Tailoring the Basic and Acid Sites by Thermal Treatments of Mg Al Hydrotalcites for their Use in Aldol Condensation

Doina Lutic*

Department of Chemistry, "Al.I. Cuza" University Iasi, 11 Carol I Bd, Iasi 700506, Romania

Abstract: The activation regime of a MgAl-LDH type catalyst is of of prime importance on its activity and selectivity in a acid-base catalyzed reaction, the aldol condensation between acetaldehyde and heptaldehyde. The optimal activation temperature was determined exprrimentally and comparisons were possible with the commercial hydrotalcite KW2200. The optimal activation temperature is 723K, allowing a heptaldehyde conversion rate of 30% and a selectivity towards 2-nonenal of 47%.

Introduction

Hydrotalcites are hydrated layered double hydroxides of global formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-}_{x/n}).mH_2O$, containing divalent cations M^{2+} (Mg^{2+} and/or Ni^{2+}, Zn^{2+}, Co^{2+}, Zr^{2+}), trivalent cations M^{3+} (Al^{3+} and/or Fe^{3+}, Ga^{3+}, Cr^{3+}) and charge compensating anions A^{n-} (HO^-, CO_3^{2-}, NO_3^-, Cl^-, SO_4^{2-}). Their structures are similar to brucite, the cationic sheets being made of 6-fold bonded $[M(OH)_6]$ units, separated by a sheet of A^{n-} compensating

anions and water. When hydrotalcites are calcined, the water is eliminated and eventually the volatile anions are decomposed, while important structural and compositional changes occur. The so-called mixed oxide form of the hydrotalcite is formed. In certain conditions, water can regenerate the double-layered structure [1-3].

The presence of O^{2-} and/or HO^- anions in the interlayer and the ratio between divalent and trivalent cations in their lattice allows obtaining wide strength range for the acidic and basic sites in hydrotalcites. Strong basic Lewis sites are associated with the presence of O^{2-} and mild acid sites are due to Al^{3+} cations. Rehydration of O^{2-} results in HO^- formation, acting as Brőnsted acid sites. In other words, in the mixed oxide form the basic Lewis sites are predominant and their rehydration gives rise to acidic Brőnsted sites. The extent of interlayer decomposition and the degree of rehydration can be more or less complete, so this is a convenient way to balance the acid-base properties of the solids [3-5].

The aldol condensation is a very sensitive reaction to the balance of basic and acid sites from the surface of a solid catalyst [6-8]. In consequence, minor changes in the activation treatment of the catalyst bring important changes in the conversion degree and on the product distribution, since both depend a lot on the strength of the basic sites [7,8]. Moreover, when two different aldehydes with short (C2) and long (more than C6) carbon chain participate at the reaction, their peculiar hydrophilic/hydrophobic character, volatilities and reactivities involve a strongly different chemisorption behavior. The ability of the catalyst to prefer one species as respect to the other is very important on the product distribution and yields to target product. From the applicative perspective, it

is usually interesting to find the best possible conditions to obtain the linear condensation product with the highest selectivity and yield.

The aim of the present work is to highlight the important effects of the composition and of the calcination temperatures values of Mg-Al hydrotalcites on the aldol condensation between acetaldehyde (AA) and heptaldehyde (HA), in terms of product yields and distribution. The definition of the optimal values which allow obtaining of the target product is also possible. This investigation of this condensation could serve as a model reaction applicable to a whole family of similar catalytic processes.

Experimental

Two Mg-Al hydrotalcites with Mg/Al mole ratios of 2/1 and 3/1 (labeled Mg2Al and Mg3Al) were prepared by the coprecipitation method [1], using a mixture of the two nitrates as precursors. At a 2.5 ml/min flowrate of the above salts solution (1M), mixed initially with 2 g of Na_2CO_3 dissolved in 50 ml of water, a solution of NaOH 2M was added dropwise using a titrator (718 Stat Tritino, Metrohm), under continuous stirring, to keep a constant pH value of 10. After about 1 h aging at room temperature, the precipitate suspension was placed for 14 h on oil bath at 353K under magnetic stirring and reflux. The hydrotalcite powder was recuperated by centrifugation and washed several times with demineralized water till pH = 7, dried at 353K overnight, crushed and sieved. The catalyst used in the condensation was the fraction between 0.0625 and 0.125 mm, in order to minimize the diffusion effects. A commercial hydrotalcite, KW2200 from Kyowa (specific surface 160 m^2/g, Mg/Al = 2.12) was used as a comparison standard.

