EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Long Term Project Report : Interim/Final

Summary Page

Proposal Number: MA4926

1. Beamtime Used

Please give a short summary of progress for each scheduling period for which beamtime has been allocated/used :

Scheduling period	Beamline(s) Used	Shifts Used	Summary of results obtained
2021/II	BM23	18	A spectral database of Pd complexes was obtained (during the beamtime MA4443) A spectral database of Ru complexes was obtained (partially during the beamtime MA4443) A speciation of ruthenium in homogenous catalytic system with ionic liquid was determined Machine learning algorithm for determining the ligand surrounding of ruthenium and Ru-ligand distances was developed based on the obtained results *In situ* experiment on homogenous-heterogenous palladium-zeolite based catalysts in the liquid phase was performed and analysed *In situ* experiment on homogenous-heterogenous copper-MOF catalysts in the liquid phase was performed and analysed A series of *ex situ*/*in situ* studies on various palladium, ruthenium and rhodium-based catalysts of industrial importance were measured ana analysed
2022/I	BM23		18 shifts scheduled
20 /II			
20 /I			
20 /II			
20 /I			

2. **Resources Provided by User team (financial, personnel, technical...):**

Financial resources.
The online mass-spectrometer for *in situ* and *operando* experiments was purchased in the end of 2021 and will be installed at BM23/ID24 beamlines in 2022.
Manufacturer: Pfeiffer Vacuum
Model: OmniStar® GSD 350 O1C, 1 – 100 u, yttrium iridium cathode, heated capillary 350 °C, 1 m
Price: 4 942 500 Russian rubbles (ca. 56.2 kEuro)

Personnel resources.
25% of the working time of our programmer Sergey Guda (SFedU, Rostov-on-Don) was devoted to the development of the machine-learning approach for the analysis of XANES spectra based on the spectral descriptors. The approach was implemented in PyFitIt code and will be soon released on a github in the new version of the code.
External programmer, Denis Ryabov (Rostov-on-Don), was involved in the development of a web-based portal for X-ray spectral data.

Financial resources.
A design of the high-temperature and high-pressure *operando* cell for liquid catalytic systems, specifically ruthenium-based catalysts in ionic liquids under harsh conditions with the possibility for fluorescence detection of XANES was made. The cell will be produced and delivered to ESRF in March 2022.

3. **Technical and Scientific Milestones Achieved** (in relation to the milestones identified in the original proposal)**:**

Year 1

According to the **milestone 1**, spectral databases of different well-defined palladium and ruthenium compounds were obtained experimentally and used as training sets for ML learning algorithms directly trained on these spectra and as test set for ML algorithms trained on the theoretical data which were calculated in frame of the scientific case of the project (more than 10,000 theoretical spectra). The web-based interface is being developed where any user will be able to identify the structure of the unknown compound (within the capacity of the database) in the online regime.

According to the **milestone 2**, the developed ML methodology was applied identify the speciation of active sites in the series of palladium and ruthenium catalytic systems based on the *ex situ* and *in situ* XANES data, including the experiments performed for low concentrated catalysts, in liquid phase and in presence of gaseous and liquid substrate. These studies will be continued in 2022.

Year 2

Year 3

4. List of publications directly resulting from beamtime used for this Long Term Project:

Publications based on the data from Proposal MA-4443:

A. Martini, A. L. Bugaev, S. A. Guda, A. A. Guda, E. Priola, E. Borfecchia, S. Smolders, K. Janssens, D. De Vos, and A. V. Soldatov. Revisiting the Extended X-ray Absorption Fine Structure Fitting Procedure through a Machine Learning-Based Approach. *The Journal of Physical Chemistry A* **2021** *125*(32) 7080–7091
DOI: 10.1021/acs.jpca.1c03746

Publications based on the data from Proposal MA-4926:

V. Lemmens, C. Vos, A. L. Bugaev, J. Vercammen, N. Van Velthoven, J. Gascon, D. E. De Vos. Ru-Bipyridine Entrapped in the Supercages of EMC-1 Faujasite as Catalyst for the Trifluoromethylation of Arenes. *ACS Applied Materials & Interfaces* **2022** *14*(1) 971–977
DOI: 10.1021/acsami.1c19655

E. G. Kozyr, A. L. Bugaev, S. A. Guda, A. A. Guda, K. A. Lomachenko, K. Janssens, S. Smolders, Dirk De Vos, and A. V. Soldatov. Speciation of Ru Molecular Complexes in a Homogeneous Catalytic System: Fingerprint XANES Analysis Guided by Machine Learning. *The Journal of Physical Chemistry C* **2021** *125*(50) 27844–27852
DOI: 10.1021/acs.jpcc.1c09082

W. Stuyck, A. L. Bugaev, et al. Sustainable formation of tricarballylic acid from citric acid over highly stable Pd/Nb_2O_5.*n*H_2O catalysts. *Journal of Catalysis* **2022** (Under review, submitted in Dec 25th 2021).