Base-catalyzed condensation of citral and acetone at low temperature using modified hydrotalcite catalysts

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Abstract

A study on the catalytic properties of properly activated hydrotalcite (HT) with special attention to the nature and amount of active sites present in this solid base catalyst has been undertaken. Only a small fraction (5%) of the available basic sites in the rehydrated calcined HT is active in liquid-phase aldol condensations. These sites exhibit high catalytic activity and are most likely localized at the edges of the HT-platelets. Besides a high activity, these modified HTs also show a high selectivity. No further condensation products other than diacetone alcohol (DAA) in the acetone self-condensation could be observed. Initial results with the citral–acetone condensation show that even at 273 K this reaction is catalyzed by modified HTs with a conversion of 65% and a selectivity of 90%, when the citral concentration is not too high ($\sim$1 wt.%). At higher citral concentrations, no reaction is observed indicating a negative order in citral concentration. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrotalcite; Solid base catalysts; Citral; Basic sites; Aldol condensation

1. Introduction

In the fine chemical industry, a common method of coupling organic molecules via C–C bond formation is the base-catalyzed aldol condensation. When executed in the liquid-phase, currently homogeneous alkaline bases are used as catalysts, which brings about large waste streams, while re-use of the catalyst is not practical. A key starting material for the commercial production of vitamin A (and of various carotenoids, flavors and fragrances) is pseudoionone (PS), which is synthesized by condensating citral and acetone (see Fig. 1a). Commercial citral is a mixture of two isomers due to the *cis–trans* isomerism at the C=C bond near the aldehyde group. Besides the desired reaction, several side-reactions can take place too. Especially,

self-condensations of citral and secondary reactions of PS are potential problems [1].

Some of these problems might be avoided using solid base catalysts. A promising candidate is hydrotalcite (HT), an anionic clay showing high activities and selectivities in these type of reactions [2,3]. The structure of HT, $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, resembles that of brucite, $Mg(OH)_2$. In the latter structure, the magnesium cations are octahedrally coordinated by hydroxyl ions, resulting in stacks of edge-shared layers of the octahedra. In the HT structure, part of the Mg^{2+} ions are replaced by Al^{3+} ions resulting in positively charged layers, whose charge is compensated by interlayer anions, in the above case carbonate. Furthermore, water molecules are present in the interlayer [4–6]. To bring about catalytic activity in aldol condensation reactions, the HT has to undergo a specific treatment. For gas-phase condensation reactions at high temperature, calcination at 723–773 K is sufficient [7]. The

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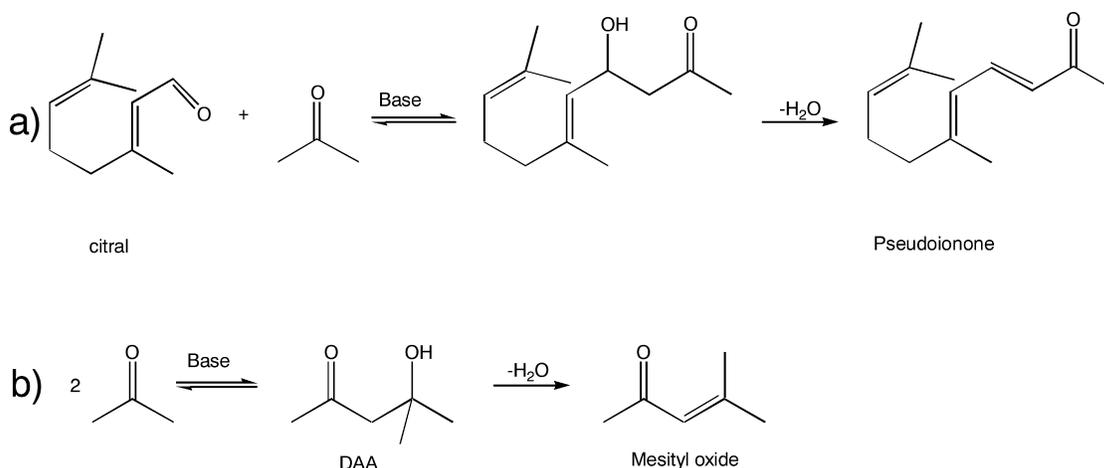
Fig. 1. (a) Base-catalyzed condensation of citral and acetone yielding PS after dehydration; (b) base-catalyzed self-condensation of acetone to DAA, followed by dehydration yielding MO.

