Room temperature synthesis of glycerol carbonate catalyzed by spray dried sodium aluminate microspheres

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Abstract

Nanostructured $NaAlO_2$ microspheres are produced from an aqueous solution, by a one-pot spray drying route. The obtained solids are composed of spherical aggregates of sodium aluminate with small crystallite size and strong surface basicity. This makes them highly active catalysts in the base-catalyzed synthesis of glycerol carbonate from glycerol and dimethyl carbonate. The new catalyst does not leach and is recyclable. $NaAlO_2$ microspheres outcompete commercially available $NaAlO_2$ as well as other basic catalysts in the usual reaction conditions, i.e. at relatively high reaction temperature. Remarkably, the new catalyst also catalyze efficiently the room temperature synthesis of glycerol carbonate.

Keywords

$NaAlO_2$; glycerol; aerosol; dimethyl carbonate; heterogeneous catalysis; biomass conversion

1. Introduction

Glycerol – produced in large excess by the biodiesel industry – can be profitably converted into several value-added chemicals. Among those products, glycerol carbonate (GC) received significant attention due to its wide industrial applications [1,2]. It is a green alternative for petroleum derivative such as ethylene or propylene carbonates and its production from renewable resources using environmentally friendly routes is of high interest [3]. Industrially GC is currently mainly obtained by transesterification of glycerol with – for instance – ethylene carbonate. This leads to ethylene glycol as by-product, making product purification complicated [1,4,5]. Another possible method is to produce GC by the reaction of glycerol with urea in the presence of a Lewis acid catalyst. The reaction must be carried out in vacuum in order separate ammonia and shift the equilibrium [6,7]. One greener alternative is the use of dimethyl carbonate (DMC) as co-reagent for the transesterification of glycerol, leaving only methanol as a by-product, easy to separate from the reaction medium [8]. This catalytic reaction requires the development of highly active catalysts that can work under mild conditions to make this process completely environmental friendly.

Comprehensive reviews have been published recently, reckoning a large series of working catalytic systems for the synthesis of GC from glycerol and DMC, including acid, base and enzyme catalysts [1,2,9,10]. To date however, drawbacks of existing GC synthesis from glycerol and DMC include: relatively high reaction temperature, long reaction period (slow reaction rates), mediocre environmental performance (depending on the solvent used), and high cost for the catalyst. For example, N-heterocyclic carbenes were reported as active homogeneous catalysts at room temperature [11] but are not recoverable and therefore expensive for large scale industrial application. Thus, there is a need for the development of processes that can be run under mild and solvent-free conditions, with a cheap, recoverable, recyclable, and highly active catalyst.

In contrast to solid acid catalysts, less effort has been devoted to solid base catalyst [12]. The interest for basic catalysts is currently rising due to their applications in biomass conversion to value added products. $NaAlO_2$ is a strongly basic compound which finds important applications in zeolite synthesis, as a bleaching agent in industrial and chemical waste management, and in the construction and textile industry [13-15]. $NaAlO_2$ is soluble in water but insoluble in alcohol, which makes it a suitable heterogeneous catalyst candidate for base-catalyzed organic reactions in alcoholic solvent. It was recently reported as catalytically active for transesterification [16-18] and condensation [19] reactions. $NaAlO_2$ is inexpensive and widely available.

In here, we report that $NaAlO_2$ is highly active for the synthesis of GC from glycerol and DMC. Commercial $NaAlO_2$, however, is characterized by high crystallinity and relatively low surface basicity. Since catalytic transesterification is known to occur on strong basic sites at the solid surface, it appears reasonable to attempt to improve the textural and basic properties of the solid catalyst. The purpose of the present study is two-fold: (i) developing a more active form of $NaAlO_2$ using a cheap and scalable preparation method and (ii) investigating the possibility to run the glycerol carbonate synthesis under mild conditions (room temperature).

2. Experimental

We propose a one pot preparation of highly active $NaAlO_2$ catalysts by a fast and scalable spray drying method [20,21] starting from a commercially available $NaAlO_2$ solution. The aerosol catalyst preparation is described in details in the electronic supplementary information (ESI). Briefly, an aqueous sodium aluminate solution (25 wt.% $NaAlO_2$, Dequenne Chimie) was sprayed in an atomizer from TSI and the aerosol was dried rapidly by passing through a tubular furnace maintained at 700°C (sample denoted “AerW”). Alternatively, the solution was first blended with ethanol before spray drying (sample denoted “AerWE”). The commercial solid $NaAlO_2$ from Carlo Erba (denoted “CM”) was used as such as a benchmark. Additionally, the $NaAlO_2$ solution was vacuum dried in a static autoclave to yield another reference solid (denoted “VD”). Procedures for the characterization of the solids, reaction conditions and analytic details are provided in ESI.

