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SCIENTIFIC PAPER

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## ALDOL CONDENSATION OF THE INFERIOR ALDEHYDES OVER DEALUMINATED CLINOPTILOLITE

*The catalytic performances of dealuminated clinoptilolite in the vapour-phase condensation of acetaldehyde and formaldehyde were investigated. The activity of dealuminated clinoptilolite in terms of the overall conversion of the acetaldehyde is comparable with that of the cation-exchanged forms (Na<sup>+</sup>, Ni<sup>2+</sup>, Fe<sup>3+</sup>). The dealumination process of clinoptilolite exhibits a favourable effect on the catalytic selectivity toward crotonaldehyde formation.*

*Key words: Aldol condensation, Acrolein, Crotonaldehyde, Dealuminated clinoptilolite.*

Recent advances in the field of natural zeolites confirm their catalytic performances in many chemical reactions such as: separation of gases [1–6], the oxidation of CO and H<sub>2</sub>S [7,8], the reduction and disproportionation of NO [9,10].

Previous studies [11,12] made evident the possibility of using clinoptilolitic volcanic tuff modified by ionic exchange with metallic cations as a catalyst in the condensation reactions of lower aldehydes. At the same time, volcanic tuff modified by acid–basic treatment was successfully used for catalysing this reaction [13,14].

For practical applications of these catalysts, it is very important to promote the catalytic activity by a series of treatments. Since the decrease in the aluminium content in the structure of the natural zeolite results in an activity improvement [15–17], our studies were focused on dealuminated volcanic tuffs.

In the present study, the catalytic properties of dealuminated volcanic tuff in the condensation reaction of aldehydes were investigated. A comparison was also made of the catalytic performances of the dealuminated volcanic tuff and that modified by ionic exchange.

### EXPERIMENTAL

#### Volcanic tuff modified by ionic exchange

The volcanic tuff (deposit in Marsid, Romania) taken in this study contains 70% clinoptilolite of the following chemical composition: 68.54% SiO<sub>2</sub>; 11.95% Al<sub>2</sub>O<sub>3</sub>; 0.40% Na<sub>2</sub>O; 2.8% K<sub>2</sub>O; 3.35% CaO; 0.70% MgO and 0.86 wt.% Fe<sub>2</sub>O<sub>3</sub> [18].

The native volcanic tuff was washed with distilled water and dried at 333 K. It was then crushed and screened to obtain particles of 0.25–0.50 mm size.

The volcanic tuff samples thus obtained were submitted three times to ionic exchange with a 1 M NaCl solution for 24 hours at 353 K, followed by washing with distilled water and finally dried at 333 K. The ionic exchange capacity of the tuff for the Na<sup>+</sup> ion was 2.05 mEq/g tuff. The volcanic tuff thus modified was submitted to ionic exchange with solutions containing Ni<sup>2+</sup> and Fe<sup>3+</sup> ions. The ionic exchange process was carried out under the previously described experimental conditions.

#### Dealuminated volcanic tuff

The dealuminated volcanic tuff was obtained by acid treatment. Thus, samples of volcanic tuff, both native and Na<sup>+</sup> form, were treated with 6M HNO<sub>3</sub> solution in a zeolite/solution volume ratio of 1/20, at 353 K for 10 hours. The samples were then washed with distilled water and dried at 333 K. The samples of dealuminated volcanic tuff thus obtained and their corresponding designations are presented in Table 1.

Table 1. The obtained samples of dealuminated volcanic tuff

No	Initial samples	Dealuminated samples
1	Native tuff	Native tuff d
2	Na-tuff	Na tuff d

The chemical composition of the dealuminated samples were determined by chemical analysis. The degree of crystallinity was estimated by means of the X-ray diffraction method.

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## Reaction Procedures

A 37% aqueous solution of formaldehyde (FA), Merck stabilized with 12% methanol was used without further treatment. Acetaldehyde (AA) was a pure Fluka reagent.

