University
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Faculty
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Opponent's report on the dissertation thesis

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Title: Design and catalytic application of novel nanostructured materials
Supervisor: Dr. Maksym Opanasenko
Study program: Physical Chemistry

Brief characterization of the work

Presented dissertation thesis deals with preparation of nanostructured zeolites and their catalytic applications in order to gain insight into the relationship between their key properties (texture and morphology, composition and accessibility of active sites) and catalytic performance. Theses consists of four partial studies. First part deals with synthesis of Al-containing isoreticular zeolites of IPC-x family and their catalytic activity in ethanol dehydration and tetrahydropyranylation reactions, in which the influence of pore size on catalytic activity is discussed. Second part reports on synthesis of aluminated **AFI** zeolites and their activity in aromatics alkylation. This study led to the finding of a successful two-step process of post-synthetic isomorphous substitution of germanium for aluminium. Third part of dissertation describes the surface modification of nanosized **MFI** zeolite with silanes in order to prepare aggregation-resistant catalytic material. The last part of the thesis is devoted to the synthesis of cobalt-containing **MWW** zeolites with different layer arrangements. Architecture and acidity of these materials was correlated with their activity in catalytic elimination of VOC like propane and toluene. The dissertation is written as a full text supplemented by three publications co-authored by student. All three papers were published in renowned journals (ACS Catalysis, Applied Catalysis A and Catalysis Today). The majority of the presented results have already successfully passed the review procedure in these journals, which testifies to their quality. However, while reading the dissertation, I had several questions that I would like to present to the student for discussion.

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Comments and questions

1) Figure 4-10 displays comparison of the alcohols conversions in tetrahydropyranylation reached over IPC-6 and mixture of IPC-2+IPC-4, having similar textural properties and total content of acid sites as IPC-6 catalyst. Differences in catalytic activity for more bulky alcohols is ascribed to the differences in the population of "external sites" (sites accessible to quinoline). But, both catalytic systems differ not only in amount of such external sites but also in the fraction of Lewis and Brønsted sites (roughly estimated from Fig. 4-6). As mentioned in the thesis, tested reaction takes place on both Brønsted and Lewis sites. Can be difference in activities related also to the different population of both acid sites? Do they differ in intrinsic activity?
2) In second part, the activity of aluminated **AFI** zeolites and other zeolitic materials in toluene alkylation is studied. The conversion of toluene is almost independent on TOS or even slightly decline in TOS (see Fig. 4-17)! Why? Can you explain this behaviour? In addition, it is claimed in the thesis that toluene conversion was mainly influenced by B/L ratio. The conversion should be dependent also on total amount of acid sites. What role do play Lewis sites?
3) For synthesis of isoreticular Al-IPC-x zeolites and Al-**AFI** zeolites, post-synthetic incorporation of Al to the framework was applied. I would like to know your opinion on whether there is some limit in amount of incorporated Al and if there is possibility to shift B/L ratio in favour of Brønsted sites.
4) It is claimed in the thesis that surface silanol groups are almost completely consumed in silylated **MFI** samples based on Si NMR spectra (Fig. 4-22). But IR spectra of the same samples (Fig. 4-20) exhibit quite intense band at the position coincided with vibration of silanols. What would you assign to this band in IR spectra of silylated **MFI** zeolites?
5) Redox behaviour of the cobalt in Co-**MWW** zeolites was studied by CO-TPR (see Fig. 4-37). How are reduced bare cobalt cations (Co^{2+}) in exchangeable site of zeolites? How quantitative is reduction of cobalt in zeolites studied by carbon monoxide?

The formal aspects of the dissertation:

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- Text contains typos in an amount not exceeding the normal level.
- On page 46, frequency of hydroxyls in IR spectra is reported to be 3620 cm^{-1}, but in the Fig. 4-5 the position of the band is highlighted at 3610 cm^{-1}.
- The order of the Co-**MWW** samples according to the intensity of IR band at 2185 cm^{-1} reported on page 88 contain twice the unlabelled Co/MCM-22(30) (A or B label is missing).

In conclusion, the doctoral dissertation by Mgr. Yong Zhou contains interesting results of scientifically sound research. The results reported in this work were published in three papers, therefore thesis fulfils all requirements for this type of work, the PhD student has proven the ability to conduct independent scientific work, cooperate with colleagues and therefore, despite the above mentioned comments and reservations, I recommend the work for defense.

Pardubice, September 1st 2020

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