CATALYTIC TRANSFORMATIONS OF BIOETHANOL

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Objectives

This work is focused on the catalytic transformation of bioethanol into industrially significant alkenes. Catalytic transformation of ethanol was studied using catalysts based mainly on nanostructured materials as hydrotalcites, sepiolites and zeolites doped with Cu, K, Sr, Zn and Mn. The catalytic tests were carried out in a plug-flow reactor at a temperature range of 350-550 °C. The impact of the preparation method of hydrotalcites on their structure and catalytic activity is reported.

Hydrotalcites

Hydrotalcites, also known as layered double hydroxides or Feitknecht compounds with the general formula: $M^{2+}_{1-x}M^{3+}_x(OH)_2(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are divalent (e.g., Mg, Ni, Zn, Cu, Mn) and trivalent (e.g., Al, Fe, Cr) metal ions, A^{n-} is an anion (most commonly $(CO_3)^{2-}$, but also $(SO_4)^{2-}$, $(NO)^{3-}$, Cl^-, OH^-), and the value of x is 0.1 - 0.5.
Hydrotalcites have also received increasing attention due to their cheap and easy synthesis. Their acid-base properties depend on their chemical composition and methods of preparation.
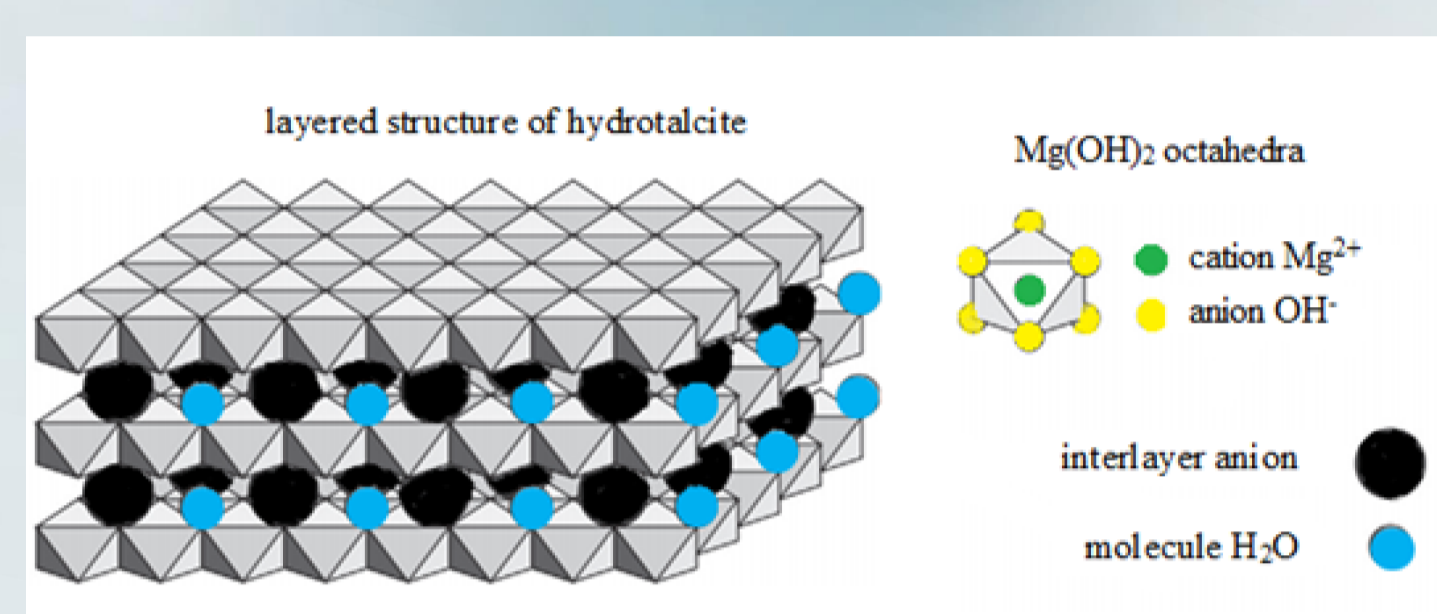

Fig.1. The layered structure of hydrotalcite.

layered structure of hydrotalcite — Mg(OH)₂ octahedra — cation Mg²⁺ — anion OH⁻ — interlayer anion — molecule H₂O

Coprecipitation method

In this method inorganic Mg and Al salts are supersatured in an alkaline media either at increasing pH or at constant pH.

