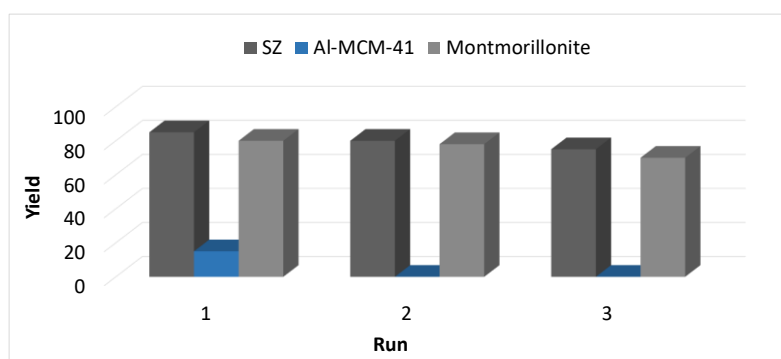
Table 2. Hydroacylation reaction in the presence of solid acids^{a,b}

<p>3a SZ = 90% Al-MCM-41 = 85% Montmorillonite = 87%</p>	<p>3b SZ = 91% Al-MCM-41 = 80% Montmorillonite = 85%</p>	<p>3c SZ = 90% Al-MCM-41 = 82% Montmorillonite = 86%</p>
<p>3d SZ = 91% Al-MCM-41 = 80% Montmorillonite = 85%</p>	<p>3e SZ = 92% Al-MCM-41 = 84% Montmorillonite = 88%</p>	<p>3f SZ = 91% Al-MCM-41 = 83% Montmorillonite = 94%</p>
<p>3g SZ = 90% Al-MCM-41 = 80% Montmorillonite = 92%</p>	<p>3h SZ = 90% Al-MCM-41 = 81% Montmorillonite = 90%</p>	<p>3i SZ = 93% Al-MCM-41 = 84% Montmorillonite = 95%</p>
<p>3j SZ = 92% Al-MCM-41 = 83% Montmorillonite = 95%</p>	<p>3k SZ = 55% Al-MCM-41 = 32% Montmorillonite = 40%</p>	<p>3l SZ = 61% Al-MCM-41 = 30% Montmorillonite = 55%</p>

^a Reaction conditions: aldehyde 1 (1 mmol), alkene or alkyne 2 (1.5 mmol), $RhCl(PPh_3)_3$ (5% mmol), 2-amino-3-picoline (20% mmol), aniline (20%) solid acid (50 mg) and toluene (3 mL). ^b Yield of the isolated product after chromatographic purification.

2.3. Reuse of solid acids

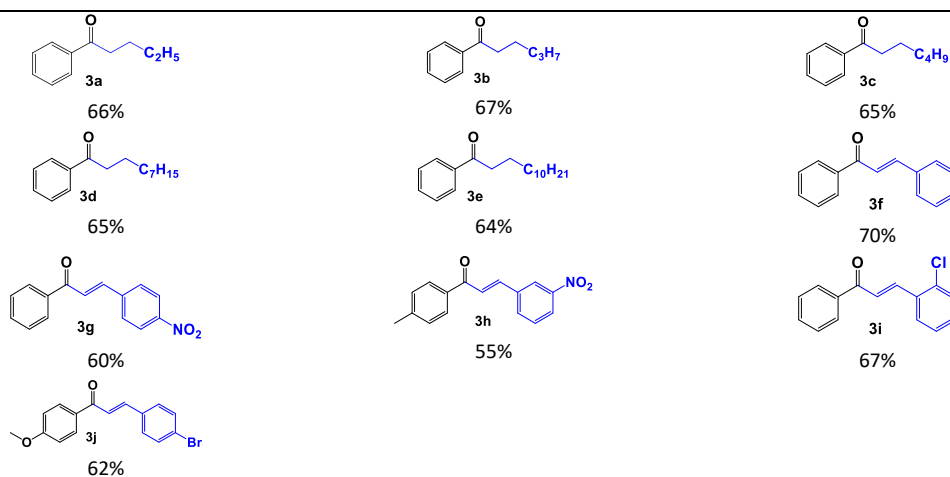
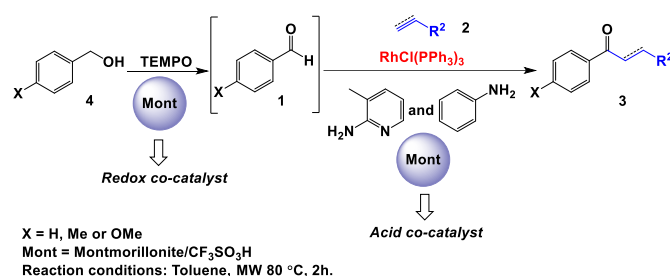
We studied the reuse of solid acids in the hydroacylation of 1-butene with benzaldehyde to form **3a** by reactivation of the materials at $100\text{ }^\circ\text{C}$ in an oven under an O_2 atmosphere for 12 h. In the case of modified montmorillonite and SZ, the reaction yield did not decrease significantly after three reuses. After two runs, Al-MCM-41 lost its original structure and catalytic activity (Fig. 2).

