Combined temperature-programmed reaction and *in situ* x-ray scattering studies of size-selected silver clusters under realistic reaction conditions in the epoxidation of propene

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The catalytic activity and dynamical shape changes in size-selected nanoclusters at work are studied under realistic reaction conditions by using a combination of simultaneous temperature-programmed reaction with *in situ* grazing-incidence small angle x-ray scattering. This approach allows drawing a direct correlation between nanocatalyst size, composition, shape, and its function under realistic reaction conditions for the first time. The approach is illustrated in a chemical industry highly relevant selective partial oxidation of propene on a monodisperse silver nanocatalyst. The shape of the catalyst undergoes rapid change already at room temperature upon the exposure to the reactants, followed by a complex evolution of shape with increasing temperature. Acrolein formation is observed around 50 °C while the formation of the propylene oxide exhibits a sharp onset at 80 °C and is leveling off at 150 °C. At lower temperatures acrolein is produced preferentially to propylene oxide; at temperatures above 100 °C propylene oxide is favored. © 2009 American Institute of Physics. [doi:10.1063/1.3237158]

The catalytic performance of nanometer size catalysts has been the subject of extensive theoretical and experimental studies within the catalysis and surface science communities.^{1–4} However, in order to elucidate the structure-reactivity relationship in catalysis, well defined particles as well as the use of industrially relevant supports are required.^{5,6} In addition to the high-precision fabrication of the catalysts, the catalyst's activity needs to be followed under realistic reaction conditions and the evolution of catalyst's size and shape be monitored during the course of the reaction using *in situ* characterization tools.^{6,7}

This communication focuses on gaining a direct correlation between nanocatalyst size and shape and its catalytic properties by combining unique methods of (1) size-selected nanocatalyst synthesis, (2) mass spectrometry, and (3) *in situ* imaging of size-selected nanocatalysts at work under realistic reaction conditions.

Deposition of size-preselected clusters from molecular beams is an ideal method for preparing a wide palette of nanostructures and compositions on virtually any surface, for example, highly uniform model nanocatalyst systems.^{1,2,8} The present monodispersed silver clusters were produced using an arc cluster ion source.⁹ The subsequent mass separation of the desired cluster size was achieved by an electrostatic quadrupole deflector. As support material, a 3 ML (monolayer) thick amorphous alumina film prepared by atomic layer deposition on the top of a naturally oxidized silicon wafer was used.^{2,8,10} The lateral diameter and number of the supported clusters were determined by high-resolution scanning electron microscopy (SEM) on a Zeiss Field Emission SEM. Supra VP55 apparatus (Fig. 1) yielding 23.3 nm mean value and 1.6 nm width distribution at an average particle density of 1.8×10^8 clusters/cm².

Grazing incidence small angle x-ray scattering (GISAXS) was used to determine cluster size and shape during temperature-programmed reaction (TPRx). This technique has been proven to be very powerful to study particles

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FIG. 1. SEM image of the silver nanocatalyst as deposited, with average particle size of 23.3 nm and width distribution of 1.6 nm.

at surfaces and their transformations under vacuum conditions and low-pressure reactive gas environment at the nanometer^{2,11,12} and the subnanometer⁸ scales. GISAXS is sensitive to particles in the surface region and in addition to particle size, it provides particle size distribution, distance between particles and average aspect ratio of metal particles.^{2,8,12,13} The GISAXS experiments were performed at the 12-ID of the Advanced Photon Source using x rays of 12.0 keV energy in a reaction cell of our own design. The cell was sealed with mica windows and mounted on a computer controlled goniometer. As shown in Fig. 2, the x-ray beam was scattered off the surface of the sample near the critical angle ($\alpha_c=0.18$) of the substrate. A 1024×1024 pixel two-dimensional Marresearch MAR160 CCD camera was used for recording the GISAXS images from the sample. GISAXS data were collected as a function of reaction temperature and time. The two-dimensional x-ray images were analyzed by taking cuts in the q_y direction for horizontal information and in the q_z direction for vertical information. Scattering vectors q are calculated from $(4\pi/\lambda)\sin\theta_f$, where θ_f is the scattering half angle and λ is the wavelength of the x rays.^{2,12} Based on the high uniformity of the silver clusters and assuming a spherical shape, the data were analyzed by the Guinier analysis,¹⁴ providing

FIG. 2. Schematic of GISAXS experiment: incident angle $\alpha_i=0.18^\circ$ and scattered beam angle α_f .

the horizontal and vertical particle radii of gyration R_{gH} and R_{gV} , respectively. The diameter and height of the nanoparticles can be calculated from the radii of gyration as $2.58R_{gH}$ and R_{gV} , respectively. The aspect ratio of the particles is given as R_{gH}/R_{gV} .