Urea hydrolysis

Another precipitating agent can be urea. Urea hydrolyzes slowly at elevated temperature, releasing ammonia and carbonate anion, which leads to a slow supersaturation.

Sol-gel method

Sol-gel method is reported to lead to hydrotalcites of high phase purity. Hydrolysis of metal-organic compound occurs in organic solvents at elevated or room temperature.

Combustion Synthesis

During combustion synthesis an explosive decomposition of organometallic precursors take place, leading to a formation of mixed metal oxides. Hydrotalcites have a peculiar feature known as a memory effect. This allows a (re)generation of layered structure from mixed oxides leading to (re)gain a hydrotalcite structure.

Microwave treatment

Using microwave treatment in the above-mentioned synthesis methods not only reduces the synthesis time but also decreases the crystallite size.

Hydrothermal Treatment

Hydrothermal treatment in the presence of water vapor improves the crystal sizes of hydrotalcites. Such treatment also maintains or compensates water molecules in the interlayer.

The effect of the preparation method

The difference between precipitation methods is that upon precipitation with Na_2CO_3 a precipitate is formed almost immediately. On the other hand, in the urea precipitation method, urea slowly hydrolyses to form NH_3 which gradually precipitates hydrotalcite. This is also reflected in the morphology of the precipitate formed. Upon precipitation with urea a regular lamellar structure typical of hydrotalcite was formed, however upon precipitation with Na_2CO_3 an irregular morphology was formed (Fig. 3).
Upon calcination at 450 °C the XRD structure of hydrotalcites gets lost, resulting in Al – Mg mixed oxides. However, exposing to humidity and CO_2, a reorganization of the original structure of the hydrotalcite takes place (Fig. 4).
A correlation was found between the method of preparation and the catalytic activity of these hydrotalcites. In the one hand, one can see that at a reaction temperature of 500 °C and above, the yields of butadiene were significantly reduced. Hence, it can be concluded that the loss of the hydrotalcite structure is not beneficial for the formation of butadiene. It has also been found that the highest yields of butadiene are obtained on a catalyst with a regularly developed lamellar structure (Figs. 5, 6).
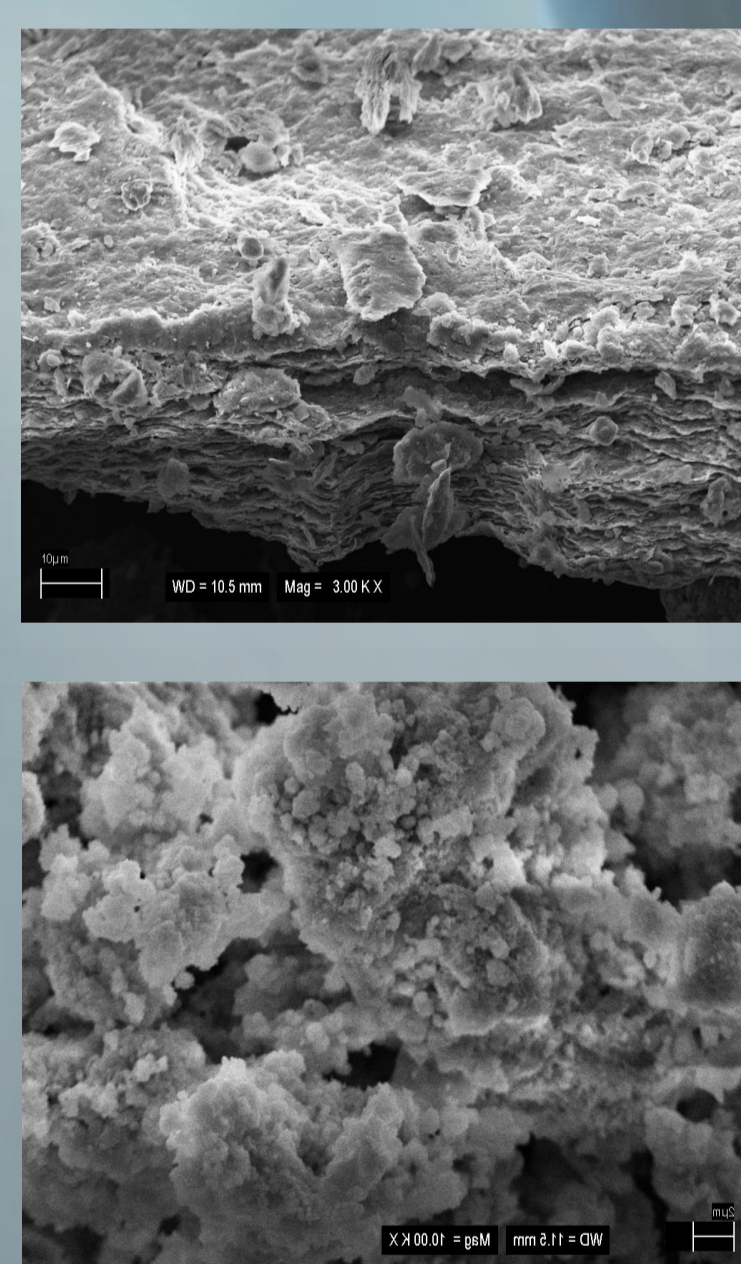

