

Synthesis of carbonate esters by carboxymethylation using NaAlO_2 as a highly active heterogeneous catalyst

*Sreerangappa Ramesh, Kiran Indukuri, Oliver Riant, and Damien P. Debecker**

UCLouvain, Institute of Condensed Matter and Nanosciences (IMCN), Place Louis Pasteur 1, box L4.01.09, 1348 Louvain-La-Neuve, Belgium, damien.debecker@uclouvain.be

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Abstract. Sodium aluminate is presented as a highly active heterogeneous catalyst able to convert a range of alcohols into the corresponding unsymmetrical carbonate esters by reaction with dimethyl carbonate. Preparing NaAlO_2 via spray drying allows to boost the basic properties and the activity of the catalyst.

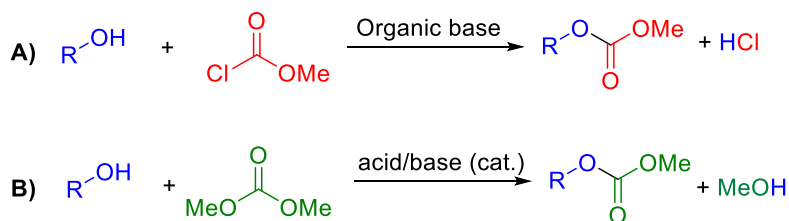
Carbonate esters are important compounds in the bulk chemicals industry, as they find applications as green solvents, lubricating oils and fuel additives.¹⁻² Carbonates esters are also key compounds in organic synthesis.³⁻⁵ They are used as synthetic intermediates in the total synthesis of biologically active natural products such as atomoxetine, nephrosteranic acid, and roccellaric acid.⁶ They serve as protecting groups of alcohols owing to their higher stability compared to the corresponding esters under basic conditions.⁷⁻⁸ In particular, allylcarbonates are valuable intermediates in asymmetric allylic substitution reactions.⁹

Unfortunately, the currently applied routes toward these chemicals rely on toxic reagents – e.g. chloroformates, trimethylamine, pyridine, phosgene – and on the use of homogeneous catalysts, which are non-reusable and require onerous separation procedures (Scheme 1A).¹⁰ A greener alternative is the carboxymethylation reaction using (i) environmental friendly reagents and (ii) heterogeneous catalysts.

Dialkyl carbonates are interesting reagents for the synthesis of mixed carbonate esters from alcohols. For example, dimethyl carbonate (DMC) – which can be obtained by the reaction of methanol with CO₂¹¹⁻¹³ – is emerging as a green and versatile reagent for a wide range of chemical transformations, including carboxymethylation.¹⁴⁻¹⁵ Various homogeneous acid or base catalysts have been reported for the carboxymethylation reactions using DMC (Scheme 1B). For example, *in situ* generated lanthanum(III) nitrate alkoxide was proposed by Hatano et al.¹⁶ Recently, McElroy et al. reported various homogeneous acids as efficient catalysts.¹⁷ While primary alcohols were efficiently converted, secondary alcohols required stoichiometric amounts of acids to undergo the carboxymethylation reaction. An attractive route was proposed by Mutlu et al., using an organo catalyst (1,5,7,-triazabicyclo[4.4.0]dec-5-ene) able to convert a large range of alcohols

– including tertiary alcohols – to the corresponding unsymmetrical carbonates in a solvent-less reaction with DMC.¹⁸

Heterogeneous catalysts would offer an even greener pathway, provided they can demonstrate high efficiency, selectivity, and recyclability. However, up until now, only a handful of heterogeneous catalysts showed significant activity for the synthesis of mixed carbonate esters using di alkylcarbonate (Scheme 1B). Sartorio *et al.* developed an efficient hybrid organic-inorganic catalyst by anchoring Triazabicyclodecene (TBD) onto a MCM-41 silica.¹⁹ Figueras *et al.* used fluorinated hydrotalcites, MgLa mixed oxides and CsF/ α -Al₂O₃ as basic solid catalysts, demonstrating that the rate of the reaction was roughly proportional to the number of strongly basic sites present on the catalyst.²⁰ Kantam *et al.* proposed a nano crystalline magnesium oxide showing good efficiency, selectivity and stability.²¹ Stanley *et al.* used various basic catalysts for the carboxymethylation of cinnamyl alcohol.²² Tabanelli *et al.* used MgO for the synthesis of aliphatic mixed alkyl-methyl carbonates and catechol carbonate.²³



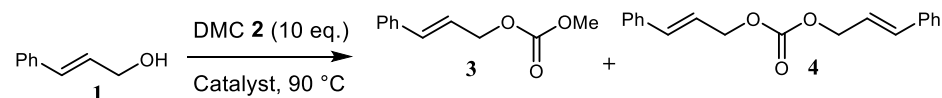
Scheme 1. Methods for the carboxymethylation of alcohols.