3. Results and discussions

Aerosol-made $NaAlO_2$ catalysts consist of spherical particles in the 0.1-5.0 μm size range (Figure 1 and ESI, Figure S1). Their spherical shape is linked to the preparation process in which particles are produced after the evaporation of solvents contained in spherical aerosol droplets [22-23]. CM and VD samples on the other hand show a platelet-like morphology (Figure S2).

All $NaAlO_2$ samples studied here exhibited the expected XRD patterns (Figure 2). Three phases are systematically detected in similar relative proportions: $NaAlO_2 \cdot 1.25H_2O$ (JCPDS 00-044-0430), $NaAlO_2$ (JCPDS 00-033-1200) [24,25] and Na_2CO_3 (JCPDS 53-61386). No other crystalline species was detected. The average $NaAlO_2$ crystallite size for each catalyst was approached using the Debye-Scherrer formula applied on the $2\theta = 35.0°$ diffraction line of $NaAlO_2$. Catalysts made through aerosol exhibited relatively small crystallites (16 and 17 nm for AerWE and AerW respectively), as compared to CM (36 nm) and VD (42 nm) samples.

FT-IR spectra were recorded in ATR mode (ESI, Figure S3). The intensity of the peak at 1420 cm^{-1} – attributed to carbonates – increased with the decrease in particle size, which figures a higher amount of adsorption sites for carbonate species on the samples with smaller crystallites (i.e. aerosol-made catalysts). 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}.

The basicity of the catalysts was evaluated using temperature programmed CO_2 desorption (CO_2-TPD) (Figure 3). The method is known to allow a quantitative analysis of basicity, with a distinction between weak, moderate and strong sites [26,27]. It should be noted, however, that a bulk gas/solid reaction may also occur during CO_2 adsorption, transforming sodium aluminate into sodium carbonate. So in the present case, CO_2-TPD is not strictly a surface reactivity analysis. Nevertheless, the CO_2 desorption profiles allow visualizing the ability of the sample to interact with acidic CO_2 and to retain it upon heating. Here, the preparation method dictates the behavior of the sodium aluminate catalysts: amount of adsorbed CO_2 increases as follows VD < CM < AerW < AerWE. Also, the high temperature desorption peak is getting larger as the crystallite size decreases. This has to be correlated with crystallinity: samples with smaller crystallites exhibit higher concentration and/or accessibility of strongly basic edge ions (defects) [28].

XPS experiments were carried out to gain insights into the surface composition and the nature of the phases present in the catalysts (Figure 4 and ESI Table S1). For all the samples investigated, the XPS survey showed Na, Al, O and C to be the main elements, along with small but significant contamination by Cl (2-5 atomic %). The surface Na/Al ratio is systematically higher than the theoretical ratio of 1 expected from the stoichiometry of $NaAlO_2$. This may be related to the presence of Na_2CO_3 on the surface. For all samples, the Na 1s peak is aligned to the expected value of 1071.2 eV. The Al 2p peaks systematically falls at relatively low binding energy, as compared to the Al species found in the 73.9-74.6 eV range for $Al(OH)_3$ or Al_2O_3 [29,30]. Lower binding energy indicates a higher electron density around Al atoms – itself resulting from a less electronegative environment in $NaAlO_2$ as compared to alumina of Al hydroxides or oxides. It is interesting to note that this downward shift in BE is particularly pronounced for the samples for which large crystals of $NaAlO_2$ have formed (especially VD and CM) and less pronounced for aerosol-made samples. This may be correlated with the presence of more abundant defects in which surface Al atoms are not strictly in a $NaAlO_2$ environment.

From the catalytic point of view, all four $NaAlO_2$ samples catalyze the synthesis of GC from glycerol and DMC, exhibiting full selectivity for GC (see NMR results, Figure S4). In the literature, activity is often reported at relatively high temperature and with an excess of DMC. Here, at 90°C and with a glycerol: DMC molar ratio of 1:2, $NaAlO_2$ catalysts (3 wt.%) reached the thermodynamic equilibrium (~94% yield) after 40 min (Figure S5). This outcompetes reported performance for other basic catalysts or ionic liquids [31-33], which all need higher reaction temperatures, or longer reaction times to reach similar yield (Table 1). Remarkably, aerosol made catalyst showed much faster kinetics as compared to the commercial solid (Figure S5). Equilibrium conversion was almost reached (93%) after 20 min with AerWE, when CM only reached 46% conversion.