The catalyst was activated in a glass tube inserted in a vertical oven, by calcination to the desired temperature, under nitrogen flow, at a rate of 1K/min, maintained for 6 hours, then cooled down spontaneously. The activation temperatures were comprised between 643 – 823K.

The rehydration of the mixed oxide was performed by contacting the solid with a 100 ml/min nitrogen flow saturated with water, at temperatures comprised between ambient to 353K, for variable durations. The samples were denoted as $T_1 - t - T_2$, where T_1 is the activation temperature, t the rehydration duration in hours and T_2 the rehydration temperature.

The aldol condensation between AA and HA (analytical grade) was carried out in a sealed stainless steel autoclave, equipped with temperature control and regulation system, mechanical stirring system and sampling device. The reaction was performed in ethanol (analytical grade) as solvent, in order to diminish the secondary self-condensation reactions, as showed in a previous paper [8]. A part of the solvent and the catalyst powder (2g) were introduced in the autoclave, sealed, purged with nitrogen, in order to avoid the possible oxidation processes on the aldehydes, then pressurized at 2 atm. The aldehyde mixture diluted with the rest of solvent was pumped within a few minutes in the autoclave, as presented in a previous work [8].

Samples from the reaction mixture were taken every 60 minutes and measured using a gas-chromatograph HP 4890 equipped with a HP-5 column. The product identification was performed by means of GC-MS, using a database accessible on the apparatus computer.

The reaction advancement was expressed in terms of AA and HA conversion degrees, selectivity or yield towards a certain product defined as:

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

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

⇒ 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

The surface area of the samples was determined by BET method, on an ASAP 2000 Micromeritics machine, on samples outgassed at 473K and 10^{-4} Pa for 2 hours.

Results and discussions

The lamellar structure of the MgAl LDH was confirmed by X-Ray diffraction pattern, as well as the mixed oxide formation upon calcination and the rehydration of the sample (diffractograms not shown). The BET surface had were quite close values for all the calcination temperatures in the investigated range, comprised between 217-238 m^2/g.

The reaction network from the aldol condensation (Figure 1) between two aldehydes is complex, since cross- and self-condesations are possible, both aldehydes can act as methylene components and furthermore, the Meerwein-Pondorf-Verley reaction and acetalization of the aldehydes with the ethanol used as solvent are possible [7, 8]. The main, target reaction in the perspective of practical application is the formation of nonenal (**1**), a longer linear aldehyde molecule.
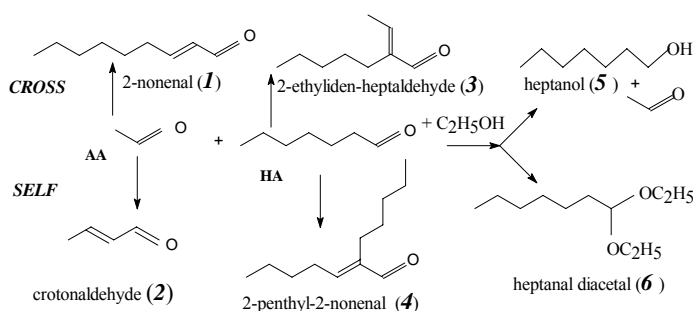
Figure 1. The reaction network in cross-aldol condensation

The aldol condensation between AA and HA was performed at 120°C, using ethanol as solvent at a 5/1 mole ratio to reactants, as previously determined by a parametric study for operating optimization [8].