resulting mixture of oxides exhibits strong Lewis basicity [8–11] capable of catalyzing various reactions like the self-condensation of acetone [12] and the condensation of formaldehyde and acetone [13]. However, these calcined samples are significantly less active and selective in liquid-phase condensations at lower temperatures [14,15] due to, amongst others, the presence of Lewis acid sites [16]. To enhance the catalytic activity at these lower temperatures, the calcined samples have to be rehydrated at room temperature under exclusion of CO_2, a treatment which results in the restoration of the original layered structure but now with OH^- ions in the interlayer. This catalyst brings about, for instance, the condensation of benzaldehyde with acetone giving high yields and selectivities even at 273 K [3,15]. Still, little is known about the nature and number of active Brönsted basic sites and the mechanism involved. A useful and relatively well described condensation reaction in the liquid-phase using rehydrated calcined HT is the self-condensation of acetone yielding diacetone alcohol (DAA) [14,17–19], shown in Fig. 1b. It may be concluded that a reaction temperature of 273 K is advantageous to prevent the dehydration of DAA to mesityl oxide (MO), and thus, to avoid the liberation of water which could influence the accessibility and the reactivity of the catalyst. Furthermore, the conversion of acetone to DAA is a reversible process and the equilibrium is favoring acetone with increasing temperatures [18].

Recently, Noda et al. [20] studied the production of PS at 330 K using a calcined HT. These authors concluded that at lower temperatures, the condensation of citral with acetone requires stronger basic sites than for the self-condensation of acetone and preferably has to be executed at higher temperatures. We concluded from their results that with a more suitably pretreated HT-catalyst better results, even at lower temperatures, are not to be excluded. In this study, we tested our catalyst in the citral–acetone condensation and the self-condensation of acetone at 273 K with special attention to the nature and number of active basic sites present in the HT-catalyst.

2. Experimental

2.1. Preparation of the catalyst

An aqueous solution (45 ml) of 0.1 mol $Mg(NO_3)_2 \cdot 6H_2O$ and 0.05 mol $Al(NO_3)_3 \cdot 9H_2O$ was added all at once to a second solution (70 ml) containing 0.35 mol NaOH and 0.09 mol Na_2CO_3 at 333 K. The mixture was maintained at this temperature for 24 h under vigorous stirring, after which the white precipitate was filtered off and washed several times. Drying of the HT took place for an additional 24 h at 393 K. ICP-analysis revealed an Mg/Al ratio of 2/1. Using this ratio and thermogravimetric analysis (TGA) results,

the HT-structure ($Mg_6Al_3(OH)_{18}(CO_3)_{1.5} \cdot 4H_2O$) was calculated.

After drying, the HT was heated in a nitrogen flow up to 723 K with a heating rate of 10 K/min and kept at this temperature for 8 h. Samples (typically 0.5 g) were rehydrated at 303 K by use of a decarbonated water-saturated nitrogen flow of 100 ml/min for 48 h. The rehydration procedure has been adapted from Rao et al. [3].

2.2. Reaction procedures

The self-condensation reaction of acetone was performed in a stirred double-walled cooled glass reactor, equipped with baffles. Typically, an amount of 2 mol acetone was cooled to 273 K and 0.3 g freshly prepared catalyst was added under a low flow of nitrogen to exclude atmospheric carbon dioxide. The amount of catalyst was varied in the range 0.2–0.8 g and this did not affect the results. Aliquots of 1 ml were taken from the reaction mixture during the 24 h reaction period and analyzed using a Chrompack CP 9001 GC provided with a Chrompack CP 9050 autosampler. *iso*-Octane was used as internal standard to calculate the amount of DAA formed.

The procedure used for the citral–acetone condensation was similar to the procedure used with the self-condensation of acetone. The reaction mixture contained 1 wt.% citral (Aldrich). Tetradecane was used as the internal standard. Product identification is complicated because of the facile dehydration reaction of the β-hydroxy-ketone (Fig. 1a) under the conditions needed for product analysis. To get around these problems, we decided to monitor the decrease of the citral concentration in time. In addition, no citral self-condensation was found to proceed while the amount of PS was monitored. The selectivity has been calculated by using both the β-hydroxy-ketone and PS signals from GC-analysis and comparing these with the amount of reacted citral.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were obtained by using an Enraf Nonius FR 590 with Co Kα radiation. Thermal analyses with a heating rate of 6 K/min were done on a Perkin Elmer TGS-2, equipped with a Fisons Instruments Thermo-lab quadrupole mass spectrometer. After outgassing under vacuum at 393 K, a Micromeritics ASAP 2400 analyzer was used for N_2-physisorption to determine surface areas and pore volumes.

