$NaAlO_2$ supported on titanium dioxide as solid base catalyst for the carboxymethylation of allyl alcohol with DMC

Sreerangappa Ramesh, François Devred, Damien P. Debecker*
Institute of Condensed Matter and Nano sciences (IMCN), UCLouvain, Place Louis Pasteur, 1, box L4.01.09, 1348 Louvain la-Neuve, Belgium. Email: damien.debecker@uclouvain.be

Abstract

$NaAlO_2$-based heterogeneous catalyst efficiently convert allyl alcohol and dimethyl carbonate with high selectivity to allyl methyl carbonate. While sodium aluminate is highly active for the synthesis of such unsymmetrical carbonate, its handling is problematic because it is highly corrosive and hygroscopic. Here a simple impregnation method is applied to obtain $NaAlO_2/TiO_2$ catalysts, which are characterized by XRD, N_2-physisorption, Raman spectroscopy, SEM, TGA, CO_2-DRIFTS and CO_2-TPD. The carboxymethylation activity of these impregnated catalysts linearily correlates with their $NaAlO_2$ content. Yet, the catalyst loaded with only 20% active phase reaches the same activity as that of the pure $NaAlO_2$ phase. Importantly, our study demonstrates that this solid base catalyst is truly heterogeneous, stable, and reusable, paving the way to other potential applications in organic synthesis.

Keywords: Carboxymethylation, Solid base catalyst, Unsymmetrical carbonate esters, Titania, Sodium aluminate

1. Introduction

Allyl carbonates find many applications as monomers for organic glasses, as solvents, in the manufacture of lithium batteries and more widely as chemical intermediates for organic synthesis [1-6]. Such unsymmetrical carbonates are normally obtained by the reaction of alcohols with noxious reagents such as phosgene, dimethyl sulphate and pyridine. However, these reagents are toxic and suggested to be blacklisted in the context of green chemistry [7, 8]. It is therefore necessary to develop more convenient and environmentally benign catalytic routes for the synthesis of such carbonate esters [9]. Dimethylcarbonate (DMC) – which can be obtained from methanol and CO_2 in a relatively green way – features high biodegradability and low toxicity [10]. It has been proposed as an alternative green carboxymethylation agent, provided a strongly basic catalyst is employed [9]. Recently, for example, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) – an organo catalyst – has been reported as an active homogeneous catalyst for allyl carbonates synthesis using DMC [3].

For commercial scale applications, however, homogeneous catalysts face limitations in terms of reusability and price [11]. Hence, there is a need for the development of heterogeneous catalysts that better address the principles of green chemistry by providing the ease of separation and reuse [12]. Solid base catalysts are widely employed in many industrial processes for bulk, fine chemical synthesis and biomass conversion [13-16]. In the perspective of sustainable chemistry, innovative catalyst formulations are needed, with specific requirements (e.g. high surface basicity, low cost, made of earth abundant materials, stable, selective, etc.). Over the past few decades, research on solid-base catalysts, such as metal oxides [17-19], apatites [20, 21], layer double hydroxides [22-25], alkali doped zeolites [26-28] and metal–organic frameworks [29] has increased rapidly [30].

In particular, the carboxymethylation reaction of alcohols with DMC was investigated with different types of solid basic catalysts such as Mg-La mixed oxides [31], CsF/Al_2O_3 [32] and nano-crystalline MgO [1]. Very recently, we reported that $NaAlO_2$ is highly active for the carboxymethylation of various organic alcohols with DMC, outcompeting other reference basic solids [33]. Sodium aluminate ($NaAlO_2$, abbreviated 'SA' in the following) belongs to a class of solid super bases [34]. SA is highly soluble in water, but insoluble in most organic solvents, including alcohols, which makes it suitable for being used as a heterogeneous basic catalyst for organic reactions. In the early 70s, sodium aluminate was reported for the first time as solid catalyst for the oxidative coupling of methane to produce ethylene and it showed excellent conversion and selectivity among the catalysts studied [35]. Recently, it was found to be very active for transesterification [36-38], isomerisation [39, 40] and condensation reactions [41]. Thus $NaAlO_2$ is emerging as a promising solid catalyst for a range of base-catalysed organic reactions.

Nevertheless, $NaAlO_2$ is highly corrosive and hygroscopic, which complicates its use in the pure form, especially if large scale industrial applications are envisaged. In addition, pure $NaAlO_2$ possess low surface area (typically lower than 5 $m^2.g^{-1}$) which limits the amount of active basic sites and therefore its performance as a heterogeneous catalyst. Hence supporting a $NaAlO_2$ phase on a suitable support appears as a reasonable strategy to (i) benefit from more attractive textural properties and disperse $NaAlO_2$ to create more abundant basic sites and (ii) improve the handiness of the catalyst. Thus, in the present work, we describe the preparation of a new type of solid base catalysts obtained by supporting $NaAlO_2$ onto a titanium dioxide support. A very common commercial TiO_2 (Degussa P25) was selected as a support. It is widely available and is known to be chemically and thermally stable. As a non-porous material, it is also well adapted to undergo a wet impregnation process with the starting $NaAlO_2$ solution. The catalytic performance of the catalysts were studied in the carboxymethylation of allyl alcohol with DMC serving both as reactant and solvent.

2. Experimental section

2.1 Chemicals

Titanium dioxide purchased from Degussa (P25). Dequachim, Belgium kindly provided the sodium aluminate solution (25 wt %). Allyl alcohol (AA, Sigma-Aldrich, >99%), ethanol (VWR chemicals, >99%), dimethyl form amide (DMF, Sigma-Aldrich, >99.8%), allyl methyl carbonate (AMC, Sigma-Aldrich, >98%), di-allyl carbonate (DAC, Sigma-Aldrich, >99%), and dimethyl carbonate (DMC, Sigma-Aldrich, >99%) were obtained and used as received.

2.2. Catalyst preparation

The pure $NaAlO_2$ catalysts was prepared by spray drying (“Type II” aerosol processing [42]) according to our earlier reported procedure [36]. Briefly, 10 ml of sodium aluminate solution (25 wt.%) was diluted in demineralized water (100 ml) and the mixture was sprayed with a 6-Jet 9306A atomizer from TSI with an air pressure of 30 psi and the aerosol was dried by passing through a tubular quartz tube set at 700°C. The recovered powder was further dried for one night at 120°C under vacuum and then stored in a desiccator.

