Dependence of Hydrogen Peroxide Decomposition on the Size of Catalytic Gold Nanoparticles

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Introduction

Due to its environmental friendliness, H_2O_2 is a desirable oxidizing reagent in the chemical industry. Formation of H_2O_2 as a target product in the direct synthesis from H_2 and O_2 and as a reaction intermediate for in situ selective hydrocarbon oxidant over Au-based catalysts is actively studied [1]. One of the main challenges is that catalysts that are efficient in H_2O_2 synthesis are also active in its decomposition [2]. In order to deconvolute the reaction mechanism, it is useful to study H_2O_2 decomposition separately [3]. In this work, the dependence of H_2O_2 decomposition on the size of Au nanoparticles was studied with kinetic measurements, surface-enhanced Raman spectroscopic (SERS) measurements and density functional theory (DFT) calculations.

Materials and Methods

Four Au/SiO_2 catalysts were prepared in order to evaluate Au particle size effects using monodisperse 5, 50, 100 and 400 nm Au particles (Figure 1). Kinetics of H_2O_2 decomposition over the Au/SiO_2 catalysts were measured in a batch reactor at room temperature. In situ SERS measurements for identification of reaction intermediates on Au were performed with H_2O_2 and D_2O_2 using a laser with the 632.8 nm excitation wavelength. DFT calculations were performed with the DMol^3 code in Materials Studio software by BIOVIA using Au_5, Au_{13}, and Au_{55} clusters, and periodic unit cells of Au(211) and Au(111), which allowed evaluation of Au particle size effects.

Results and Discussion

The rate of H_2O_2 decomposition increased with decreasing Au particle size (Figure 2). When a blank experiment was conducted in the absence of Au, the rate of H_2O_2 decomposition was dramatically lower over the SiO_2 support. The in situ SER spectra collected after 15 min of reaction time for the 50 and 400 nm Au/SiO_2 in Figure 3 exhibit four bands. The band at 590 cm^{-1} was observed only for the 400 nm Au particles and assigned to ν_s(O-Au-O) of an atomic oxygen structure, based on results of the DFT calculations. The band at 822 cm^{-1} was assigned to ν(O-O) of OOH surface species on Au. This assignment was confirmed with D_2O_2 measurements: the band due to OOD surface species shifted to 824 cm^{-1}. The band at 875 cm^{-1} is due to ν(O-O) of liquid-phase H_2O_2 (877 cm^{-1} for D_2O_2). DFT calculations suggest that because of weak adsorption, the band for H_2O_2 adsorbed on Au overlaps with the band for liquid-phase H_2O_2 and, as a result, was not observed. Finally, the constant band at 940 cm^{-1} is due to the SiO_2 support.

Since the spectroscopic results in Figure 3 show the presence of OOH species on Au surfaces under reaction conditions, reaction energies for decomposition of H_2O_2 to OOH and H were evaluated on model Au surfaces with DFT calculations. The computational results

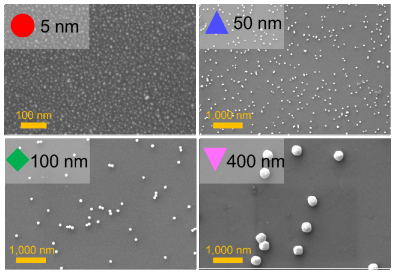

Figure 1. SEM images of catalysts with monodisperse Au particles supported on SiO_2: 5, 50, 100 and 400 nm Au particles.

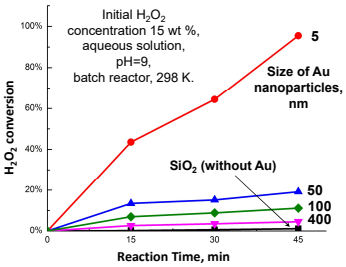

Figure 2. Kinetic measurements for H_2O_2 decomposition over Au/SiO_2. The results for the SiO_2 support (without Au) are included for comparison.

Table 1. DFT calculated reaction energies for O-H bond splitting, H_2O_2* + *= OOH* + H*, kJ/mol.

Au_5	Au_{13}	Au_{55}	Au(211)	Au(111)
Particle size decreases ←				
-70	-1	80	82	122

in Table 1 demonstrate that adsorbed H_2O_2 becomes progressively less thermodynamically stable on Au surfaces with decreasing size of Au particles (from the flat surface of Au(111), representing very large Au particles, to progressively smaller Au particles), explaining the activity trend in Figure 2.

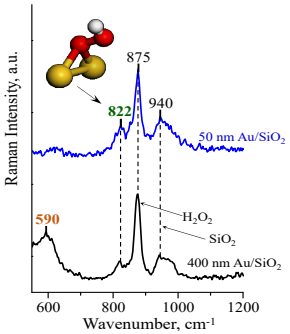

Figure 3. In situ SER spectra collected after 15 min of reaction time for the 50 and 400 nm Au/SiO_2.

Significance

Kinetic measurements with monodisperse Au nanoparticles showed that the rate of H_2O_2 decomposition increases with decreasing size of the Au particles. Ultra-high sensitive SERS measurements for the first time allowed direct in situ observation of an OOH intermediate on Au surfaces during H_2O_2 decomposition. By comparing calculated and experimental vibrational frequencies, DFT calculations with vibrational analysis allowed for the determination of structures and relative stability of surface species as well as better interpretation of the experimental spectra.

References

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