Nano-design of Zeolites Biomass Wastes Valorization: Dehydration of Lactic Acid into Acrylic Acid

Izabela KURZYDYM, Izabela CZEKAJ[1)]

[1)] Cracow University of Technology, Faculty of Chemical Technology, Warszawska 24, 31-155 Cracow, Poland;
email: iczekaj@chemia.pk.edu.pl

http://doi.org/10.29227/IM-2019-01-32

Submission date: *11-07-2018* | Review date: *02-04-2019*

Abstract

The valorization of waste from biomass currently arouses great interest. In the present study we concentrate on the design of innovative BEA zeolite catalysts with applied metal nanoparticles - copper, vanadium and manganese for the dehydration of lactic acid to acrylic acid. The ab initio method based on density functional theory (DFT) was used to calculate the electron structure of the analyzed molecules. The non-local generalized gradient corrected functionals GGA-RPBE was used to in order to account for electron exchange and correlation. The cluster model was represented by a hierarchical zeolite $M_2Al_2Si_{12}O_{40}H_{22}$ *(M = Cu, V, Mn). The stabilization of the* $M\text{-}O_b\text{-}M$ *dimer complex in the hierarchical structure of BEA, mechanism of adsorption of lactic acid on BEA zeolite with applied metal dimers and formation of acrylic acid on these zeolites were investigated. The examined metals form stable dimers interconnected by a bridge oxygen (Ob). Adsorption of lactic acid takes place in the vicinity of a dimer of* $M\text{-}O_b\text{-}M$*. The dehydration of lactic acid to acrylic acid in all cases consists in the separation of the hydroxyl group and creating a connection with a metal center of dimer and disconnection of a single hydrogen atom from the methyl group and its interaction with bridge oxygen of dimer.*

Keywords: DFT method, metalic nanoparticles, lactic acid dehydration, acrylic acid

Introduction

Major challenge of society research is to build fuels and chemical intermediates from available and renewable materials that do not compete with food crops for water or fertilizer (Pacala et al.,2004). The urgent needs for a more sustainable production of chemicals from renewable feedstock, like biomass, have caused intensive research efforts in search for novel porous nano-materials (Corma et al., 2007). Such materials may combine high catalytic activity, selectivity and a long-term stability by controlling their structure, porosity and functionalities. Knowledge about catalysts molecular structure and reaction mechanism is necessary to design and synthetize optimal materials. Due to ability to catalyze many types of hydrocarbon reactions as well as due to specific structure of active sites zeolites are ideal candidates for the production of chemicals from biomass, e.g. dehydration reactions (Rinaldi et al., 2009, Stöcker et al., 2008). Additionally, zeolites are effective three dimensional supports for active nanoparticles as well as there are flexible for metal exchange inside framework.

Acrylic acid is currently used as a starting material to produce many chemicals and polymers for example in the textile industry (Xu et al., 2006). At the present time acrylic acid is produced in a two-step reaction by partial oxidation of propylene (Lin, 2001). Due to the increased use of renewable sources, the production of acrylic acid as a result of dehydration of lactic acid is an attractive alternative.

In the present part of study, we are interested in designing a new approach for the synthesis of acrylic acid from lactic acid over zeolite catalysts. The theoretical modeling of lactic acid dehydration would help in further development and synthesis of zeolite with declare structure, e.g. proper metallic nanoparticles in the zeolite frame.

Computational method

The ab initio method based on density functional theory (DFT) was used to calculate the electronic structure of the analyzed molecules (StoBe code). The exchange and electron correlation is taken by using for the calculation of the generalized non-local functional GGA-RPBE (Pardew et al., 1996; Hammer et al., 1999). The use of extended Gauss functions allowed for the presentation of all Kohna-Sham orbits by a linear combination of atomic orbitals (LCAO's) (Lebanowski, Anzelm, 1991; Godbout et al., 1992). The Mulliken population analysis for a detailed analysis of the electron structure (Mulliken, 1955), and the Mayer procedure to interpret the rows of bonds was used (Mayer, 1983; Mayer, 1987). In the studies of stabilization of dimeric M-O-M complexes we based on previous theoretical studies on iron dlimers in the ZSM-5 framework (Czekaj et al., 2013).