Titanium dioxide (support) was pre-treated at 400 °C in a muffle furnace under static air for 4 h. A series of catalysts with $NaAlO_2$ (SA) content ranging from zero to 20 wt. % was prepared by an impregnation method. The required quantity of $NaAlO_2$ (25 wt.% aqueous solution) was diluted with distilled water (100 ml) and the resulting solution was added to the support (10 g) to form a slurry, kept under continuous mixing for 2 h. The excess of water was removed by rotavapor. The solid powders were collected, dried at 100 °C overnight and calcined under static air at 400 °C (5°C/min) for 4 h. The samples are denoted as $xSATiO_2$, where 'x' indicates the nominal $NaAlO_2$ weight loading, in percentage. MgO (Sigma-Aldrich) and Hydrotalcites (Mg:Al ration = 2:1) (Kisuma chemicals, Netherlands) were calcined at 400 °C and used as benchmark catalysts.

2.3 Catalyst characterization

Powder X-ray diffraction (XRD) analysis were recorded on a Siemens diffractometer model D5000 fitted with a Cu Kα (1.541˚) radiation source. Data were recorded over a 2θ range of 10–80° with an angular step of 0.05° at 3 s/step which resulted in a scan rate of 1°/min. Patterns were identified using files from the Joint Committee on Powder Diffraction Standards (JCPDS).

Raman spectra were recorded at room temperature on a Thermo Scientific DXR Raman microscope using the 780 nm laser with 14 mW power. The resolution was 4 cm^{-1}. Acquisition time was 10 s, and 32 scans recorded and averaged for each sample.

N_2 adsorption and desorption isotherms were determined by nitrogen adsorption at liquid nitrogen temperature using the Tri-Star 3000 equipment from Micromeritics. Samples were previously degassed in-situ at 120 °C under vacuum overnight. Surface areas were calculated using the Brunauer–Emmet–Teller (BET) methods over a p/p_0 range where a linear relationship was maintained (0.05-0.30).

Scanning Electron Microscope (SEM) images were used to determine the morphology of the studied catalysts. SEM images were taken with a JEOL 7600F with a 15.0 kV voltage. Catalysts were dried under vacuum at 60 °C for 24 h and then placed on a piece of carbon black tape on an aluminium stub. A chromium sputter coating of 10 nm was applied under vacuum with a Sputter Metal 208 HR (Cressington).

CO_2 adsorption was explored by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), with a Bruker EQUINOX 55 spectrometer. The sample was heated to 400 °C in He flow and held at this temperature for 1 h prior to experiment in order to remove absorbed water. Then, it was cooled to 30 °C and 140 scans were recorded and averaged. High-purity carbon dioxide was introduced to the cell at 50 $cm^3.min^{-1}$ for 1 h. Then, a He flow of 50 cm^3 / min was admitted and spectra of adsorbed CO_2 were recorded using a resolution of 4 cm^{-1} (average of 140 scans).

To evaluate the basicity of the prepared catalysts, CO_2 temperature-programmed desorption (TPD) experiments were conducted using the CATLAB apparatus from Hiden equipped with QGA mass spectrometer for gas analysis. Approximately 80 mg of each sample was loaded in a quartz micro reactor supported by quartz wool. Samples were degassed at 400 °C for 1 h using a heating rate of 10 $°C.min^{-1}$ in flowing Argon (at a flow rate of 50 $cm^3.min^{-1}$). Next, the samples were cooled to 50 °C and exposed to flowing 15% CO_2-Ar (50 $cm^3.min^{-1}$) for 1.5 h and finally purged in flowing Argon for 3 h. In the TPD experiments, the samples were heated up to 850 °C using a heating rate of 5 $^{\circ}C.min^{-1}$. The amount of desorbed CO_2 was obtained by integration of the desorption profiles and referenced to the TCD signals calibrated for known volumes of analyzed gases.

TGA analyses were carried out in a TA Instruments TGA Q500. The samples were heated up from room temperature to 800 °C, at 10 °C/min, under airflow (60 mL/min). The weight loss was recorded as a function of temperature.

2.4. Catalytic evaluation

Carboxymethylation of allyl alcohol (AA) with dimethyl carbonate (DMC) was carried out at 90°C, under reflux, in a 25 mL round-bottom flask fitted with a water-cooled condenser. In a typical study, the reaction was initiated by introducing 10 mmol of AA (0.58 g), 50 mmol of DMC (4.5 g), 0.2 g of DMF internal standard and the catalyst (0.1 g). An excess of DMC is used to drive the equilibrated reaction forward and to simplify the process (DMC is used both as a reactant and as the solvent). Then, the reaction mixture was heated to the desired temperature and stirred at 800 rpm using an oil bath mounted on a hot plate equipped with a magnetic stirrer and a thermocouple.

The reaction products were analysed by gas chromatography (5µl injection volume) (GC-456 Scion Bruker) equipped with a flame ionization detector, split/split less injection unit and a capillary column (DB-WAX, 30 m, 0.25 mm, 0.25 m). Helium was used as the carrier gas. The injection was performed with a split ratio of 100:1. Initially, the oven temperature was set at 100 °C and then increased at the rate of 15 $°C.min^{-1}$ until it reached 240 °C and then it was maintained at this temperature for 15 min. The FID and injection temperatures were fixed at 270 °C and 300 °C, respectively. The experimental runs were repeated three times (reproducible results with a maximum deviation of 3%).

2.5 Heterogeneity and reusability studies

Leaching tests were carried out to investigate the stability of the catalysts and to confirm they act as heterogeneous catalysts. The reaction was carried out with $20SATiO_2$ at reaction temperature of 90 °C with AA: DMC molar ratio of 1:5. After 4 h of reaction, the catalyst was filtered off the hot reaction mixture. Then, the filtrate was further maintained under reaction conditions for another 12 h and the reaction mixture was analysed to determine the AA conversion.

3. Results and discussion

3.1. Characterization of the catalysts

The crystalline structure of the prepared catalysts was confirmed by XRD and Raman spectroscopy. **Fig. 1** shows the XRD patterns of the TiO_2, SA and TiO_2-supported SA. The bare TiO_2 support calcined at 400 °C showed the expected XRD patterns, with only anatase (JCPDS 21-1272) and rutile (JCPDS 21-1276) TiO_2 as crystalline phases [43]. The anatase crystal size approximated by the Debye-Sherrer equation (applied on the most intense peak at $2\theta = 25°$) was ~20 nm. In the catalysts loaded with 5 and 10 wt.% of SA, no additional crystalline phases are observed, suggesting that sodium aluminate is well dispersed on titania and does not form any crystallites larger than the detection limit (~5 nm). The onset of crystalline $NaAlO_2$ was observed for the catalysts with 15 wt.% SA. In $20SATiO_2$, the characteristic diffraction pattern of sodium aluminate is clearly observed (2θ = 20.8, 30.2, 33.6, 35.0, 45.8, 48.4, 51.8, 58.1, 61.1, 63.0 as per JCPDS 00-019-1179 and 01-083-0316) [36, 37] (**Fig. 1**). The absence of peaks at 10.5° and 24.3° indicates that there is no formation of crystalline sodium titanate [44, 45].

