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Short communication

# Combined $H_2O_2$/nitrile/bicarbonate system for catalytic Baeyer-Villiger oxidation of cyclohexanone to ε-caprolactone over Mg—Al hydrotalcite catalysts

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ABSTRACT

Magnesium-aluminium hydrotalcite-like compounds (Ht) with molar ratios of Mg/Al = 2, 3, 4 and 6, were synthesized and used as catalysts in the Baeyer-Villiger oxidation of cyclohexanone to ε-caprolactone. Oxidation was carried out in mild conditions (70 °C, atmospheric pressure) either with conventional $H_2O_2$/acetonitrile oxidizing mixture, or with a newly designed $H_2O_2$/acetonitrile/bicarbonate system. The presented results show clearly superiority of bicarbonate-containing setup, which provides a significant increase of the ε-caprolactone yield. The neutralizing effect of bicarbonate, strongly limiting leaching of magnesium from Ht, is considered the main cause of the improved catalytic performance.

## 1. Introduction

Baeyer-Villiger (BV) oxidation of ketones to esters and cyclic ketones to lactones yields products of immense practical importance, ranging from fine chemicals to intermediates for the high tonnage commodities [1]. In particular, BV transformation of cyclohexanone gives ε-caprolactone, a monomer used in manufacturing of biodegradable polymers, finding application in tissue engineering, biocompatible coatings, or drug delivery systems [2]. Industrially, ε-caprolactone is obtained with the use of organic peroxy acids [3], which is environmentally burdensome due to the explosive nature of the oxidants and generation of acid by-product. For this reason a trend emerged aiming at substitution of peroxy acids with other, more benign oxidants, for instance $H_2O_2$, in combination with an appropriate catalyst [1], e.g., Sn-beta-zeolite, pioneered by Corma et al. [4]. Another frequently investigated system is based on the use of hydrogen peroxide in combination with nitrile solvent, in the presence of basic solid catalysts, such as Mg—Al hydrotalcites [5–13]. Mg—Al hydrotacites are layered compounds with the general formula $[Mg_{1-x}Al_x(OH)_2]^{x+}(A^{n-}_{x/n})\cdot mH_2O$, where "x" is the degree of Al for Mg substitution, $A^{n-}$ denotes anion and "m" indicates the content of water of hydration [14]. The materials are widely used in base catalysis, since the change of "x" offers means for tuning their basic character to the requirements of a particular reaction. The role of nitrile compound goes beyond that of a solvent, because, due to its reaction with perhydroxyl anion species ($HOO^-$), a peroxycarboximidic anion is generated, the active intermediate oxidant [15,16]. Although benzonitrile has been shown to ensure best ε-caprolactone yields [8], acetonitrile is significantly cheaper and less toxic [17]. Therefore, in pursuance of the greener character of the overall reaction system, in our studies we focus on the use of acetonitrile solvent [11–13]. Reaction of peroxycarboximidic anion formation from acetonitrile is illustrated in Fig. 1a.

The attractive features of Mg—Al Ht catalysts are the relatively easy and cheap synthetic methods, nontoxicity, facile modification of chemical composition and, most importantly, capability of activating rather inert hydrogen peroxide. However, recent studies from our laboratory indicated that the acidic environment of the reaction mixture, stemming from the presence of hydrogen peroxide, results in leaching of magnesium from the hydrotalcite catalyst, and causes partial deactivation of the Ht catalyst [11,13]. Although the catalytic activity can be restored by soaking of the used catalyst in the solution of $Mg(OH)_2$, the problem of leaching remains non-trivial, especially that it has been repeatedly demonstrated that catalytic performance of Mg—Al Ht is enhanced by low crystallinity of the catalysts [12,13,18–27]. This advantage is limited by the fact that small crystallites are more susceptible to leaching effects [13]. The problem cannot be solved by simple

