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Use of polyoxometalate catalysts in extraction coupled oxidative desulfurization

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In the last decade, much attention has been paid to the desulfurization of fossil fuels. Due to environmental regulations, fossil fuels have to be desulfurized to very low levels. Currently, the technology used for this purpose is hydrodesulfurization (HDS). An alternative approach to remove sulfur from fossil fuels is the oxidative desulfurization (ODS). In common, ODS sulfur compounds are oxidized to their corresponding sulfoxides and sulfones. These oxidation products are significantly more polar and can be removed from the fossil fuel by subsequent extraction. A promising class of catalysts used for ODS are polyoxometalates. The most common oxidizing agent used in ODS is hydrogen peroxide. Only in some cases oxygen can be used as oxidizing agent. In comparison to HDS, ODS can be performed at relatively mild reaction conditions. Temperatures from 40-120°C are sufficient for oxidative desulfurization. In our recent studies, we investigate extraction coupled oxidative desulfurization using different sulfur-containing compounds (benzothiophene, dibenzothiophene, 4,6-dimethyldibenzothiophene) in different oil matrices (aliphatic, aromatic moieties) as the model oil and water as the in-situ extracting agent containing the dissolved polyoxometalate catalyst and oxygen as the oxidant. Our studies show that all different sulfur-containing compounds can be completely removed from the oil matrix in a temperature range from 90-140°C at 20 bar oxygen pressure. Moreover, they can be fully oxidized to water-soluble sulfur compounds. These sulfur compounds are extracted in-situ into the aqueous catalyst solution. Hereby, sulfate is found to be the major sulfur component in the aqueous phase. The other aqueous sulfur compounds are found to be sulfoacetic acid, 2-sulfobenzoic acid and 2 (sulfoxy) benzoic acid. Other non-sulfur containing decomposition products are carbon dioxide, carbon monoxide, formic acid, acetic acid and oxalic acid. We can demonstrate that the oil matrix has a major influence on the performance of the desulfurization. Additionally, the stability of the organic moiety under reaction conditions was proven and no catalyst leaching into the organic phase takes place. We systematically investigated the influence of different parameters such as temperature, pressure, water/oil volume ratio, concentration etc., in order to improve our oxidative desulfurization system. Our optimization studies showed that high water/oil volume ratios and high amounts of catalyst improve desulfurization of the model fuel significantly.

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Synthesis and characterization of supramolecules and their application as a chemosensor for drugs

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The monitoring of pharmaceutical drugs in the environment is of great importance worldwide. For example, in Karachi, Pakistan due to contaminated water, six children died and about 200 fell ill in 2005. A large number of pharmaceutical drugs in highly alarming amount were found in different components of drinking water (surface water, drainage, and effluent) of Karachi in the microgram-per-liter range during bioassay directed chemical analysis. The photophysical evaluation of supramolecular organic molecules as optical probes for detection of water toxins has been recognized to be very selective, sensitive, and economical as compared to the previously used methodologies. Synthesis, characterization and molecular recognition properties of fluorene based supramolecular cleft is reported. The cleft molecule was prepared in a single-step with good yield (85% yield), by linking fluorene with 1-ethyl piperazine. The cleft molecule was carefully characterized using various spectroscopic techniques such as NMR and mass spectrometry. The supramolecular interaction of cleft with amoxicillin, 6APA, aspirin, captopril, cefotaxime, ceftriaxone, cefuroxime, diclofenac, penicillin, and cephradine was evaluated by fluorescent spectroscopy. The molecular recognition studies showed that amoxicillin selectively binds with cleft in the presence of other drugs. The analytical method developed for the supramolecular interaction of molecular cleft and amoxicillin was validated at varying pH, concentration and temperature during recognition process. Job's plots indicated that the stochiometry of the interactions between the cleft and the amoxicillin was 1:1.

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