# Dealuminated Natural Zeolites for Applications in Catalytic Processes with Formation of C-C Bonds

## II. Aldol condensation over natural clinoptilolite modified by dealumination

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*The vapor-phase aldol condensation of acetaldehyde and formaldehyde over the natural volcanic tuff, dealuminated by acidic treatment, was studied. The condensation reactions were performed over a temperature range from 250° to 400°C. The catalytic properties were analyzed taking into account both, the influence of the reaction temperature and the effect of the acidic treatment applied to the natural volcanic tuff.*

*Keywords: aldol condensation, dealumination, natural zeolites, clinoptilolite*

The condensation of the carbonyl compounds is a very important reaction, as the resulting products are found in numerous industrial applications. This reaction, which could take place in liquid or gaseous phase, may be performed both on Br nsted and Lewis acidic sites as well as on basic sites on the surface of the catalyst. Numerous studies on this topic showed that catalysts like alkaline hydroxides deposited on silica gel [1,2], alkali and the alkaline earth metals deposited on silica [3,4], oxides modified with various metals or deposited on synthetic zeolites [5,6], synthetic zeolites [7-9], hydrotalcite–like materials [10] are efficient for this process.

It was also noted that the two types of the active sites present on the catalyst surface lead preferentially to the condensation products and less to the other reaction types. As a consequence, the selectivity of the condensation process is in direct corelation with the nature and the strength of the acid-base sites. Therefore, the advantage of using catalysts with medium acidity and/or basicity for the condensation reaction of the acetaldehyde with formaldehyde is that only acrolein and crotonaldehyde could be obtained as reaction products.

The natural zeolites are a category of catalytic materials of particular interest. Among them, the clinoptilolite is the most known one and could be found in concentrations up to 70% in volcanic tuff. The catalytic performance of the natural zeolite as well of its modified forms, obtained by suitable treatments of the volcanic tuff, in the reaction of the aldol condensation has been the subject of some previous papers [11-13]. Among applied treatments, we can mention the hydrothermal and the acidic ones.

In a previous study [14] we showed that, the dealumination of the volcanic tuff by treating with nitric acid leads to decreased crystallinity and aluminium content (with notable consequences over concentration and distribution upon strength of the active sites). At the same time, a considerable increase of the specific surface and of the porous volume, depending on the duration of treatment, was observed. Thus, using this treatment one can fine tune the properties of the native material in order to obtain an efficient zeolitic material with high activity and selectivity with regard to a certain reaction.

Taking as a model the same reaction of aldol condensation, we propose here to investigate the catalytic properties of the following volcanic tuff samples: TD1, TD2 and TD3 modified by acidic treatment and obtained in first part of our study.

### Experimental part

The samples TD1, TD2 and TD3, dealuminated by acidic treatment, were used as catalytic materials in the aldol condensation reaction. The synthesis route, the applied treatments and the characteristics of these samples were presented in the first part of our study [14]. The reaction between the acetaldehyde (AA) and the aqueous solution containing 36% of formaldehyde (FA) was carried out in a isothermal system, under nitrogen flow, in a pulse type microreactor (stainless steel, i.d. 3 mm and 80 mm length) and coupled with a gas chromatograph equipped with two columns, one filled with Carbowax 20M on Chromosorb W and the second filled with Porapak N. Every catalyst sample (weight of catalyst 0.03 g; particle size 0.25..0.50 and 5 mm high bed) was activated before in situ under air flow (20 mL $min^{-1}$) at 450°C for 3 h (5°C/min ramp), then it was cooled down to the reaction temperature under a stream of nitrogen.

### Results and discussions

As was already mentioned, the objective of our study is to investigate the catalytic properties of the TD1, TD2 and TD3 acidic dealuminated samples in the condensation reaction of acetaldehyde with formaldehyde performed in the gas phase. In order to better emphasize the catalytic performances of the mentioned samples, we presented, comparatively, the results obtained on a sample of the native volcanic tuff.