CO_2 adsorption measurements were performed at 273 K using a Micromeritics ASAP 2000. After calcination and/or rehydration as described above, the samples were quickly stored under nitrogen to avoid CO_2-uptake from the atmosphere. Before measurements were performed, the samples were outgassed under vacuum at 393 K.

3. Results

The XRD pattern of the synthesized HT compound exhibits the typical features of a HT (Fig. 2a). From the position of the 003 peak, the lattice distance of 7.8 Å (corresponding to the sum of one cation layer and one interlayer distance) can be calculated [4]. By heating the samples up to 773 K, the lattice structure is destroyed and a mixed oxide of the Mg(Al)O type is formed (Fig. 2b). Restoration of the original layered structure can be achieved to a large extent by rehydration of the calcined product at 303 K (Fig. 2c). In this last compound, the weak base CO_3^{2-} (respectively, HCO_3^-) has been replaced by the strong Brönsted base OH^- (via rehydration). The lattice distance is not affected by this replacement.

TGA and differential thermogravimetric analysis (DTG) results with the HT with CO_3^{2-} as the compensating anion are shown in Fig. 3. The weight loss of HT-like compounds at increasing temperatures is well described in literature [10,21–23]. First, up to about 393 K, adsorbed water is lost followed by interlayer water up to 540 K. We ascribe the weight loss at higher temperatures (maximum between 640 and 720 K) to dehydroxylation of the cation layers and the removal of carbonate via the formation of carbon dioxide. The monitored mass signals in terms of water and carbon dioxide confirm these findings (data not shown). There has been some discussion in the literature about the starting temperature of these processes. Kloprogge and Frost [24,25] found that carbonate decomposition starts even at 343 K. We are inclined to agree with these authors that it is possible for surface carbonate groups to decompose at these low temperatures but, in view of our own results, we are convinced that
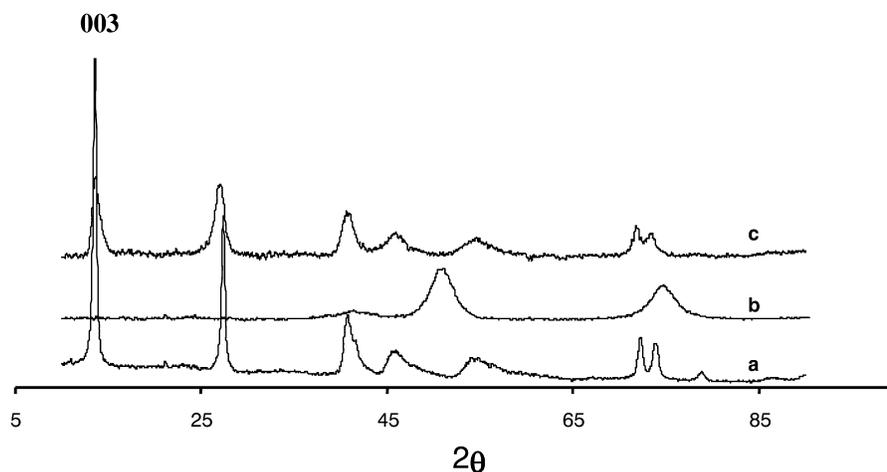
Fig. 2. XRD patterns of (a) HT as synthesized; (b) HT heated in N_2 atmosphere at 723 K; (c) HT after 48 h rehydration at 303 K.
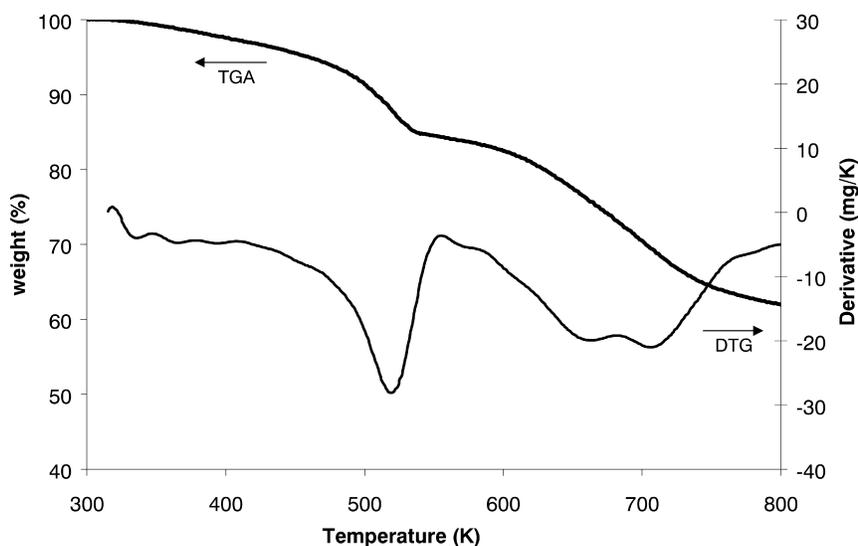