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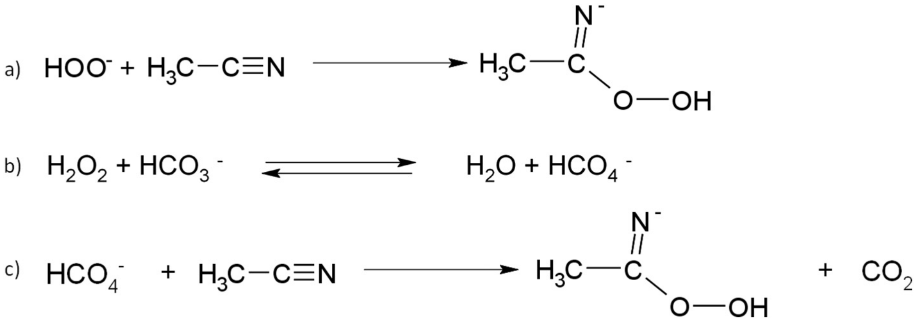

**Fig. 1.** Generation of a) peroxycarboximidic anion from acetonitrile, b) peroxymonocarbonate anion in BAP system, c) peroxycarboximidic anion from acetonitrile and peroxymonocarbonate anion in BAP system.

alkalization of the reaction medium, because hydrogen peroxide is prone to the alkali-induced decomposition [28]. It is therefore highly desirable to find means to counteract the negative impact of the acidic reaction environment, without causing excessive unproductive destruction of the $H_2O_2$ oxidant.

In search for the solution to this problem we turned our attention to the joined use of $H_2O_2$ and sodium bicarbonate as a reagent active in epoxidation reactions, discovered by Richardson et al. [29]. The key aspect of this system, referred to as bicarbonate-activated peroxide (BAP), is that hydrogen peroxide reacts with bicarbonate to form peroxymonocarbonate, which acts in the capacity of the actual oxidant (Fig. 1b). Of particular importance for the present work is that the BAP system operates at nearly neutral pH.

In view of this we decided to check on the effect of bicarbonate addition to the cyclohexanone/$H_2O_2$/nitrile/Ht system, in expectation that it might alleviate the effect of hydrotalcite catalyst deactivation, while simultaneously introducing the BAP-related activity.

## 2. Experimental

Mg-Al Ht compounds with nominal Mg/Al ratio = 2, 3, 4, 6 were synthesized by the co-precipitation at pH = 10, described in details earlier [30] (see Supporting Information). The materials were characterized with ICP OES, PXRD, Raman and FTIR spectroscopies, and basicity determination by means of benzoic acid adsorption [31] and measurement of pH of aqueous suspensions [32]. Results and measurement details are provided in the Supporting Information file. The amounts of metal cations leached to the solution during catalytic experiments were determined with AAS using a Thermo Scientific ICE 3500 AAS spectrometer. Catalytic tests were carried out for 3 h at 70 °C in a glass reactor nested in a magnetic stirrer equipped with the heat-on system in the presence of 0.2 g of catalyst. Reaction mixture consisted of 0.025 mol of cyclohexanone, 0.2 mol of 30% hydrogen peroxide and 0.4 mol of acetonitrile. In the experiments with bicarbonate, 4 × 0.05 g of $NaHCO_3$ was added after 1, 15, 30 and 120 min of reaction duration. Recovery of catalyst was performed by centrifugation of reaction mixture. Liquid reactants were decanted and catalyst was reintroduced into the reactor without drying or purification. Centrifugation vessel was washed with acetonitrile in order to transfer all of the catalyst into the reactor. After that substrate and hydrogen peroxide were added into the reactor. Reaction mixture was analyzed by gas chromatography using Thermo Trace GC Ultra instrument fitted with TR-5 capillary column with flame ionization detector. Identification of products was performed using GC–MS analysis with Thermo Trace GC Ultra equipped with TR-5-MS capillary column and DSQ 2 mass detector. Hydrogen peroxide efficiency was determined on the basis of iodometric titration of the reaction mixture.

