CARL VON OSSIETZKY universität OLDENBURG
FAKULTÄT V
MATHEMATIK- UND NATURWISSENSCHAFTEN

Institute of Chemistry
Chemical Technology 1
Photocatalysis & sustainable feedstock utilization

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OLDENBURG

Date
November, 14th, 2020

PhD Thesis Committee

Natalya Karpova

St. Petersburg State University

Dear committee members,

On the next passages you find my report on the PhD thesis
Petr Dmitrievich Murzin entitled:
Effect of heterovalent cation doping on activity of titanium dioxide in molecular photoprocesses in heterogeneous systems.

In summary I can confirm that the thesis fulfills the requirements established by the degree of "On Order of Granting Degrees in St. Petersburg University".
Thus, Mr. Petr Dmitrievich Murzin deserves to be granted with the Degree of Candidate of Physico-mathematical Sciences (Scientific specialization 01.04.07 — «Condensed matter physics»).

To my opinion the thesis fulfills all criteria for the grade:
"magna cum laude".

Yours sincerely

Prof. Dr. Michael Wark

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Report on the PhD thesis (dissertation) of **Petr Dmitrievich Murzin** entitled:
Effect of heterovalent cation doping on activity of titanium dioxide in molecular photoprocesses in heterogeneous systems

Mr. Petr Murzin studied the well-known photocatalysts TiO_2, which he doped with the trivalent ions Sc^{3+}, Al^{3+} as well as the five-valent ions Nb^{5+} and V^{5+}. He also produced samples, in which the four-valent Ti^{4+} was replace with a combination of Sc^{3+} and V^{5+} ions in order to conserve electron neutrality.
The idea of replacing some Ti^{4+} ions with ions of higher or lower valence is not new; several hundreds of papers on doping have been published. Nevertheless, the exact nature of the defect sites of the vacancies formed in the structure due to this doping is still not known very well.
Thus, the presented measurements of electronic work functions via the Kelvin probe method, EPR spectroscopy studies as well as the investigations on the photoinduced coloration of the doped samples are very fruitful for a better understanding of the formed defective structures.

Mr. Murzin found that for doping ions which radii do not differ much from the ionic radius of Ti^{4+} ions the percentage of doping leading to the highest increase in photoactivity is higher than for ions which size is more different to that of the Ti^{4+} ions (summary in Fig. 97).
This confirms older results from heterogeneous catalysis that the oxide structures tolerate only weak structural distortion.
A bit surprising is in the discussion of Table 8 that about 3-times higher concentration of Al^{3+} ions than V^{5+} ions are needed for highest photoactivity. Possibly, the charge relative to TiO_2 has an effect, a fact which should be more discussed in future.
However, Figure 96 shows that the changes in the work functions (although the errors in the measurements are quite high) go in-line with the changes in photoactivity and indicate that the effects induced are higher for doping with Al than with V ions.

As an important factor induced by doping Mr. Murzin could identify the redistribution of defective states. EPR studies and photoinduced coloration showed that TiO_2 doped with trivalent ions causes a higher concentration of Ti^{3+} centers, which behave as shallow traps, being ineffective as recombination centers, thus increasing the photoactivity.

For the five-valent ions Mr. Murzin could see that it is important whether the electronic levels of the doping ions lie within the band gap of the TiO_2 (and may be in general of the doped semiconductor) or not. Doping states within the band gap lead to a competitive population with Ti^{3+} centers. In contrast, if the doping centers are not lying in the band gap, there is a clear tendency to form deep traps which are acting as unwanted recombination centers. This is clearly seen in the strongly increased work function.

For the co-doping the surprising result was observed that not a 50:50 ratio but a 75:25 ratio led to the highest photoactivity. Furthermore, the activity increase was lower than that observed Sc^{3+} doping alone. Although the shallow trap formation dominates there is no simple effect of a summation of the effects of the two doping ions.

To my opinion all these are very interesting for the scientific community working in heterogeneous photocatalysis.
However, especially the findings about co-doping are helpful, since they contradict the dominant opinion in literature. Nevertheless, especially these results also require more confirmation – and the widening of the measurements to other semiconductors.
Mr. Murzin also discussed mainly the rutile modification of TiO_2, a future confirmation of the results for anatase and brookite or even for mixtures of them would be very fruitful.

Until now Mr. Murzin could publish his results in 4 publications in international journals. The paper from January 2020 in Catalysis Today was already cited 9 times and is thus marked in Web of Science as “highly cited paper”. Since this paper is a result of a collaboration with colleagues from other Russian Institutes and from Italy Mr. Murzin is not first author, but I´m very convinced that he made important contributions to that successful paper.

Looking on the PhD thesis presented by Mr. Murzin it becomes easily clear, that Mr. Murzin has conducted all his experiments very precisely. The accuracy of the obtained data is always discussed.
Also, the given explanations and the quality of presentation (in figures) are over the whole thesis on a high level. The extended literature list with over 250 citations documents that Mr. Murzin was very active in getting deep into the knowledge on his topic and he could demonstrate that he achieved a high level of understanding.

Thus, in summary Mr. Murzin presents a very clear and interesting to read PhD thesis.
To my opinion there is no doubt that Mr. Petr Dmitrievich Murzin deserves to be granted with the Degree of Candidate of Physico-mathematical Sciences (Scientific specialization 01.04.07 — «Condensed matter physics»).
In the German system I would judge the presented dissertation with the grade:
“magna cum laude”.

Best regards

Prof. Dr. Michael Wark