Results and discussion

The stabilization of dimer complexes M-Ob-M (where M=Cu, V, Mn) on the BEA zeolite surface obtained by simulation of hierarchization in the alkaline environment was investigated (Figure 1). All analyzed structures revealed stabilization of the dimer around the aluminum and oxygen atoms in the BEA zeolite structure. This indicates a strongly active acid center on the aluminum atom. Stable dimers are formed by connection of metal atoms witch bridge oxygen. Bond lengths between the metal atoms and bridge oxygen atom are slightly different depending on the element and are equal: for

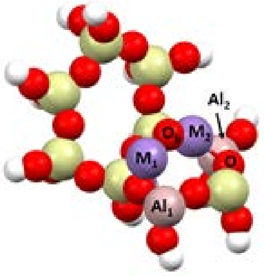

Fig. 1. Metal dimer M-Ob-M (where M= Cu, V or Mn) in the hierarchical BEA zeolite
Rys. 1. Dimer metaliczny M-Ob-M (gdzie M = Cu, V lub Mn) w hierarchicznym zeolicie BEA

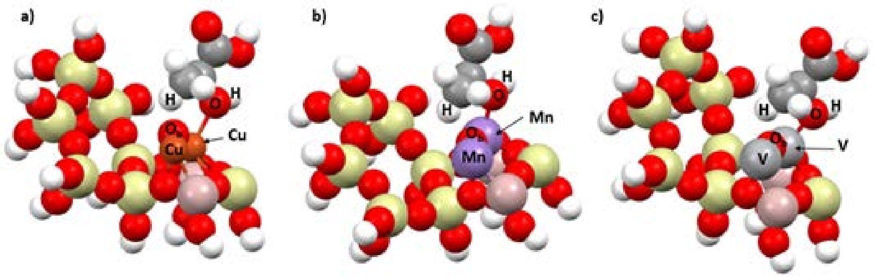

Fig. 2. Hierarchical model of BEA zeolite with a metallic dimer and adsorbed lactic acid a) Cu, b) V, c) Mn
Rys. 2. Hierarchiczny model zeolitu BEA z dimerem metalicznym i zaadsorbowanym kwasem mlekowym a) Cu, b) V, c) Mn

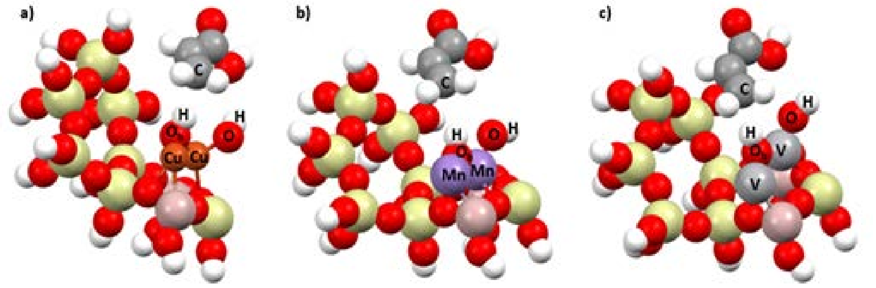

Fig. 3. Hierarchical model of BEA zeolite with a metallic dimer and desorbed acrylic acid a) Cu, b) V, c) Mn
Rys. 2. Hierarchiczny model zeolitu BEA z dimerem metalicznym i desorbującym kwasem akrylowym a) Cu, b) V, c) Mn

Cu – 1.81 and 1.86 Å, V – 1.76 and 1.77 Å, Mn – both 1.68 Å. Despite these small differences, the mechanism of dimer deposition on BEA zeolite is basically the same. A strong correlation between vanadium and manganese metallic centers was also demonstrated (bond order Mn-Mn 1.90 and V-V 1.88) while in copper these interactions are negligible and around 0.17 for Cu-Cu.