The catalytic reaction was performed in a pulse type microreactor (stainless steel, o.d. 6 mm, i.d. 3.5 mm, length 80 mm) containing 30 mg of catalyst with particle size 0.25–0.50 mm. Generally, each catalyst was previously calcined under nitrogen flow at a heating rate of 273 K/min up to 723 K, then calcined for 2 hours under air flow, after which the catalyst was cooled at reaction temperature by a stream of nitrogen. Samples of 0.5  $\mu$ l of the reagents were injected under nitrogen flow (30 mL/min, 130–140 kPa). The reaction products were analysed using a gas chromatograph equipped with one column on the basis of Carbowax 10M on ChromosorbW.

## RESULTS AND DISCUSSION

### Analysis of Catalysts

As can be seen in Table 2, the Si/Al ratio is much higher for the dealuminated and ionic exchanged volcanic tuff than for the native tuff (Si/Al = 4–5.3) [18].

Table 2. The value Si/Al ratio of the catalyst sample

No	Samples	Native tuff	Fe-tuff	Ni-tuff	Native tuff d
1	Si/Al	5.530	5.640	5.600	13.070
2	Na/Al	0.046	0.413	0.450	0.055

It may also be noticed that the compositions of the samples differ after ion exchange with a Na<sup>+</sup> containing solution, as proved by the Na/Al ratio values (Entry 2, Table 2). A possible explanation is that some of the cations in natural tuff were replaced by Na<sup>+</sup> during the first ion exchange with Na salt solution. A significant increase in the Si/Al ratio was noticed in dealuminated clinoptilolite which proves the extraction of Al<sup>3+</sup> ions from the zeolite network during dealumination in acid medium.

Table 3. The X-ray diffraction analysis of the sample

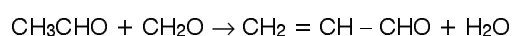
No	Samples	Crystallinity, %
1	Native tuff	54.4
2	Na-tuff	65.3
3	Fe-tuff	47.4
4	Ni-tuff	50.0
5	Native tuff d	36.7

The data in Table 3 show that acid treatment induces a modification in the zeolite crystalline network, the crystallinity of the dealuminated samples being lower compared to the ionically exchanged samples.

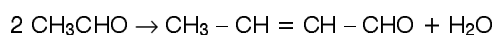
### Aldol Condensation

Samples of dealuminated volcanic tuff and of that submitted to ionic exchange were tested as catalysts in the aldol condensation reactions of acetaldehyde and formaldehyde. Three pathways of consumption of the reagents were identified depending on the experimental conditions (reaction temperature and dealumination treatment).

a. The mixed condensation of lower aldehydes resulting in the formation of acrolein



b. The self-condensation of acetaldehyde leading to crotonaldehyde



c. Reactions leading to light hydrocarbons (methane, ethane, propylene, etc.) involving both the reagents and condensation products.

### Effect of temperature on catalytic activity

In order to observe the influence of temperature on the catalytic activity every sample of volcanic tuff was submitted to catalytic tests within the temperature range 523–673 K and the total conversion of acetaldehyde determined. The experimental results are presented in Figure 1.

The total conversion of acetaldehyde was much higher in the case of the ionically exchanged samples (Figure 1, a) than in the case of the dealuminated ones (Figure 1, b). Although the specific surface of the volcanic tuff samples increased by the dealumination treatment, the number of active centers decreased drastically. At the same time, the number of basic centers able to catalyse the condensation reactions also decreased.

### Effect of temperature on catalytic selectivity

The reaction temperature relevantly affected the selectivity of the condensation based on the competition between the above mentioned reactions. In order to observe the way that temperature influenced the selectivity, the native and the dealuminated tuffs were discussed since they gave the most relevant results (Figure 2).

