In situ TEM studies of catalysts for diesel engine exhaust abatement

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Publication date:
2010

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):
In situ TEM studies of catalysts for diesel engine exhaust abatement

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One of the most important areas in nanotechnology is catalysis, which is applied e.g. in environmental protection, fuel upgrading and supply of chemicals. In situ TEM has become a powerful tool in heterogeneous catalysis e.g. due to its ability to directly monitor catalysts during exposure to reactive gases at elevated temperatures. These years catalysts for diesel exhaust abatement receive increasing interest. The present contribution will therefore give examples of how in situ TEM can be applied to obtain a fundamental understanding regarding challenges in diesel emission exhaust reduction (e.g. nanoparticle sintering and removal of soot from the diesel engine exhaust).

The experiments are carried out using a CM300 FEG ETEM \cite{1}. Different model catalysts are exposed to an oxidizing gas environment at elevated temperatures, and time resolved images series monitor dynamical changes of the nanoparticles. To model e.g. a diesel oxidation catalyst, Pt nanoparticles are dispersed on a planar, amorphous Al\textsubscript{2}O\textsubscript{3} support. The Pt/Al\textsubscript{2}O\textsubscript{3} model catalyst is monitored during the exposure to 10 mbar air at 200-650°C as an approximation to the lean burn conditions of the diesel engine exhaust. To model soot deposited in a diesel particulate filter, a carbon black powder was mixed with a CeO\textsubscript{2} catalyst powder. The soot-CeO\textsubscript{2} samples were exposed to 2 mbar O\textsubscript{2} and a temperature in the interval 300-600°C. From in situ TEM images, quantitative measurements of the magnitude of the combined effects of the electron beam and the gas environment was obtained. This made it is possible to define experimental conditions where the beam effects are negligible.

The time-resolved in situ TEM image series directly reveal mechanistic information. For example the image series clearly show that sintering of the Pt nanoparticles is mediated by an Ostwald ripening process (fig 1a). Another series provide direct observations of soot particles during the CeO\textsubscript{2}-catalyzed oxidation process, and show that the reaction centers are closely confined to the soot-CeO\textsubscript{2} interface (fig 2). Furthermore, from the image series kinetic information is derived in such a way that the in situ TEM results become comparable either with results from other techniques or with kinetic models. Examples are: an activation energy barrier for catalytic soot oxidation or time-resolved particle size distributions for the Pt/Al\textsubscript{2}O\textsubscript{3} model catalyst (fig 1b).

References
1 P.L. Hansen et al., \textit{Adv. Catal.}, 50 (2006), 77
2 S.B. Simonsen et al., submitted 2009
3 S.B. Simonsen et al., \textit{J. Catal.}, 255 (2008), 1
Figure 1: (a) Time-lapsed TEM images recorded in situ of the same area of a Pt/Al₂O₃ model catalyst during exposure to 10 mbar air at 650°C. To guide the eye an example of a growing and of a shrinking particle is indicated with arrows. (b) Particle size distributions based on TEM images obtained in situ. A lognormal (left) and a Lifshitz-Slyozov-Wagner (LSW) (right) distribution are fitted to the data. Acquisition time after initiation of the experiment is indicated for each image and histogram. Scale bar = 10 nm. The figure is adapted from [2].

Figure 2: A time-lapsed ETEM image series of soot in contact with a CeO₂ catalyst acquired during the exposure to 2 mbar O₂ at 550°C. The time interval between the images is ~2min. Scale bar = 90 nm. The figure is adapted from [3].