In agreement with the XRD results, Raman spectra of TiO_2 exhibited the six characteristic Raman active modes of anatase at 144, 197, 399, 513, 519 and 639 cm^{-1} [46]. The band at 144 cm^{-1} is the strongest one observed for anatase. After the impregnation of SA, the Raman spectra were not modified (**Fig. 2**). Again, the absence of Raman peaks at 200, 250 and 300 cm^{-1} confirmed that there is no formation of sodium titanate [47].

The textural properties of the catalysts were analysed by N_2 physisorption (Table 1). The pristine P25 support expectedly showed a surface area of 44 $m^2.g^{-1}$ with pore volume of 0.12 $cm^3.g^{-1}$ created by inter particle voids. Upon impregnation of SA, the specific surface are and pore volume dropped dramatically. The effect was more pronounced as the SA loading increased. This suggests that $NaAlO_2$ acts as a cement around TiO_2 particles, plugging the interparticle voids.

The morphology of the catalysts was inspected by SEM (**Fig. 3**). The titania calcined at 400°C showed aggregates of the typical particle structure, which with a sponge-type aspect (see Electronic Supporting Information (ESI), **Fig. S1**). Visually, the structure seemed preserved on 10 $SATiO_2$ but the roughness of the aggregates clearly decreased when the $NaAlO_2$ loading was further increased, leading to relatively smooth structures at higher $NaAlO_2$ loading. The EDX probe mounted on the SEM allowed to map the different elements on the catalyst and to show that $NaAlO_2$ was homogeneously impregnated over the titania support, leading to a uniform distribution of the active phase throughout the sample (**Fig. S2**).

The basic properties of the prepared catalysts were probed by CO_2-DRIFTS and by CO_2-TPD methods. **Fig. 4** shows the CO_2-DRIFTS spectra of the prepared catalysts. While titanium dioxide only showed a very weak band at 1550 cm^{-1}, pure $NaAlO_2$ showed intense vibration bands at 1328, 1540 and 1678 cm^{-1}. The same pattern was found for the $SATiO_2$ catalysts. Expectedly, the intensity of these signals increased with the $NaAlO_2$ loading. Monodentate bonding of CO_2 with SA gives the count of strong basic sites (1328 cm^{-1} and 1540 cm^{-1} for symmetric and antisymmetric stretching respectively) [48]. The peak at 1678 cm^{-1} corresponds to bridged carbonate and contributes to weak basic sites.

The basicity of the solid catalysts was also approached by temperature programmed desorption of CO_2 (CO_2-TPD). The total amount of CO_2 desorbed is taken as an indication of the amount of basic sites (Table 1). Expectedly, bare titania possess only few basic sites (0.04 mmol of CO_2 per g of TiO_2), consistent with the weak signal detected in CO_2-DRIFTS. The catalysts prepared by impregnation of $NaAlO_2$ on titania showed an increasing amount of desorbed CO_2 (from 0.09 to 0.22 mmol per g of catalyst) as the $NaAlO_2$ loading increases (from 5 to 20 wt.%). From pure SA, CO_2 desorption accounts for 0.80 mmol per g of SA. This trend is not compatible with the marked drop in specific area observed when SA content increase, because it would imply a remarkable increase in the surface density of basic sites. In fact, it is known that $NaAlO_2$ can also react with CO_2 to give sodium carbonate, which can then decomposes during the temperature programme. This means that CO_2-TPD does not give a quantitative value of surface basic sites but an overall indication of the amount of CO_2 that the sample is able to both adsorb and react with in the conditions where the saturation is carried out. Overall, the amount of CO_2 that is quantified by CO_2-TPD is roughly proportional to the amount of $NaAlO_2$ present in the material.

3.2 Catalytic activity studies

The reaction of allyl alcohol with DMC in excess was tested in the absence of a catalyst and the AA conversion was nil after 8h (blank reaction). Sodium hydroxide (1.2 equivalents) was tested as a reference homogeneous base and showed only 30% of AA conversion. Using a large excess of trimethylamine as a homogeneous base, it was shown that full conversion can be obtained, with high selectivity [33]. Yet, as stated above, recyclable heterogeneous catalysts are more desirable.

The pristine TiO_2 calcined at 400°C exhibited very low activity (Table 2), which is consistent with the fact that it is virtually not basic. MgO and hydrotalcites – widely reported as efficient heterogeneous solid catalysts for various base-catalysed organic transformations in the liquid phase [24, 49-51] – are here used as references. Both catalysts were indeed active for the reaction studied, showing respectively 45 % and 63 % AA conversion after 8h of reaction. Consistent with its strong basicity, pure $NaAlO_2$ reached higher conversion (85 %). After standard workup, H-NMR analysis of the crude mixture showed that, only allyl methyl and diallyl carbonates are the products with 96% selectivity towards allyl methyl carbonate and 4 % diallyl carbonate (**Table 2** and **Fig. S3**).

Despite its appealing activity, SA is highly corrosive and difficult to handle and hence unfavourable for industrial applications [38]. This can be observed by manipulating pure $NaAlO_2$ (the solid is sticky and corrodes glassware). The catalysts prepared by impregnating SA onto TiO_2 all behaved like dry powders and could be manipulated easily. $SATiO_2$ catalysts showed significant activity, and, expectedly, the conversion increased with increasing SA loading. The catalyst with 20% SA showed almost the same AA conversion as that of pure SA after 8 hours of reaction (**Table 2**). Selectivity for AMC always remained high (between 96 and 100%).

To allow for a better comparison of the intrinsic activity of the SA-based catalysts, a kinetic study was performed (**Fig. 5**). For pure SA the AA conversion increased with reaction time and reached 98% AA conversion after 16h. Further increase in time did not increase the AA conversion, suggesting that the thermodynamic equilibrium was reached. Using TiO_2, the AA conversion remained as low as 14 % even after in 24 h. Loading $NaAlO_2$ onto titania leads to a drastic increase in AA conversion. The activity clearly increases with the $NaAlO_2$ loading, which is fully consistent with the parallel increase in basic strength observed in DRIFTS and CO_2-TPD (Table 1). The catalyst loaded with 20 wt. % SA (20SATiO$_2$) reached 94% conversion after 24h of reaction, similar to pure SA.

