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Theoretical Investigation of Properties of 3D and 2D Zeolites

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Disertační práce

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Praha, 2016
Declaration of Authorship

I, Ho Viet Thang, declare that this dissertation titled, “Theoretical Investigation of Properties of 3D and 2D Zeolites” and the work presented in it are my own. All the literature is properly cited, and I have not been yet awarded any other academic degree or diploma for this thesis or its substantial part.

Signed: ____________________________

Date: ____________________________
Acknowledgments

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Zeolites have been widely used in many different fields including catalysis, adsorption and separation, ion exchange, or gas storage. Conventional zeolites have three-dimensional (3D) structures with microporous channel system; typical pore sizes are well below 1 nanometer, therefore, diffusion limitation plays important role in many process and bulkier reactants (or products) cannot enter (or leave) the zeolite channel system. Two-dimensional (2D) zeolites prepared in last years can lift all diffusion limitation and they thus offer a very attractive alternative to conventional 3D zeolites. 2D zeolites attracted considerable attention on the experimental side; however, understanding of 2D zeolites based on computational investigation or on a combination of experimental and computational investigation is limited. A motivation for the computational work presented here is to improve our understanding of properties of 2D zeolites based on computational investigation.

The originality of the research presented herein is in the strategy: we carried out systematic investigation of properties of corresponding 2D and 3D zeolites and we focus on the identification of similarities and differences. The most important zeolite properties, i.e., presence of Brønsted and Lewis acid sites, are investigated. A number of different characteristics of acid sites are considered, focusing on those that can be also obtained experimentally. Our computational results are compared with experimental results available in literature and with those newly obtained by collaborating experimental research groups. Several zeolite topologies are investigated, including, UTL, MFI, MWW, and FAU; properties of traditional 3D zeolite as well as of corresponding 2D one are considered in all cases.

The results obtained were found to be in a good agreement with available experimental data. This agreement entitles us to outline a general connection between the properties of 3D and 2D zeolites. Two-dimensional zeolites with relatively thick layers (above 2 nm) and low concentration of surface silanol have almost identical properties as their corresponding 3D counterpart (MWW). Two-dimensional zeolites with thick layers and high concentration of surface silanols show rather different properties for the same crystallographic sites in 3D and 2D materials; however, averaged properties remain similar. Two-dimensional zeolites with thin layers (1 nm) appear to be less acidic than
corresponding 3D zeolites. In summary, our results indicate that neither Brønsted nor Lewis acidity is significantly influenced by the transition from 3D to 2D zeolites.
Abstrakt

Zeolity jsou široce využívány v řadě oblastí včetně katalýzy, adsorpce a separací, ioničtých výměn a ukládání plynů. Běžné zeolity mají trojrozměrnou (3D) strukturu obsahující systém mikoporézních kanálů. Typická velikost těchto kanálů je pod 1 nm, v důsledku čehož je řada procesů limitována rychlostí difúze a větší reaktanty (produkty) nemohou vůbec vstoupit (opustit) do kanálového systému. Dvojrozměrné (2D) zeolity připravené v posledních letech mohou zmírnit nebo zcela eliminovat problémy spojené s difúzí a představují velmi zajímavou alternativu k běžným 3D zeolitům. 2D zeolity byly intenzivně zkoumány v posledních letech zejména experimentálně, zatímco porozumění jejich vlastností na základě teoretických výpočtů či na základě kombinace experimentu a teorie je zatím značně omezené. Práce zde předkládaná je motivována snahou vyjasnit vlastnosti 2D zeolitů na základě výpočetní studie.

Originalita našeho výzkumu je ve zvolené strategii – na základě systematického výzkumu vlastností 2D a korespondujících 3D zeolitů chceme nalézt a pochopit podobnosti a rozdílnosti mezi 3D a 2D zeolity. Soustředíme se na studium nejvýznamnějších vlastností zeolitů, tedy na popis Bronstedovské a Lewisovské kyselosti. Zabýváme se studiem různých charakteristik kyselých center v zeolitech a zejména takových charakteristik, které jsou experimentálně dostupné a mohou být porovnávány s experimentálními daty. Naše teoretické výsledky jsou srovnávány nejen s experimentálními daty dostupnými v literatuře, ale také s nově získávanými daty ve spolupracujících experimentálních laboratořích. V práci se zabýváme zeolity s různou strukturou (UTL, MFI, MWW a FAU), vždy studujeme stejné vlastnosti v běžném 3D zeolitu a v jeho 2D analogu.