These reports prompted us to investigate strongly basic catalysts. Over the past few decades, research on solid basic catalysts, such as magnesium oxides, apatites, layered double hydroxides, alkali doped zeolites and basic metal-organic frameworks has gained interest.²⁴⁻³⁰ Sodium aluminate (NaAlO₂) is a highly basic material, inexpensive and readily available in the solid form or as a concentrated solution. It finds applications in water purification, paper industry and as a

precursor in zeolite synthesis.³¹ Being insoluble in various organic solvents, NaAlO₂ can be used as a true heterogeneous catalyst.³² Nevertheless, only a small number of publications have reported NaAlO₂ as an active heterogeneous catalyst for a limited number of base-catalyzed reactions such as isomerisation,³²⁻³³ transesterification,³⁴⁻³⁵ and condensation.³⁶ Recently, we showed that NaAlO₂ is an excellent catalyst for the production of glycerol carbonate in mild conditions.³⁷⁻³⁸ Earlier, the in-situ formation of NaAlO₂ from NaOH and γ -alumina was indeed also reported during this reaction.³⁹ Thus, we anticipated that NaAlO₂ would also catalyze transcarbonation reactions between DMC and other types of alcohols.

Here, NaAlO₂ is probed as a catalyst for the carboxymethylation reaction. Various mixed carbonate esters are synthesized by reacting the corresponding alcohols with DMC, acting both as the reagent and the solvent. The NaAlO₂ catalysts are either readily acquired from commercial sources or prepared using a spray drying process⁴⁰ aiming at increasing the concentration of defects, responsible for the formation of strong basic sites.

Table 1. Screening of common heterogeneous and homogeneous basic catalysts for the carboxymethylation of cinnamyl alcohol (**1**) with DMC and comparison with sodium aluminate.^a



Entry	Catalyst	Time (h)	Conversion (%) ^b	Selectivity for 3:4 (%) ^b
1	Blank	24	0	---
2	Triethylamine ^c	24	100	97:3
3	NaOH ^c	24	15	15:0
4	K ₂ CO ₃ ^d	96	91	90:10
5	CsF/Al ₂ O ₃ ^d	50	94	94:6

6	NaX, NaY ^d	24	0	---
7	MgO	24	30	100:0
8	Hydrotalcite	24	40	99:1
9	NaAlO ₂	24	52	99:1
10	SD-NaAlO ₂	24	76	99:1

^aReaction conditions: 5 mmol of **1**, 50 mmol of DMC, 0.10g of catalyst at 90 °C. ^bConversion and selectivity were determined by gas chromatography. ^c1.2 equivalent basic homogeneous catalyst. ^dResults from Stanley et al.²²

The carboxymethylation of cinnamyl alcohol (CA, **1**) with DMC in the liquid phase was used as a probe reaction (Table 1). After 24h reaction at 90°C the reaction did not proceed at all in the absence of a catalysts (Table 1, entry 1). Using an excess of triethylamine as a conventional homogeneous basic catalyst, a total conversion of could be achieved with 97% selectivity. Using NaOH, the conversion reached only 15%. K₂CO₃ was also reported to catalyse the reaction but longer reaction times had to be used to reach decent conversion.²² In the same conditions, basic NaX and NaY zeolites were reported to be inactive but CsF/Al₂O₃ showed significant activity after a long reaction time (50h).²² Here, common solid base catalysts such as MgO and hydrotalcites were tested as benchmarks and showed only moderate CA conversion (entries 7 and 8). On the contrary, sodium aluminate showed high CA conversion (entries 9 and 10). Interestingly, the NaAlO₂ catalyst prepared by spray drying (vide infra) was even more active than the commercial NaAlO₂. After standard workup, H-NMR analysis of the crude mixture showed purity well above 95% (see ESI), excluding the need for purification. Selectivity towards cinnamyl methyl carbonate (**3**) was close to 100%. Thus, among the tested catalysts, NaAlO₂ showed the best performance and appeared as a highly promising catalyst for the carboxymethylation reaction.