## 3. Results and discussion

In this research note we report on the effect of joined use of $H_2O_2$, nitrile and bicarbonate in the Mg—Al hydrotalcite catalyzed reaction of cyclohexanone lactonization and demonstrate that this novel combination brings about an improvement of the catalytic performance with respect to the separate action of either $H_2O_2$/nitrile/Ht or BAP systems.

Catalytic activity of Mg—Al Ht compounds is known to increase with the relative Mg content, therefore the catalysts with nominal Mg/Al ratio = 2, 3, 4, and 6, referred to as $Mg_2Al$, $Mg_3Al$, $Mg_4Al$ and $Mg_6Al$ were used in this study. Detailed physico-chemical characterization of such samples is given elsewhere [30], but the most important feature, confirming the structural identity of the materials, is that they show XRD patterns typical of a hydrotalcite structure (Supporting Information Fig. S1) [14]. Crystallographic data revealed that both the $d_{003}$ (related to the interlayer distance) and $d_{110}$ (related to the mean cation–cation distance) values increase with decreasing Al content, the former due to the weakening of electrostatic attraction between the positively charged layers and interlayer anions, the latter due to the difference in ionic radii between $Mg^{2+}$ and $Al^{3+}$(0.072 and 0.054 nm, respectively). The actual Mg/Al values, were close to the intended ones, i.e. 1.9, 2.9, 3.8 and 5.6 for $Mg_2Al$, $Mg_3Al$, $Mg_4Al$, and $Mg_6Al$, respectively. The phase purity of the samples is further confirmed by Raman spectroscopy, which shows that even in the Mg-rich samples no segregation of other phases, in particular brucite, occurs (Fig. S2, Supporting Information) [30].

Catalytic activity of the samples was investigated in the Baeyer-Villiger oxidation of cyclohexanone to ε-caprolactone with $H_2O_2$/acetonitrile system. The results, presented in Fig. 2a, show that the catalytic performance of the as received Ht catalysts improves with increasing Mg content, i.e. with the catalysts basicity, in agreement with the literature data [7,11]. The increase of the Ht samples basicity with growing Mg content has been confirmed by measurements of benzoic acid adsorption and determination of the pH of aqueous suspensions of the catalysts (Table 1S, Supporting Information). In the absence of any additive, the best caprolactone yield of 33% is obtained for the $Mg_6Al$ sample.

However, when the catalysts were subjected to recycling experiments, in all cases a significant loss of the activity, selectivity and the ε-caprolactone yield was observed (Fig. 2b). This loss of activity has been previously attributed to partial leaching of Mg in the slightly acidic environment of the $H_2O_2$-containing reaction mixture [11]. Indeed, the AAS analysis of the liquid phase separated from the reaction mixture after the first catalytic run revealed that some magnesium initially present in the catalysts was transferred to the solution, the amount growing with the catalyst Mg/Al ratio from ca. 5% for $Mg_2Al$ to ca. 10% for $Mg_6Al$ sample. The amount of leached Al was two orders of magnitude lower, indicating that the loss of Mg takes place in a selective manner. Since the occurrence of a homogeneous catalytic reaction with participation of leached $Mg^{2+}$ has been excluded [11], the observed

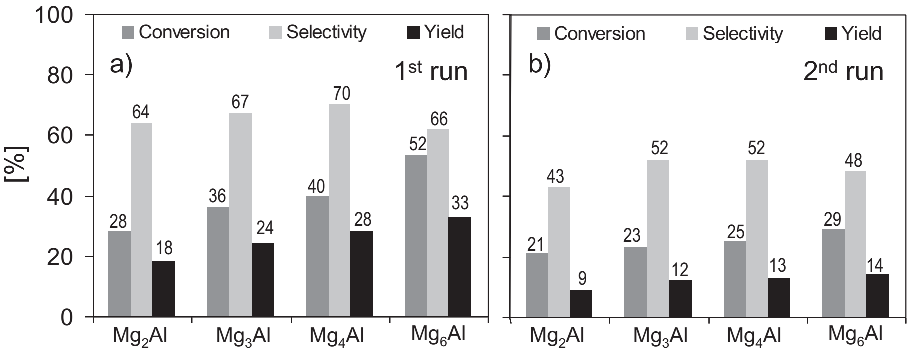

**Fig. 2.** Catalytic oxidation of cyclohexanone to ε-caprolactone with $H_2O_2$/acetonitrile system over $Mg_nAl$ catalysts: a) first run, b) second run.