Výsledky získané teoreticky jsou v dobré shodě s dostupnými experimentálními daty. Tato shoda nás opravduje k formulaci obecných vzácních mezi vlastnostmi 3D a 2D zeolitů. Dvojrozměrné zeolity s relativně silnými deskami (silnějšími než 2 nm) a nízkou koncentrací povrchových silanolů mají prakticky totožné vlastnosti jako jejich 3D analog (například zeolity s MWW topologií). Dvojrozměrné zeolity s silnými deskami a vysokou koncentrací povrchových silanolů mají rozdílné vlastnosti pro jednotlivá krystalografická kyselá centra ve 3D a 2D materiálech, ale zprůměrová vlastnosti jsou velmi podobné. A dvojrozměrné zeolity s tenkými deskami (okolo 1 nm) mají o něco
slabší kyselá centra než korespondující 3D zeolit. Získané výsledky indikují, že ani Brønstedovská ani Lewisovská kyselá centra nejsou významně ovlivněna přechodem od 3D ke 2D zeolitům.
Contents

Declaration of Authorship.....................................................................................................i
Acknowledgments............................................................................................................... ii
Abstract .............................................................................................................................. iii
List of Figures ..................................................................................................................... ix
List of Tables ................................................................................................................... xiii
Abbreviations ..................................................................................................................... xv
Introduction .......................................................................................................................... 1
General background .......................................................................................................... 4
  2.1. Zeolites ...................................................................................................................... 4
    2.1.1. Zeolites of IPC-1P family ................................................................................... 6
    2.1.2. 3D and 2D zeolites with MWW topology .......................................................... 8
    2.1.3. 3D and 2D zeolites with MFI topology .............................................................. 8
    2.1.4. FAU zeolite and FAU layered material .............................................................. 9
  2.2. Brønsted and Lewis acidity in zeolites .................................................................... 10
  2.3. Characterization of acid sites in zeolites – adsorption of probe molecules .......... 11
  2.4. Vibrational dynamics of adsorbed probe molecules ............................................. 12
Zeolite models .................................................................................................................... 14
  3.1. Zeolites of IPC-1P family ........................................................................................ 14
  3.2. Materials with MWW topology .............................................................................. 17
  3.3. 3D and 2D zeolites with MFI topology ................................................................... 18
  3.4. FAU zeolite and layered FAU material ................................................................... 19
Methods .............................................................................................................................. 21
  4.1. DFT methods ........................................................................................................... 21
4.2. Non-local vdW functionals ........................................................................................................... 23
4.3. Atom-atom dispersion corrections (DFT-D) ................................................................................. 23
4.4. DFT/CC method .............................................................................................................................. 24
4.5. Calculations details ......................................................................................................................... 24

Results and Discussion .......................................................................................................................... 26
5.1. Understanding the Lewis acidity in 3D and 2D zeolites ................................................................ 27
5.1.1. 3D UTL vs. 2D IPC-1P zeolites ................................................................................................. 28
5.1.2. 3D and 2D zeolites derived from IPC-1P – effect of zeolite pore size on Lewis acidity ................. 33
5.1.3. 3D vs. 2D zeolites with MWW topology .................................................................................... 37
5.1.4. 3D vs. 2D zeolites with MFI topology ....................................................................................... 41
5.2. Understanding the Brønsted acidity in 3D and 2D zeolites ......................................................... 45
5.2.1. 3D and 2D zeolites derived from IPC-1P – effect of zeolite pore size on Brønsted acidity. ............... 46
5.2.2. 3D vs. 2D zeolites with MWW topology .................................................................................... 53
5.2.3. 3D vs. 2D zeolites with MFI topology ....................................................................................... 56
5.2.4. Characterization of 3D and 2D zeolites with MFI topology with the $^{31}$P NMR of adsorbed TMPO ................................................................. 60
5.3. Hierarchical Na-USY zeolite .......................................................................................................... 66
5.3.1. Nature of active sites in hierarchical Na-USY ........................................................................ 67
5.3.2. Theoretical investigation of reaction mechanisms of aldol condensation catalyzed by the hierarchical USY zeolite ......................................................... 69