The calcination temperature has, as we expected, a prime role in the catalytic activity and product distribution. There is a tight connection between the basic sites number and the conversion value, while their strength will determine the nature of the products of the catalytic reaction. It has been shown previously [7, 8] that the key in the catalytic reaction products is the species chemisorbed on the catalyst, which will further add to a free aldehyde molecule from the liquid to form an aldol, via an Langmuir - Hinshelwood heterogeneous mechanism [9]. The cross-condensation, linear product *1* is formed when the AA molecule is chemisorbed on the basic site, forming an anion, which adds to the HA free molecule. The acidity of AA is only slightly stronger than that of HA, so the strength of the basic sites for the AA selective adsorption must be extremely finely tuned. Moreover, the high volatility of AA makes even more difficult to adsorb it selectively on the catalyst surface at high temperatures. The product distribution for different calcination temperatures of the Mg3Al hydrotalcite, Mg2Al calcined at 723 K and KW2200 calcined at 723K, in terms of selectivity to *1* versus conversion degree of HA are presented in figure 2. The performance displayed by the Mg2Al catalyst was weaker than those of Mg3Al and the forthcoming studies were focused on the better sample.
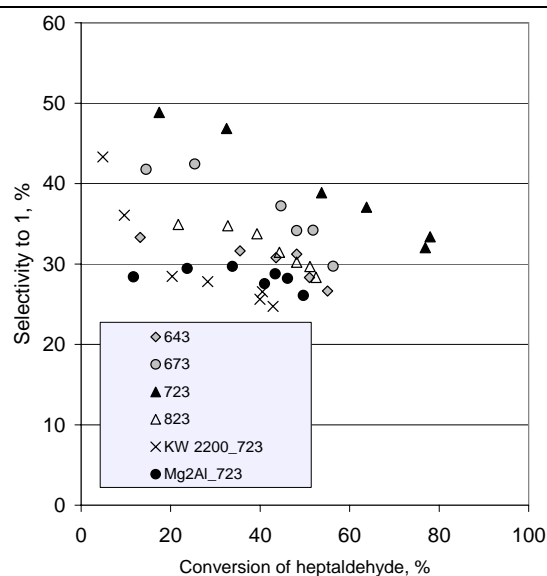
Figure 2. Selectivity to *1* versus HA conversion for different calcination temperatures of the Mg3Al hydrotalcite, Mg2Al and KW2200

The results displayed in Figure 2 indicate that there are major differences between the behaviors of the solids calcined at different temperatures. From far, the value of 723 K is favorable to the formation of *1*, since a reasonable value of 30% conversion of HA will give 45-50% selectivity. For all the calcination temperatures, the Mg3Al hydrotalcite synthesized by us gave better results with respect to Mg2Al and KW2200 used for comparison. Both lower and higher temperatures than 723 K are not suited for the main reaction evolution, due, respectively, to the incomplete decomposition of the initial anions at low temperatures and to the partial structure collapse at too high temperatures [1, 3]. The general tendency of selectivity decrease with the conversion indicates unfavorable structural changes of the active sites during the reaction evolution, possible associated to the production of water during the dehydration following the condensation step and the hydration of the active sites, whose basicity

decreases in this process below that of the ones able to give the target reaction.

If a practical application of this condensation is previewed, an important parameter for appreciating the evolution of the reaction is the value of the yield towards a certain product. The results presented in Figure 3 indicate that a time on stream of about 4 - 6 h gives an optimal yield value to *1* of about 25%.
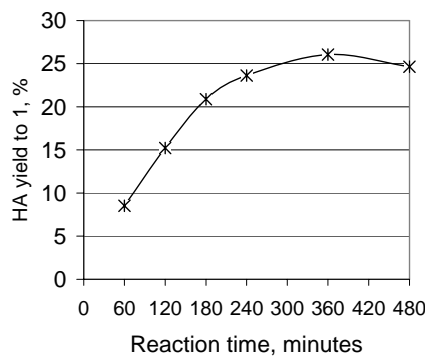
**Figure 2.** HA transformation yield to *1* in time

The ratio between different secondary products gives good information about the nature of the active sites. It is also interesting to see what the ratio between the other products involving HA transformation is. In this respect, we found interesting to compare the selectivity ratios towards *1* divided by the selectivities towards products *3*, *4* and *5*. The results are presented in Figure 4.

The product *5*, the diacetal, is formed on strong acid sites and the ratio of 10 or more noticed at times on stream of 150-300 min indicate a relatively low amount of HA transformed by this way.