*Influence of the temperature over the catalytic activity*

In a first phase of our study, we analysed the influence of the thermodynamic parameters, especially of the reaction temperature over the general behaviour of the zeolitic materials. Thus, the catalytic tests for the aldol condensation reaction of acetaldehyde with formaldehyde have allowed us to study the influence of the temperature reaction on the activity of the catalysts over the temperature range of 250–400°C. The total conversion of acetaldehyde (this beeing susceptile also of self condensation) was analysed. In this case, for our investigation we used only

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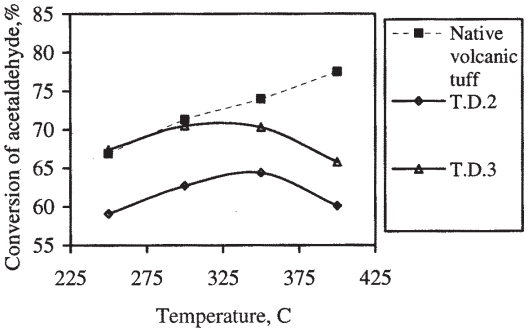



Fig. 1. Influence of the reaction temperature on the catalytic activity. Catalysts: volcanic tuff, TD2 (the volcanic tuff, dealuminated by acidic treatment for 5h); TD3 (the volcanic tuff, dealuminated by acidic treatment for 10 h)

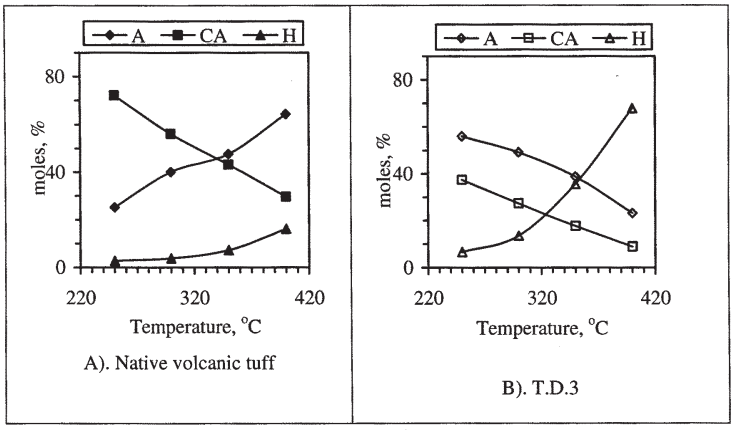



Fig. 2. Effect of the reaction temperature over the distribution of the reaction products. A – acrolein; CA - crotonaldehyde; H - hydrocarbons; AA/FA = 1/1.

the TD2 and TD3 samples because their structural and textural characteristics were stronger affected by the acidic treatment than the TD1 sample, fact which was earlier emphasized [14].

The obtained experimental results were depicted in figure 1.

In comparison with the sample of the native volcanic tuff, which is the most active for the acetaldehyde coversion, the TD2 and TD3 - dealuminated samples have a different behaviour. While in the case of the native tuff, the conversion of the acetaldehyde increases nearly linear with temperature, the conversion increases up to 325°C for the TD2 sample and up to 350°C for the TD3 sample but then decreases. Concerning the native volcanic tuff, it is known the fact that it contains sites of medium and weak acid strengths. The analysis of the thermoprogrammed desorption of ammonia has confirmed this fact [14]. Moreover, in the structure of the zeolite exist also alcaline cations with basic properties [15] which confer to the zeolite a good stability toward the coking process. Thus, the evolution of the acetaldehyde conversion with the temperature fits to general behaviour with regard to the effect of the temperature over the rate of the catalytic reactions (fig. 1). In case of the TD2 and TD3 samples, their behaviour could be explained taking into account the modifications of the acid-base properties induced by the acid treatment.

