Dynamic observation of nanocatalysts deformation during carbon nanotube growth in an environmental TEM

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Abstract

In situ observation of the formation of the carbon nanotubes by acetylene decomposition on Co catalysts inserted in mesoporous silica (SBA-15) was performed in an FEI Titan 80-300 environmental TEM equipped with an objective lens spherical aberration corrector[1]. Prior to acetylene decomposition, the catalyst nanoparticles were reduced *in situ* in a flow of hydrogen. Electron energy-loss spectra taken before and during reduction showed that the Co oxide nanoparticles were reduced to metallic Co. *In situ* high resolution TEM images were consistent with cubic Co. Two types of tubular carbon structures were observed: smaller nanotubes with internal diameters seemingly regulated by the size the Co nanoparticles formed within the SBA-15 pores and larger nanotubes. Real-time morphological changes of the catalyst were observed during growth (Figure 1) and are consistent with previously reported results on other catalysts[2,3]. The Co nanoparticle pulsated (elongated and contracted) during growth of the nanotube. This sequential elongation/contraction, which is often associated with the formation of a narrow neck, is thought to be responsible for the presence of small nanoparticles found within the nanotubes after growth. Consistency of these *in situ* results with *ex situ* carbon nanotube growth as a function of experiment conditions (T, P) and electron-beam damage during *in situ* growth will also be discussed.

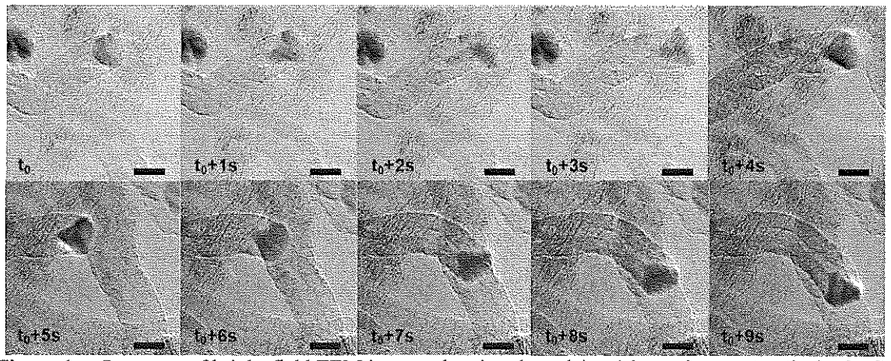

Figure 1. Sequence of bright-field TEM images showing the pulsing (elongation-contraction) of a Co nanoparticle during MWNT growth. (Scale bar: 10 nm).

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Noble metal catalyst reduction in hydrogen, a quasi and in-situ TEM study

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Abstract

$Pt/\gamma\text{-}Al_2O_3$ catalyst was reduced under H_2 at 250 °C in the quasi in-situ TEM mode. The results will be compared with in-situ TEM experiment using MEMS-based nanoreactor. The particle motion inside the nanoreactor during loading was studied using fluorescence microscope.

Introduction

Calcination and reduction are essential procedures in the activation and regeneration of catalyst. Knowledge about the reaction mechanism of the process is important to achieve optimum performance of the catalyst. Quasi in-situ is one method to study this mechanism [1]. The results will be compared with in-situ TEM experiments using MEMS-based nanoreactor [2].

Methods

The as-calcined $Pt/\gamma\text{-}Al_2O_3$ catalyst precursor was reduced under H_2 environment in the quasi in-situ mode, in which contact with air was avoided. A combination of a leak-tight U-shaped reactor and a TEM transfer sample holder were being used. The sample was transferred to the TEM holder inside a glove box. The influence of the reaction temperature was studied in detail by stepwise heating of the sample up to 250 °C and monitoring the changes in the particles for each step. For in-situ TEM experiment, the catalyst will be loaded into surface micromachined nanoreactor. In order to study the flow pattern as well as the motion of the particles inside the nanoreactor during the loading process, fluorescence tracer particles suspended in ethanol were loaded into the nanoreactor and visualized by means of flow visualization fluorescence microscopy.

Results and discussions

The quasi in-situ experiment was performed on the sample that was deposited on Quantifoil® microgrid carbon film on Au mixed mesh TEM grids which allows us to monitor the same particles during the experiment. Figure 1 shows that the PtOx particle size decreases after reaction under hydrogen at room temperature. Then the Pt particle size increases as the temperature increases.

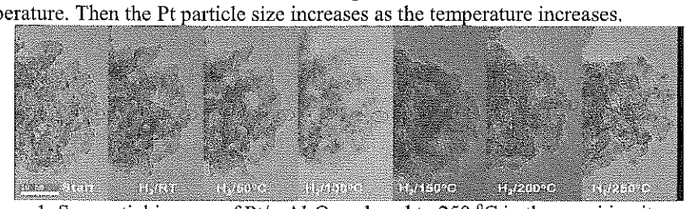

Figure 1. Sequential images of $Pt/\gamma\text{-}Al_2O_3$ reduced to 250 °C in the quasi in-situ mode.

The in-situ TEM experiment started with the study on the nanoreactor loading. The geometry and design of the nanoreactor affects the flow of the catalyst particles suspension (Figure 2). Flow visualization study on the behavior of the particles shows that drop loading in both inlet and outlet seems to be quite effective to load the particles onto the central area of the nanoreactor.