In order to compare the intrinsic activity of all catalysts, the initial activity can be approximated by looking at the conversion at an early stage of the batch reaction (2 hours). In these conditions, AA conversion is as low as 2% with the titania alone. By promoting the titania with only 5 wt.% $NaAlO_2$ (5 SATiO$_2$), AA conversion increased to 10%. AA conversion at 2 hours increased further to 16%, 21% and 28% with further increase in SA loading to 10 wt.%, 15 wt.%, and 20 wt.%. Thus, intrinsic activity increases steadily with the $NaAlO_2$ loading, consistent with the idea that the impregnation of increasing amounts of $NaAlO_2$ on TiO_2 allows to proportionally enhance the surface basicity. However, pure $NaAlO_2$ only reaches 29% conversion at 2h, very close to the conversion obtained with 20SATiO$_2$. In its pure form, $NaAlO_2$ exhibits a lower amount of surface basic sites as compared to its supported form, consistent with its very low specific surface area.

3.3 Catalyst stability

To investigate the heterogeneous nature of the SATiO$_2$ catalysts, a hot filtration test was conducted to investigate the leaching of active species into the solution.

Carboxymethylation reaction of AA with DMC was carried out using 20 SATiO$_2$ and interrupted after 4 h (conversion = 50%). The reaction mixture was filtered to remove the catalyst. The filtrate was then refluxed at 90 °C for an additional 12 h in the absence of the solid catalyst. Analysis of the final reaction mixture showed that the conversion did not evolve (**Fig. 6**). This test confirms that the catalysis is truly heterogeneous and not due to putative leached species.

The reusability was studied by running 4 consecutives runs with the same catalyst. For each run, the catalyst was filtered off after 4h of reaction, washed twice with 5 mL of methanol, and dried at 120 °C for 4 h. The results presented in **Fig. 7** indicate that the catalyst can be recycled and reused at least three times with no significant loss in catalytic activity.

The used catalyst (20 SATiO$_2$) was characterised in XRD and TGA. After the reaction, the reaction mixture was allowed to cool to room temperature and the solid catalyst was separated by filtration, washed twice with 5 mL of methanol, and dried at 120 °C for 4 h. The catalysts recovered after reaction showed a similar XRD pattern as compared to the fresh sample (**Fig. S4**). Further, TGA performed on the fresh and used 20SATiO$_2$ gave very similar thermogravimetric profiles (**Fig. S5**). The total weight loss was in the same range for both catalysts (15% and 11%), indicating that no organic matter was accumulated on the catalyst sample after reaction and washing.

4. Conclusions

NaAlO$_2$ is confirmed to be an attractive active phase for base-catalysed organic reactions, showing high activity in the carboxymethylation reaction. Using sodium aluminate as a catalyst, it is possible to synthesise allyl methyl carbonate from allyl alcohol and dimethyl carbonate, with good to excellent selectivity. Pure $NaAlO_2$ outcompetes other reference basic catalysts. Yet, a supported version of this catalyst is more desirable for practical reasons. Here, we showed that this phase can be impregnated onto TiO_2 to exploit its highly basic properties and obtain highly active carboxymethylation catalysts. In particular, the catalyst loaded with 20 wt.% of $NaAlO_2$ performed as well as the pure version. Importantly, the catalysts truly acts as a recyclable heterogeneous catalyst.

Acknowledgements

Authors gratefully acknowledge the Walloon Region for the financial support (BEWARE programme, convention n° 1410279). SR thanks Gabriel Hidalgo for his assistance with the Raman analysis and Debobrata Sheet for the TGA analysis.

References

[1] M.L. Kantam, U. Pal, B. Sreedhar, B.M. Choudary, Adv. Synth. Catal., 349 (2007) 1671-1675.
[2] T. Tabanelli, E. Monti, F. Cavani, M. Selva, Green Chem., 19 (2017) 1519-1528.
[3] H. Mutlu, J. Ruiz, S.C. Solleder, M.A.R. Meier, Green Chem., 14 (2012) 1728-1735.
[4] J.N.G. Stanley, M. Selva, A.F. Masters, T. Maschmeyer, A. Perosa, Green Chem., 15 (2013) 3195-3204.
[5] P. Tundo, F. Aricò, G. Gauthier, L. Rossi, A.E. Rosamilia, H.S. Bevinakatti, R.L. Sievert, C.P. Newman, ChemSusChem, 3 (2010) 566-570.
[6] B. Schäffner, F. Schäffner, S.P. Verevkin, A. Börner, Chem. Rev., 110 (2010) 4554-4581.
[7] A.-A.G. Shaikh, S. Sivaram, Chem. Rev., 96 (1996) 951-976.
[8] S. Jin, Y. Tian, C.R. McElroy, D. Wang, J.H. Clark, A.J. Hunt, Catal. Sci. Technol., 7 (2017) 4859-4865.
[9] G. Fiorani, A. Perosa, M. Selva, Green Chem., (2017).
[10] Z. Hou, B. Han, Z. Liu, T. Jiang, G. Yang, Green Chem., 4 (2002) 467-471.
[11] J.R. Ochoa-Gómez, O. Gómez-Jiménez-Aberasturi, C. Ramírez-López, M. Belsué, Org. Proc. Res. Dev., 16 (2012) 389-399.
[12] M.J. Climent, A. Corma, S. Iborra, Green Chem., 13 (2011) 520-540.
[13] T.C. Keller, K. Desai, S. Mitchell, J. Pérez-Ramírez, ACS Catal., 5 (2015) 5388-5396.
[14] D. Kishore, S. Kannan, Green Chem., 4 (2002) 607-610.
[15] M. Pelckmans, T. Renders, S. Van de Vyver, B.F. Sels, Green Chem., (2017).
[16] R. Gérardy, R. Morodo, J. Estager, P. Luis, D.P. Debecker, J.-C.M. Monbaliu, Top. Curr. Chem., 377 (2018) 1.

