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Review Report on the PhD thesis submitted to the University of Pardubice
Faculty of Chemical Technology
Department of Physical Chemistry

Author: **Ing. Jan Vaculík**
Title: **Acidobazické vlastnosti zeolitů**
Scientific supervisor: **Prof. Ing. Roman Bulánek, Ph.D.**

The thesis written by Ing. Jan Vaculík is focused on the development of the method for the analysis of the strength of Brønsted acid sites in zeolites with various topology and dimensions (3D vs 2D). The analysis of the strength of acid sites in zeolites represents one of the crucial factors influencing the catalytic activity of zeolites. Thus, the studies presented in the thesis meet the requirements of the current industry to obtain highly active and stable zeolite-based catalysts.

The thesis consists of the detailed description of performed studies and the analysis of the obtained data (59 pages) supported by five scientific papers published in impacted international journals. Ing. Jan Vaculík is a co-author of four original papers, and the first author of one paper. The thesis is divided into seven chapters. In the first chapter, the author describes precisely the motivation of the work, which lies in finding the best method for the determination of the strength of Brønsted acid sites in zeolites. In the second chapter of the thesis, the properties of zeolites and their hierarchical analogues were clearly described. The aim of the work and scientific questions (third chapter) were unambiguously formulated. Chapter four is focused on the presentation of characterization methods used for the determination of acid sites in zeolites. This part is an overview of acid-base theory, available characterization techniques, and methods for studying the strength of acid sites. All discussed aspects are well supported by the literature data. The fifth chapter is the list of the scientific papers being part of the dissertation.

The discussion of the obtained results is presented in the sixth chapter. Ethanol dehydration was chosen as a testing reaction to determine the strength of acid sites in zeolites with different topologies (MFI, MWW, and CHA). It was shown that this is not a plausible method for determining the strength of acid sites in zeolitic materials due to the strong influence of diffusion limitations, formation of several reactions by-products, and complex reaction mechanism. However, the author proposed another method for determining the strength of acid sites, which was based on the interaction of zeolite isotopically marked by deuterium with ethane followed by FTIR. It was shown that the employment of this method together with NH₃-TPD for acid site monitoring confirmed that the strength of Brønsted acid sites of MFI is higher than in MWW. The study of acid sites in 2D and 3D zeolites with MFI, MWW, and PCR framework using FTIR spectra after interaction with CO and deuterium isotopic exchange revealed no significant difference in the strength of acid sites between 2D and 3D zeolites.

A novel method enabling the disclosing of the acid site location is presented in the following part of the thesis. This method is based on blocking the external acid sites by an organic molecule, which is large enough to prevent its entering into zeolite channels, and subsequent analysis of internal Brønsted acid sites using deuterium isotopic exchange monitored by FTIR spectroscopy. The results indicated that in the MFI zeolite, the strength of external and internal Brønsted acid sites is similar. The presented results confirmed that the author has proven satisfactory knowledge and research methodology. The last chapter concludes the obtained results. This chapter is short and to the point.

While studying Ing. Jan Vaculík's thesis, a few questions arise that I would like the candidate to answer during the defence:

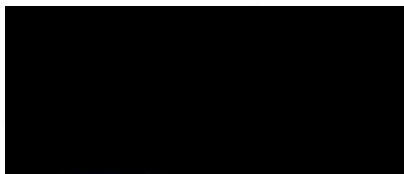
1. Following the unsuccessful attempt to employ ethanol dehydration as a characterization reaction, a novel approach suitable to distinguish between external and internal Brønsted acid sites was proposed. On the other hand, it may be discussed what should be the reason for the different strength of internal vs. external acid sites, which however both arise from the same zeolite structure and therefore the same acidity may be expected and was indeed proven.

2. What were the criteria for the selection of various zeolite structures studied in this work? Ethanol dehydration was examined over MFI, MWW, and CHA. On the other hand, the FTIR study after interaction with CO was done with MFI, MWW, and PCR. Finally, the distinguishing between external and internal Brønsted acid sites was studied using only the MFI zeolite.
3. What was the reason for selecting ethanol dehydration as a testing reaction? What are the commonly used methods for acid sites characterization and what could be the advantages of their characterization using ethanol dehydration?
4. What is the influence of the Al organization in the studied zeolites on the strength of acid sites?
5. Why the author decided to analyze the FTIR spectra after interaction with ethane in the region of 4000-2250 cm^{-1} only (cf. Fig. 29 in the thesis, and Fig. 5 in Appl. Catal. A 575 (2019) 180)? The interaction of zeolites with ethanol is usually analyzed simultaneously in the region 1800-1400 cm^{-1} , where the formation of H-bonded species and carbenium ions can be followed.
6. Please ascribe the vibrations in Figs. 28 and 29 to particular species formed on zeolites.
7. What was the origin of the studied zeolites? Were they home-made or commercial?

Below I have listed the flaws and errors that appeared in the thesis:

1. CO and deuterium isotopic exchange was studied over PCR zeolite. However, this sample is first mentioned on p. 44, is not included in the Abbreviation list and there is no description of the PCR zeolite in the whole thesis.
2. Abbreviation *BEA should be written instead BEA as the author studied the partially disordered structure (p. 8).
3. P. 22, line 8, "...podle Benesiho." – the reference is missing.
4. P. 23, third paragraph, references describing probe molecules are missing.
5. The quality of Figs. 16, 23, and 28 is low. It would be better to keep the same quality as in the papers.
6. Fig. 28 – the scale on the Y-axis is missing.

Ing. Jan Vaculík presented a scientifically important PhD dissertation entitled “Acidobazické vlastnosti zeolitů” dealing with the development of methods for determining the strength of acid sites in zeolites. The thesis is based on several studies on the acidic properties of zeolites that were published in five impacted scientific papers. The interpretation of obtained results was performed according to good scientific practice. Ing. J. Vaculík demonstrated the ability for creative and independent scientific work in the physicochemical analysis of zeolite-based catalysts. In my opinion, Ing. J. Vaculík fulfils the conditions for obtaining a Ph.D. degree in chemistry pursuant to Section 47(4) of Act No. 111/1998 Coll. on Universities. Based on my evaluation of the presented dissertation, I recommend his thesis for public defense.



Doc. Mgr. Edyta Tabor, Ph.D.