This high activity of $NaAlO_2$ microspheres prompted us to investigate the room-temperature synthesis of GC. Indeed, while the thermodynamic equilibrium is less favorable at lower temperature – thus limiting the achievable yield, a room temperature process may prove more attractive both in economic and environmental terms. Up to now, however, only homogeneous catalysts (N-heterocyclic carbenes) have been reported as highly active catalysts at room temperature (Table 1) [11].

At 30°C, the AerWE catalyst reached the equilibrium value (75% yield) after 30 min (Figure 5). To validate the heterogeneous nature of the catalyst, a leaching test was conducted using the catalyst filtration method. After 10 min reaction, the catalyst was filtered off and stirring at reaction temperature was continued. Glycerol carbonate yield remained constant 58% (Figure 5). Hence the solid used is truly a heterogeneous catalyst.

To compare the different catalysts, we approximate initial activity by looking at the GC yield at after 5 min of reaction (Figure 6). Levels of activity varied noticeably with respect to catalyst preparation; aerosol catalysts being significantly more active than the two benchmark catalysts. Despite marked differences in surface composition, both aerosol catalysts exhibit similar performance. The most active catalyst (AerWE) is ~5 times more active, reaching already 43% yield after 5 min of reaction. Vacuum dried sample with the largest crystallite showed the lowest GC yield (9%). An evident link is found between $NaAlO_2$ crystallite size and initial activity: aerosol prepared catalysts – exhibiting smaller particle size – are identified as highly active catalysts for the studied reaction. This has to be related to the enhanced basic properties of aerosol-made $NaAlO_2$ catalysts, because basicity also increases when the particle size decreases, as discussed above.

To push the equilibrium toward the formation of GC, an appropriate strategy is to introduce DMC in excess. For example, a glycerol: DMC molar ratio of 1:3 allowed to reach the equilibrium GC yield of 83% at 30°C, after 30 min, with 3 wt. % of AerWE catalyst. Under these conditions, recycling tests were performed by re-using spent catalyst several times. Spent catalyst was separated by centrifugation after completion of the reaction (30 min) and washed twice with ethanol (5ml) followed by vacuum drying at 100 °C for 4h. The dried catalyst was further used in the reaction with a fresh reaction mixture. The catalyst maintained the same high activity even after the 4th run (Figure S6).

4. Conclusion

Sodium aluminate, as a cheap, available, recoverable, reusable, and highly active solid material is a promising heterogeneous catalyst for the room temperature synthesis of glycerol carbonate from glycerol and DMC. While solid $NaAlO_2$ obtained commercially or by simple vacuum drying is active in the reaction, it is advantageous to prepare it in a more divided form, by the spray drying method presented here. The latter allows the continuous, one-step and scalable preparation of nanostructured spherical sodium aluminate catalysts with small crystallite size and high surface basicity. These properties make these materials very attractive for the glycerol carbonate synthesis under environmentally benign conditions, even exhibiting high activity at room temperature.

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Table 1. One-pot synthesis of glycerol carbonate from glycerol and DMC with various catalysts.

Catalyst	T (°C)	Time (min)	Glycerol:DMC molar ratio	GC yield (%)	Catalyst/glycerol wt. ratio (%)	Reference
Zn-Al hydrotalcite	120[a]	60	1:3	93	50	[25]
Acidic ionic liquids	100	30	1:3	98	2.5	[31]
KF/ Alumina	75	120	1:2	96	3	[32]
Gypsum	150	240	1:1.5	92	2.5	[33]
N-hetrocyclic carbenes	30	60	1:3.5	95	4	[11]
AerWE	90	30	1:2	94	3	This work
AerWE	30	30	1:3	83	3	This work