Fig. 3. SEM images of samples prepared by urea- (upper) and Na_2CO_3 precipitation

Introduction

Butadiene is historically one of the most important substances in the industry. Prior to the invention of butadiene polymerization technology, the only way to produce tire elastomers was to vulcanize natural caoutchouc.
Recently, there has been a resurgence of academic interest in transformation of ethanol to butadiene, driven mainly by economic (oil price) and environmental factors. There is a relatively well-established opinion on the reaction mechanism. In the first reaction step, in an acid- or metal-catalysed reaction, ethanol is dehydrogenated to acetaldehyde. Subsequently, in the second condensation - dehydration step acetaldehyde reacts with unreacted ethanol. This second set of base-catalysed reactions will lead to the formation of butadiene [1-6].

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \quad (1)$$
$$C_2H_5OH + CH_3CHO \rightarrow \rightarrow CH_2CHCHCH_2 + 2H_2O \quad (2)$$
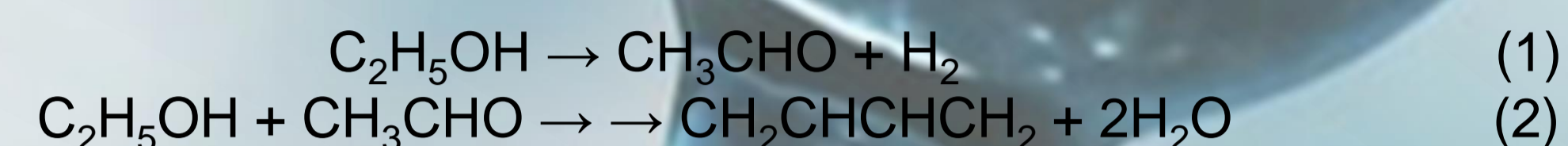
Our research has been mainly focused on finding suitable basic nanostructured catalysts, especially hydrotalcites and sepiolites. For the sake of completeness, zeolitic catalysts are briefly discussed as well.