[17] L. Grazia, A. Lolli, F. Folco, Y. Zhang, S. Albonetti, F. Cavani, Catal. Sci. Technol., 6 (2016) 4418-4427.
[18] F. Li, H. Li, L. Wang, P. He, Y. Cao, Catal. Sci. Technol., 5 (2015) 1021-1034.
[19] S.-Y. Peng, Z.-N. Xu, Q.-S. Chen, Z.-Q. Wang, Y. Chen, D.-M. Lv, G. Lu, G.-C. Guo, Catal. Sci. Technol., 4 (2014) 1925-1930.
[20] M. Gruselle, J. Organometallic Chem., 793 (2015) 93-101.
[21] K. Kaneda, T. Mizugaki, ACS Catal., 7 (2017) 920-935.
[22] G.M. Lari, G. Pastore, C. Mondelli, J. Perez-Ramirez, Green Chem., (2017).
[23] S. Nishimura, A. Takagaki, K. Ebitani, Green Chem., 15 (2013) 2026-2042.
[24] D.P. Debecker, E.M. Gaigneaux, G. Busca, Chem. Eur. J, 15 (2009) 3920-3935.
[25] W.Y. Hernandez, J. Lauwaert, P. Van Der Voort, A. Verberckmoes, Green Chem., (2017).
[26] E.Y.C. Jorge, T.d.M. Lima, C.G.S. Lima, L. Marchini, W.N. Castelblanco, D.G. Rivera, E.A. Urquieta-Gonzalez, R.S. Varma, M.W. Paixao, Green Chem., 19 (2017) 3856-3868.
[27] M. Selva, M. Fabris, A. Perosa, Green Chem., 13 (2011) 863-872.
[28] G.M. Lari, P.Y. Dapsens, D. Scholz, S. Mitchell, C. Mondelli, J. Perez-Ramirez, Green Chem., 18 (2016) 1249-1260.
[29] L. Zhu, X.-Q. Liu, H.-L. Jiang, L.-B. Sun, Chem. Rev., 117 (2017) 8129-8176.
[30] L. Chen, J. Zhao, S.-F. Yin, C.-T. Au, RSC Adv., 3 (2013) 3799-3814.
[31] B. Veldurthy, F. Figueras, Chem. Commun., (2004) 734-735.
[32] B. Veldurthy, J.-M. Clacens, F. Figueras, Eur. J. Org. Chem. 2005 (2005) 1972-1976.
[33] S. Ramesh, K. Inukuri, O. Riant, D.P. Debecker, Org. Proc. Res. Dev. 22 (2018) 1846-1851.
[34] V. Mutreja, S. Singh, A. Ali, J. Oleo Sci., 61 (2012) 665-669.
[35] H.B.A. Hamid, R.B. Moyes, Catal. Today, 10 (1991) 267-274.
[36] S. Ramesh, D.P. Debecker, Catal. Commun., 97 (2017) 102-105.
[37] T. Wan, P. Yu, S. Wang, Y. Luo, Energy Fuels, 23 (2009) 1089-1092.
[38] S. Ramesh, F. Devred, L.v.d. Biggelaar, D.P. Debecker, ChemCatChem, 10 (2018) 1398-1405.
[39] M. Wang, M.A.A. Gasmalla, H. Admassu Tessema, X. Hua, R. Yang, Food Chem., 233 (2017) 151-158.
[40] S. Despax, B. Estrine, N. Hoffmann, J. Le Bras, S. Marinkovic, J. Muzart, Catal. Commun., 39 (2013) 35-38.
[41] R. Bai, P. Liu, J. Yang, C. Liu, Y. Gu, ACS Sus. Chem. Eng., 3 (2015) 1292-1297.
[42] D.P. Debecker, S. Le Bras, C. Boissière, A. Chaumonnot, C. Sanchez, Chem. Soc. Rev., 47 (2018) 4112-4155.
[43] A. Kim, D.P. Debecker, F. Devred, V. Dubois, C. Sanchez, C. Sassoye, Appl. Catal. B, 220 (2018) 615-625.
[44] D.R. Zhang, C.W. Kim, Y.S. Kang, J. Phys. Chem. C, 114 (2010) 8294-8301.
[45] Y. Ishikawa, S. Tsukimoto, K.S. Nakayama, N. Asao, Nano Letters, 15 (2015) 2980-2984.
[46] T. Ohsaka, J. Phys. Soc. Jpn, 48 (1980) 1661-1668.
[47] R.A. Zárate, S. Fuentes, J.P. Wiff, V.M. Fuenzalida, A.L. Cabrera, J. Phys. Chem. Solids, 68 (2007) 628-637.
[48] V.F. Kiselev, O.V. Krylov, Adsorption and Catalysis on Transition Metals and Their Oxides, Springer-Verlag, Berlin Heidelberg, 1989.
[49] J.I. Di Cosimo, V.K. Díez, C. Ferretti, C.R. Apesteguía, Chapter 1 Basic catalysis on MgO: generation, characterization and catalytic properties of active sites, in: Catalysis: Volume 26, The Royal Society of Chemistry, 2014, pp. 1-28.
[50] N. Sutradhar, A. Sinhamahapatra, S.K. Pahari, P. Pal, H.C. Bajaj, I. Mukhopadhyay, A.B. Panda, The J. Phys. Chem. C, 115 (2011) 12308-12316.
[51] Z. Bai, Y. Zheng, W. Han, Y. Ji, T. Yan, Y. Tang, G. Chen, Z. Zhang, CrystEngComm, 20 (2018) 4090-4098.

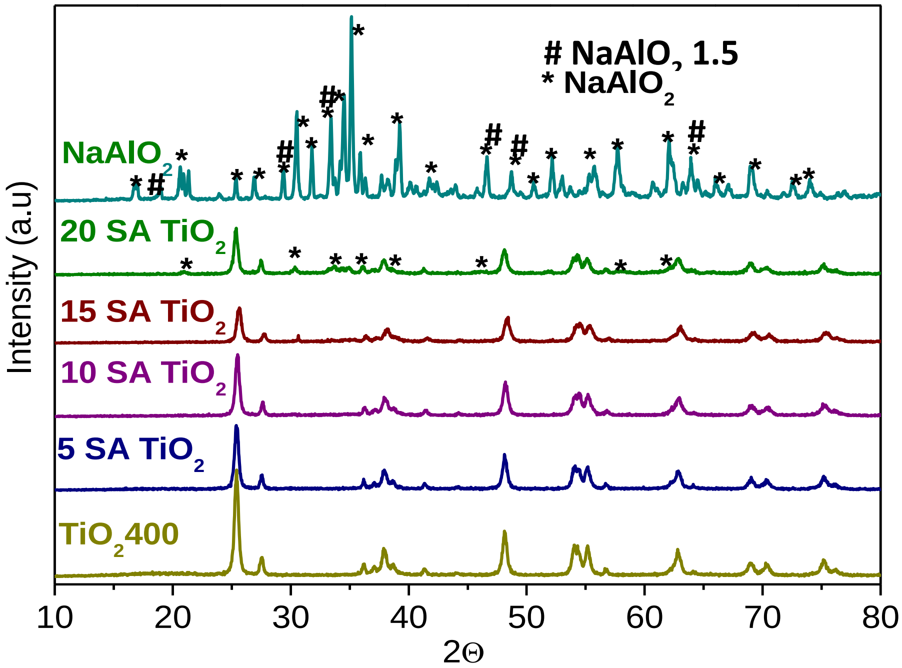

Fig. 1. Powder XRD patterns of the TiO_2 support ($TiO_2$400), SATiO_2 catalysts, and pure $NaAlO_2$.