leaching-induced loss of Mg is assumed to be the chief cause of deterioration of the catalytic performance. Due to the complex composition of the reaction medium it was not possible to conclude on the presence or absence of the leached carbonate species, but in view of the well-known affinity of carbonate anions to the Ht lattice and difficulty of their deintercalation/desorption, it seems unlikely that Mg leaching is accompanied by a meaningful loss of interlayer carbonate. It is tentatively proposed that the Mg-depleted areas resemble nonstoichiometric Al hydroxycarbonate, known to form easily at the surface of $Al(OH)_3$ [33].

In order to get better insight into the changes of acid-base properties of the reaction medium during the course of the catalytic process, the pH value of the reaction mixture was monitored, and, as an example, the data for the $Mg_4Al$ catalyst are shown in Fig. 3.

The reaction mixture without the catalyst was characterized by pH around 4.5. Addition of the catalyst raised the pH value to ca. 6.7, and, subsequently, a gradual fall of pH was observed to the final reading of 5.3, thus confirming that the acid-base interaction between the catalyst and the reaction medium occurred.

Prior to the tests with the joint use of a Ht catalyst and sodium bicarbonate, a blank experiment, checking on the $NaHCO_3$ effect on the reaction mixture in the absence of the catalyst has been carried out. The result showed that BAP system itself is active in the Baeyer-Villiger transformation of cyclohexanone, and gives 35% cyclohexanone conversion. However, the 51% reaction selectivity is less than in any process carried out with the use of Ht samples (64–70%). As a result, the observed order of ε-caprolactone productivity is: BAP = $Mg_2Al$ < $Mg_3Al$ < $Mg_4Al$ < $Mg_6Al$. Monitoring of pH during oxidation with the neat BAP system, i.e. with $NaHCO_3$ but without the Ht catalyst, (Fig. 3) shows that after initial increase to ca. 7.3, the pH falls and stabilizes slightly above 6. A similar experiment carried out for the $Mg_4Al$ + $NaHCO_3$ system, showed that, due to the buffering properties of $NaHCO_3$ solution, the pH changes were quite similar to those observed for $NaHCO_3$ without the catalyst. This confirms that in the presence of $NaHCO_3$ a more favorable environment for the operation of a Ht catalyst is created. Indeed, upon addition of $NaHCO_3$ to the reaction systems containing Ht catalysts a significant improvement of the catalytic performance is observed, as indicated by the data in Fig. 4. The efficiency of $H_2O_2$ utilization measured as the selectivity towards ε-caprolactone was 23 ± 2% without bicarbonate, and 19 ± 2% in tests with $NaHCO_3$ addition.