The next step of the analyzed mechanism of dehydration of lactic acid to acrylic acid is the adsorption of lactic acid on the metallic dimer deposited on the surface of the BEA zeolite (Figure 2). It can be seen that lactic acid interacts via its hydroxyl group of α-carbon with the metallic center of the dimer. Bond order between oxygen of hydroxyl group and the metallic center are equal: for Cu-O 0.14, Mn-O 0.24 and V-O 0.29. The single hydrogen atom of methyl group also participates in the lactic acid adsorption process. It interacts with the bridge oxygen of the dimer. In all cases the bond order between hydrogen and bridge oxygen is about 0.01–0.05.

The last step of dehydration is the desorption of acrylic acid (Figure 3). Visualization of results allows us to state that the water molecule separates from lactic acid in the form of two hydroxyl groups at metal dimer. The first hydroxyl group attaches to the metallic center, while second hydroxyl group is formed at bridge position between metal centers of dimer. The bond between β-carbon of acrylic acid and the hydrogen of bridge hydroxyl group is broken. This indicates the complete formation of acrylic acid and its desorption from the BEA zeolite surface. The bond order of the formed hydroxyl group H-Ob is about 0.6 for each dimer. In contrast, the hydroxyl group attached to the metallic center shows the following bonds order between metal and oxygen: Cu-OH 0.73, Mn-OH 1.12, V-OH 1.07. After desorption, the dimers occur in a hydrated form.

Analyzing the length of bonds between individual atoms, we can notice that the attachment of a hydroxyl group and a single hydrogen atom to the dimer causes structural changes of metal dimer. Mainly, the metal-bridge oxygen bond lengthen by 0.15-0.2 Å (Figure 4). The interaction of the hydrated form of the dimer with acrylic acid is negligible. The newly formed hydroxyl groups have the lengths of bonds typical for these types of moieties (about 1Å).

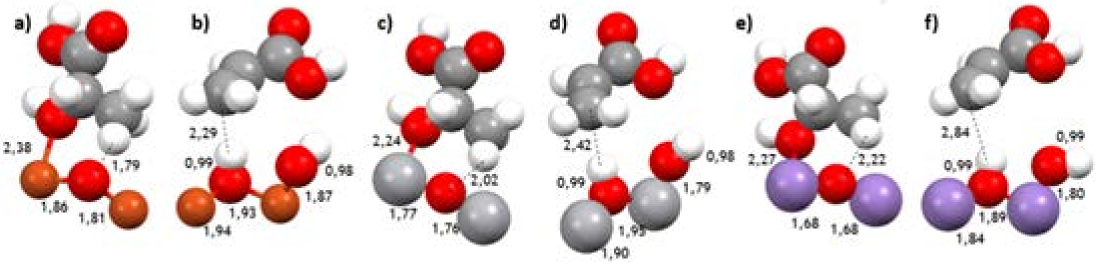

Fig. 4. Structure of lactic acid and acrylic acid: a) LA with Cu_2O dimer, b) AA with Cu_2O dimer, c) LA with V_2O dimer, d) AA with V_2O dimer, e) LA with Mn_2O dimer, f) AA with Mn_2O dimer

Rys. 4. Struktura kwasu mlekowego i kwasu akrylowego: a) kwas mlekowy z dimerem Cu_2O, b) kwas akrylowy z dimerem Cu_2O, c) kwas mlekowy z dimerem V_2O, d) kwas akrylowy z dimerem V_2O, e) kwas mlekowy z dimerem Mn_2O, f) kwas akrylowy z dimerem Mn_2O

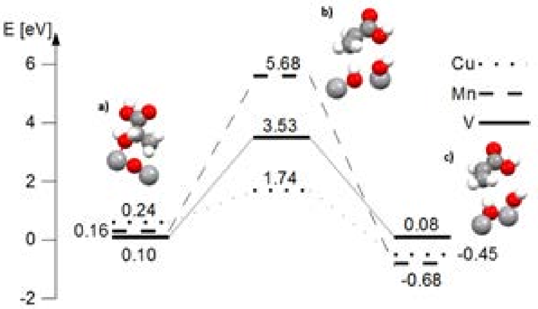

Fig. 5. Energy diagram of lactic acid dehydration into acrylic acid over dimeric M-O_b-M complex in the BEA zeolite, where M= Cu, V, Mn, a) lactic acid adsorption, b) intermediate stage, c) desorption of acrylic acid

