Understanding Real World Catalysts: A Challenge for Spectroscopy and Engineering

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Introduction and Objectives

Detailed understanding of the structure of catalysts is required for a rational design of new or improved catalysts. Thereby the establishment of structure-performance relationships gained by studying catalysts at work is considered one of the key steps [1]. Furthermore, the development of appropriate in situ cells is decisive. The spectroscopic setup should resemble as much as possible the catalytic experiment [2,3]. Nevertheless, in most cases it is a compromise between the spectroscopic experiment and the real working conditions and engineering issues. Preferentially, for each study both the spectroscopic side and the engineering solution should optimised to finally find the best compromise.

Since in situ X-ray absorption spectroscopy (XAS) is a well-suited method for the establishment of structure-activity relationships, in this contribution different facets for the understanding of real world catalysts are outlined using XAS and related techniques. Additionally, structure-performance studies on gas sensors are presented to demonstrate that the concepts can also be transferred to related topics. Finally, the potential of time-resolved studies, new photon-in/out techniques and spatially resolved studies is outlined.

Results and Discussion

Structure of noble metals during catalytic partial oxidation of natural gas and total oxidation of methane: The partial oxidation of methane to hydrogen and carbon monoxide over Pt- and Rh-based catalysts [4] and the total combustion of hydrocarbons over Pd [5] are good examples for the importance of structural identification of catalysts in its working state during. The measurement of the catalytic performance is essential and for studies during the total oxidation of methane XRD, XAS and Raman spectroscopy were combined. In order to study the ignition of the catalytic partial oxidation of methane over Pt and Rh-catalysts as well as chemical oscillations over Pd-based catalysts measurements in the subsecond time scale were recorded in the QEXAFS scanning mode [6].

Hydrothermal synthesis of transition metal oxides and C-C coupling reactions over Pd-catalysts (Heck-reaction): The hydrothermal synthesis of metal oxides and the study of

sold/liquid reactions like Heck reactions require studying both the liquid and the solid phase. For this purpose a specially designed in situ cell was used. During the preparation of transition metal oxide catalysts both the evolvement of liquid species and the transformation of the solids could be monitored; the occurrence of intermediates was detected using the QEXAFS technique [7]. This approach together with special analysis tools also allowed gaining new insight into the Heck reaction starting with solid Pd-catalysts [8].

Understanding SnO_2-based gas sensors: A new cell and a special sensor device were designed to derive structure-performance relationships during gas sensing and the catalytic action of Pt and Pd promoters in SnO_2. Using a high resolution fluorescence detector for acquirement of the XAS data uncovered that the noble metal ions remain – in contradiction to previous studies – mostly in oxidized state under working conditions [9].

Spatially resolved studies: Spatially resolved studies become important if gradients occur in catalytic reactors and/or catalyst shaping comes into play [10]. This appears for example important during the catalytic partial oxidation of methane as well as time-resolved studies during the ignition of reactions (ref. [10,11]).

Significance

The case studies demonstrate not only the importance of in situ studies and the engineering of appropriate in situ cells. Equally important are the application of better time-resolution, new analysis methods and spatially resolved methods. This allows tracking the catalytic structure from its evolvement (preparation and activation), via its active state (structure-activity relationship) and finally deactivation and regeneration.

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