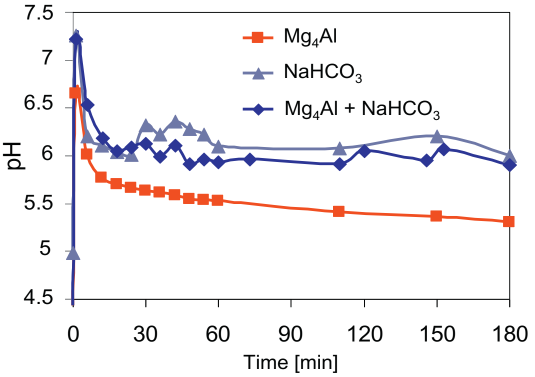

**Fig. 3.** Dependence of the pH of the reaction medium on time of the catalytic process.

The relative increase of ε-caprolactone yield with respect to that observed in the absence of bicarbonate is 205, 188, 179 and 127% over $Mg_2Al$, $Mg_3Al$, $Mg_4Al$, and $Mg_6Al$, respectively. This shows that the beneficial influence of $NaHCO_3$ addition is most pronounced in the catalysts least susceptible to the elution of Mg. Analysis of the liquid phase after completion of the reaction over $Mg_4Al$ showed that the amount of leached Mg was ca. 1.5% of the total Mg, i.e. much lower than the 8.5% loss observed without bicarbonate addition. The effect is understandable, since the equilibrium between Mg bound in the Ht lattice and Mg leached to the solution is pH dependent, according to the Eq. (1):

$$[Mg - OH]^{+}_{Ht} + H^{+} \leftrightarrow Mg^{2+} + H_2O \quad (1)$$

In consequence, alkalization of the reaction medium by addition of bicarbonate, evidenced by pH measurements, suppresses the leaching of Mg. It should be noted that the unique property of bicarbonate is that it not only ensures pH more favorable for the catalyst stability, but in combination with $H_2O_2$ forms a system capable of cyclohexanone transformation into ε-caprolactone, the ability which other possible alkalizing agents (e.g., NaOH) don't have.

As to the impact of treatment with BAP on the composition of Ht catalyst interlayer, FTIR spectra show that the main effect is a certain increase of the carbonate content due to the replacement of nitrate impurity with carbonate anions from bicarbonate solution, while no meaningful change in the intensity of bicarbonate-related bands is observed (Fig. S3, Supporting Information).

The enhanced stability of the Ht catalysts in the bicarbonate-containing reaction medium brought about a spectacular improvement of the catalysts recyclability. The data in Fig. 4 show that in the second catalytic run the used $Mg_2Al$, $Mg_3Al$, $Mg_4Al$, and $Mg_6Al$ samples perform nearly as well as the fresh ones, and the observed ε-caprolactone yield corresponds to 97, 91, 88 and 83% of the first run values.

Noteworthy, while in the absence of $NaHCO_3$ the best performance in terms of the ε-caprolactone yield is given by the most basic $Mg_6Al$ catalyst, in the combined $H_2O_2$/nitrile/bicarbonate system, the optimum catalytic properties are achieved for the $Mg_4Al$ sample, which yields 50% ε-caprolactone. Apparently, in the case of $Mg_6Al$, the neutralizing effect of $NaHCO_3$ addition is not sufficient to enable satisfactory retention of Mg in the catalyst structure. Chemical analysis of Mg content in the $NaHCO_3$ containing reaction mixture separated from the $Mg_6Al$ catalyst shows 4.5% loss of Mg, which, although significantly lower than the 10% observed without $NaHCO_3$, is the likely reason for

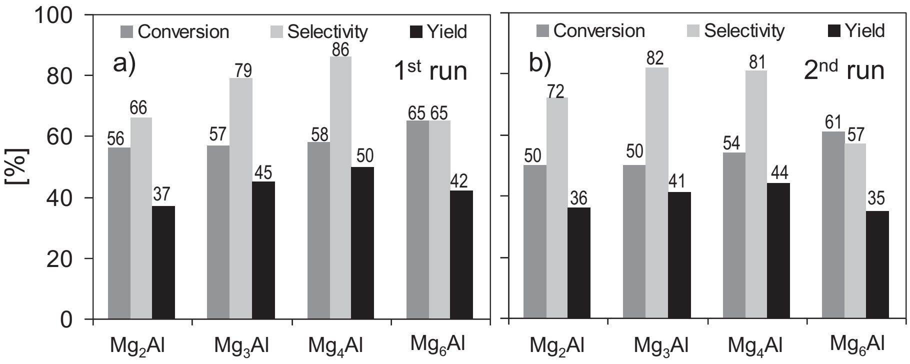

**Fig. 4.** Catalytic oxidation of cyclohexanone to ε-caprolactone with $H_2O_2$/acetonitrile/bicarbonate system over MgnAl catalysts: a) first run, b) second run.

the poorer performance of $Mg_6Al$.