The reactants used were gases at 1% concentration in He, the ratio for C_3H_6 and O_2 was kept 2:1 by preparing the mixture in a remotely controlled gas-mixing unit consisting of calibrated mass flow controllers (Brooks model SLA5850). The reaction cell was operated in a continuous flow mode at 133 kPa pressure and 30 SCCM (SCCM denotes cubic centimeter per minute at STP) gas flow. The products were analyzed using a differentially pumped mass spectrometer (Pfeiffer Vacuum Prisma QMS 200); the reaction rates were calculated using calibrated gas mixtures and the count of deposited clusters. The temperature of the catalyst was controlled using a ceramic heater (Momentum Performance Materials Inc.) allowing heating of samples up to 600°C . The sample temperature was measured with a K -type thermocouple attached to the edge of the heater surface. To achieve thermal equilibrium between the heater and sample during the application of a temperature ramp, a low heating rate ($<1.5^\circ\text{C}/\text{min}$) was used.

The evolution of the particle aspect ratio determined from GISAXS during the experiment is depicted in Fig. 3. In Fig. 3(a) the first data point (square) represents the aspect ratio of the clusters under pure helium with average diameter (21.3 nm) and height (13.6 nm) as determined by GISAXS, before introducing the reactant gas mixture. The lateral dimension of the clusters determined from GISAXS is in very good agreement with the mean cluster diameter determined

FIG. 3. (a) Square: aspect ratio of silver nanoclusters in pure helium atmosphere at room temperature. Triangles: time-dependent change in the aspect ratio after the introduction of the propene and oxygen mixture. (b) Triangles: temperature-dependent aspect ratio of the silver nanocatalyst. (c) Triangles: time-dependent aspect ratio at constant 200°C . Star: aspect ratio after cooling back to room temperature.

from SEM. The second data point reveals an abrupt and remarkable change at room temperature of the silver nanoparticle shape immediately after admitting propene and oxygen into the reaction cell, followed by a monotonic increase in the aspect ratio during the 30 min observation at room temperature. An increasing aspect ratio hints at a flattening of the silver particles, most probably driven by a significant change in the surface and interface energy, as reported by Hansen *et al.*¹⁵ for Cu nanoparticles with similar sizes. With increasing temperature, first no notable change in cluster aspect ratio is observed up to approximately 60 °C, when cluster aspect ratio starts to decrease [Fig. 3(b)]. After reaching 200 °C, no further change in particle aspect ratio is observed during an additional hour of the reaction at constant 200 °C [Fig. 3(c)]. The star in Fig. 3(c) represents the aspect ratio of the particles after cooling back to room temperature.

No indication of sintering was observed based on GISAXS data, which was confirmed by SEM performed after the reaction, yielding an unchanged particle size of 23.1 ± 0.5 nm. To identify the cause of shape change observed at room temperature, a series of experiments was performed with various gas compositions containing only oxygen, only propene, or a mixture of both reactants. Having only oxygen present in the helium carrier gas no noticeable change in cluster aspect ratio was detected. However, a mixture of propene with oxygen in helium or propene alone induced the same changes in cluster shape, which indicates that propene induces changes in the cluster shape at room temperature. This is supported by an earlier study of Argo *et al.*,³ revealing that propene ligands cause changes in interatomic distances in clusters and affect cluster/support interaction in Ir/Al₂O₃ and Ir/MgO catalysts. Moreover, Nijhuis *et al.*¹⁶ found significant adsorption of propene to titania-supported gold nanoparticles and the formation of bidentate propoxy species being a critical step in the epoxidation of propene on Au/TiO₂. The binding of ligands may alter the surface energy of the nanoparticle and the strengths of the interaction at the nanoparticle-support interface inducing dramatic shape changes similar to the observations by Hansen *et al.*¹⁵