Catalyst preparation

We doped several catalysts with Cu, Zn, Mn by wet impregnation method using a 3% solution of metal nitrates in amount as to the metal content of the resulting material was 5%. The catalyst samples were calcined in static air at 500 °C.
Faujasite Y (module: 2.5), SDUSY (module: 30), mesostructured MCM-22 (module: 30) (Zeolyst) were used as supports for the zeolite-based catalysts. To prepare sepiolite-based catalysts commercial sepiolite (Sigma) was impregnated with metal nitrate solutions following the above-mentioned procedure.
To prepare hydrotalcite-based catalysts using a precipitation method, 0.1 M solutions of $Mg(NO_3)_2$ and $Al(NO_3)_3$ were used. The pH of the mixture was adjusted to 10 ± 0.1 during the precipitation adding appropriate amounts of a 0.2 M NaOH solution. To prepare hydrotalcie-based catalysts using the urea method, urea was added to the solution of Al and Mg nitrates in a molar ratio of urea : (Mg + Al) = 4 : 1. The mixture was refluxed for 24 h, filtered, washed and dried at 110 °C overnight.
Templated hydrotalcite-like materials were prepared by the precipitation method with addition of Pluronic123 surfactant (Sigma) along with n-octane.
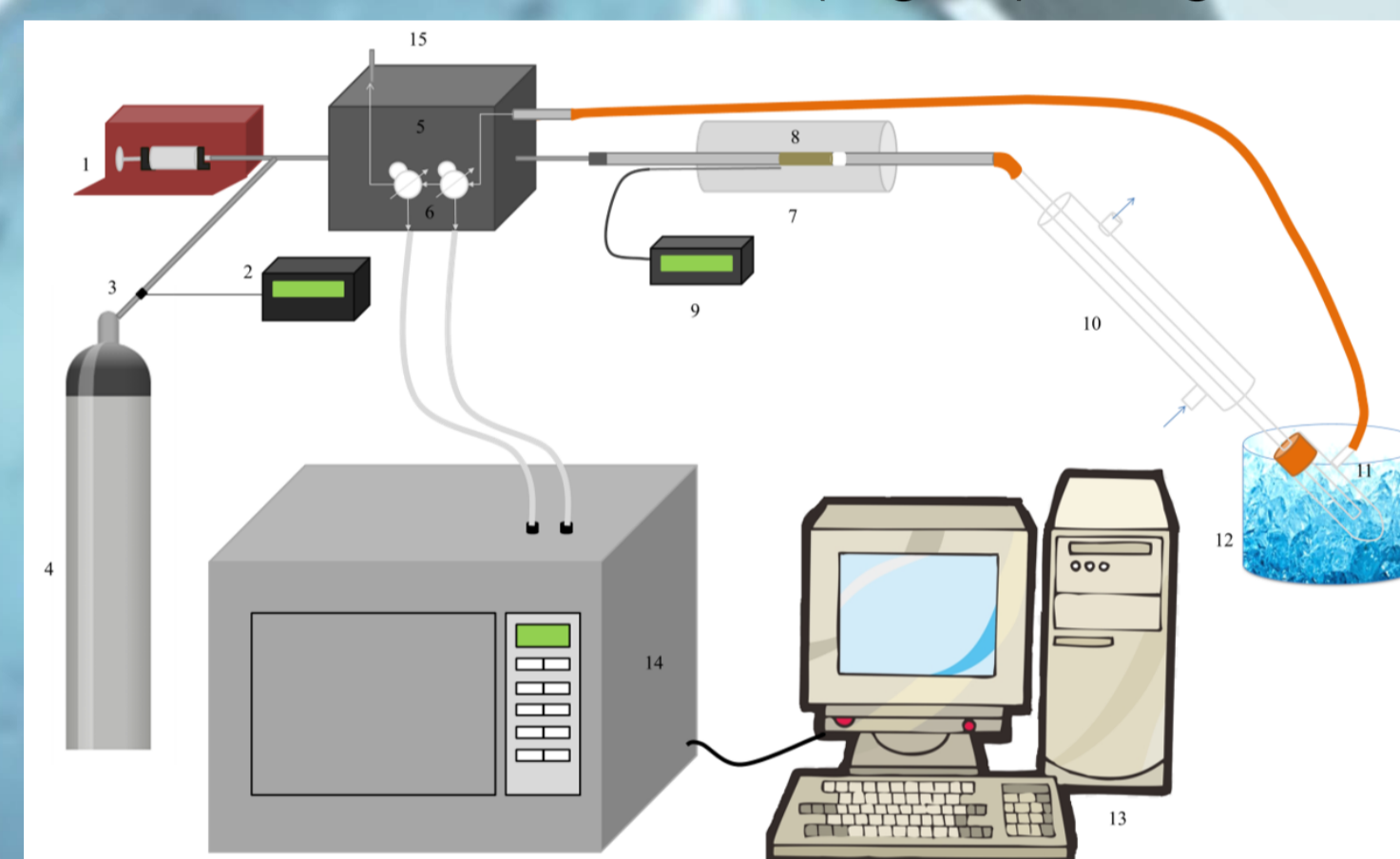
Fig. 2. Scheme of the apparatus for catalytic tests: 1 syringe pump; 2 PID controller; 3 solenoid valve; 4 nitrogen cylinder; 5 heated chamber; 6 six-way valves; 7 reactor; 8 catalyst in the reactor; 9 temperature controller; 10 condenser; 11 liquid products collector; 12 pot with ice; 13 computer; 14 gas chromatograph; 15 off-gas.

