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Efficient hydroalkoxylation of alkenes to generate octane-boosting ethers using recyclable metal triflates and highly active metal triflate/Brønsted acid-assisted catalysts

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ABSTRACT

gem-Disubstituted alkenes are directly and readily etherified with alcohols using Al(OTf)$_3$ and Zr(OTf)$_4$ as recyclable Lewis acid catalysts. In contrast, primary or secondary alkene analogues were inert under these conditions, enabling excellent chemoselectivity. Lanthanide triflates are inactive as catalysts for such reactions, as is phosphoric acid. But a combination of these two otherwise inactive entities led to an 'assisted acidity' scenario that saw significant unmatched catalyst activity. All catalysts of this study are recyclable a number of times without loss of activity.

1. Introduction

Methyl *tertiary*-butyl ether (MTBE) is an octane enhancer that has clean burning properties. It is prepared *via* the reaction of isobutylene and methanol in the presence of an acid catalyst [1]. However, its solubility in water causes environmental problems due to migration of this material through soils and natural water bodies [2]. Consequently, alternative oxygenates are required as gasoline additives which, amongst others, reduce carbon monoxide emissions [3]. *tertiary*-Amyl methyl ether (TAME) and *tertiary*-amyl ethyl ether are viable alternative octane-boosting petrol additives [4] with which to substitute MTBE for gasoline blending [5] to enhance gasoline burning properties. Furthermore, *tertiary* ethers have high octane numbers, low viscosities and low densities [6], properties essential for gasoline blending [7].

Ether formation may be effected using the traditional Williamson transformation [8] or by the hydroalkoxylation of alkenes [9]. Typically, the latter requires rather harsh conditions and strong Brønsted acids such as triflic acid or sulfuric acid for a successful outcome [10]. Acidic resins are commonly used catalysts in the industry for such reactions [11,12]. The preferred large scale synthesis of *tertiary* ethers is *via* the hydroalkoxylation of an alkene with an alcohol, typically employing sulfonic acid-based resins such as Amberlyst 15 [13,14]. Other catalysts such as supported sulfated zirconia [15], Si-MCM-41 [1], zeolites [5], homogeneous heteropoly acids [16] and certain palladium complexes are also used [17].

Metal triflates promote various organic reactions [18]. Duñach and co-workers [9] recently investigated the hydromethoxylation of terpene-type substrates with various metal triflates. They often found mixtures of products (regioselectivity) even in alkenes in which a *gem*-disubstituted carbon centre is present. They furthermore found Al(OTf)$_3$ to be less useful as a catalyst than, for example, Sn(OTf)$_4$. We have shown such triflate catalysts, particularly Al(OTf)$_3$, to be extremely useful in epoxide ring-opening reactions with a range of nucleophiles [19], to be capable of effecting highly efficient acetal formations [20] and to readily produce highly active Pd catalysts for the co-catalysed methoxycarbonylation reaction of alkenes [21]. Importantly, metal triflates are readily recycled [19-23] and are capable of catalysing organic reactions in a hydrous or protic environment as opposed to their corresponding metal halides that typically require anhydrous reaction conditions [24].

In this paper, we report the use and recycling of aluminium and zirconium triflates as effective catalysts for the highly selective etherification of branched alkenes with alcohols. Lanthanide triflates were poor catalysts for this transformation. However, a synergistic activation was achieved when adding phosphoric acid to the lanthanide triflates, to generate 'assisted acidity' [25] catalysts. Remarkably, the

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catalytic activity of the mixed system exceeds those of aluminium- and zirconium triflates as well as that of triflic acid, while the individual components show essentially no activity. Recycling of these catalyst systems is efficient with no observable loss of activity.

2. Experimental

Reagents were obtained from commercial sources and used as received. The phosphoric acid used was an 85% aqueous mixture. The alcohols used were HPLC grade with water content of <0.03% for methanol and <0.1% for ethanol, determined by Karl Fischer titration. All samples were analysed using gas chromatography, employing a computer loaded with Class-VP software for recording and processing of chromatograms. A free fatty acid analytical column (50 m, internal diameter 0.2 mm) was utilised together with a flame ionisation detector, and the dip tube sampler was directly connected to the GC inlet to ensure sample integrity. Calibration curves were developed to accurately quantify the reaction components against authentic samples. A GC–MS (Varian Spectrum CX spectrometer) was also used to characterise the compounds against authentic samples (retention times and fragmentation patterns). Isolated materials gave satisfactory ^{1}H and ^{13}C NMR spectra (Varian 400 MHz spectrometer). pH measurements in water were performed on a Hanna Instruments HI 111 pH/ORP Meter, using a Mettler Toledo Inlab® Routine Pro pH electrode filled with 3 M aqueous KCl as the electrolyte. For the measurements in water/methanol and neat methanol, an Orion Ross Electrode Flow Combination pH electrode (Orion 8172BNWP) connected to a Thermo Electron Corporation pH meter (Orion 3 star), suitable for pH measurements in organic solvents, was used. The filler solution was saturated LiCl in MeOH. The temperature of the solutions was maintained at 25 °C.