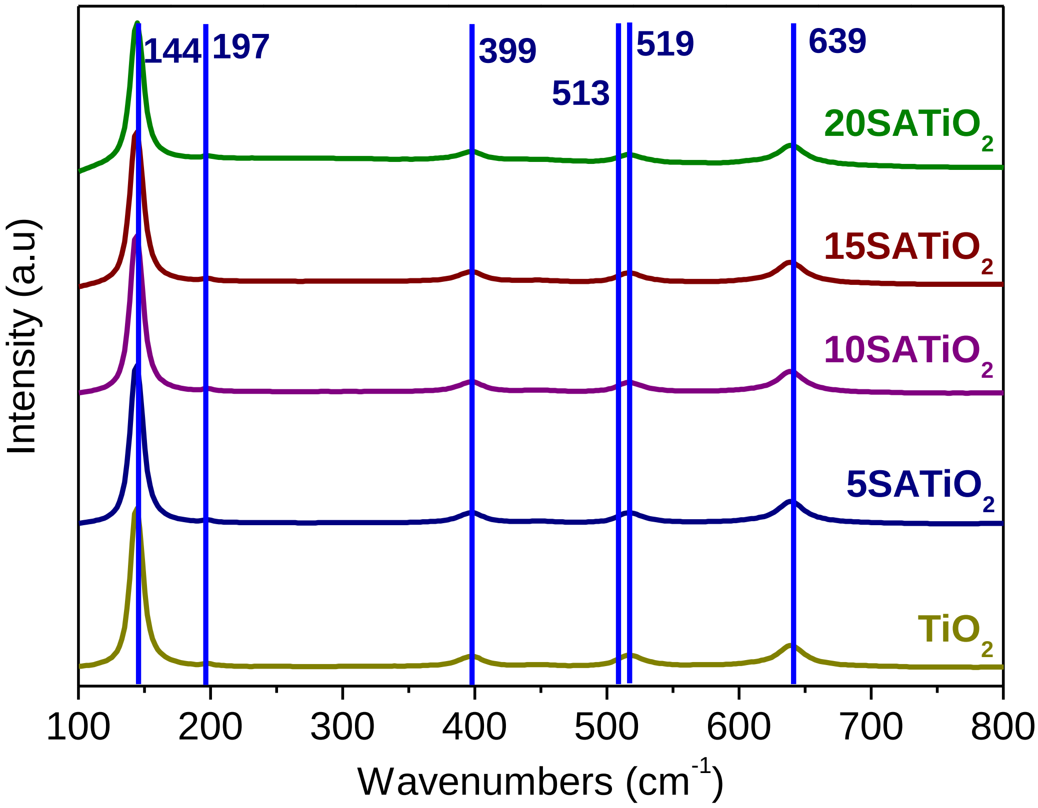

Fig. 2. Raman spectra of the TiO_2 support and of $SATiO_2$ catalysts.

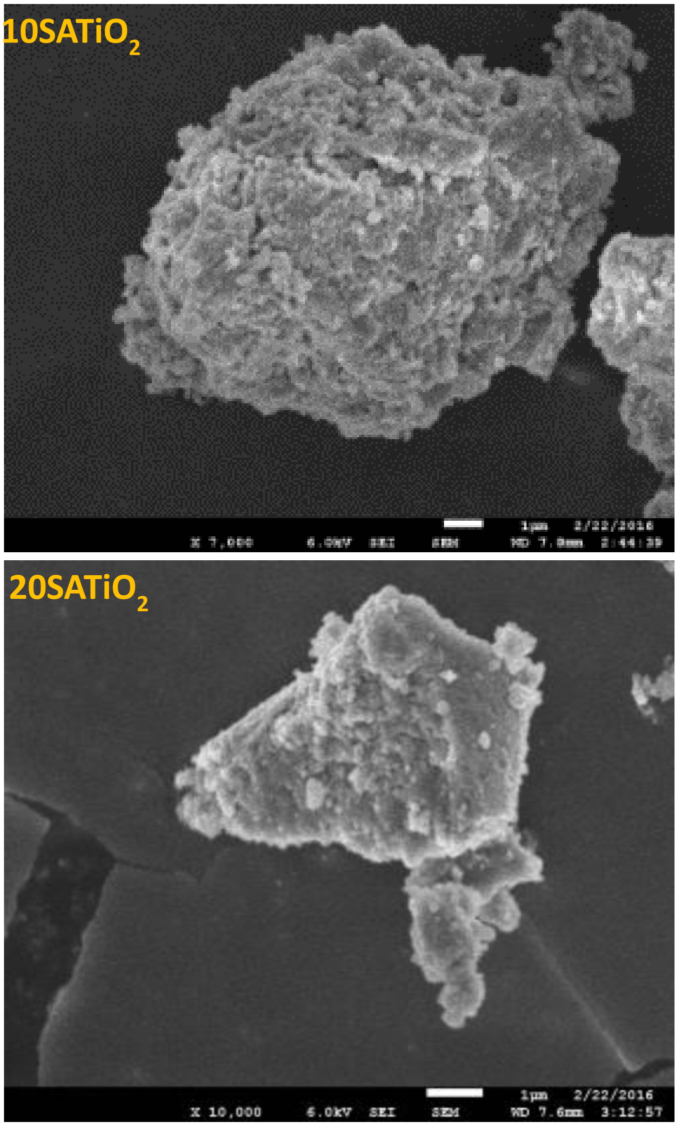

Fig. 3. SEM micrographs of SATiO$_2$ catalysts.