As far as the temperature-dependent shape change above 60 °C is concerned, in addition to the interaction of the reactants with the clusters several other factors can be considered, such as the change in the chemistry of the support and surface oxide formation on the silver clusters. The alumina surface is OH terminated¹⁷ with water adsorbed on it. As reported, water starts to desorb from a hydroxylated α -alumina surface at 47 °C, reaching maximum desorption rates at 102 °C.¹⁸ In a control experiment, desorption of water from our support was observed as well, which may also cause morphology changes in nanoparticle morphology. Moreover, partial dehydroxylation of the support during the reaction can affect support-metal particle interactions which may lead to changes in particle morphology as well.¹⁹ Another possible factor leading to morphology changes is the reduction and reoxidation of the surface of the metal clusters during the reaction.^{20–23}

To study the catalytic activity, we measured the production of propylene oxide as a function of temperature. Figure

FIG. 4. Top: rate of propylene oxide (circles) and acrolein (triangles) formed per surface silver site as a function of temperature. Bottom: temperature-dependent selectivity toward propylene oxide (solid) and acrolein (stripes).

4 shows the rate of propylene oxide and acrolein formation per surface silver atom after correction to background signal levels. The background ion signal intensities for propylene oxide and acrolein measured on a blank alumina support were below 4% and 15% of the corresponding ion signals in the presence of the silver nanocatalyst, respectively. The intensity of the ion signal of CO₂ was flat over the entire temperature range.

The catalyst exhibits a sharp onset of activity at around 50 and 80 °C for acrolein and propylene oxide, respectively, with the propylene oxide formation leveling off at 150 °C. No further change in activity was observed during an additional hour of reaction at constant 200 °C. Acrolein formation is preferred to propylene oxide formation at temperatures up to 100 °C; at higher temperatures propylene oxide production prevails. It is noteworthy that the onset of catalytic activity takes place in the identical temperature range as the change in cluster shape (cf. Fig. 3). Moreover, 150 °C is the temperature at which a formation of subsurface oxygen in silver with molecular oxygen was reported on silver catalysts.^{21,24} The role of oxygen on silver particles in oxidation reactions was described in several papers,^{21,22,24,25} including oxide formation²⁶ (see above).

The epoxidation of propene on silver catalysts with molecular oxygen has been a topic of a large number of papers, including the role of promoters. These catalysts possess low conversion and poor selectivity toward propylene oxide.^{23,27,28} However, it is not clear whether the intrinsic properties of the silver nanoparticles or wide distribution of silver particle sizes are the main cause of the poor selectivity

reported by Zemichael *et al.*²³ for unpromoted and *K*-promoted silver catalysts. Moreover, the used *K* promoter also affected the size of silver particles formed, producing 20–40 nm or 4–70 nm size distributions with and without the promoter, respectively. Similar effect of promoter on the particle size was also reported by Yao *et al.*²⁸ A very elegant illustration of the size effect and possible reaction channels in silver-mediated propene oxidation was reported by Roithova and Schroder²⁹ on gas-phase Ag₂O⁺ clusters—the smallest model of silver epoxidation catalysts—revealing a competing C–H bond activation channel resulting in poorer selectivity toward epoxide formation.

In conclusion, we have shown that the combination of size-selected cluster deposition, TPRx and *in situ* x-ray scattering techniques, allows the catalytic properties of size-preselected catalyst to be studied while simultaneously monitoring the evolution of particle shape under realistic reaction conditions. As an example we have investigated the reactivity of 23 nm sized silver clusters in the epoxidation of propene. Our approach revealed that the silver clusters are highly fluxional, reversibly changing their shape depending on the environment even at room temperature. The shape changes were accompanied by distinct changes in the acrolein and propylene oxide formation during the reaction. This demonstrates the promising potential of this new approach, where the catalytic activity of nanocatalysts is accompanied by dramatic changes in their shape and thus, opens new ways to elucidate the correlation between catalyst function and catalyst size, composition, and shape.

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