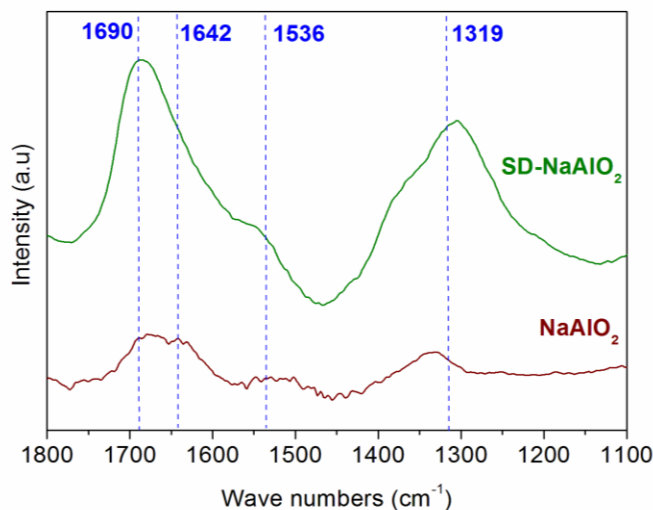


Figure 1. CO₂-DRIFT spectra of NaAlO₂ and SD-NaAlO₂ catalysts

The superior activity of NaAlO₂ catalysts has to be related to the strongly basic properties of this crystalline material.³¹ XRD confirmed that the main crystalline phases were NaAlO₂·1.25H₂O, NaAlO₂ and Na₂CO₃ (see Figure S1).⁴¹⁻⁴² Consistently, DRIFT spectroscopy coupled with CO₂ adsorption showed the abundance of surface basic sites (Figure 1). Bridged bidentate carbonate (1690 and 1642 cm⁻¹) and chelating bidentate carbonate (1536 cm⁻¹) adsorption can be assigned to moderate or weak basic sites.⁴³⁻⁴⁴ CO₂ adsorbed on oxygen ions with the lowest coordination number (usually monodentate) leads to strong basic sites (1319 cm⁻¹). FTIR spectra obtained on NaAlO₂ catalysts feature an intense band at 1420 cm⁻¹, attributed to carbonates (Figure S2A). The other main IR peaks correspond to O-O bonds at 794 cm⁻¹ and vibrations of the Al-O bond at 558 cm⁻¹ and 627 cm⁻¹, and O-Na-O bonds at 454 cm⁻¹. Compared to the commercial sodium aluminate (NaAlO₂), the catalyst prepared by spray drying (denoted SD-NaAlO₂; see supporting information for the preparation procedures) was significantly more active. This catalyst consists of spherical particles in the 0.1–5.0 μm size range (Figure 2). Their spherical shape is linked to the preparation process in which particles are produced after the evaporation of the solvent contained

in aerosol droplets.⁴⁵ Such spray drying method favors the formation of smaller crystallites (Figure S1), which leads to a higher concentration and/or accessibility of strongly basic edge ions (defects).³⁷ Indeed, CO₂-DRIFTS shows that SD-NaAlO₂ globally exhibits higher basicity compared to the commercial NaAlO₂, and especially a larger contribution of strong basic sites (Figure 1). CO₂-temperature programmed desorption (TPD) experiments (Figure S2B and Table S1) provide a more quantitative analysis of the total basicity of the catalysts, and confirm that the spray dried catalysts showed higher surface basicity (0.80 mmolCO₂.g⁻¹ for SD-NaAlO₂ vs. 0.47 mmolCO₂.g⁻¹ for commercial NaAlO₂). With this highly efficient catalyst in hand, the reaction was further studied and optimized to boost conversion levels, check for the stability of the catalyst, and expand its scope.