[a] under microwave heating

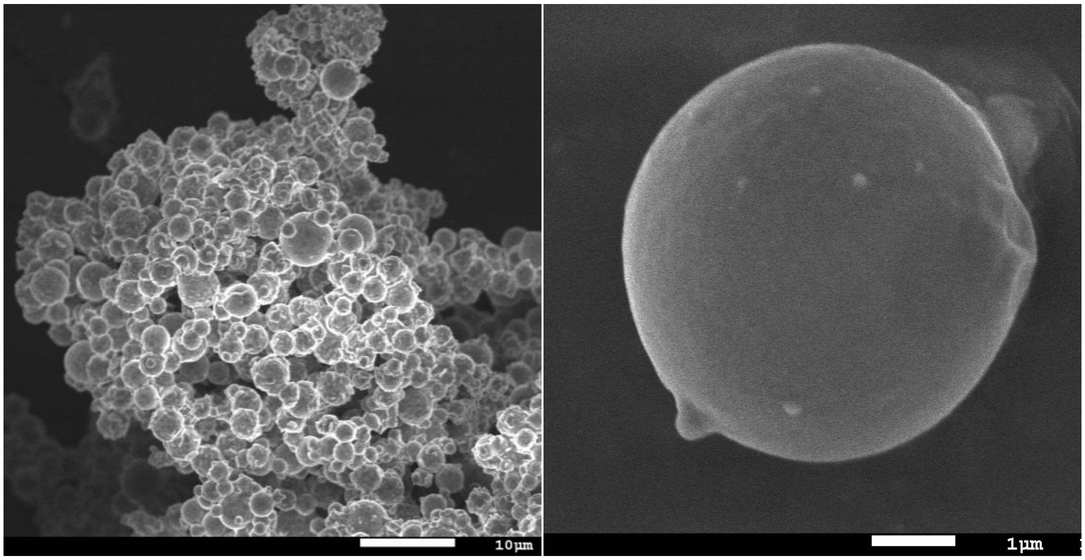

Figure 1. SEM micrographs of aerosol-made sodium aluminate catalyst (AerW).

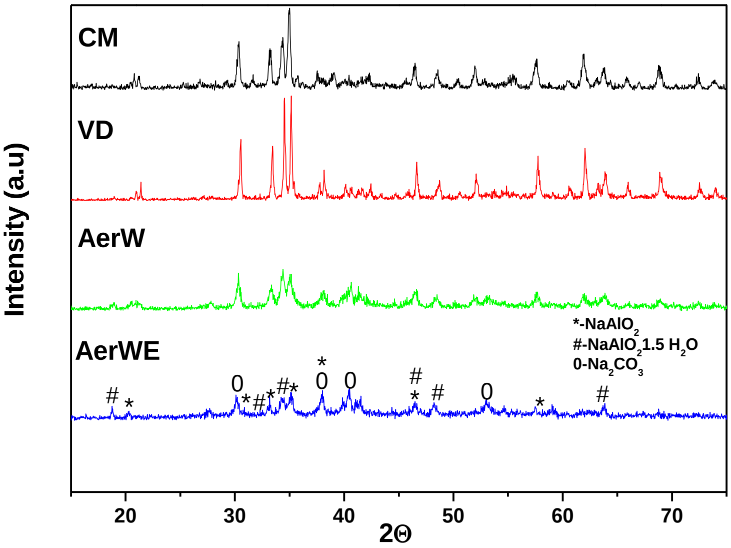

Figure 2. X-ray diffraction patterns for sodium aluminate catalysts.

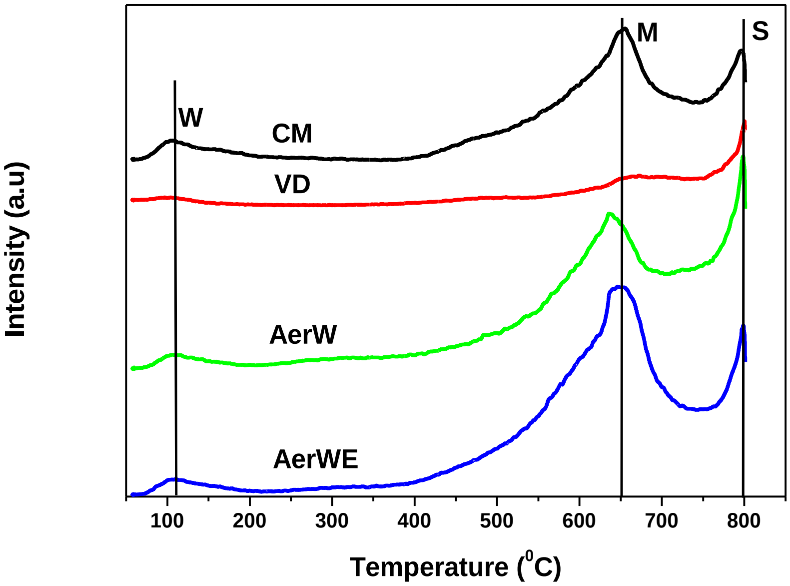

Figure 3. CO_2-TPD of sodium aluminate catalysts. Vertical lines are guide to the eye indicating weak (W), medium (M) and strong (S) CO_2 adsorption sites.