**Fig. 2** Reuse of materials in the synthesis of **3a**

2.4. Oxidation of benzylic alcohols and hydroacylation

In previous studies, we observed that montmorillonite modified with $\text{CF}_3\text{SO}_3\text{H}$ can participate as a Brønsted or Lewis acid catalyst in organic reactions²⁰ or as a generator of free radical species in redox processes.²¹ From this double behaviour, we focus on studying the hydroacylation reaction of alkenes and alkynes with benzylic alcohols.²² The process begins with the *in situ* oxidation of benzyl alcohol **4** to aldehyde **1** in the presence of modified montmorillonite and TEMPO²³ to subsequently catalyse the hydroacylation of alkene or alkyne **2** and generate corresponding ketone **3** (Table S11, SI). This strategy allowed us to obtain saturated (**3a-3e**) and α - β unsaturated (**3f-3j**) ketones in good yields (55-70%). In the case of aliphatic alcohols, the formation of the final product was not observed, as only the corresponding carboxylic acid was obtained.

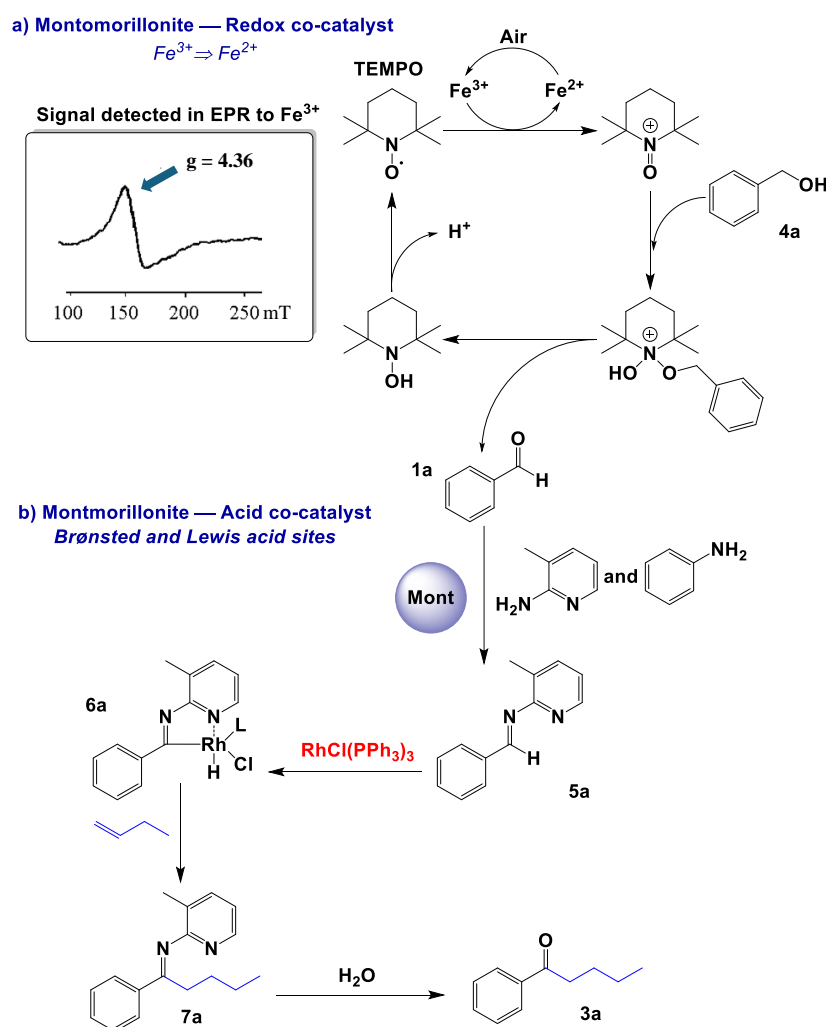
Table 3. Hydroacylation of benzylic alcohols^{a,b}



