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

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Nanostructured $NaAlO_2$ microspheres are produced by one-pot spray dried route, and are characterized by various physico-chemical methods. 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 catalyst does not leach and showed good reusability up to three cycles.

1. Scope

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] 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.[2] 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[3] 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.

$NaAlO_2$ 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. $NaAlO_2$ 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 and condensation reactions.[4] $NaAlO_2$ is inexpensive and widely available.

In here, we report for the first time 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 based on spray drying and (ii) investigating the possibility to run the glycerol carbonate synthesis under mild conditions (room temperature).

The catalysts are prepared by using an aqueous sodium aluminate solution (25 wt.% $NaAlO_2$, Dequenne Chimie) which was sprayed in an atomizer from TSI. 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 ("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"). The prepared catalysts are characterized by an array of physical and chemical methods (XRD, SEM, CO_2TPD, SEM and XPS).

Glycerol transesterification with DMC was carried out in liquid phase with a magnetic stirrer at 30° and 90° C and products were analyzed by gas chromatography and confirmed by ^{1}H-NMR analysis.

2. Results and discussion

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

From XRD patterns (Figure 2) three phases are systematically detected: $NaAlO_2 \cdot 1.25H_2O$, $NaAlO_2$ and Na_2CO_3. 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. The basicity of the catalysts was evaluated using temperature programmed CO_2 desorption (CO_2-TPD). 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.

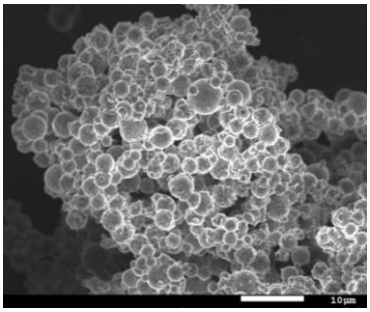

Figure 1. SEM image of AerW catalyst.

The XPS survey showed Na, Al, O and C to be the main elements. 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. 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. This downward shift in BE is particularly pronounced for the samples for which large crystals of $NaAlO_2$ have formed (VD, CM) and less pronounced for aerosol-made samples.

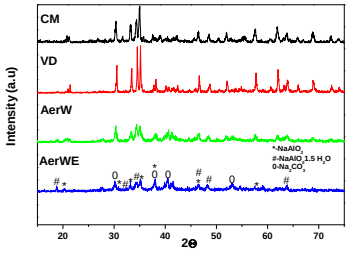

Figure 2. XRD pattern of $NaAlO_2$ catalysts.

From the catalytic point of view, all four $NaAlO_2$ samples catalyze the synthesis of GC from glycerol and DMC. In the literature, activity is often reported at relatively high temperature and with an excess of DMC. Here, at 90°C $NaAlO_2$ catalysts (3 wt.%) reached the thermodynamic equilibrium (~94% yield) after 40 min. This outcompetes reported performance for other basic catalysts or ionic liquids, which all need higher reaction temperatures, or longer reaction times to reach similar yield. Remarkably, aerosol made catalyst showed much faster kinetics as compared to the commercial solid. 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. At 30°C, the AerWE catalyst reached the equilibrium value (75% yield) after 30 min. 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%. Hence the solid used is truly a heterogeneous catalyst.

3. Conclusions

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. One post spray dried sodium aluminate resulted with small crystallites and high surface basicity which enhances the activity for glycerol carbonate synthesis. Such nanostructured $NaAlO_2$ catalysts are expected to find applications in various other base-catalyzed reactions like isomerization, hydrolysis, and condensation reactions.

References

1. R. M. Hanson, Chem. Rev,**1991**, 91, 437-475.
2. M.O. Sonnati, S. Amigoni, E. P. Taffin de Givenchy, T. Darmanin, O. Choule, F. Guittard, Green Chem, **2013**,15, 283-306.
3. B. Hervert, P. D. Mc Carthy, H. Palencia, Tetrahedron Lett, **2014,** 55,133-136.
4. A. V. Agafonov, I. A. Yamanovskaya, V. K. Ivanov, G. A. Seisenbaeva, V. G. Kessler, J. Sol-Gel Sci. Technol, **2015**,76 90-97.