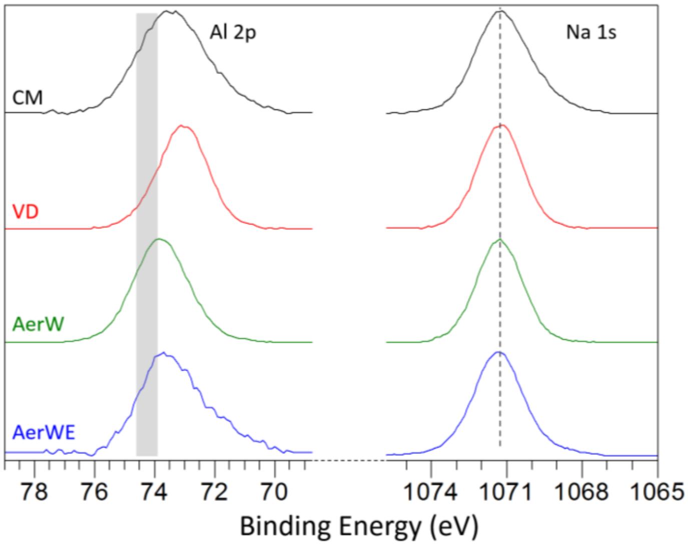

Figure 4. Al 2p and Na 1s XPS spectra of sodium aluminate catalysts. The grey zone is a guide to the eye representing the typical position of Al 2p in Al oxides or hydroxides. The dotted line is a guide to the eye showing that Na 1s peak is aligned to the expected position of 1071.2 eV.

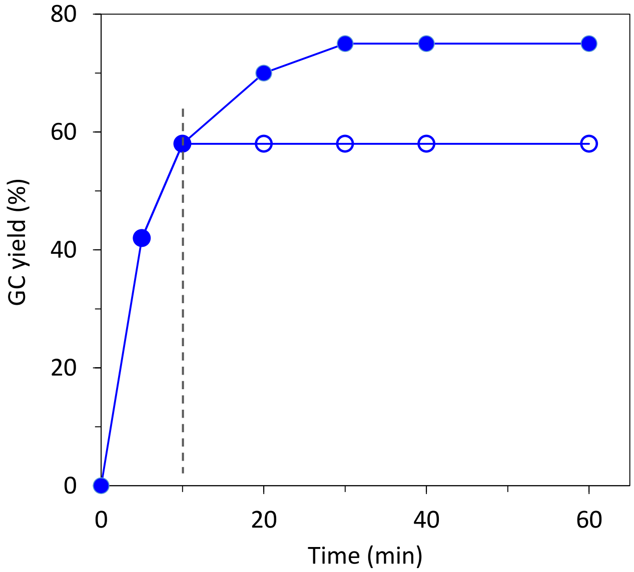

Figure 5. Evolution of the glycerol carbonate (GC) yield with time (●). Reaction conditions: 3wt. % of AerWE catalyst, 1:2mol ratio (Glycerol:DMC) at 30°C. In the leaching test (○), the solid catalyst was filtered off after 10 min of reaction and the reaction was continued without solid catalyst.

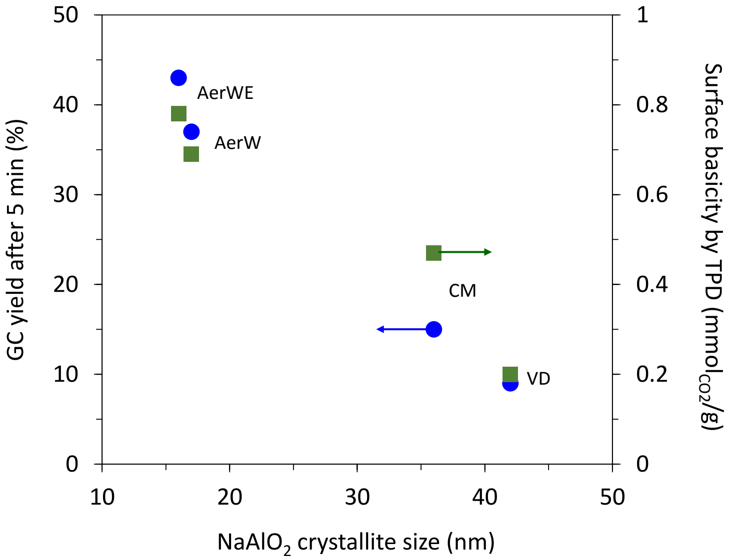

Figure 6. (●) Initial activity (approached by looking at the GC yield after 5 min of reaction), and (■) surface basicity (approached by integrating the CO_2-TPD curve) plotted as a function of $NaAlO_2$ crystallite size. Reaction conditions: 3wt. % of catalyst, 1:2 mol ratio (Glycerol:DMC) at 30°C.