The experimental data presented in Figure 2 show the secondary that the reactions leading to hydrocarbons have a higher proportion of about 60%, with dealuminated volcanic tuff (Figure 2,b) at

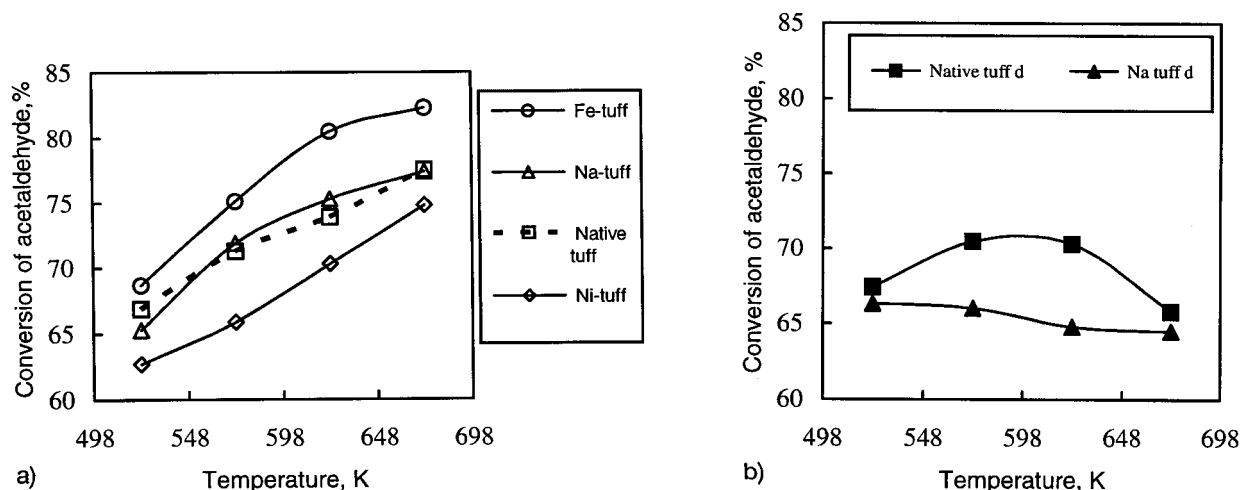


Figure 1. The effect of temperature on catalytic activity; a) on volcanic tuff ionic exchanged ( $\text{Na}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$ ); b) on dealuminated tuff (Native tuff d; Na tuff d)

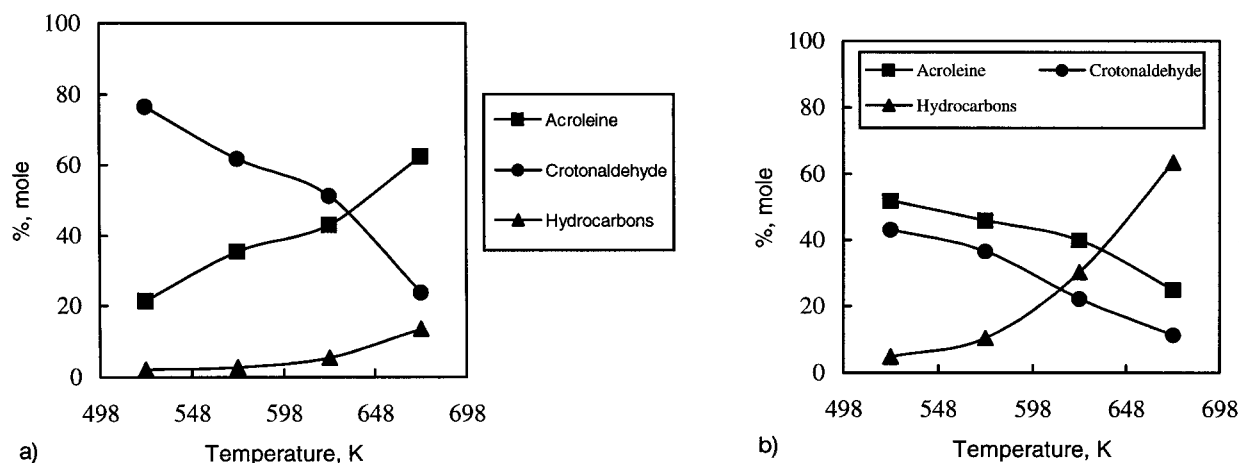


Figure 2. The effect of temperature on catalytic selectivity. a) on native volcanic tuff (Native tuff); b) on dealuminated tuff (Native tuff d);

temperatures above 673K, in comparison with native tuff (Figure 2,a). It follows that in both cases the reaction of mixed condensation competes with the secondary reaction giving hydrocarbons, which would imply that either the molecular species or the formed acrolein are converted into hydrocarbons.