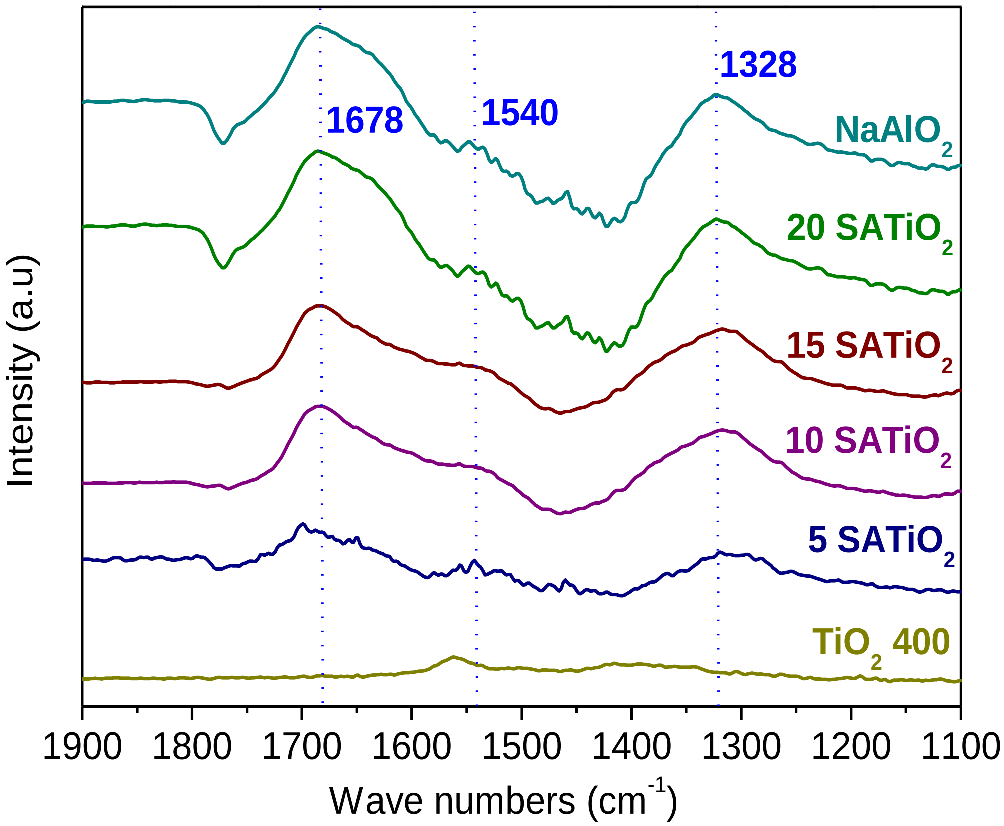

Fig. 4. IR spectra obtained in the DRIFTS mode on the pristine TiO_2 support (TiO_2 400), on $SATiO_2$ catalysts, and on pure $NaAlO_2$. Samples were exposed to a CO_2: He atmosphere (1:1 vol ratio) at 30 ^{0}C and He flush for 30 min.

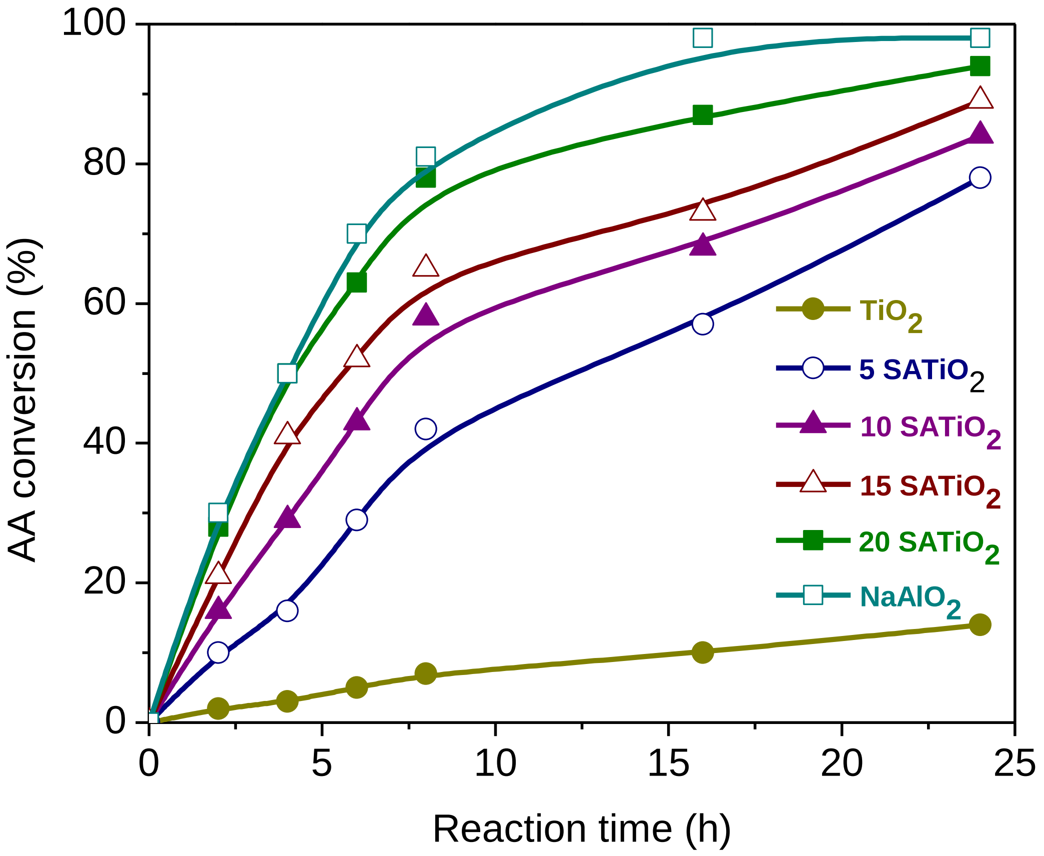

Fig. 5. Catalytic activity of TiO_2 support, $SATiO_2$ catalysts and pure $NaAlO_2$. Reaction conditions: 0.1g of catalyst, 1:5 mol ratio (AA:DMC) at 90 ^{0}C.