Catalysts testing

Bioethanol as a reactant was injected at the flow rate of 5 ml.h^{-1} by a syringe pump. A fixed bed inox reactor and nitrogen as a carrier gas was used. The catalytic tests were carried out in the temperature range of 350 °C to 550 °C. Liquid products were collected in a refrigerated flask. Liquid products were analysed using a Shimadzu QP-2010 Ultra GC/MS. Gaseous products were analysed by GC connected on-line via a 6-way valve (Fig. 2).

Results and discussion

Zeolite-based catalysts

The acid – catalysed dehydration of ethanol is well documented. Magnesium is supposed to neutralize the acidic sites in zeolites. The suppression of the formation of ethylene was observed at lower temperatures (300 °C), however at elevated temperatures (above 400 °C), the dehydration of ethylene turned to be the most dominant reaction pathway in most cases.
To further elucidate the possibility of the improvement of the catalytic performance, several types of zeolitic catalysts were prepared: unmodified MCM-22 and SDUSY with modules 30, and Y – 5%Mg – 5%Zn and Y – 5%Cu – 5%Zn. The yields of the main reaction products are summarized in Tab. 1.

MCM-22, Y and SDUSY themselves catalyse efficiently the formation of ethylene. For Y, copper, as expected, enhances the dehydrogenation of ethanol to acetaldehyde, improving the acetaldehyde yield to 22.7% in contrast with 1.4% for the undoped catalyst.

Table 1: Yields of the main reaction products over selected zeolytic catalysts.

Catalyst / yields %	ethylene	propylene	butadiene	acetaldehyde
MCM-22	31.5	4.2	1.6	8.8
SDUSY	35.3	2.5	0.8	5.2
Y13	47.2	3.5	1.8	1.4
Y13 – 5Mg	14.3	2.6	2.3	9.7
Y13 – 5Cu	38.8	4.8	4.0	22.7
Y13 – 5Mg – 5Zn	12.7	8.2	12.6	6.7
Y13 – 5Cu – 5Zn	35.5	7.2	18.5	7.4

Zinc was found promoting the formation of heavier hydrocarbons both over Mg- and Cu – doped catalysts, These observations necessitate the existence of two different consecutive reaction paths, necessary for increased butadiene formation: first the formation of acetaldehyde, second the consumption of acetaldehyde to form butadiene.
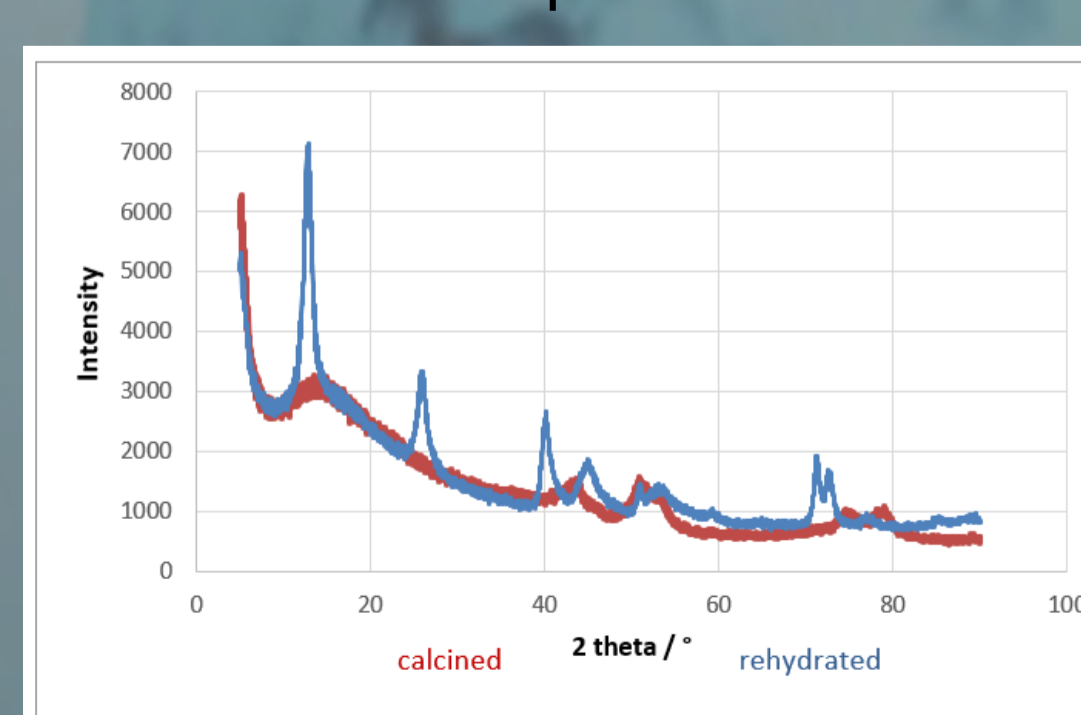
Fig. 4. XRD evidence of the memory effect of hydrotalcites