Rys. 5. Schemat energetyczny odwodnienia kwasu mlekowego do kwasu akrylowego nad dimerycznym kompleksem M-O_b-M w zeolicie BEA, gdzie M = Cu, V, Mn, a) adsorpcja kwasu mlekowego, b) etap pośredni, c) desorpcja kwasu akrylowego

The energies of individual steps of lactic acid dehydration were also analyzed (Figure 5). The first step illustrates the energy required for the adsorption of lactic acid on the surface of the catalyst (Figure 5a). The lowest energy has adsorption on vanadium dimer (0.10 eV). In all cases this step is slightly endothermic and the energies are comparable. The next step is a transitional state consisting in the formation of acrylic acid (Figure 5b). This reaction is strongly endothermic and the energies are varied depending on the metal in the dimer. The highest energy is shown for manganese dimer (5.68 eV), the lower for vanadium dimer (3.53 eV) and the lowest in case of copper dimer (1.74 eV). The last step is the desorption of acrylic acid (Figure 5c). This step is exothermic for manganese and copper dimer (-0.68 and -0.45 eV), and endothermic for vanadium dimer (0.08 eV). Comparing the energy barriers, it can be concluded that the most energy-efficient catalyst would be BEA zeolite with an embedded copper dimer.

Conclusion

The hierarchical structure of the BEA zeolite has been considered, which allowed the analysis of the reaction directly on the surface of the BEA catalyst. The metal M-Ob-M dimers (M=Mn, Cu, V) have been found to be stable above oxygen bound with aluminum centers of BEA zeolite. The geometric compatibility of the metallic dimers and lactic acid allows for the proposed direct dehydration mechanism, where the oxygen center of the hydroxyl group of the α-carbon interacts with the metal center of the dimer and hydrogen is subtracted from the β-carbon and bound with the bridge oxygen of the metal dimer. The most energy-efficient catalyst would be BEA zeolite with an embedded copper dimer.

Acknowledgement

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 665778 (Polonez-1 no. 2015/19/P/ST4/02482 of National Science Centre, Poland). This work was supported in part by the PL-Grid Infrastructure.

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Abstrakt

Waloryzacja odpadów z biomasy cieszy się obecnie dużym zainteresowaniem. W niniejszych badaniach koncentrujemy się na projektowaniu innowacyjnych katalizatorów zeolitowych BEA z nanocząstkami metali - miedzi, wanadu i manganu w celu odwodnienia kwasu mlekowego do kwasu akrylowego. Metoda ab initio oparta na teorii funkcjonalności gęstości (DFT) została wykorzystana, przy użyciu nielokalnego funkcjonału korelacyjno-wymiennego GGA-RPBE, do obliczenia struktury elektronowej analizowanych cząsteczek. Hierarchiczny zeolite BEA był reprezentowany przez model klasterowy $M_2Al_2Si_{12}O_{40}H_{22}$ (M = Cu, V, Mn). Badano stabilizację dimeru M-O_b-M w hierarchicznej strukturze BEA, mechanizm adsorpcji kwasu mlekowego na zeolicie BEA z zastosowanymi dimerami metali i tworzenie kwasu akrylowego na tych zeolitach. Badane metale tworzą stabilne dimery połączone wzajemnie tlenem mostkowym (O_b). Adsorpcja kwasu mlekowego odbywa się w pobliżu dimeru M-O_b-M. Odwodnienie kwasu mlekowego do kwasu akrylowego we wszystkich przypadkach polega na oddzieleniu grupy hydroksylowej i utworzeniu połączenia z jednym z metali dimeru i odłączeniem pojedynczego atomu wodoru od grupy metylowej kwasu mlekowego i jego oddziaływaniem z tlenem mostkowym dimeru.

Słowa kluczowe: metoda DFT, nanocząstki metaliczne, odwodnienie kwasu mlekowego, kwas akrylowy