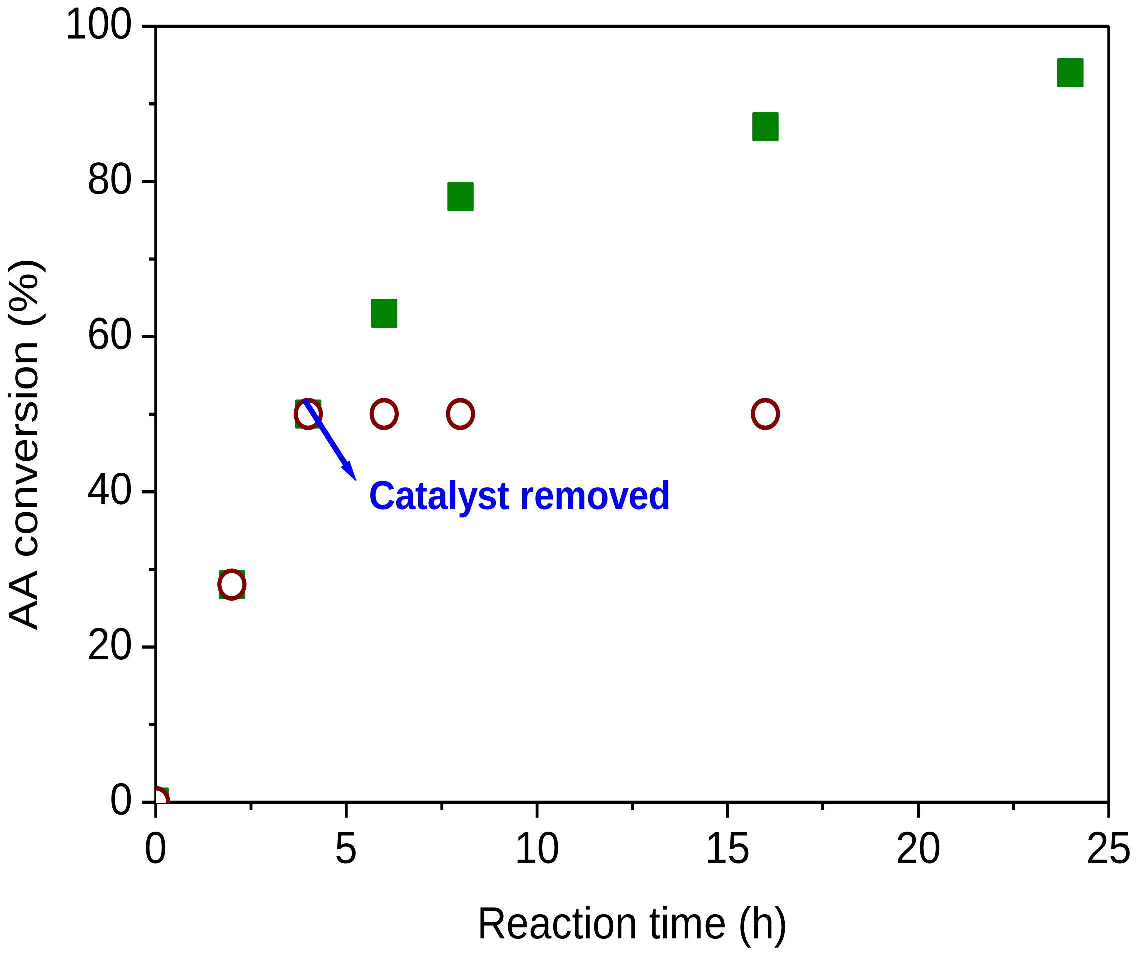

Fig. 6. Leaching test. Reaction conditions: 0.1 g of 20 $SATiO_2$, 1:5 mol ratio (AA: DMC) at 90 °C. (In the leaching test (red line), the solid catalyst was filtered off after 4 h of reaction and the reaction was continued without solid catalyst).

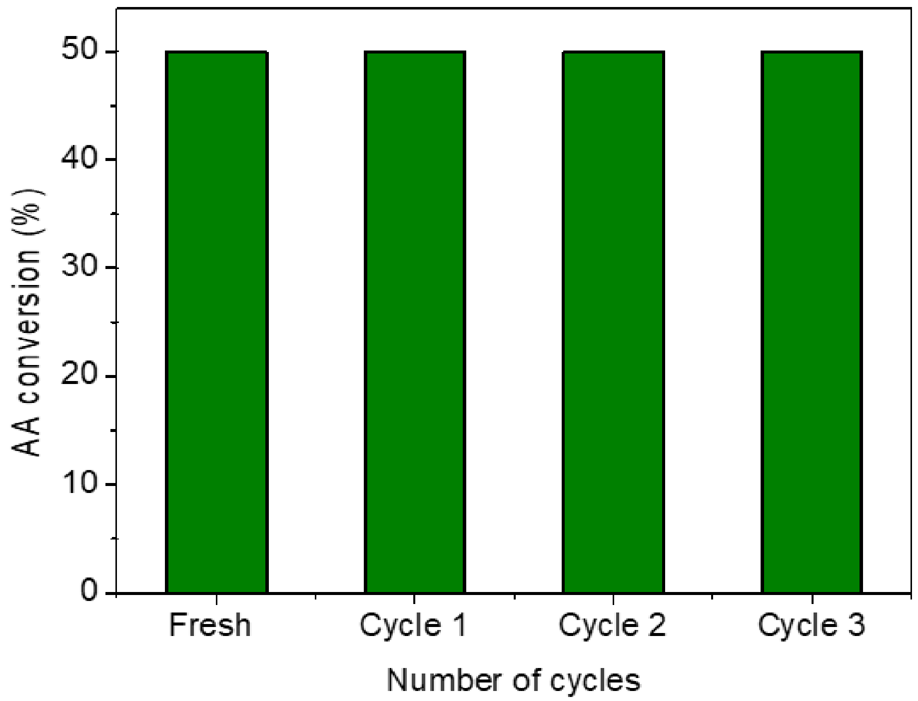

Fig. 7. Reusability studies with 20 $SATiO_2$ catalyst. Reaction conditions: 0.1 g of 20 $SATiO_2$, 1:5 mol ratio (AA: DMC) at 90 °C for 4h.

Table 1. Texture (N_2 physisorption) and basicity (CO_2-TPD) of the catalysts

Catalyst	A_{BET} ($m^2.g^{-1}$)	V_p ($cm^3.g^{-1}$)	Basic sites ($mmol_{CO2}/g_{cat}$)
TiO_2	44	0.12	0.04
5 $SATiO_2$	25	0.19	0.09
10$SATiO_2$	11	0.08	0.15
15$SATiO_2$	9	0.08	0.19
20 $SATiO_2$	5	0.04	0.22
$NaAlO_2$	2	0.01	0.80

Table 2. Catalytic activity of the tested catalysts.

Catalyst	AA conversion (%)	Selectivity AMC:DAC (%)
Blank	0	-
TiO_2	7	100:0
MgO	45	98:2
Hydrotalcites	63	92:8
NaOH	30	85:15
$5SATiO_2$	42	100:0
$10SATiO_2$	58	100:0
$15SATiO_2$	65	98:2
$20SATiO_2$	78	96:4
$NaAlO_2$	81	96:4

Reaction conditions: 0.1g of catalyst, 1:5 mol ratio (AA: DMC) at 90 °C for 8 h.