Conclusions ........................................................................................................................................ 72

References ........................................................................................................................................... 75

List of Attached Publications ............................................................................................................... 85

Attached Publications ......................................................................................................................... 86
List of Figures

FIGURE 1. Examples of secondary building units of zeolite, shown for a) 4-ring, b) 6-ring, c) 8-ring, and d) 12-ring.................................................................5

FIGURE 2. Framework structure of a) UTL and b) MFI zeolites, viewed along main channel systems...............................................................5

FIGURE 3. Structures of IPC-1PI, UTL, OKO and PCR consist of the same dense 2D layers (in green color) but different linkers (in red color) leading to the different pore sizes; shown along the main (left side) and perpendicular channels (right side). ...........................................................7

FIGURE 4. Structure of MCM-22 (left) and MCM-22P (right), The H, O and Si atoms are depicted in white, red, and gray color, respectively...............8

FIGURE 5. Structure of 3D-ZSM-5 (left) and 2D-ZSM-5 (right). The H, O and Si atoms are depicted in white, red, and gray color, respectively...............9

FIGURE 6. Structure of FAU zeolite (a) and layered FAU zeolite terminated with D6R-S6R (b). The H, O and Si atoms are depicted in white, red, and gray color, respectively..........................................................10

FIGURE 7. A Brønsted acidic site (a) and a Lewis acidic site (b). The atoms are depicted with following colors: Si (yellow), O (red), H (white) and extra-framework cation (purple). .................................................................11

FIGURE 8. Harmonic vibration potential (green curve) and anharmonic vibration potential (blue curve). ...............................................................12

FIGURE 9. Notation used for extra-framework Li$^+$ cation sites in IPC-1P, UTL, OKO and PCR. Sites in the main and perpendicular channels are denoted as Mx and Px, respectively, where x stands for the size of the ring on the channel wall where the Li$^+$ cation is located. A new surface site in IPC-1P formed upon the removal of D4R is denoted S8b. Two sites in PCR at the location of P5 and M5 in UTL are denoted M6 and P6 (depicted in the inset). The
numbering scheme of T’ atoms based on the UTL numbering is also shown.

FIGURE 10. Structure of MCM-22 framework, numbering scheme and extra-framework cation positions; view along the a (or b) direction (a) and view along the c direction (b). O and Si atoms are depicted in red and gray color, respectively.

FIGURE 11. Numbering scheme and channel systems of MFI zeolite.

FIGURE 12. The structure of faujasite (FAU); extra framework cation sites (depicted as purple balls) sites are labeled with Roman numerals. O and Si atoms are depicted in red, and gray color, respectively.

FIGURE 13. Model of a layered FAU zeolite terminated with D6R-S6R structural units exchanged with Na⁺ cations. Si, O, H, and Na atoms are depicted in gray, red, white, and purple, respectively.

FIGURE 14. Two types of LA sites in zeolite: a) the type I site, b) the type II site.

FIGURE 15. CO adsorption energies (lower part) and CO stretching frequencies (upper part) for the most stable Li⁺ sites in IPC-1P, UTL, OKO and PCR.

FIGURE 16. The CO adsorption complexes in the most stable position of Li cation in IPC-1P, UTL, OKO and PCR (from left to right); shown for Al in T4’ (a-d); T3’ (e-h); T10’ (i-l) and T7’ (m-p). The Al, O, and Si atoms are depicted in black, red and grey color, respectively while Li, C, and O atoms are depicted as purple, grey and red balls, respectively.

FIGURE 17. FTIR spectra of CO adsorbed at liquid nitrogen temperature on Li-IPC-1P (a), Li-UTL (b), Li-OKO (c), and Li-PCR (d). The intensity of spectra obtained upon CO adsorption decreases with evacuation. Insets in individual panels show theoretical spectra at corresponding Li-zeolites calculated for 0.75, 0.50, 0.25, 0.10, and 0.05 coverages (CO:Li ratio) in cyan, green, blue, red, and black, respectively.