Analysis of the catalytic data indicates that the observed substantial increase of the ε-caprolactone yield occurs both on the account of higher conversion and of enhanced selectivity. Variations in selectivity may be attributed either to changing contribution of consecutive transformation of ε-caprolactone, such as hydrolysis or polymerization, and/or to some parallel processes, which consume cyclohexanone. Reaction mixtures were subjected to GC–MS analysis which identified the presence of compounds such as acetamide, dimethoxycyclohexanone, epoxycyclohexanone, cyclohexanone oxime, nitrocyclohexane. The presence of acetamide confirms that reaction follows the mechanism proposed by Jimenez-Sanchidrian et al. [6] involving formation of peroxycarboximidic acid and a Criegee adduct, which rearranges to lactone with release of an amide. This conclusion is further supported by lack of cyclohexanone conversion when acetonitrile is substituted with dioxane or methanol (Table S2, Supporting Information). The occurrence of other nitrogen-containing products suggests that the nonselective routes also involve participation of the acetonitrile solvent. On the other hand, no evidence of products expected upon hydrolytic decomposition of ε-caprolactone have been found, such as 6-hydroxyhexanoic acid, the product of lactone ring opening upon reaction with water, thus eliminating significant hydrolysis as a possible cause for the lowering of selectivity. Another possibility is some contribution of the radical reaction pathway, occurring parallel to the desired route which involves consumption of perhydroxyl anions formed over Mg-OH Brønsted basic sites. To check on this, an experiment was performed with addition of butylated hydroxytoluene (BHT), a radical scavenger, to the reaction mixture over $Mg_4Al$ catalyst. As a result, the cyclohexanone conversion fell from 40 to 24%, but the selectivity increased from 70 to 96%, thus confirming the role of parallel radical reactions in lowering the selectivity to ε-caprolactone. In view of this, it is suggested that the addition of $NaHCO_3$, by stabilizing the Ht catalyst surface against leaching of magnesium, preserves Brønsted basic sites responsible for activation of $H_2O_2$ to $OOH^-$ – perhydroxyl anions required for the selective BV process, and promotes its occurrence.

In view of the essential role of acetonitrile in ε-caprolactone synthesis with use of the Ht-activated $H_2O_2$/nitrile system, it was of interest to check whether there is any involvement of acetonitrile in the BV oxidation of cyclohexanone with neat BAP system (without the Ht catalyst). To this end the reaction with BAP was carried out with other solvents (methanol and dioxane) instead of acetonitrile. The results (Table S2, Supporting Information) show that BAP was capable of oxidizing cyclohexanone to ε-caprolactone only in the presence of acetonitrile as a solvent. This suggests that, similarly as in the case of Ht-activated $H_2O_2$/nitrile system, the oxidizing species is the peroxycarboximidic anion, formed by reaction of peroxybicarbonate anion with acetonitrile (Fig. 1c).

## 4. Conclusions

Results presented in this study show clearly the superiority of the $H_2O_2$/acetonitrile/bicarbonate/Ht setup described in this work, over conventional $H_2O_2$/acetonitrile/Ht system. Joint operation of both the catalytic and the non-catalytic processes brings about two positive effects: a) significant increase of the lactone yield, and b) catalyst stabilization enabling efficient operation upon recycling. Formation of ε-caprolactone with the use of BAP system requires the use of a nitrile solvent, suggesting a mechanism involving peroxycarboximidic anion as an oxidizing intermediate. Full understanding of the observed phenomena requires further studies, but it appears that the neutralizing effect of bicarbonate, rendering the Ht catalyst less susceptible to magnesium leaching, is the main cause of the observed changes. The proposed novel, experimentally facile reaction setup, represents an attractive option for any catalytic process in which basic catalysts susceptible to acidic environment are used in combination with $H_2O_2$ solution.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2019.105821.

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