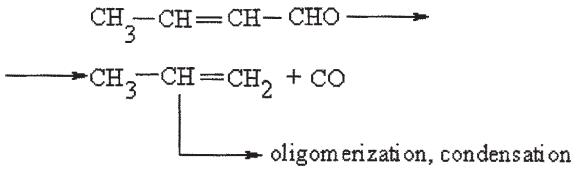
As we showed in the first part of our study [14], the dealumination of the volcanic tuff by acidic treatment leads to a solid material with bigger specific surface and porous volume than the initial one. Moreover, these parameters increase proportionally with the duration of the acidic treatment. But, beside increasing the surface and the porous volume, it also causes a very important modification to the distribution spectrum of the acid sites upon their strength. Therefore, the percentage of the strong acid sites becomes much higher than the one of the weak acid sites. But, at temperatures higher than 325°C, these centers have negative effects, either by accelerating the formaldehyde descomposition (it is known the thermodinamic instability at high temperature of this acetaldehyde), or by becoming blocked with the heavy condensation products, for instance with coke which is quickly formed.

As a rule of proportions, also in this case, the conversion of the acetaldehyde increases with the duration of the acid treatment, fact depicted in figure 1.

*The influence of the temperature on the catalytic selectivity*

The variation of molar concentrations of the two condensation products are depicted in figure 2, namely: the acrolein resulted from the cross-condensation of the two aldehydes and the crotonaldehyde resulted from the self-condensation of the acetaldehyde, respectively. Both of them were obtained on the TD3 sample which shows the best characteristics. The information obtained upon these investigations give us important suggestions toward the competition of the two processes of catalytic condensation.

In comparison to the sample of the native tuff (fig.2.A), which at 250°C shows high selectivity for the formation of the crotonaldehyde (approx. 75%), the TD3 sample (fig. 2.B) shows a low selectivity for for the same reaction (approx. 35%). In this case, the decrease of the crotonaldehyde concentration in the reaction products could be caused either by the decreased probability of the self condensation process or by the decomposition of the crotonaldehyde with propene formation as showed below [13]:




In the first section of our study [14] we demonstrated that by acidic treatment, two maximum peaks appear in the TPD ammonia profile of the TD3 sample. The first peak indicates the presence of weak and medium acid sites. The second one accounts for the strong acid sites which result from the ionic exchange between the metallic cations and protons. According to the literature data [10] we can assign the behaviour of the TD3 sample (fig. 2.B) to the fact that, on weak acidic sites, the acetaldehyde is preferentially chemosorbed and therefore, the formation of the crotonaldehyde is favoured. On the strong acidic sites, besides acetaldehyde, an important amount of formaldehyde is chemosorbed. As a consequence, the amount of the acrolein increases.

Therefore, it can be said that the stregth of acid sites may influence the ratio between the two catalytic condensation processes.

Besides this, the TD3 sample shows a great selectivity toward the acrolein formation over the investigated temperature range. The changes of the acid-base properties of the surfaces could account for this behaviour. In addition, as noticed in figure 2B, with increasing temperature the concentration of the two condensation products decreases and the amount of hydrocarbons increases. In order to explain this aspect, we additionally studied the self

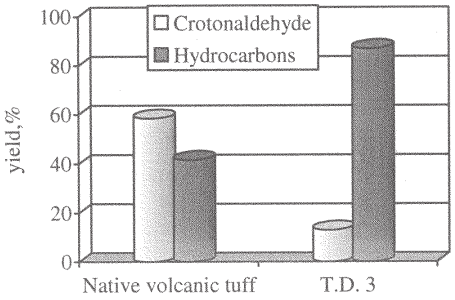



Fig. 3. Competition between the self condensation of acetaldehyde and the hydrocarbons formation. T=400°C

condensation of acetaldehyde (without the formaldehyde in feeder) under similar conditions.

The analysis of the reaction products showed that two important processes were identified, namely: the self condensation of the acetaldehyde with the formation of the crotonaldehyde and the formation of lower hydrocarbons (mainly propene) as a result of its decomposition. The competition between the two reactions is depicted in figure 3.

In comparison with the native tuff, in the presence of the TD3 sample an almost duble amount of the hydrocarbons is formed at high temperatures which leads to the assumption that, the strong acidity is responsible for formation of the these secondary products.