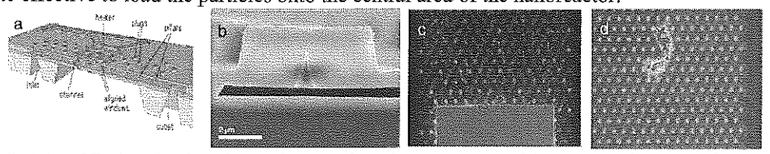

Figure 2. (a) A 3D sketch of surface micromachined nanoreactor, (b) cross section SEM image of the plug, (c) image of polystyrene particles flow inside the nanoreactor channel and (d) polystyrene particles during drying taken by fluorescence microscope.

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Quantifying Pt/Zeolite Y Hydrocracking Catalysts Using Electron Tomography and Image Analysis

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Abstract

Supported noble metal catalysts are of great importance to various industrial processes. In particular, the industrially relevant bi-functional zeolite supported Pt catalyst has been the subject of numerous studies. Assessing particle size distribution and their location within zeolite support is crucial for understanding the reaction mechanisms as well as for optimizing preparation procedures. To characterize such catalysts, usually bulk techniques are being used (EXAFS, NMR, H_2 chemisorption), while TEM is the most direct technique which enables visualization and manual measurement of Pt particles [1]. However, size measurement using common TEM micrographs is limited by low sampling and detection difficulties caused by overlapping features in 2D projections i.e. TEM micrographs. Therefore, we used electron tomography (3D-TEM) [2] coupled with image processing for a detailed characterization of the commercially available zeolite Y (Zeolyst CBV760) loaded with 1 wt% Pt.

Results

For the first time we were able to visualize, locate and measure thousands of Pt particles as small as 1 nm, extract valuable information (Figure 1) and compare the impact of preparation procedures (loading techniques, reduction temperatures) on particle sizes, particle locations and particle-particle distances. In all of the analyzed crystals prepared by incipient wetness impregnation (IWI), the Pt size distribution was narrow with a mean value of 1.0-1.3 nm, which matches the size of the zeolite Y micropore cavities. Careful observation of the reconstructed volumes suggests that most of the Pt particles were located inside the microporous crystalline regions, while only few of the largest (>4 nm) were in the mesopores. A homogeneous distribution of Pt particles was observed in all of the imaged zeolite crystals, however, calculated Pt loading varied among crystals from 0.2 to 8.4 wt% suggesting drawbacks of IWI procedures.

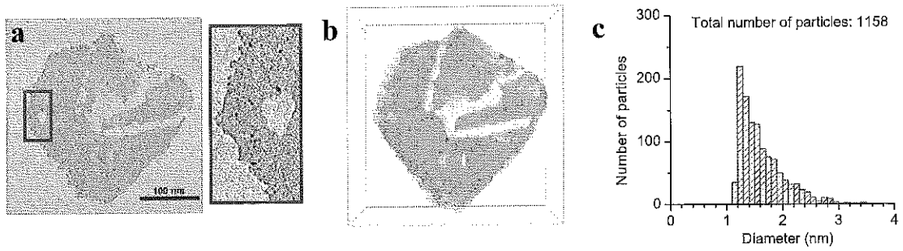

Figure 1. An example of an overloaded zeolite Y crystal with 2.6 wt% Pt: a) Virtual cross-section through the reconstructed volume, b) Volume rendered representation of the reconstructed crystal (green) with mesopores (white) and Pt particles (blue), c) Pt size distribution.

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Transmission electron microscopy characterization of photocatalysts for water splitting

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Abstract

As a result of diminishing fossil fuel reserves, there is an increasing need to switch energy dependence to renewable resources such as sunlight. Photocatalysts provide a viable route for converting solar energy into chemical bonds. In order to optimize the performance of such materials, it is necessary to understand the fundamentals of their reaction mechanisms, chemical behavior, structure and morphology before, during and after reaction using *in situ* investigations. Here, we focus on the *in situ* characterization of photocatalysts [1] in an environmental transmission electron microscope (ETEM) [2]. Such fundamental insight can be used for further material optimization with respect to performance and stability [3].

In this work, we combine conventional TEM analysis of photocatalysts with environmental TEM (ETEM) and photoactivation using light. A novel type of TEM specimen holder that enables *in situ* illumination is developed to study light-induced phenomena in photoactive materials at the nanoscale under working conditions.

Our experiments are aimed at exposing a specimen to light and detecting resulting microstructural and chemical changes using *in situ* TEM techniques. It is important to investigate photoactive materials under light illumination in order to remove the effects associated with handling of the specimen between *ex situ* reactions and TEM experiments. Two representative photoinduced phenomena are studied: the photodegredation of Cu_2O and the photodepositon of Pt onto a GaN:ZnO photocatalyst (Figure 1).

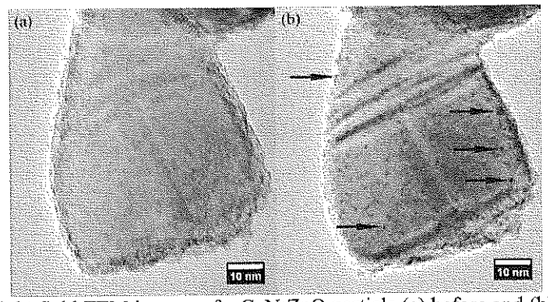

Figure 1: (a,b) Bright field TEM images of a GaN:ZnO particle (a) before and (b) after reaction in 5 mbar H_2O and with 6 W cm^{-2} light at 405nm wavelength.

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