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Heterogeneous Acid-Base Catalyzed Aldol Condensation: Acetaldehyde and Heptaldehyde on Hydrotalcites. Optimization of Operatory Conditions

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Abstract: The aldol condensation between acetaldehyde and heptaldehyde, aiming the cross-condensation as a way to increase the length of the linear carbon chain, was investigated in heterogeneous system, using the commercial hydrotalcite KW2200 as catalyst. A parametric study allowing to find the optimal operatory conditions was performed. The yield values towards the target compound were around 25%, suggesting to continue the work and synthesize new more performant catalysts for this purpose.

Keywords: Aldol cross-condensation, hydrotalcite, selectivity, operatory parameters

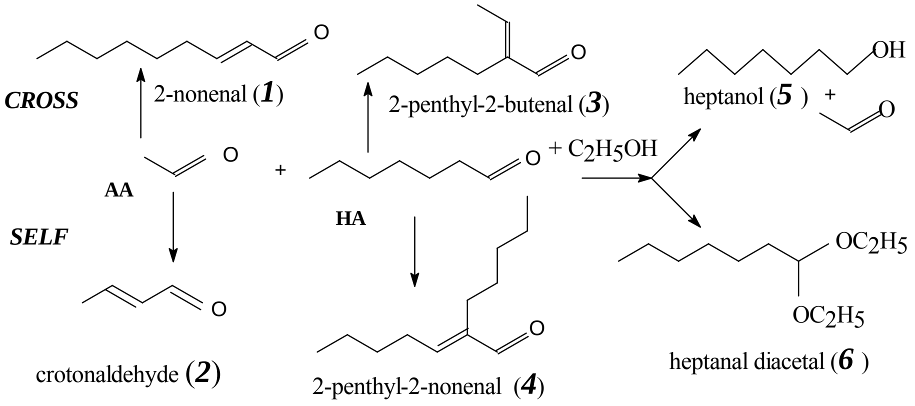
Introduction

The aldol condensation of aldehydes is a convenient way to increase the carbon chain length with important application in organic synthesis, for high molecular weight aldehydes, valuable for the obtaining of solvents, perfumes and flavoring agents or as intermediates in the manufacture of plastics, dyes and pharmaceuticals. Usually, the condensation step is followed by the dehydration of the aldol. Since the first reaction occurs mainly on base sites and the second on acidic sites, the formation of the unsaturated carbonyl product can be considered the result of the collaboration between acidic and base sites [1-3].

The use of solid catalysts in organic synthesis is preferable for environmental reasons, due to the simple separation of the catalyst at the end of the process and for the possibility to achieve good selectivity values towards the target product. The hydrotalcites are hydrated Layered Double Hydroxides (LDH) containing divalent (M^{2+}) and trivalent (M^{3+}) cations, with the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-}_{x/n})$ mH_2O; A^{n-} is the charge compensating anion. The most common cations in LDH are Mg^{2+}, Ni^{2+}, Co^{2+}, Zr^{2+}, Al^{3+}, Fe^{3+}, Ga^{3+}, Cr^{3+} while the compensating anions are HO^-, CO_3^{2-}, NO_3^-, Cl^-, SO_4^{2-}. The structure of hydrotalcites consists of two cationic sheets of $[M(OH)_6]$ octahedral units assembled by the edges, similar to brucite lattice. The anions and water molecules are placed between two cationic layers [4]. Upon calcination, water is eliminated and most of the volatile anions are decomposed. The hydrotalcite is transformed into a mixed-oxide form. The structure of the solid changes as compared to the initial product, but the change is reversible in a certain extent, by contacting the calcined form with water [4, 5]. The mixed oxides contain strong Lewis basic sites (oxygen atoms in low coordination) and mild acidic sites [4-6]. The fine-tuning of the catalytic properties of LDH is possible by the appropriate choice of the calcination regime.