The disappearance of active centers is usually associated with broad specific surfaces. The behaviour of the dealuminated tuff in the condensation reaction in comparison with the native tuff (the specific surface of dealuminated tuff is about eight times larger than that of the native volcanic tuff) is indicative of structural degradation occurring simultaneously with dealumination when the number of acid and base active centers decreases sharply.

#### Effect of dealumination on catalytic activity and selectivity

The results obtained at 523 K, when the percentage of reactions giving hydrocarbons is lower

(2–7% on all the dealuminated catalysts), provided more relevant information on how the dealumination process affected the competition between the two condensation reactions (AA+FA; AA+AA).

Figure 3 shows the proportions of the two condensation products (acrolein and crotonaldehyde) resulting using both volcanic tuff submitted to ionic exchange and the dealuminated one. The obtained results fall into two categories:

1. High selectivity for acrolein formation: Native tuff d; Na tuff d.
2. High selectivity for crotonaldehyde formation, when the self condensation reaction is promoted: Native tuff; Na tuff; Fe-tuff; Ni-tuff.

As already mentioned above, the condensation reaction is accompanied at high temperatures by secondary reactions of hydrocarbon formation. Thus, within the 523–573 K temperature range, the percentage of secondary reactions is rather low (about 15%)

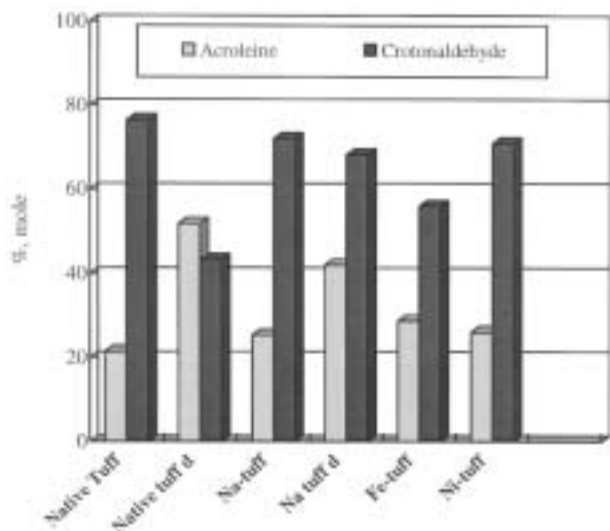


Figure 3. The proportion of two condensation products (acrolein and crotonaldehyde) on ionic exchanged and dealuminated volcanic tuffs:  $T = 523\text{ K}$ ; AA/FA = 1/1;  $30\text{ mL N}_2/\text{min}$ .

subsequently increasing with increasing temperature (75% at 673 K).

The experimental data on the catalytic selectivity attained with the dealuminated and ionic exchange volcanic tuffs at 673 K are illustrated in Figure 4.

It may be noticed that the dealuminated tuff samples showed good selectivity in the condensation reaction at even this temperature. In the case of the dealuminated tuff sample, a selectivity decrease for aldehyde condensation was observed in favour of the secondary reactions due to the total disappearance of the basic centers by dealumination. It can thus be concluded that high acidity is unfavourable to the