Fig. 3. TGA–DTG of HT as synthesized.

interlayer carbonate groups are stable at this low temperature. We ascribe evolution of CO_2 above 673 K to the decomposition of intermediately formed $MgCO_3$.

The results from our physisorption measurements are given in Table 1. Calcination results in a large increase in BET surface area from 88 to 253 m²/g. This is partly due to the formation of micropores as well as mesopores as can be concluded from the large increase in total pore volume. The micropores vanish

Table 1
Results from N_2-physisorption measurements

|	BET surface area (m²/g)	Micropore volume (ml/g)	Total pore volume (ml/g)
HT	88	Nil	0.77
HT calcined	253	0.06	1.10
HT rehydrated	57	Nil	0.66
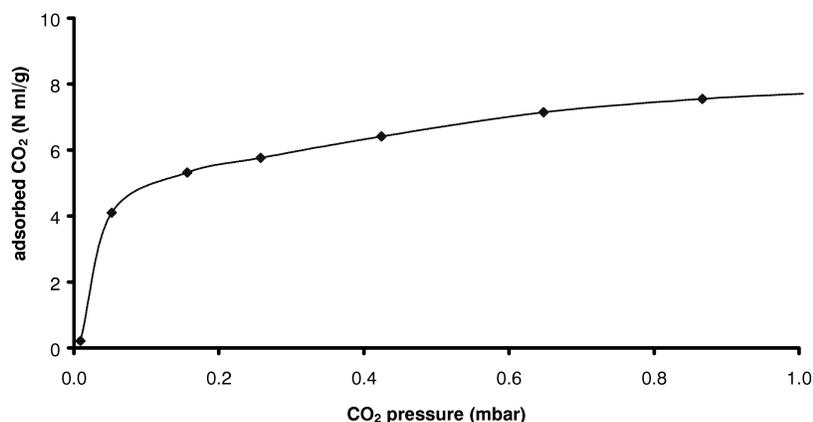
Fig. 4. Adsorption isotherm of CO_2 on the modified HT at 273 K.

during rehydration while the layered structure is restored resulting in a significant decrease of the BET surface area, from 253 to 57 m^2/g.

In order to estimate the total amount of accessible Brönsted basic sites present, CO_2 adsorption measurements have been performed at low pressures. The results of such an experiment are shown in Fig. 4. Rao et al. [3] found a similar CO_2-uptake at these low pressures. The total number of basic sites in the HT can be calculated from the number of Al^{3+}-ions present as established by ICP analysis. This number is proportional to that of the compensating anions, OH^- in case of the rehydrated HT. From the above results, we estimate that only 5% of the totally available basic sites participate in the condensation reactions, which indicates that the reaction most likely takes place at the edges of HT-platelets. Further work will concentrate on elucidation of this hypothesis by varying the platelet size and measuring of changes of the catalytic activity due to this variation.

We tested the catalytic activity of HT as synthesized, the calcined HT and the rehydrated calcined HT samples in the self-condensation of acetone. The results are shown in Fig. 5. The HT with carbonate as the compensating anion shows no significant activity. The calcined sample formed after heating in N_2 exhibits an activity comparable to that of MgO [14,26]. Its activity in the benzaldehyde–acetone condensation has been ascribed to strongly bound hydroxyl groups still present at the surface after calcination at 773 K. The Lewis basic sites (O^{2-}) are not expected to cat-
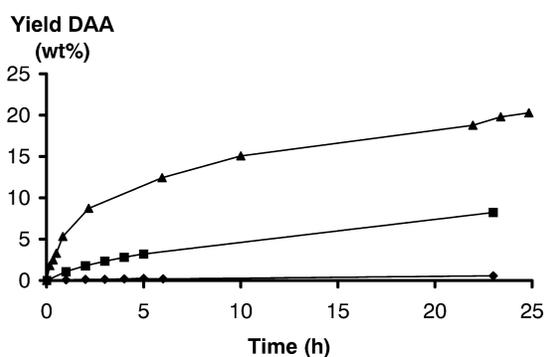