2.1. Etherification experiments

The etherification reactions were performed in a 300 mL stainless steel autoclave fitted with a gas entrainment stirrer and a dip tube for sampling. Methanol (57.7 g, 1.800 mol) and 2-methyl-2-butene (11.39 g; 0.163 mol) were weighed into the reactor vessel, and the reactor was assembled, pressurised to 3 bar with N_2 gas (to retain the reagents in the liquid phase) and heated to 100 °C. The $Zr(OTf)_4$ catalyst (0.112 g, 0.163 mmol, 0.1 mol%), dissolved in methanol (10.0 g, 0.312 mol, to make total of 2.112 mol MeOH), was transferred into a 50 mL high pressure sample holder using a syringe, and the sample holder was pressurised to 6 bar with N_2 gas. The catalyst mixture was introduced into the reactor at 100 °C and the pressure brought to 6 bar with N_2 gas (time = 0). Samples were taken over time during 2.5 h using a dip tube coupled directly in line with a GC, and analysed using GC-FID.

2.2. Catalyst recycling of $Zr(OTf)_4$ and $Al(OTf)_3$

The etherification reactions were performed in a 300 mL stainless steel autoclave reactor as described in Section 2.1 above. At the end of each experiment, the reaction medium was transferred to a glass round bottomed flask and the catalyst was recovered by removal of the liquid phase by distillation using a rotary evaporator. The catalyst residue so recovered was dissolved in 10 g of methanol and transferred into a 50 mL stainless steel sample holder, which was pressurised to 6 bar with N_2 gas. Fresh reagents (alcohol and olefin, as per the descriptions in Section 2.1 above) were charged into the reactor (so as to match the constitution of reagents described in Section 2.1 above) and the mixture heated to operating temperature prior to addition of the recycled catalyst to the autoclave from the pressurised sample holder.

2.3. pH measurements

Samples were prepared in deionised water, water/MeOH (1:1 m/m) and MeOH, respectively. The pH of the solutions was measured in triplicate at the given temperature. For measurements in neat MeOH, the probe was immersed in deionised water and gently dried with a soft absorbent material after each measurement to regenerate the hydration layer on the glass membrane of the probe. This protocol ensures improved probe stability during the individual readings.

3. Results and discussion

In time-limited reactions (2.5 h) designed to highlight rate differences between the catalysts, triflates of Zr and Al (Table 1, entries 1 and 2) were found to efficiently catalyse direct methyl ether formation from 2-methyl-2-butene and methanol.

$Sc(OTf)_3$ showed significantly lower activity (Table 1, entry 3) while lanthanide triflates (of Yb, La, Sm, Gd) and $AlCl_3$ and $ZrCl_4$ were found to be virtually without activity. There is a loose correlation between catalyst activity and the ionic radius of the metal triflate concerned (Table 1, entries 1–7), which ties the catalytic activity of the triflates in this instance more strongly to charge density, being the ratio of charge to ionic radius (z/r) [26]: the harder metals showed improved catalytic activity for these reactions over the softer metals. The lack of activity with the metal chlorides also mirrors the relative hardness of given metal systems with different counterions (in this case triflate versus chloride) and the influence thereof on the activity of the Lewis acid as a catalyst. Thus, for a given metal with a given charge density, the counterion plays a role in determining the hardness and hence also the activity of the catalyst [27]. It should also be noted, though, that the metal chlorides involved here are hydrolytically sensitive and may have undergone methanolysis to some extent leading to lower catalyst activity $M(OMe)_x(Cl)_n$ materials. The metal triflates do not readily suffer the same fate because they are generally resistant to hydrolysis [21,23,28], rendering them particularly useful Lewis acid catalysts in protic media. In fact, they may be isolated and recovered for recycling by aqueous extraction [19b]. We have also shown various examples of differential activity between triflic acid and metal triflates [19–21,28–30], which collectively point away from triflic acid as being the active catalyst in such systems. Additionally, the metal triflate catalyst may be recovered by various means, including extraction into water and subsequent drying of the catalyst by heating to 120 °C under vacuum [19b] and by distillation of the product (this work and in references 20 and 30), conditions under which triflic acid, if it forms, should be removed.

Minor levels (<1%) of isomerisation of 2-methyl-2-butene to 2-methyl-1-butene were observed in the process (by GC-FID analysis). In the event, these two isomers provide the same ether product and this side reaction is of no consequence here. In the cases of $Zr(OTf)_4$

Table 1
Catalysed reaction of methanol with 2-methyl-2-butene and correlation to ionic radii[a].

Entry	Catalyst	Yield (%)	Ionic radius (Å) [26]
1	$Al(OTf)_3$	55[b]	0.675
2	$Zr(OTf)_4$	55[b]	0.860
3	$Sc(OTf)_3$	16	0.885
4	$Yb(OTf)_3$	7	1.008
5	$Sm(OTf)_3$	3	1.078
6	$La(OTf)_3$	2	1.098
7	$Gd(OTf)_3$	2	1.172

[a] 100 °C, 6 bar N_2 pressure, 2.5 h, MeOH (65.72 g; 1.960 mol, 13 eq.), 2-methyl-2-butene (11.39 g; 0.163 mol), 0.1 mol% catalyst with respect to the alkene.

[b] 55% is the equilibrium conversion of the alkene to the ether product (that equilibrium is reached is clear from Fig. 2, see below).