FIGURE 18. Adsorption heats of CO on Li-zeolites and Li-IPC-1PI measured by microcalorimetry at -100°C as a function of coverage.
FIGURE 19. CO adsorption complexes of MCM-22 (left column) and MCM-22P (right column), shown for Al in T1 (a,b), T2 (c,d), T6 (e,f) and T8 (g,h). ............40

FIGURE 20. The IR spectra of CO adsorption complexes in Li-MCM-22 (a) and Li-MCM-36 (b), adapted from Ref. [81]. .......................................................41

FIGURE 21. CO adsorption complexes of 3D-ZSM-5 (left column) and 2D-ZSM-5 (right column), shown for Al in T4 (a,b), T9 (c,d), T10 (e,f) and T12 (g,h). ........44

FIGURE 22. Two types of BA sites in zeolite: a) the type of isolated BA site, b) the type of H-bonding BA site ...................................................................................46

FIGURE 23. OH frequency of bare BA sites for 10 distinguishable framework Al position in IPC-1P, UTL, OKO and PCR ....................................................47

FIGURE 24. The shift of OH frequencies upon CO adsorption in IPC-1P, UTL, OKO, and PCR .......................................................................................................49

FIGURE 25. Adsorption energies and CO frequencies of CO adsorption complexes in IPC-1P, UTL, OKO and PCR. ..............................................................50

FIGURE 26. The CO adsorption complexes in the most stable BA sites in IPC-1P, UTL, OKO and PCR (from left to right); shown for Al in T4’ (a-d); T8’ (e-h); T6’ (i-l) and T12’ (m-p). The H, Al, O, C, and Si atoms are depicted in white, black, red, grey, and light gray color, respectively. ..................................................51

FIGURE 27. IR spectra of CO adsorbed on H-zeolites of IPC-1P family ..................52

FIGURE 28. CO adsorption complexes at the most stable Bronsted acid sites in MCM-22 (left column) and MCM-22P (right column), shown for Al in T4 (a,b), T6 (c,d) and T7 (e,f) and T5 (g,h) .................................................................55

FIGURE 29. CO adsorption complexes at the most stable Bronsted acid sites in 3D ZSM-5 (left column) and 2D ZSM-5 (right column), shown for Al in T1 (a,b), T3 (c,d) and T5 (e,f) and T8 (g,h). .................................................................59

FIGURE 30. TMPO adsorption complexes with BA sites in 3D MFI, shown for Al in T1 (a) and Al in T6 (b). .............................................................................62
FIGURE 31. TMPO complexes with BA sites in 2D MFI, shown for Al in T1 (a) and Al in T6 (b); a complex with both BA site and silanol, shown for Al in T12 (c) and in T9 (d); complexes only with silanol, shown for T12 (e) and T7 (f). 63

FIGURE 32. $^{31}$P NMR chemical shifts of adsorbed TBPO on the surface sites (top) and TMPO on sites inside the channel system (bottom) of the lamellar MFI zeolite; experimental data taken from Ref. [40] (depicted in black) are compared with the DFT results (red bars). .................................................. 66

FIGURE 33. CO adsorption complexes formed on (a) S$_{D6R}$, (b) S$_{S6R}$, (c) S$_{06R}$, (d) B$_{1T}$, (e) S$_{1T}$, and (f) S$_{2T}$ Na$^+$ sites in Na-hUSY. Si, O, H, and Na atoms are depicted in gray, red, white, and purple, respectively. All distances are in Å. The notations details can be found in Attachment E. ..................................... 68

FIGURE 34. Schemes of aldol condensation; acetone-acetone (left column), acetone-furfural (right column). ................................................................. 70

FIGURE 35. Reaction profiles of condensation reactions in acetone and furfural mixture catalyzed by Na-hUSY represented by a S$_{S6R}$ site. All minima were obtained using periodic model and PBE+D3 method and corrected for B3LYP based on cluster model results; the reaction barriers were obtained from cluster model using B3LYP functional. .............................................. 71
List of Tables

TABLE 1. The numbering of T sites in IPC-1P, UTL, OKO and PCR was taken from IZA database. The common numbering of the T’ sites are chosen following numbering of UTL structure.................................................................17