The use of hydrotalcites in aldol condensation had been approached in papers and patents, due to the practical applications. The self-condensation of acetaldehyde [4, 7], butyraldehyde [8] and acetone [9] and in cross-condensation of formaldehyde with butyr- and isobutyraldehyde [10] are some examples.

In this paper, the study of the cross-condensation reaction between acetaldehyde (AA) and heptaldehyde (HA) was approached. The use of AA in aldol condensation allows increasing the linear hydrocarbon chain with two carbon atoms.



Scheme 1. Reaction network in AA and HA aldol condensation

The aldol condensation taking place on solids supposes the chemisorption of the aldehyde molecule on the base sites, by the subtraction of a proton from the alpha-carbonyl position of the aldehyde, forming its adsorbed anion. This anion then adds at the carbonyl group of another aldehyde molecule, forming an aldol. From the reaction network in Scheme 1, we can observe that there are four different reactions of condensation, two cross-condensations and two self-condensations. Only product ***1*** is desirable to form, since only this molecule is linear and interesting for practical applications.

The target compound ***1*** is obtained when AA is chemisorbed and the formed anion attacks a HA molecule. Since there is a big difference in the physical properties of these two species, especially their volatilities (boiling points: 20.2°C for AA and 150°C for HA), an excess of AA is requested to favor its adsorption on the surface. But the excess will also increase the probability of the self-condensation of AA to occur, giving crotonaldehyde (***2***)**.** This compound is extremely reactive [11] and leads easy to C6, C8, C10, and C12 products when combined with more AA molecules.

The aim of this work is to settle the operational conditions for the obtaining in the highest yield the 2-nonenal (***1***), by cross-condensation between AA and HA, on a synthetic commercial hydrotalcite (KW2200).

Experimental

The acetaldehyde (95%) and heptaldehyde (98%) were Aldrich products, the absolute ethanol was from Carlo Erba and the decane (98%+) used as internal standard was a Fluka product. A commercial hydrotalcite, KW2200 ($Mg_{0.7}Al_{0.3}O_{1.15}$, BET surface area of 160 m^2g^{-1}, Kyowa), was used as catalyst.

The reaction was performed in liquid phase, in a sealed stainless steel autoclave with a volume of 100 ml, equipped with mechanical agitation and sampling device. In most cases, about 70% of the solvent, the internal standard (decane) and 2 g of catalyst powder were put in the autoclave and sealed. Before beginning the reactants addition, the free space in the autoclave was purged with nitrogen for one minute, sealed and pressurized at 2 atm. The reactants diluted with the rest of solvent were introduced in the autoclave with a pump, as soon as the programmed temperature in the autoclave was reached. This manipulation was necessary because of the high volatility of acetaldehyde. We minimized in the same time the temperature fluctuations during the initial heating period.

The reaction products were identified by a mass spectrometer coupled to a gas chromatograph HP 5890. The quantitative measurement of reaction mass was done periodically on a HP 4890 gas chromatograph equipped with a HP-5 column, using decane as internal standard.

The results were expressed in terms of acetaldehyde and heptaldehyde conversion degrees, as well as selectivity towards a certain product.

⇨ Conversion at time t, $C_t^R = (R_0\text{-}R_t)/R_0$

⇨ Selectivity of reactant R towards product P, $S_P^R = R_P/(R_0\text{-}R_t)$

⇨ The yield of reactant R towards product P, in time t, $Y_R^{P,t} = C_t^R * S_P^R$,

where: R_0 – initial amount of reactant R; R_t – amount of R unreacted till time t; R_P – reactant transformed in product P, in time t

Before running an experiment, the catalyst was activated by heating under 100ml/min air flow, with a rate of 1°C/min to the desired temperature value, kept constant for 6 hours and cooled at about 2°C/min to the room temperature.