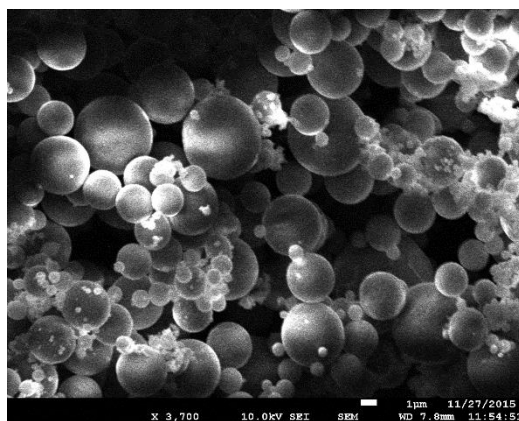


Figure 2. Scanning electron micrograph of SD-NaAlO₂ catalyst.

Under atmospheric pressure, the maximum reaction temperature is 90°C (the boiling temperature of DMC). Lower conversion was obtained at lower temperature but the selectivity reached 100% instead of 99% (Figure S3). Almost quantitative conversion of CA into cinnamyl methyl carbonate can be reached by increasing the catalyst amount to 0.2 g (Table S2). The recyclability of SD-NaAlO₂ was tested by performing 5 consecutive runs of reaction (Figure 3).

After each reaction, the catalyst was centrifuged, washed three times with 5 mL ethanol, and dried at 120°C for 6h before being used with fresh reactants. In these recycling experiments, no significant activity drop was observed. Additionally, a “hot filtration” experiment was run, demonstrating that the activity is strictly arising from the solid catalyst (Figure S5). The integrity of the spent SD-NaAlO₂ catalyst was also verified by XRD, FTIR and CO₂-TPD. Both the crystalline structure (Figure S1) and the surface basicity (Figure S2B) of the used solid were unaffected after the reaction. Thus, the catalyst can be described as truly heterogeneous, stable, resistant to leaching during the reaction, and therefore recyclable.

The scope of the catalyst was evaluated with a large series of alcohols, at 8h and 24h of reaction. Various primary allylic alcohols **2a-d** afforded the corresponding carbonate esters with high conversion and selectivity after only 8 hours of reaction. Secondary allylic alcohol **2f** gave only 31% of conversion after 8h and 45% by increase in reaction time to 24h. In this case, we did not observe any diallylcarbonate product **4f**. No conversion was observed from the tertiary allylic alcohol, linalool (**2e**). Steric hindrance is probably the reason for the lower activity when going from the primary to the secondary and then tertiary allyl alcohols. Primary benzylic alcohols like 3,5-dimethoxy benzyl alcohol and 3,5-di(trifluoromethyl) benzyl alcohol **2h-j** afforded the corresponding carbonate esters in good yields. Secondary benzylic alcohols such as, 1-phenylpropan-1-ol and 1-(naphthalen-2-yl)ethan-1-ol were also converted to the corresponding carbonate esters **3k** and **3l** with 100% selectivity but with moderate conversion. Interestingly, alcohols bearing a hetero aryl group (e.g. furfural **1m**) can also be converted. 2-furfurmethylester carbonate **3m** was obtained after 8h with 78% conversion and full selectivity. The same reaction after 24h gave 100% conversion with 93% selectivity. The carboxymethylation reaction of primary aliphatic alcohols (**1n**) was also established, with quantitative conversion and selectivity at 24h

reaction time. Menthol **1o** reacted with 100% of selectivity, with 45% of conversion. We also tested this reaction for obtaining propargyl carbonates, which are important synthetic precursors in the synthesis of allenes and various heterocyclic compounds.⁴⁶ After 24h, the reaction showed 93% conversion of 2-butyne-1-ol **2g** with 100% selectivity to **3g**.

Table 2: Scope of the reaction for the NaAlO₂-catalysed carboxymethylation of alcohols.

$\text{R-OH} + \text{MeO-CO-OMe} \xrightarrow[8 \text{ or } 24 \text{ h}]{\text{NaAlO}_2, 90^\circ \text{C}}$
 $\text{R-O-CO-OMe} + \text{R-O-CO-O-R}$