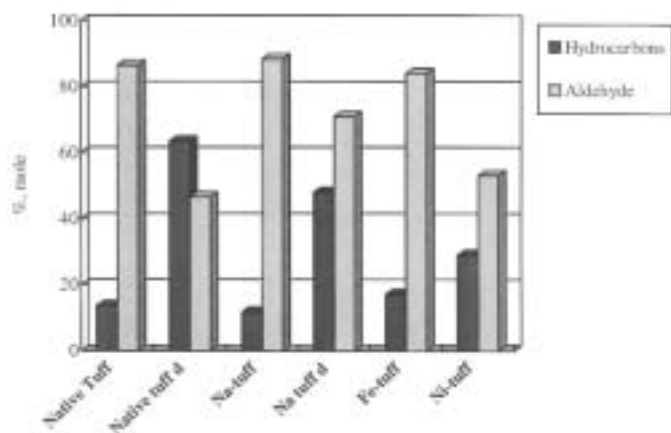


Figure 4. The effect of the ionic exchange process and dealumination treatment on catalytic selectivity:  $T = 673\text{ K}$ ; Aldehydes = acrolein + crotonaldehyde; AA/FA = 1/1;  $30\text{ mL N}_2/\text{min}$ .

process because the secondary reactions are mainly catalysed.

## CONCLUSION

The properties of dealuminated volcanic tuffs and their catalytic performances were studied in the condensation reaction of lower aldehydes. A comparison was made between the ionically exchanged and dealuminated tuffs.

Dealumination by acid treatment allows the obtaining of a volcanic tuff with uniform properties and higher activity and catalytic selectivity for crotonaldehyde formation in comparison with the native and ionically exchanged volcanic tuffs. At high temperatures secondary reactions with hydrocarbon formation are promoted.

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## IZVOD

### ALDOLNA KONDENZACIJA INFERIORNJIH ALDEHIDA PRIMENOM DEALUMINIZIRANOG KLINOPTILOLITA

(Naučni rad)

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U radu je ispitivana katalitička aktivnost dealuminiranog klinoptilolita u reakciji kondenzacije acetaldehida i formaldehida. Kao katalizator je korišćen polazni materijal vulkanskog porekla koji je prethodno obrađen posebnim postupkom. Ovaj materijal (depozit iz Marsida, Rumunija) koji sadrži 70% klinoptilolita ispran je destilovanom vodom, samleven i prosejan, a za dalju obradu uzeta je frakcija 0,25-0,50 mm. Pripremljene čestice su tretirane u trostepenom postupku u cilju jonske izmene sa 1 M NaCl (kapacitet jonske izmene u odnosu na Na<sup>+</sup> bio je 2,05 mEq/g). Ovako modifikovana vulkanska masa je podvrgnuta jonskoj izmeni sa rastvorima koji sadrže Ni<sup>2+</sup> i Fe<sup>3+</sup>.

Dealuminizirana vulkanska masa je dobijena kiselinim tretmanom (originalna i u pripremljenom Na<sup>+</sup> obliku) sa HNO<sub>3</sub>. Katalitička reakcija je ispitivana u mikroreaktoru od nerđajućeg čelika (o.d. 6 mm, i.d. 3,5 mm, dužina 80 mm) u kome se nalazilo 30-mg pripremljenih čestica katalizatora. Prethodno je katalizator kalciniran u struji azota a zatim ohlađen na temperaturu na kojoj je ispitivana reakcija aldolne kondenzacije u internoj atmosferi (azot). Uzorak od 0,5 μl reaktanata je injektiran u struju azota (30 mL/min, 130-140 kPa) a proizvodi reakcije analizirani gasnom hromatografijom (kolona Carbowax 10M na ChromosorbW).

Aktivnost ovako pripremljenog katalizatora definisana je na osnovu merenja konverzije acetaldehida i vrednosti upoređivane sa katjonskom izmenjivačkom smolom (Na<sup>+</sup>, Ni<sup>2+</sup>, Fe<sup>3+</sup>). Proces dealuminacije klinoptilolita se pokazao kao efikasan način za povećanje katalitičke aktivnosti i selektivnosti u pravcu stvaranja krotonaldehida.

Ključne reči: Aldolna kondenzacija, Akrolein, Krotonaldehid, Dealuminiziran klinoptilolit.