Results and discussions

1. Opportunity of solvent use and reactants mixing protocol

A preliminary set of experiments were performed in order to investigate the reactivity of AA in comparison with that of HA, working at an equimolar ratio between the two aldehydes. HA is the limitative reactant in the reaction, due to its price higher than that of AA and to its lower availability. The catalyst was placed in the autoclave with the HA, purged with nitrogen, pressurized at 2 atm and sealed, then the AA was dropwise added with a pump. It was aimed thus to minimize the AA self-condensation which is known to occur very easily [11] and introduce it approximately at its consumption rate. There were not detectable amounts of products at temperatures lower than 80°C. In these conditions, the catalyst was rapidly deactivated by strongly adsorbed bulky species colored in brown. It was impossible to establish if the reaction products came from AA or HA. It indicated that the active sites were quickly blocked by heavy products adsorbed on the catalyst surface, formed because of the high density of reactive molecules.

Several solvents were tested in this reaction system, namely ethanol, 1-propanol and hexane. The best behavior was displayed by ethanol, due to its good solving ability, for both initial reactants and products, as well as for its acid-basic almost neutral character. The conversion degree of HA and its selectivity of transformation towards the target compound ***1*** (2-nonenal) and compound ***4*** (2-penthyl-nonenal) (the latter consuming two molecules of HA for the formation of one of its molecule) are presented in Table 1.

Two modes of contacting the reactants were tested. In the first one, HA was mixed with 50-100% of the solvent and the catalyst, then AA, eventually diluted with the rest of solvent was pumped quickly in the autoclave. In the second version, the catalyst was dispersed in 70-80% of the solvent amount, heated at regime temperature, and then the mixture of the two aldehydes with the rest of ethanol was pumped in the autoclave.

The results displayed in the first two lines in Table 1 show very different selectivity values towards ***1*** and ***4***, at very similar conversion degrees of HA.

Table 1. Selected preliminary experiments for establishing the reaction conditions; HA/AA = 1/1 (moles), reaction temperature: 120°C; time on stream: 6h

Test no.	Initial autoclave content	Components pumped later	Solvent / reactants ratio, mole/mole	C^{HA}, %	S_1^{HA}, %	S_4^{HA}, %
1	HA+ solvent + catalyst	AA or AA + solvent	0.65	32	9	74
2	HA + solvent + catalyst	AA or AA + solvent	2	32.5	18	58
3	Solvent + catalyst	HA + AA + solvent	5	28.3	27	25

The net increase of selectivity towards ***1*** in the same time with the decrease of selectivity towards ***4*** indicates that the use of ethanol as solvent is beneficial and the effect is better when the dilution radio increases. Despite the initial suppositions, big amounts of ***4*** were obtained even at very slow addition rate of AA. It means that in the given conditions, the catalyst is able to produce the chemisorption of both initial aldehydes and not only of AA as expected. The formation of HA anion allows its self-condensation giving ***4*** and also forming ***3*** (when HA works as the methylene component in the reaction), both of them undesirable products. It is worth noting that the manipulation of AA was easier after its dilution (1/1 moles) in ethanol. Its low boiling point makes technically impossible its addition along more than 2 hours.

The results from the second scheme for reactants mixing with the catalyst are presented in test 3 (Table 1). The two aldehydes were mixed and diluted with 30% of the solvent, pumped as fast as possible in the autoclave, previously charged with the catalyst and 70% of the solvent and heated at the desired reaction temperature. This mode of reactant addition was superior to the precedent ones, with respect of selectivity towards ***1*** at similar HA conversion degree.

This set of tests allowed concluding that the reactivities of the two aldehydes are very close to each other. In order to increase the selectivity of transformation towards ***1***, we had to work on "fine tuning" of the basicity strength of the catalyst, so that it interacts with the acetaldehyde rather than with heptaldehyde for the anion formation.

The data in Table 1 indicate that solvent use is beneficial and furthermore, the selectivity towards the target product ***1*** is favored by higher solvent/reactants (S/R) ratio. In order to find out if a higher solvent content of the reaction mixture gives better results, we also tested the evolution of the reaction at an S/R ratio of 10/1. The efficiency of the solvent was expressed by the value of the yield of transformation of heptaldehyde to ***1***, see figure 1.