*Influence of the acidic treatment over the catalytic activity and selectivity*

The previous discussions have already emphasized the influence of the acidic treatment, applied the volcanic tuff, over the catalytic properties of the resulted materials.

However, to better emphasize how the acidic treatment affects the competiton between the two condensation reactions (AA+FA; AA+AA), in figure 4 are showed the ratios between the two condensation products (acrolein and crotonaldehyde) which were obtained with the volcanic tuff and the TD3 sample, respectively. The results are obtained at T=250°C, temperature at which the probability of the reactions with hydrocarbons formation is lower.

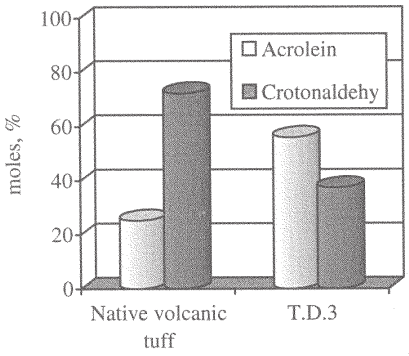



Fig. 4. Distribution of the condensation products during the reactions performed on the native tuff and on the TD3 samples (acidic modified); T = 250°C

In comparison with the native catalyst, the amount of the acrolein obtained on the TD3 sample is evidently higher. This fact confirms again that, upon the acidic treatment, strong acidic sites of Bronsted type occur which lead to a superior catalytic activity in the process of aldol cross condensation. Therefore, by using the adecvate treatment, one could obtain efficient catalysts for certain processes from natural materials such as the volcanic tuff. Of course, the catalytic performances are also influenced by other factors, as we showed in our study by peforming catalytic tests at different temperatures.

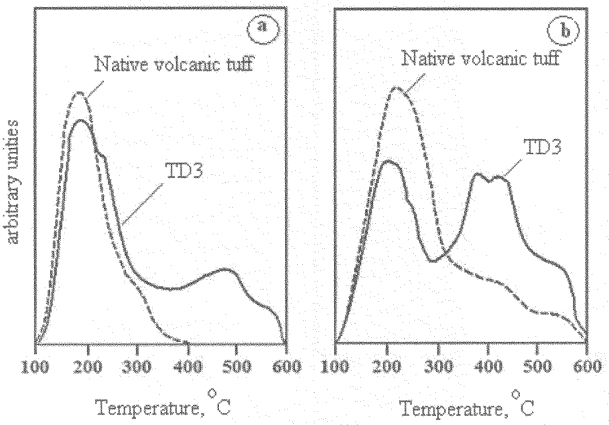



Fig. 5. Thermo-programmed desorption of the formaldehyde (a) and acetaldehyde (b); heating rate: 17°C/min

Although, the TD3 catalyst maintains its high selectivity towards the cross condensation, the decomposition reactions of the condensation products and those with the formation of heavy products (which led to the desactivation of the catalyst) are accelerated by increasing the process temperature. To support our previous statements, we want to use the results of the thermo-programmed desorption of the two aldehydes, using as solid adsorbent the native tuff and the one acidic treated, respectively (fig. 5).

The experiments of the thermo-programmed desorption were conducted similarly to those for the thermo-programmed desorption of $NH_3$, described in the first section. Instead of $NH_3$ we introduced either the gaseous formaldehyde (obtained by thermocatalytic decomposition of the paraformaldehyde and dried on the silica gel) or the acetaldehyde under $N_2$ flow.

As we can observe in figure 5, at low temperatures the amount of the formaldehyde retained on the acidic treated catalyst is comparable or even higher than the one of the acetaldehyde. This fact could explain the intensification of the cross condensation on the TD3 sample. At high temperatures we notice a high retention of the acetaldehyde, fact which should favour its self condensation, but, due to the strong retention, the condensation products are afterwards decomposed to hydrocarbons and carbonic oxide which are easily liberated.

Figure 6 clearly shows the modification of the ratio between the condensation products at high temperature on the two catalysts: the native tuff and the acidic treated tuff.

