Chemical Imaging of Catalytic Solids at the Micron- and Nanoscale

B.M. Weckhuysen*
Debye Institute for Nanomaterials Science, Utrecht University,
*Sorbonnelaan 16, 3508 TB Utrecht, The Netherlands;*b.m.weckhuysen@uu.nl*

Introduction

Most characterization studies of catalytic solids focus on ensemble-averaged measurements, assuming that catalytic solids are spatially homogeneous materials when placed in a reactor. Structure-performance relationships can then be obtained by relating activity and selectivity with a multitude of spectroscopic signatures. However, these signatures are not necessarily identical across e.g. a catalyst grain or fixed bed reactor. Detailed knowledge on these spatial heterogeneities is required to better understand reaction and deactivation mechanism. This keynote lecture discusses the potential of spectroscopic methods for chemical imaging spatial heterogeneities within catalytic solids at the micron- and nanoscale. Special emphasis will be on the use of in situ Scanning Transmission X-ray microscopy (STXM), UV-Vis microscopy, synchrotron IR microscopy, Coherent Anti-Stokes Raman Scattering (CARS) microscopy and (confocal) fluorescence microscopy.

Results and Discussion

Two showcases will be discussed, namely Fe-based Fischer-Tropsch Synthesis (FTS) and H-ZSM-5 zeolites, catalyzing the oligomerisation of styrene and methanol to hydrocarbons. For the latter showcase, large coffin-shaped H-ZSM-5 crystals have been studied. During the liquid-phase oligomerization of styrene, carbocationic intermediates are formed that act as reporter molecules, which exhibit strong absorption, fluorescence as well as IR activity. Optical microscopy allows revealing a space- and time-resolved product formation, demonstrating a non-uniform catalytic behaviour [1]. Moreover, polarized light measurements showed that the product molecules are aligned within the straight pores of the zeolite. Complementary confocal fluorescence and CARS measurements visualized the 3-D distribution of respectively the products and reactants within an individual crystal [2]. By using synchrotron-based IR microscopy the chemical nature of these reaction products as well as their alignment within the zeolite pores could be unravelled [3].

The combined method was also employed to study the effect of mesoporosity, introduced via post-synthesis desilication, on the catalytic activity [4]. Apart from the visualization of the complex intergrowth structure of boat-shaped ZSM-5 crystals, it has been demonstrated that the introduction of intracrystalline mesoporosity facilitates the transport of styrene molecules inside the zeolite volume and limits the product formation to dimeric carbocation intermediates. This leads to a more uniform coloration and fluorescence pattern of the crystals. Moreover, using various styrene compounds, differing in their reactivity, a non-homogenously distributed Brønsted acidity over the crystals' volume has been demonstrated. More reactive styrene compounds react on both strong and weak Brønsted acid sites, giving rise to a uniform fluorescence pattern, whereas weaker acid sites are not capable of protonating the less reactive styrene compounds, therefore leading to fluorescence signals merely at locations of strong Brønsted acid sites. In a similar fashion it was possible to reveal reaction fronts and different pore accessibilities for the methanol-to-hydrocarbon reaction [5].

Another powerful experimental approach to study spatial heterogeneities within catalytic solids is STXM, revealing phase changes at the nanoscale and detailing the nature and location of carbon species under reaction conditions. In situ STXM has recently been applied to a SiO_2-supported Fe FTS catalyst [6]. It was found that the starting catalyst contains mainly α-Fe_2O_3 dispersed on SiO_2. After reduction in H_2 the catalyst shows significant compositional changes as Fe_2O_3 is completely converted into a mixture of Fe oxides and metallic Fe. More specifically, it was found that regions containing initially Fe_2O_3 were transformed into regions containing various amounts of Fe_3O_4, Fe_2SiO_4 and Fe^0. During the subsequent FTS reaction, the Fe_3O_4 phase is further converted to Fe^0 and Fe_2SiO_4. Interestingly, the developed method also allows characterizing the C species via its C K edge. It was found that the regions where Fe^0 was observed correspond with carbidic Fe. Furthermore, in regions where less Fe is present sp^3-like C deposits are observed, indicative for FTS reaction products. In a related study [7], the reduction behavior of the FTS catalyst in a flow of H_2 as probed with STXM was compared with the average oxidation state values obtained with temperature programmed reduction (TPR). The average oxidation state, determined by summing up the individual contributions of all STXM pixels, can be directly compared with the bulk average oxidation state as determined with TPR. A remarkable correspondence was found for these values indicating that in situ STXM allows revealing nanoscale differences in the redox behavior of a catalyst. However, these intricate differences can still be explained, as it should, in terms of the macroscopic behavior of the catalyst material.

Significance

Knowledge of spatiotemporal gradients in heterogeneous catalysts is of paramount importance for the rational design of new and more sustainable catalytic processes. Spatial heterogeneities occur at the level of e.g. catalyst grains (nm-µm scale) and active sites and metal (oxide) particles (Å—nm scale). This keynote lecture reports on the use of space and time resolved spectroscopic methods for imaging spatial heterogeneities at the micron- and nanoscale with special emphasis on the use of optical and synchrotron—based methods, their capabilities in providing space resolution, depth profiling and potential for single molecule/particle detection.

References

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