Adsorption and Decomposition of Methanol on Au Nanoclusters Supported on a Thin Film of Al_2O_3/NiAl(100)

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Methanol has been investigated because of its potential as a logistic fuel and a feed for a fuel cell. Their diverse mechanisms of decomposition on various surfaces and involving stable surface intermediates make this molecule special for investigations in surface science. As part of various methanol conversions – steam reforming, partial oxidation etc. – the decomposition of methanol as a source of hydrogen attracts intensive researches. On the other hand, oxide-supported Au nanoparticles were shown recently to have a greater catalytic activity for many reactions, encompassing oxidation of CO and hydrocarbons, water-gas shift and NO reduction. The potential of Au catalysts in fuel cells and related processing of hydrogen fuel has thus drawn attention; but little is known about the decomposition of methanol on Au catalysts. For detailed mechanisms, model systems are in great demand, to which our present work responds.

Our work has focused on the adsorption and decomposition of methanol on Au nanoclusters supported on an ordered Al_2O_3/NiAl(100) thin film. The morphology and structure of the surface and clusters were characterized with a scanning tunneling microscope and reflection high energy-electron diffraction. The adsorption and temperature-dependent decomposition of methanol were characterized by photoelectron spectroscopy with synchrotron radiation. To elucidate the effects of cluster size and structure on the methanol decomposition we grew the Au clusters by vapor deposition as a function of coverage (0.05-2.9 monolayer (ML)) and temperature (300-570 K) of the substrate. The methanol was adsorbed at 120 K; we investigated the temperature dependence of methanol decomposition by increasing the sample temperature in a stepwise manner and recording a photoelectron spectrum of the reaction mixture on the surface at each temperature step. The behavior of methanol is reflected in the temporal variation of C 1s photoelectron spectra. The results show that adsorption sites on the clusters are of two kinds: one activates the decomposition via scission of the O-H bond into CO at a temperature below 120 K, whereas the other does not. The CO on the active sites remains on the surface below 250 K, begins to desorb above 250 K and decomposes into elemental C (or mixed with some CH_x) around 350 K. The methanol on the inert sites either desorbs or dehydrogenates into methoxy with increasing sample temperature. All carbon species can be desorbed from the surface at 450 K, a temperature much lower than for other metals, implying that carbon-induced poisoning can be readily suppressed on the Au clusters. The reactivity also exhibits a dependence on the morphology of the cluster: clusters with 1-2 atomic layers do not catalyze efficiently the methanol decomposition.

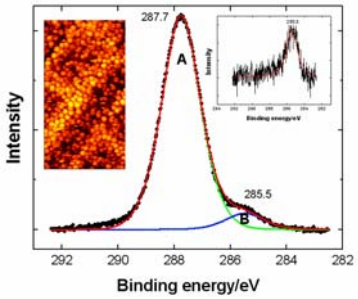

Figure 1. C 1s spectrum obtained from methanol (1 L) adsorbed on oxide-supported Au nanoclusters (2.9 ML) at 120 K and fitted with two Gaussian-Lorentzian peaks centered at 287.7 and 285.5 eV respectively. The insets are the C 1s spectrum for 1 L CO adsorbed on the oxide-supported Au nanoclusters (2.9 ML) at 120 K and the STM image for the 2.9 ML Au nanoclusters. The spectra were recorded at 120 K.

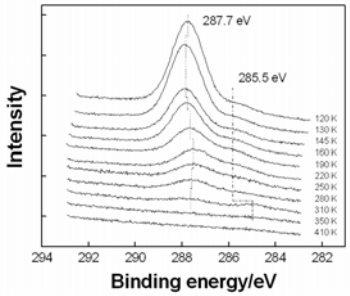

Figure 2. typical C 1s spectra for methanol (1 L) adsorbed on oxide-supported Au clusters (2.9 ML) at 120 K and annealed to specified temperatures (for 1 min). Each spectrum was recorded when the surface was cooled to 120 K after annealing to the indicated temperature.

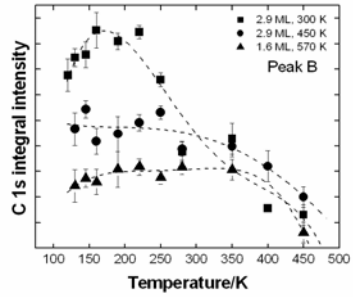

Figure 3. Variation of integral intensity of peak B with annealing temperature for methanol (1 L) adsorbed on Au nanoclusters grown on an Al_2O_3/NiAl(100) thin film at 300, 450 and 570 K. The spectra were recorded when the surface was cooled to 120 K after annealing to the indicated temperature. The dash lines are drawn to indicate the trends and the errors bars indicate possible errors due to fitting.