The values of the yield show that the S/R ratio of 5 gives a better degree of transformation of heptaldehyde to ***1***, at reaction durations longer than 3 hours. These experiments also indicated that the duration of 6 h is somehow an optimum for the catalyst lifetime, the yield value reaching a plateau at this point.

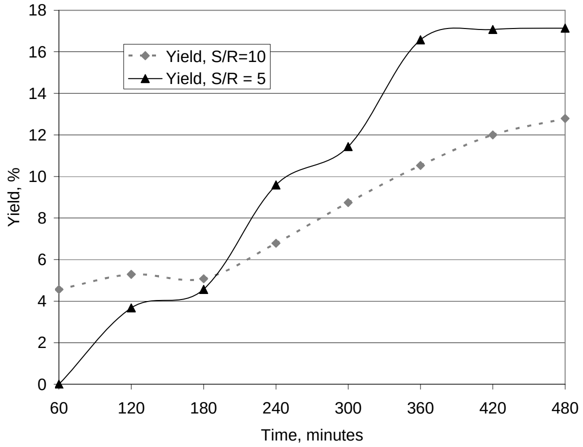


Figure 1. Dependence of the solvent/reactant ratio (reaction temperature: 120°C, catalyst calcination temperature: 450°C, initial HA/AA = 2/1, mole)

There was also a drawback connected to ethanol usage as a solvent for this reaction. The Meerwein-Pondorf-Verley reaction is possible between HA and ethanol, giving heptanol (product ***5***) [12, 13]. Also, on acidic sites, the alcohol addition to the double carbonyl bonding is possible, giving the diacetal ***6*** [13]. The importance of these reactions can be however diminished by avoiding the availability of medium to strong acidic sites on the catalyst surface.

2. The water influence

The important changes of the structure and base/acidic character of LDH occurring upon calcination and rehydration [4, 14] could be important in the product distribution of the aldol condensation between AA and HA. In order to study the influence of the rehydration on the catalytic activity and product selectivity, parallel experiments were performed where some water was introduced in the reaction vessel together with the ethanol. The water amount was calculated to be close to the necessary for the reconstruction of the LDH obtaining. The results in terms of conversion degree of AA and HA, as well as selectivity towards different reactions products are presented in Table 2.

Table 2. Evolution of the reaction in anhydrous and water-containing system*

Medium	C^{HA}, %	C^{AA}, %	$S_{\mathbf{1}}^{HA}$, %	$S_{\mathbf{2}}^{AA}$, %	$S_{\mathbf{3}}^{HA}$, %	$S_{\mathbf{4}}^{HA}$, %	$Others^{HA}$**, %
Anhydrous	22.93	32.94	12.44	32.41	16.37	25.95	12.83
Aqueous	30.52	35.08	11.58	18.26	21.24	30.05	18.88

*Batch compositions: ANHYDROUS 1 AA : 1 HA : 10EtOH; AQUEOUS 1AA : 1 HA : 9.5 EtOH : 0.4H_2O ; reaction temperature: 120°C; time on stream: 240 min; catalyst activation temperature: 550°C; **heptanol, heptanal-diacetal and heavy unidentified products of polycondensation.

The influence of water in the reaction system is very important. The catalyst activity is much higher in the reaction system containing water, both HA and AA occur higher conversion degrees. In what concerns the product selectivity, it is evident that water had a bad influence on the desired product distribution. The selectivity towards products ***3*** and ***4*** are a lot higher than in the anhydrous system. In return, the AA self-condensation forming ***2*** is also highly favored in anhydrous medium. This behavior can be attributed to the changes induced on the catalyst surface by the water resulted by the aldol dehydration, i.e., the partial rehydration of the mixed oxide and the transformation of strong Lewis base sites in hydroxyl species, which are Brőnsted sites. However, the XRD performed on the used catalyst did not show the LDH structural reconstruction. It means that the catalyst surface is very sensitive to water and the superficial groups undergo changes very easily. The conversion degree of AA is almost double with respect to HA and the highest proportion of this reactant is transformed by self-condensation. The self-condensation continues further, so that about 5-7% heavy products are obtained.

