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FINAL REPORT
on the research activity of Dr. Oxana A. Kholdeeva
in CNR-ISTM during the period of 04.11.13-16.11.13

The collaborative research between **CNR-ISTM** and **BIC** (the Boreskov Institute of Catalysis) addresses a problem of widespread and considerable importance — the development of catalysts for the selective oxidation of organic compounds with environmentally friendly and available oxidants, such as aqueous 30% H_2O_2 and *tert*-butyl hydroperoxide (TBHP). The development of clean catalytic methods for the production of oxygen-containing products like epoxides, alcohols, aldehydes, ketones and quinones is of great scientific and practical interest since these oxygenated derivatives serve as intermediates in the production of many valuable fine chemicals and nutraceuticals.

The main scientific goal of the collaborative research project between ISTM-CNR and BIC is the development of novel single-site heterogeneous catalysts that would be highly active, selective and stable under the conditions of liquid-phase oxidation. During the last years, titanium-containing catalysts were in the main focus of the collaboration because of their efficiency in liquid-phase selective oxidation of various organic compounds. **The main goal of the present visit** was to perform an exchange of the results obtained in both labs during the last two years, to make a comparison of the catalytic properties of Ti-based catalysts prepared by different techniques, including some new ones, and to start a new project devoted to the preparation, characterization and catalytic applications of Nb- and W-containing silica catalysts.

During the reporting period, samples of Ti- and Fe-silicates, prepared in BIC following a new, very simple and versatile methodology, namely, evaporation-induced self-assembly (EISA), have been examined in ISTM in several liquid-phase oxidation reactions. Specifically, the Ti-containing silica catalysts were tested in the liquid-phase oxidation of limonene (1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene) and methyl oleate (methyl (9*Z*)-9-octadecenoate) with anhydrous TBHP as oxidant, in acetonitrile. They showed a catalytic behaviour fully in line with the results previously obtained over Ti-grafted silica materials, *i.e.*, similar specific activity and selectivity, although the total conversion over the grafted catalysts was higher, most likely, due to the presence of larger mesopores in these catalytic materials. We expect that the EISA materials will, however, have a better stability toward deactivation and, therefore, their recycling performance in TBHP-based epoxidation of limonene will be studied in the near future. On the other hand, Fe-SiO_2-EISA was tested in the liquid-phase oxidation of benzyl alcohol into benzaldehyde in the presence of H_2O_2 as well as in the liquid-phase oxidation of limonene with TBHP. The Fe-containing catalyst is prone to leaching when H_2O_2 is used as oxidant and the reaction occurs mainly under homogeneous conditions, which is evidence by the presence of yellow-coloured species in solution. The reaction mixture appears colourless and free from leaching, on the contrary, when TBHP is used as oxidant. In the oxidation of benzyl alcohol, the activity of Fe-SiO_2-EISA appeared to be poor and a maximum yield of 4% to aldehyde was obtained. In limonene oxidation with TBHP, conversely, it showed a scarce activity, leading to the formation of some allylic oxidation products.

During the visit of Dr. Kholdeeva to ITSM, the catalytic behaviour of various titanium-based catalysts, including mesoporous titanium-silicates prepared by different methodologies, *viz.*, hydrothermal synthesis, evaporation-induced self-assembly (EISA) and grafting or impregnation of Ti(IV) precursors onto commercial mesoporous silica supports as well as the metal–organic framework MIL-125 and amorphous TiO_2, has been analyzed and discussed. It was concluded that the presence of di(oligo)nuclear Ti active centers (verified by DR UV-vis spectroscopy) and the lack of anatase microcrystallites (confirmed by Raman spectroscopy) in Ti-catalysts of different nature ensures nearly 100 % selectivity toward TMBQ and no formation of dimeric by-product in the oxidation of 2,3,6-trimethylphenol (TMP) to 2,3,5-trimethyl-p-benzoquinone (TMBQ, vitamin E precursor) with 35 % H_2O_2. All the catalysts studied were stable toward titanium leaching, revealed a truly heterogeneous nature of catalysis and could be easily recovered by filtration. However, they differ significantly in the efficiency of H_2O_2 utilization (which is closely related to the attainable substrate conversion with a fixed amount of oxidant) and recycling performance. Although the crystal structure of MIL-125 is destroyed by the reaction medium under these conditions, the metal–organic framework acts as a precursor for the highly active, selective and recyclable catalyst, but the week point of this catalyst is a rather low H_2O_2 efficiency (< 40 %). In contrast to crystalline anatase, amorphous TiO_2 enables TMP oxidation to TMBQ with 100 % selectivity. The substrate conversion and quinone yield have a trend to increase in the course of the TiO_2 catalyst recycling. However, bearing in mind the current cost of H_2O_2, this catalyst cannot be considered the best choice, at least on a short-term time period, because of the scarce oxidant efficiency shown in this reaction. To date, mesoporous titanium-silicates prepared by the EISA methodology reveal superior catalytic performance in terms of substrate conversion, product selectivity and reusability and can be therefore considered as prospective catalysts for the title reaction. A draft of a full paper entitled "Environmentally Benign Oxidation of Alkylphenols to *p*-Benzoquinones: A Comparative Study of Various Ti-containing Catalysts" has been completed and submitted to the special issue of *Topics in Catalysis* (The proceedings of the 25th ORCS conference).

Samples of Nb- and W-containing silica have been prepared in ISTM by two methodologies, *viz.*, dry impregnation and liquid-phase grafting, during the stay of Dr. Kholdeeva. The grafting procedure has been adopted in order to reach the concentration of Nb on the surface around 0.8 atom/nm^2 (such surface concentration was established as optimal for Ti/SiO_2 catalysts to achieve 100% selectivity toward quinones in the oxidation of alkylated phenols with H_2O_2). The catalysts prepared will be further characterized by different techniques, including elemental analysis, thermogravimetry, N_2 adsorption (ISTM), DRS-UV, FT-IR and Raman (BIC), and their catalytic performances will be assessed in the oxidation of phenols with aqueous H_2O_2 as oxidant (BIC). Structure/activity/selectivity relationships will be analyzed and, based on the analysis of the results of the catalytic and spectroscopic studies we hope to identify the structure of the active Nb and W species that would ensure high activity, selectivity and stability of these catalysts.

Signature Oxana A. Kholdeeva

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