1 2 3 4

Entry ^a	Alcohol (1)	Product (3)	Time (h)	Conversion ^b	Selectivity 3/4 (%) ^b
a			8	97%	99:1
			24	97%	97:3
b			8	85%	96:4
			24	92%	90:10
c			8	93%	97:3
			24	95%	97:3
d			8	53%	100:0
			24	76%	100:0
e			8	0%	---
			24	0%	---
f			8	31%	100:0
			24	45%	100:0
g			8	70%	100:0
			24	93%	100:0
h			8	100%	97:3
			24	100%	96:4
i			8	79%	98:2
			24	81%	98:2
j			8	94%	94:6
			24	92%	91:9
k			8	17%	100:0
			24	69%	100:0
l			8	39%	100:0
			24	65%	100:0
m			8	78%	100:0
			24	100%	93:7
n			8	93%	100:0
			24	100%	100:0
o			8	45%	100:0
			24	45%	100:0

^aConditions: Alcohol (5.0 mmol), DMC (50 mmol) and NaAlO₂ (0.20g) at 90 °C. ^bConversion and selectivity were measured by ¹H NMR (300MHz) using the NMR integration ratio between

the desired product and the by-product (see ESI). For entry a, conversion and selectivity were measured by GC and confirmed by NMR. For entries b, c, and d, selectivity was evaluated by GC.

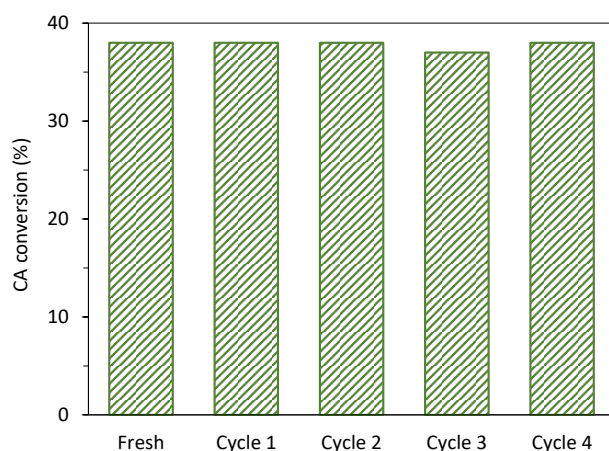


Figure 3. Regeneration studies (Reaction conditions: 5mmol of CA, 50 mmol of DMC, 0.10 g of catalyst at 90 °C for 2 h). Under these conditions, the conversion is far from equilibrium. A recycling experiment was also done at high conversion (8h reaction, 0.20 g of catalyst) to show that high yields can be achieved over several runs as well (see Figure. S4).

In conclusion, the heterogeneously catalyzed synthesis of mixed carbonate esters using sodium aluminate and DMC is demonstrated for a large range of substrates. The reaction can be considered greener than the classical routes because it is run with environmentally friendly reactants and with a recyclable solid catalyst. The preparation of NaAlO_2 by a simple spraying method yield a highly basic catalyst which shows excellent performance levels and acts as a truly heterogeneous and recyclable catalyst.

Supporting Information. General experimental procedures, additional catalyst characterization, characterization of the spent catalyst, optimization of reaction conditions, heterogeneity and leaching test, NMR spectra of the products

AUTHOR INFORMATION

Corresponding Author

*Damien P. Debecker Damien.debecker@uclouvain.be

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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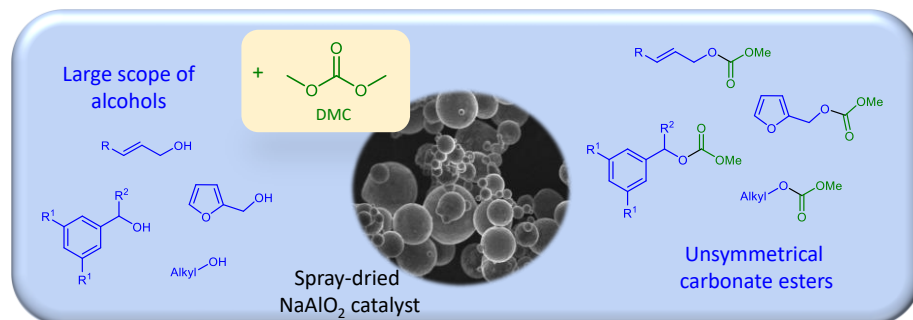
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Graphical abstract



Synopsis

A range of mixed carbonate esters are obtained in high yields, using NaAlO_2 as a strongly basic heterogeneous catalyst. The reaction is carried out starting from various alcohols and with dimethyl carbonate acting as the solvent and carboxymethylation reagent. Sodium aluminate is shown to be a cheap, stable and recyclable solid catalyst.