calcined — rehydrated — 2 theta /°
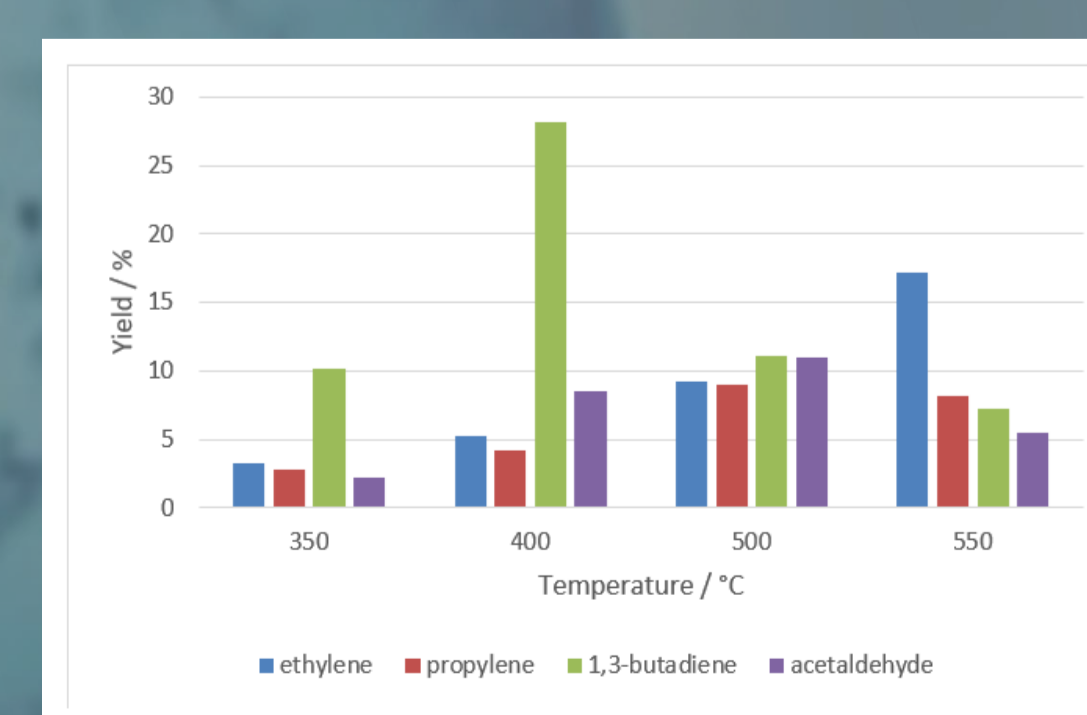
Fig. 5. Catalytic performance of the urea-precipitated sample