Although, the strong acidity would be favourable to the condensation process, the condensation products strongly retained on these sites (due to their bifunctional character) will be easily degraded to hydrocarbons due the high temperature.

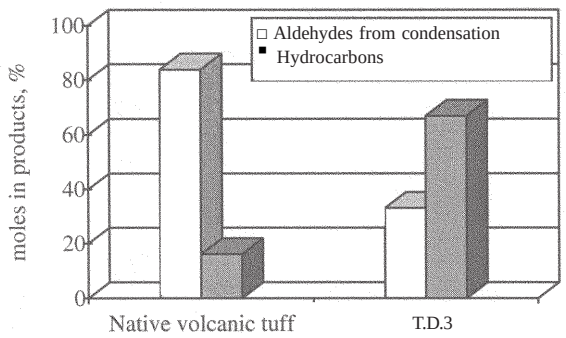



Fig. 6. Distribution of the reaction products obtained at high temperature on the native tuff and TD3 samples: T = 400°C; aldehyde = acrolein +crotonaldehyde AA/FA = 1/1.

## Conclusions

The results of this study point out the fact that, the volcanic tuff dealuminated by acidic treatment can be used as catalyst for the aldol condensation reaction of the acetaldehyde and formaldehyde with the formation of the acrolein at low temperatures (250°C). Both the catalytic activity and the selectivity of this catalyst are correlated with the nature, strength and density of the acid sites.

At high temperature (over 350°C) a significant decrease of the yield of the condensation products of aldehydes is observed due to the intensification of the secondary reactions with hydrocarbons formation.

## References


1.MALINOWSKI, S., JEDRSEJEWSKA, H., BASINSKI, S., BENEBEK, S., Chim., Ind., Genie Chim., **85**, 1961, p.885
2.MALINOWSKI, S., React. Kinet. Catal., Lett., **1**, 1974, p.73
3.AI, M., J. Catal., **107**, 1987, p.201
4.AI, M., Bull., Chem., Soc., Jpn., **64**, 1991, p.1342
5.DUMITRIU E., HULEA V., BILBA N., CARJE G., AZZOUZ A., J. Mol. Catal., **79**, 1993, p.175
6.WANG, X., LI, C., YANG, J., J. Rare Earths **22** (6), 2004, p. 848.
7.DUMITRIU, E., HULEA, V., FECHETE, I., AUROUX, A., LACAZE J-F., GUIMON, C., Microp. Mesopor. Mater., **43**, 2001, p. 341
8.UNGUREANU, A., ROYER, S., HOANG, T.V., TRONG ON, D., DUMITRIU, E., KALIAGUINE, S., Microp. Mesop. Mater., **84** (1-3), 2005, p. 283
9.DUMITRIU, E., BILBA, N., LUPASCU, M., AZZOUZ, A., HULEA, V., CIRJE, G., NIBOU, D., J. Catal., **147** (1), 1994, p. 133
10.DUMITRIU, E., HULEA, V., CHELARU, C., CATRINESCU, C., TICHIT, D., DURAND, R., Appl. Catal. A, **178**, 1999, p.145
11.DUMITRIU, E., HULEA, V., COBZARU, C., OPREA, S., Rev. Chim.(Bucharest), **54**, 2, 2003, p.142
12.COBZARU, C., OPREA, S., DUMITRIU, E., HULEA, V., Appl. Catal. Gen. **351**, 2008, p. 253
13.DUMITRIU, E., HULEA, V., Bullet. I.P.I, Tomul **XLIV**, Fasc. 1-2, 1998, p.75
14.DUMITRIU, E., COBZARU, C., HULEA, V., ROTARIU, A., OPREA, S., Rev. Chim.(Bucharest), **60**, no. 3, 2009, p. 297
15.BĂRBAT, A., MARTON, A., Tufurile vulcanice zeolitice, Ed. Dacia, Cluj-Napoca, 1989, p 39


Manuscript received: 21.09.2009