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Watching Catalysts in Action

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The rate of catalyzed chemical reactions is in general very dependent on the actual state and geometry of the catalysts surface. This state and geometry are very often dependent on the actual chemical environment the solid-state catalyst is exposed to. Electron microscopy in general and transmission electron microscopy (TEM) in particular gives unmatched detailed insight of the local chemical and structural state of the nanostructured catalysts. Adding the possibility of controlling the gaseous atmosphere around the studied sample at elevated temperature gives a unique way of watching catalysts in action.

The formation and stability of molybdenum carbide based catalysts for hydrodeoxygenation (HDO) of bio-oil has been addressed by environmental TEM (ETEM) and in situ XRD. The active molybdenum carbide has a strong tendency to oxidize at reaction temperature in presence of water (which is a product in the HDO reaction). The formation of Mo₂C from molybdenum oxide by carburization has been monitored by means of in situ XRD for further study in the ETEM. Gas-phase ETEM studies show that the active Mo₂C is fully embedded in an oxide layer during exposure to 300 Pa water vapour at 400°C as shown in Figure 1. Preliminary studies involving co-feeding of 220 Pa CH₄ in addition to the water vapour indicate a preventing effect on the surface oxidation, increasing the stability of the molybdenum carbide catalyst.

Unfortunately, the conversion of gas species in the catalytic reaction are not directly observable in ETEM. However, in the case of the process involving solid reactants as in soot oxidation, it is possible to follow the catalytic reaction by imaging the process by means of ETEM and thereby give direct visualization of the chemical reaction.

Soot particles in the exhaust from diesel vehicles are likely to cause lung cancer and to affect the climate both locally and globally. Soot particles are therefore typically removed from exhaust gases by filtration through a ceramic filter. However, increased fuel consumption due to filter regeneration demands development of soot oxidation catalysts that can lower the regeneration temperature. The heterogeneously catalyzed soot oxidation is a gas/solid/solid interaction; hence, the contact between soot and catalyst is very important for the catalytic activity.

Here, we have monitored the soot oxidation by a silver catalyst in situ in the ETEM by ramping the temperature in 300 Pa oxygen at identical rates as used in temperature programmed oxidation experiments. Small Ag particles are observed to be highly mobile at an oxidation temperature of approx. 350°C. The Ag particles travel throughout the soot partly oxidizing the carbon structures. A full oxidation of the soot is observed when the temperature reaches 700°C. Snapshots of the in situ temperature programmed soot oxidation are shown in Figure 2.
The exact pressure and temperature are essential parameters when quantifying catalytic processes. However, measuring those parameters at the sample where the chemistry is taking place is often hindered by geometrical limitations in the ETEM. By addressing this issue by means of Computational Fluid Dynamics calculations of the temperature and pressure profiles in a differential pumped ETEM as used in the above examples we show a good correspondence between the pressure and temperature at the catalysts sample and the gauges monitoring the parameters in the experimental setup.

Figure 1: Molybdenum carbide based catalyst for HDO before and after exposure to H₂O at 400 °C.

Figure 2. BF-TEM micrographs of in situ soot oxidation by a silver catalyst in the ETEM in tight contact condition. $P(O_2)=300$ Pa.