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Application for beam time at ESRF – Experimental Method

This document should consist of a maximum of two A4 pages with a minimal font size of 12 pt.

Aims of the experiment and scientific background

Mesoporous silica (MCM-41) has been prepared in 1991 for the first time by Mobil Oil scientists [1]. Since their discovery they have attracted much attention [2]. Since their discovery close to 6000 papers have already been published related to mesoporous materials. In the last two years we have applied a sonochemical technique for the fabrication of various mesoporous materials [3,4]. These papers demonstrated that the main advantages of our method is the shorter reaction times and a more stable product. In addition we have recently shown that sonochemistry can also be used for the insertion of nanosized catalysts into the mesopores of these materials. The mechanism of the role of the ultrasonic waves is not clear. How is it possible that a 200 micron size bubble collapses in a pore that is less than 10 nm? If the bubble on the other hand collapses outside the channels and microjets and shock waves are responsible for the insertion of the nanoparticles into the mesopores, then very strong chemical bonds should be formed between the mesoporous material and the inserted catalyst. The current planned experiments are aimed at investigation these bonds and their importance in the catalytic process. The system that will be investigated is mesoporous titania inserted by nanometer size particles of iron oxide (Fe_2O_3). We want to measure the XANES and EXAFS of the pristine mesoporous titania, mesoporous titania with Fe_2O_3 deposited in its pores [5], Degussa P-25 (a well known commercial catalyst), nanosized Fe_2O_3 inserted sonochemically into Degussa P-25. These measurements will be conducted on the solid powders. In addition it is our aim to conduct the same measurements on the *in-situ* catalytic reaction. Namely, the oxidation of ethanol under H_2O_2 [6], and the oxidation of cyclohexane under 1 atmosphere of O_2 [7]. These reactions are considered in our laboratory as calibration reactions for the study of various catalysts.

Mesoporous composites were also synthesized sonochemically in our laboratory. For example mesoporous SiO_2/TiO_2, and Fe_2O_3/TiO_2 have been prepared. We have obtained a stable structure with the highest titnia concentration ever reported (containing 40 % atoms of titnia). It is our aim to use EXAFS measurements to demonstrate that the skeleton of the mesoporous channels is composed from Si-O-Ti bonds and that the titania (or Fe_2O_3) is an integral part of the skeleton. This will done by comparing the EXAFS measurements of mesoporous silica, mesoporous titania, mesoporous Fe_2O_3 [8], and the composites mesoporous SiO_2/TiO_2, and mesoporous Fe_2O_3/TiO_2.

Experimental method

A. In Situ Catalysis.

The catalytic materials will be prepared in Israel. The solid samples will be taken with us to Grenoble. The weight obtained for each of the sonochemically prepared products amounts to hundred of milligrams per batch. There is therefore no shortage of this compounds and no need to save them. The measurements can be conducted in the absorption mode or even better in the emission mode. The materials (silica, titania, and iron oxide) are all safe materials and are being widely used in various industrial products. Their disposal at the end of the experiments will cause no problem. The experiment will be carried out in a quarts test tube whose length is 10 cm and its diameter is 5 cm. The total amount of materials is 6 cc. The amount of Fe_2O_3 is 25-50 mg. To guarantee that the catalytic particles will not precipitate at the bottom of the cell a stirrer is introduced in the test tube. The *in situ* catalytic experiments can be carried out in a glass test tube. The oxidation of cyclohexane is conducted at 70 ^{0} C under 1 atmosphere of O_2. It requires isobutyraldehyde as a cooxidant and minute amount of acetic acid. The oxidation of ethanol requires hydrogen peroxide. In both cases we expect to get these chemicals at Grenoble. The reaction will be followed for the first 6 hours. The composite mesoporous materials will be also brought from Israel and handled in the same way as the above-mentioned materials.

B. Composite mesostructures.

The EXAFS of the Ti and Fe edges have to be measured in these experiments in order to show that the Fe is part of the skeleton of the mesostructure and does not appear as nanoparticles deposited on the inner walls. Although these are trivial measurements we have tried to conduct these measurements in Bessy, Berlin. We were informed that the Ti or Fe K-edges (5 and 7 keV) couldn't be measured at Bessy. These experiments will be carried out on the solid substrate and the pellet will be prepared in Israel and taken with us on the plane. We will do the disposal of the pellet by returning it back to Israel. We have no experience with EXAFS measurements and therefore rejecting our project on the basis of our inability to describe the exact beamline, the monochromator, and the crystal required for the experiments will be just

Results expected

Describe the results expected from the measurements, their scientific (or technical) relevance, and how they relate to existing work on the topic.

We will try first of all to understand what changes does the mesoporous titania undergo upon depositing amorphous nanosized particles on its inner surfaces. In addition, the results will also shed light on the reaction site of a catalytic oxidation measured *in situ* and the changes in the neighborhood of the active sites during catalysis. The oxidation of hydrocarbons is a very basic reaction. Our catalytic amorphous Fe_2O_3 nanoparticles have already shown [3,4] superiority over other catalysts, and the current measurements will enable us to understand in depth its mechanism.

In a separate research we will learn on the structure of a composite mesostructure of silica and titania. It is essential to prove that the walls of the composite mesostructures are made a true alloy-like bonds, and are not a mixture of two oxides. Namely, chemical bonds are formed between the two oxides.

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