^a Reaction conditions: aldehyde **1** (1 mmol), alkene or alkyne **2** (1.5 mmol), TEMPO (10%), $\text{RhCl}(\text{PPh}_3)_3$ (5% mmol), 2-amino-3-picoline (20% mmol), aniline (20%) solid acid (50 mg) and toluene (3 mL). ^b Yield of the isolated product after chromatographic purification.

To propose a pathway for this direct hydroacylation reaction from benzyl alcohol **4a**, a series of control experiments were carried out. Fe^{+3} was detected in a sample of modified montmorillonite by EPR (150 mT and $g = 4.36$, Scheme 2); thus, the treatment with $\text{CF}_3\text{SO}_3\text{H}$ may dissolve structural iron in the montmorillonite, allowing these free cations to move to the interlayer of the montmorillonite where the oxidation of benzyl alcohol to aldehyde is catalysed. In the absence of montmorillonite or its replacement by another

free-Fe³⁺ solid acid (SZ or Al-MCM-41), ketone **3a** was only detected at 10%. When the reaction was carried out in N₂ atmosphere, no final product formation was observed. In the absence of Wilkinson's complex and long reaction times (1 to 7 h), benzoic acid was generated in 65% yield. Moreover, in the absence of TEMPO, a complex mixture of benzyl alcohol oligomerization products was observed via NMR. Based on these results, a putative reaction mechanism is shown in Scheme 2. The Fe³⁺ present in the modified montmorillonite is responsible for the oxidation of TEMPO to generate TEMPO⁺, which oxidises alcohol **4a** to aldehyde **1a**.²⁴ Air acts as an oxidant in the first step of the process, promoting the oxidation of Fe²⁺ to Fe³⁺ from montmorillonite. On the other hand, protons and aluminum ions present in solid acids (Brønsted or Lewis acid sites) are responsible for catalysing the formation of imine **5a**. Then, Wilkinson's complex participates in the second part of the process,²⁵ the hydroacylation of the imine to obtain **7a** via the rhodium-aminoacyl complex **6a**. Finally, the hydrolysis of **7a** afforded saturated ketone **3a**.



Scheme 2 Proposed mechanism for the hydroacylation of benzyl alcohols.

3. Conclusions

In summary, we demonstrated that different solid acids (sulfated zirconia, Al-MCM-41 or montmorillonite superacid) can be used as cocatalysts in the hydroacylation of alkenes and alkynes *via* an imine intermediate and in the presence of Wilkinson's complex. Due to the stability of SZ, Al-MCM-41 and modified montmorillonite under reaction conditions, the catalysts can be reused with similar yields. Additionally, the catalytic process was carried out from benzylic alcohols with *in situ* oxidation of alcohol in the presence of modified montmorillonite and TEMPO to afford the corresponding aldehyde. In the latter case, we demonstrate the usefulness of the dual character of montmorillonite by utilizing it first in a redox process and then as an acid catalyst.

Associated content

Supporting information: General information, detailed synthetic procedures, full characterization of solid acids, spectral data, and copies of NMR spectra of reaction products.

Conflicts of interest

There are no conflicts to declare.

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Author contributions

J.A.M.S. and R.G. conceived the project and acquired the funds. B.I.V.A., E.G.R., R.G., J.C. and J.A.M.S designed the experiments. B.I.V.A., E.G.R., A.M.G., E.A.J.A. and A.L.T. conducted the experimental work. J.C., R.G. and J.A.M.S. coordinated the whole project. B.I.V.A., E.G.R., R.G., J.C. and J.A.M.S wrote the manuscript. All the authors contributed to the discussions.

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