The influence of water in the initial composition of the reaction system is therefore unfavorable. It is worth noting that the attempts to rehydrate KW2200 by contacting with a humid air flow did not lead to the structure reconstruction, as shown by the XRD patterns of the powder.

3. The Influence of the Activation Temperature of the Catalyst

The catalyst was activated prior to each experiment, by heating in air flow (100 ml/min) at two temperatures values, 450 and 550^{o}C, at a rate of 1^{o}C/min. The activation below 450^{o}C risks making an incomplete activation, while temperatures higher than 550^{O}C risk inducing the spinel structure formation, catalytically inactive [4]. The HA conversion, selectivity and yield values towards to product ***1,*** for the two activation temperatures, are represented in the Figure 2.

A clear different behavior of the catalysts is noticed. The conversion values are a lot higher in the case of the activation at the lower temperature value and the shift increases a lot with time on stream. In the meantime, the selectivity remains almost the same for the catalyst activated at lower temperature but decreases constantly for the other one.

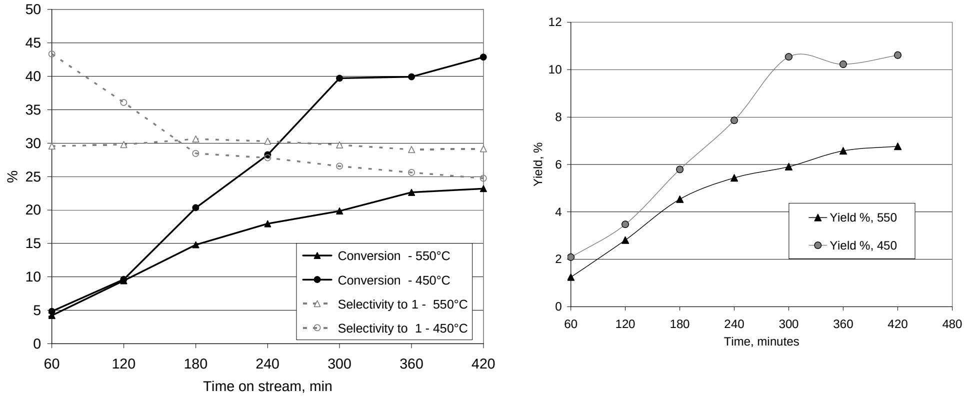


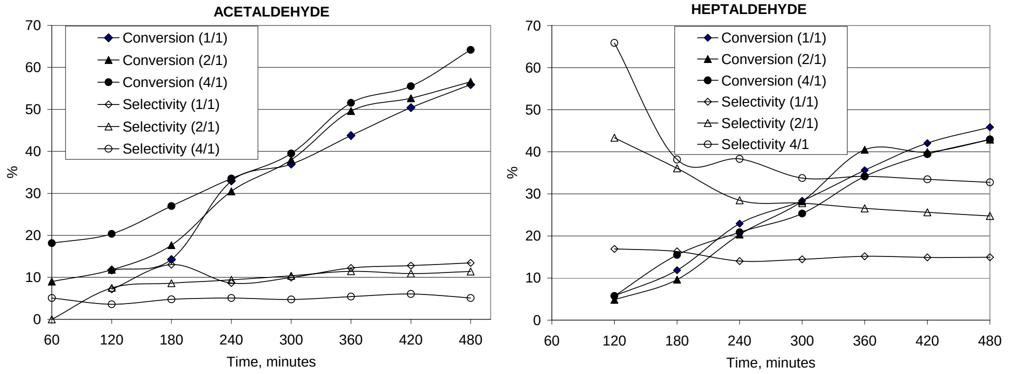
Figure 2. The influence of the activation temperature of the catalyst (reaction temperature: 120°C, initial HA/AA ratio = 5)

Since the aldol dehydrates after the aldehydes addition to each other, there is a small amount of water by the active sites. It will affect the nature and activity of the catalytic sites, increasing the acid Brőnsted ones, known as more active but less selective in the target reaction. The overall efficiency of the catalyst is better reflected by the yield values. The optimal value of the activation temperature, used for the next experiments, is 450^{O}C.