The transformation of HA to products *3* and *4* has a much higher occurrence. Both are formed from the anion of HA adsorbed as an anion on

the surface, when added respectively to AA and HA. The more volatile AA makes more difficult its access to the proximity of the surface where it can meet the chemisorbed anion and thus, the formation of product *3* is less favored than *4*. The amount of *1* is always higher than those of *3* and *4*, proving that the formation of AA anion on the catalyst surface is higher than HA, especially on the fresh catalyst (short time on stream).
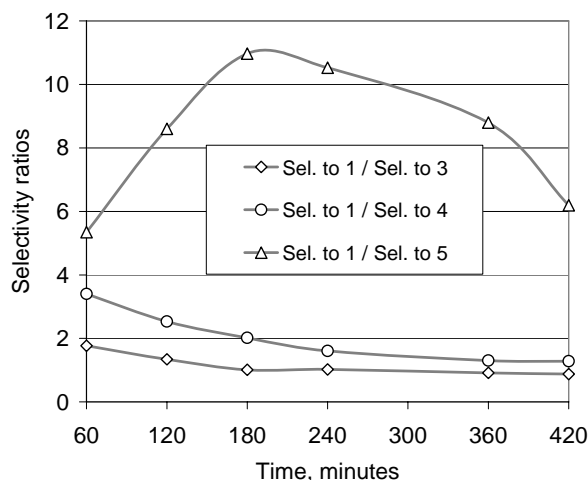
Figure 4. The secondary products distribution on the basis of HA

After having ascertained the important role of the basic strength of the catalytic sites, an attempt to convert the mixed oxide to hydrotalcite, by rehydration, before the catalytic run, was done. On our samples, the XRD patterns (not shown) indicate that quite poor regeneration occurred for both catalyst calcination temperatures, 643 and 673K. Nevertheless, the catalytic sites are transformed before structural changes could be highlighted by XRD, as shown by displaying the yield to product *1* in time for a series of rehydrated samples in comparison with the calcined samples is presented in figure 5. The catalytic performance of the rehydrated samples is inferior to

the calcined samples in terms of yield to the target product, for both calcination temperatures.
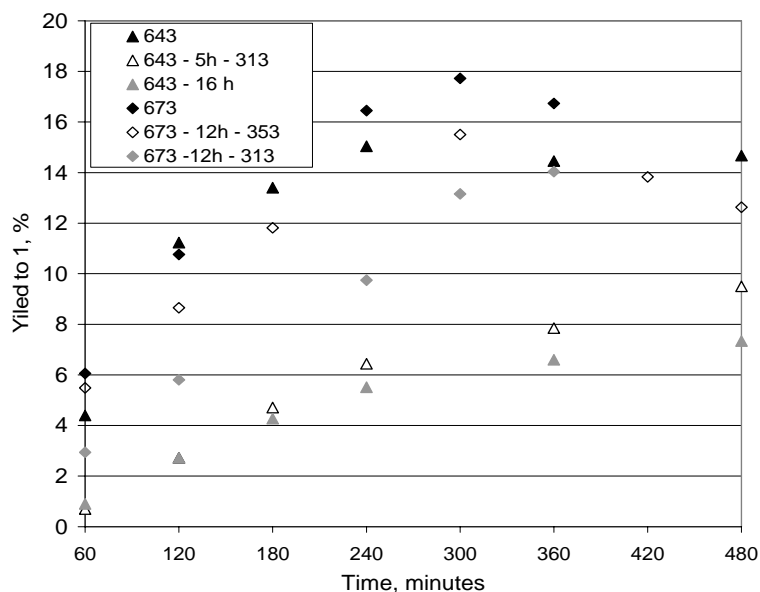
Figure 5. Evolution of the yield to product *1* for hydrated samples

In the case of the samples calcined at 643 K, a little better reconstructed by rehydration, the decrease of the catalytic performance is even deeper than in the case of the sample calcined at 673 K, where the structure regeneration did not succeed.

Conclusions

Mg-Al hydrotalcites with Mg/Al ratios of 2 and 3 were synthesized by coprecipitation from the nitrates mixture, using Na_2CO_3 and NaOH as precipitation agents. The resulted solid was used in the mixed oxide form, after calcination, as a catalyst for the aldol condensation between acetaldehyde and heptaldehyde. The activation temperature is very important on the catalyst activity and selectivity towards the target linear

reaction product. The behavior of Mg3Al sample was better than Mg2Al and detailed investigations were performed only on the first one. The temperature value of 723 K was found to be optimal for Mg3Al sample activation. The rehydration is unfavorable upon the catalytic activity and selectivity.

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