Fig. 5. DAA production with HT as synthesized($\blacklozenge$), calcined HT ($\blacksquare$) and calcined/rehydrated HT ($\blacktriangle$).

alyze this type of condensation reactions [15]. The rehydrated calcined HT-catalyst with OH^- ions between the cation layers shows a high initial activity (Table 2). Even within 1 h, the initial rate decreases due to the establishment of equilibrium at 273 K (23.1 wt.% DAA

Table 2
Initial reaction rates and conversion levels after 24 h for acetone self-condensation at 273 K with the calcined/rehydrated HT catalyst

	Initial rate ($g_{DAA}\,g_{cat}^{-1}\,h^{-1}$)	Conversion to DAA (wt.%)
HT–CO_3	<0.1	<0.1
Calcined HT	2.3	8
Rehydrated HT	13	21
Rehydrated HT from [14]	3	25
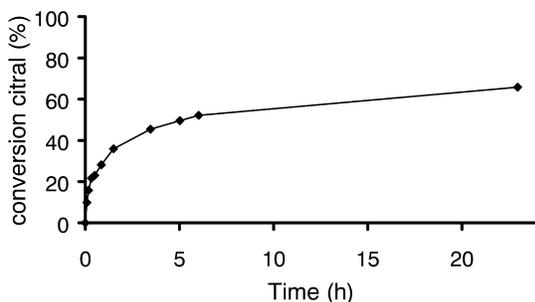
Fig. 6. Conversion of citral at 273 K with 1 wt.% citral initially present.

Table 3
Total TON and initial TOF for acetone self-condensation and for acetone–citral condensation at 273 K

	TON	TOF (h^{-1})
DAA production	2000	720
Citral conversion	35	73

[18]). The activity we measured was four times higher than that reported in literature [14] (Table 2).

To suppress self-condensation of citral in the condensation reaction of citral and acetone, a high ratio of acetone/citral was applied. Rao et al. [3] used in the benzaldehyde–acetone condensation a molar acetone/benzaldehyde ratio of 32 and obtained a conversion of 94% and a selectivity of 86% to the β-hydroxy-ketone. We found that with a molar acetone/citral ratio of 20 (corresponding to 10 wt.% of citral), no reaction took place at all. When the amount of citral was decreased to 1 wt.%, both acetone self-condensation and citral–acetone condensation were observed, which demonstrates a strong inhibition by citral at higher concentrations of citral. The reason for this observed inhibition is currently under investigation.

Fig. 6 shows the conversion of citral at 273 K when a rehydrated HT-catalyst is used. As can be seen, after 24 h 65% of the citral was converted. Furthermore, a selectivity of 90% was observed. These results show also a sharp decrease of the conversion rate in time. Deactivation could be the reason, since the accompanying self-condensation of acetone is four to five times lowered to yield 5 wt.% DAA after 24 h (data not shown). Nevertheless, these results show that the modified HT enables the desired citral–acetone condensation to proceed at 273 K. The basic sites appear to be extremely active, resulting in high turn over frequencies (TOFs). The calculated total turn over number (TON) and initial TOF for both performed condensation reactions are presented in Table 3. The calculated numbers for the citral–acetone reaction are low compared with the acetone self-condensation, due to the low concentration of citral.

4. Conclusions

We demonstrated from adsorption measurements that only a small fraction (5%) of the total number of basic sites in the rehydrated calcined HT-structure is available for liquid-phase aldol condensation reactions at low temperatures. These sites, most likely localized at the edges of HT-platelets, exhibit high catalytic activity in the condensation reactions investigated. Besides a high activity, the rehydrated calcined HTs show a high selectivity. For example, no further condensation products other than DAA in the acetone self-condensation were formed.

Our preliminary results for the citral–acetone condensation show that, even at 273 K, with 1 wt.% citral present, the condensation reaction is catalyzed by modified HTs with reasonable conversions and high selectivities [27]. At 10 wt.% citral no reaction is observed, which points to a negative reaction order in citral. Future experiments will give more insight in the mechanism involved.

Acknowledgements

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