4. Influence of the initial reactants ratio

The high extent of HA transformation by self-condensation giving product ***4*** as well as the formation of ***3*** at an equimolar mixture of HA and AA (Table 1) is due to the chemisorption of a high number of HA molecules on the catalyst surface. AA has a high volatility and tends to evaporate in the gaseous phase.

In order to investigate the effect of reactant ratio and establish an optimal value of this parameter, we performed the reaction at AA/HA ratios of 1/1, 2/1 and 4/1. In this case, we followed the reaction evolution by considering the conversion and selectivity values of both HA and AA. In the case of HA, the conversion values are practically independent of the reactant ratios. The selectivity evolution is however depending strongly of the molar ratio between the initial aldehydes. As expected, the formation of product ***1*** is favoured by high ratios of the AA/HA.



a b

Figure 3. Conversion and selectivity to ***1*** (a: HA; b: AA) in time as a function of initial molar ratio between the aldehydes (reaction temperature: 120^{o}C, reactants/solvent ratio: 1/5)

The effect is more pronounced between 1/1 and 2/1, then being diminished. In what concerns AA, the conversion value increases more seriously at higher AA/HA ratio. Also, the high values of the AA/HA ratios have a very bad influence upon AA transformation in product ***1***, the degree of its transformation by the cross-condensation reaction not exceeding 5-6%. The initial ratio AA/HA of 2 can be considered the optimal value.

5. The influence of the reaction temperature

A series of preliminary experiments put in evidence that the cross condensation reaction start only at temperatures above 80^{o}C. However, at this temperature the transformation is very slow. We tested the behavior of the reaction system at 100, 120 and 140°C. At 100°C, the HA conversion was still below 10% after 5 hours, while the selectivity to ***1*** did not exceed 20% on HA basis. In what concerns the transformation of AA, its selectivity of transformation to ***1*** remains below 10%.

The conversion values of the two reactant species are, as expected, increasing very much at 120 and 140°C. In the transformation of HA, there is an increase of 10-12% in the conversion values between 120 and 140°C, while the selectivity to ***1*** is quite similar. By contrast, the consumption of AA is extremely fast as the temperature is higher, reaching 77% after 7 hours at 140°C. The product distribution is in change very unfavorable, since no matter of the temperature the selectivity towards ***1*** remains below 10%. The main reason for this behavior is the big extent of transformation of AA by self-condensation, followed by subsequent similar transformations of ***2*** and/or AA. The best temperature value for the target reaction had been established to be 120°C.

Conclusions

The aldol cross-condensation reaction between two aldehyde molecules of different length, AA and HA, is very sensitive to both catalyst base and acidic character and the operating conditions. The target is the cross condensation product involving proton subtraction from AA followed by its addition to HA molecule. The secondary self-condensation reactions could not be avoided, whatever the reaction conditions employed, proving very close acidity values of the two reactant aldehydes.

A reliable way to improve the selectivity to the linear cross-condensation product is the synthesis of other acid-base catalysts allowing the fine-tuning of their catalytic properties.

For the case of the KW 2200 hydrotalcite, the optimal activation temperature was deduced to be 450°C. The anhydrous medium is better than when some water was added to the initial reagents. The optimal operational retrieved reaction conditions were, respectively: AA/HA mole ratio of 2, Solvent/Reactants ratio of 5 and reaction temperature of 120°C.

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