TABLE 2. The most stable Li\textsuperscript{+} sites found for all possible Al positions in Li-IPC-1P, Li-UTL, Li-OKO, and Li-PCR; Li distances (Å) to framework oxygen atoms (O\textsubscript{f}) smaller than 2.4 Å are reported.................................................................30

TABLE 3. The Li\textsuperscript{+} cation sites and Li-O\textsubscript{f} distances (in Å) of the most stable Li\textsuperscript{+} sites in the vicinity of Al in seven different framework positions found for MCM-22 and MCM-22P zeolites. .................................................................................38

TABLE 4. Characteristics of CO adsorption complexes formed on the most stable Li\textsuperscript{+} sites (the number in parentheses is the coordination numbers of Li\textsuperscript{+} cation with framework oxygen) in MCM-22 and MCM-22P. CO frequencies are in cm\textsuperscript{-1}, and adsorption enthalpies are in kJ mol\textsuperscript{-1}.................................................................39

TABLE 5. The Li\textsuperscript{+} cation sites and Li-O\textsubscript{f} distances (in Å) of the most stable Li\textsuperscript{+} sites in the vicinity of Al in all distinguishable framework positions of 3D and 2D ZSM-5 zeolites. ..............................................................................................42

TABLE 6. Characteristics of CO adsorption complexes formed on the most stable Li\textsuperscript{+} sites (the number in parentheses are CN) in 3D ZSM-5 and 2D ZSM-5. CO frequencies are in cm\textsuperscript{-1}, and adsorption enthalpies are in kJ mol\textsuperscript{-1}. ................43

TABLE 7. The Al-O-Si bond angle (deg.), OH bond distance (Å) and OH frequencies (cm\textsuperscript{-1}) of the most stable Brønsted sites in the vicinity each of 8 different framework Al positions in 3D and 2D MWW .................................................................53

TABLE 8. Characteristics of CO adsorption complexes with the most stable Brønsted sites in 3D and 2D MWW, adsorption energies and frequencies are reported in kJ mol\textsuperscript{-1} and in cm\textsuperscript{-1}, respectively. .................................................................54

TABLE 9. The Al-O-Si bond angle (deg.), OH bond distance (Å) and OH frequencies (cm\textsuperscript{-1}) of the most stable Brønsted sites in the vicinity of each of 12 distinguishable Al positions in 3D-ZSM-5 and 2D-ZSM-5 zeolites. ........57
TABLE 10. Characterization of CO adsorption complexes in the most stable BA site in each of 12 distinguishable Al position. ........................................................ 58

TABLE 11. Characteristics of TMPO adsorption complexes formed on the most stable Bronsted-acid sites in the vicinity of each of 12 distinguishable framework Al positions in 3D MFI; structural parameters, stretching frequencies, adsorption energy, and chemical shift values are given in Å, cm$^{-1}$, kJ mol$^{-1}$, and ppm, respectively. ................................................................................. 61

TABLE 12. Characteristics of TMPO adsorption complexes formed on the most stable Bronsted-acid sites in the vicinity of each of 12 distinguishable framework Al positions in 2D MFI; structural parameters, stretching frequencies, adsorption energy, and chemical shift values are given in Å, cm$^{-1}$, kJ mol$^{-1}$, and ppm, respectively. ................................................................................. 65

TABLE 13. Relative exchange energies, CO interaction energies, and stretching frequencies calculated at the PBE level for various alkali metal sites in M-hUSY zeolites. ............................................................................................................. 68

TABLE 14. Reaction profile of aldol condensation of acetone and furfural with minima obtained in periodic Na-S$_{66}$R-hUSY model and PBE+D3 functional and elementary barriers with S$_{66}$R cluster model. B3LYP corrections were added as obtained from the S$_{66}$R cluster model (as difference between B3LYP/TZVP and PBE/TVZP reaction energies). All energies in kJ mol$^{-1}$. .......................................................................................................................... 71
**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
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<tr>
<td>vdw</td>
<td>van der Waals</td>
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<td>Coupled Clusters with Singles, Doubles and perturbative Triples</td>
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<td>PBE</td>
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<td>ZSM-5</td>
<td>Zeolite with MFI topology</td>
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<td>BA</td>
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