ethylene — propylene — 1,3-butadiene — acetaldehyde — Temperature / °C
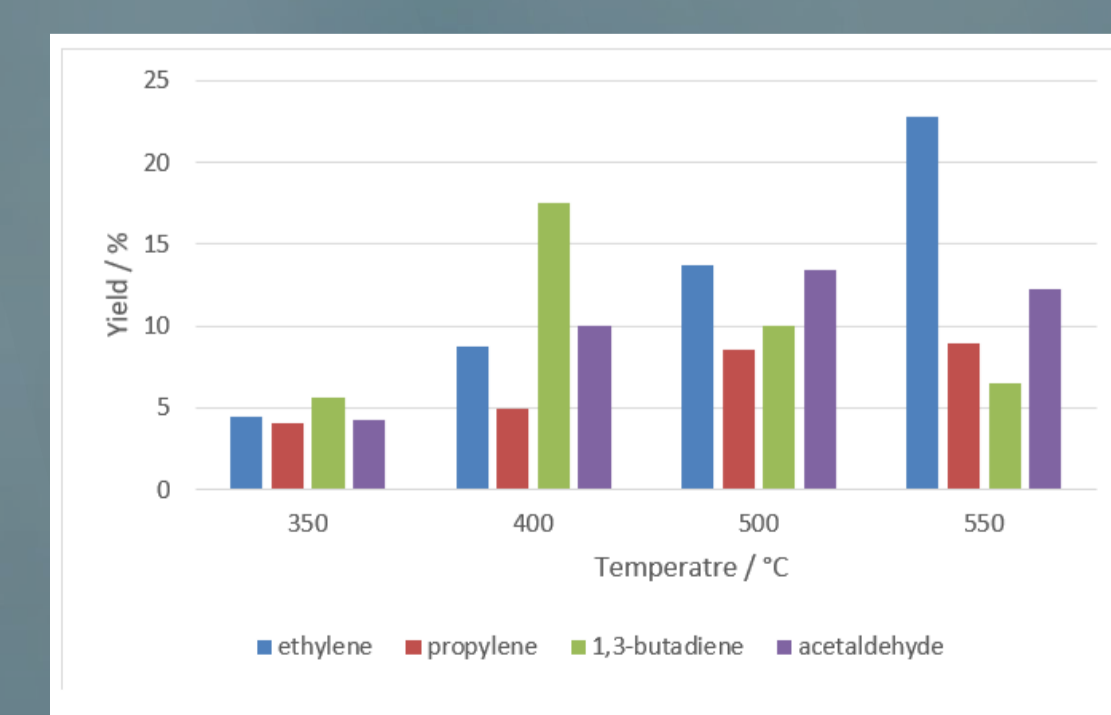
Fig. 6. . Catalytic performance of the Na_2CO_3-precipitated sample

ethylene — propylene — 1,3 butadiene — acetaldehyde — Temperature / °C

Conclusions

- Undoped zeolites promote the acid-catalysed dehydration of ethanol, while in the case of basic catalysts, such as hydrotalcites, the product distribution is shifted toward butadiene.
- Zinc was found promoting the formation of heavier hydrocarbons both over Mg- and Cu – doped zeolites. These products cannot be obtained by simple dehydration of ethanol, their formation require several reaction steps.
- Non-zeolytic nanostructured materials were found to be promising catalysts for the transformation of bioethanol into valuable chemicals with emphasis on light alkenes. It was found that hydrotalcite with well-developed layered structure, prepared by slow hydrolysis promotes the formation of butadiene. Simple precipitation failed to generate a pronounced layered structure and led to a deteriorated catalytic performance.

References

[1] Bi J, Guo X, Liu M, Wang X (2010) Catalysis Today 149: 143—147.
[2] Gao M, Jiang H, Zhang M (2018) Applied Surface Science, 439: 1072-1078.
[3] Klein A, Palkovits RRP (2017) Catalysis Communications, 91: 72-75.
[4] Tian G, Han G, Wang F, Liang J (2019) Nanomaterials from Clay Minerals: 135–201.
[5] Zhao Y, Li S, Wang Z, Wang S (2019) Chinese Chemical Letters 31(2).
[6] Zhu Q, Wang B, Tan T (2016) ACS Sustainable Chemistry & Engineering, 5(1): 722–733.