# Methanethiol chemistry on TiO$_2$-supported Ni clusters

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## ABSTRACT

The thermal decomposition of methanethiol on Ni clusters grown on TiO$_2$(110) was studied by temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and low energy ion scattering (LEIS). On all of the Ni surfaces investigated, methane and hydrogen were observed as gaseous products in the TPD experiments, and the only sulfur-containing species that desorbed from the surface was methanethiol itself at low temperatures. The two pathways for methanethiol reaction were hydrodesulfurization to produce methane and nonselective decomposition, which leaves atomic carbon and sulfur on the surface. From high resolution XPS studies, methyl thiolate was identified as the surface intermediate for reaction on TiO$_2$ and on all of the Ni surfaces investigated, similar to what is observed on single-crystal Ni surfaces. However, the binding sites for methyl thiolate on the 1 ML (monolayer) Ni clusters were different from those on the Ni clusters at coverages of 2.5 ML and higher, based on the S(2p) binding energies for methyl thiolate. No distinct changes in activity or selectivity were observed for the smaller Ni clusters grown at low coverage compared to the more film-like Ni surfaces other than what could be accounted for by changes in total surface area. Interactions between the Ni clusters and the TiO$_2$ support had two main effects on chemical activity. First, carbon was oxidized by oxygen from the TiO$_2$ lattice to produce CO at temperatures above 800 K. Second, annealing induced encapsulation of the Ni clusters by reduced TiO$_x$ and chemisorbed oxygen. At 800 K, the Ni clusters were totally encapsulated, resulting in a complete loss of methanethiol activity; partial encapsulation at 700 K caused a smaller decrease in activity accompanied by increased oxidation of carbon by lattice oxygen.

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## 1. Introduction

The chemistry of sulfur-containing molecules on transition metal surfaces has long been a topic of interest for understanding catalysts used in hydrodesulfurization reactions [1,2]. In particular, methanethiol has been well-studied as a probe molecule for hydrodesulfurization reactions on single-crystal Ni surfaces like (111) [3–5], (110) [6], and (100) [7–10], since Ni is an important component in desulfurization catalysts [11–17]. Methanethiol reactions have also been investigated on other transitions metal surfaces, including Mo(110) [18], Ru(0001) [19], Fe(110) [20], W(100) [21], and Pt(111) [22]. In almost all cases, methyl thiolate has been found to be the main intermediate formed from S–H bond scission at low temperatures. Upon heating the surfaces, methyl thiolate undergoes hydrodesulfurization to produce gaseous methane and nonselective decomposition to produce hydrogen gas and atomic carbon on the surface; both reaction pathways result in atomic sulfur left on the surface. For the Ni surfaces, the selectivity for hydrodesulfurization is ∼80% [4,6], but this value drops to

∼50% on Mo(110) [18,23], ∼40% on Pt(111) [24] and 30% on W(001) [25]. On Pt(111), CH$_2$S has been reported as a reaction intermediate in nonselective decomposition processes [22,24], and on Mo(110), gaseous methyl radicals have been observed in addition to methane [23].

In work reported here, the thermal chemistry of methanethiol is investigated on Ni clusters supported on TiO$_2$(110) as a function of Ni cluster size, coverage and interactions with the titania support. A number of studies have shown that clusters can exhibit activity different from the bulk surfaces due to particle size effects [26–30], differences in active sites [31–33], and interactions between the clusters and the supports [34–38]. Titania is a support of particular interest since highly reducible metal oxides like titania are known to strongly interact with transition metal clusters [39–43]. In addition, titania is one of the few bulk oxides that can be made semiconducting for scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and low energy ion scattering (LEIS) studies simply by heating in ultrahigh vacuum. In this process, oxygen preferentially desorbs from the crystal as O$_2$, resulting in an n-type semiconductor.

The chemistry of methanethiol has been studied by TPD and XPS on the supported Ni clusters with Ni coverages ranging from

0.25 to 5 ML. At temperatures below 600 K, the surface activity of all Ni clusters is similar to that on the single-crystal Ni surfaces; methanethiol is the surface intermediate formed at low temperature, and methane and hydrogen are the gaseous products, with atomic carbon and sulfur remaining on the surface below 700 K. For Ni coverages of 1–5 ML, the selectivity for methane production is 80%, and nonselective decomposition accounts for the remaining 20% of reaction. There is evidence that the 1 ML Ni clusters have different sites for methyl thiolate adsorption compared to the 5 ML Ni clusters. However, the selectively for methane production remains at 80% for coverages between 1 and 5 ML, and total reactivity of the surfaces appears to scale with Ni surface area. The major difference between methanethiol chemistry on the clusters compared to on single-crystal Ni surfaces is that interactions with the titania support influence chemical activity. For example, atomic carbon is oxidized by lattice oxygen from $TiO_2$ to produce gaseous CO at temperatures above 700 K. The extent of CO production increases with increased interactions between the Ni clusters and titania in the form of partial encapsulation of the clusters by $TiO_x$ and chemisorbed oxygen. Furthermore, the complete encapsulation of the Ni clusters after heating to 850 K results in total loss of activity for methanethiol reaction. This result is consistent with previous work in which Ni encapsulation was proposed to be the cause of the loss of activity for dimethyl methylphosphonate decomposition on titania-supported Ni clusters [34].

## 2. Experimental

All experiments except for the high resolution XPS were conducted in two ultrahigh vacuum chambers ($P \leqslant 1.5 \times 10^{-10}$ Torr) that have been previously described. In the first chamber, temperature programmed desorption (TPD) studies were carried out with a Hiden HAL 301/3 F quadrupole mass spectrometer [44]. In second chamber, an Omicron variable-temperature STM (VT25) was used for imaging the Ni clusters, while LEIS and XPS studies were carried out with an Omicron EA 125 hemispherical analyzer [34,45–47].

The rutile $TiO_2(1\,1\,0)$ surface was prepared by $Ar^+$ sputtering for 15 minutes at a beam energy of 1 kV and 2–5 µA current to the sample, followed by heating to 950 K for 5 min. The resulting surface exhibited a sharp ($1 \times 1$) LEED pattern and was free of surface contamination, as established by Auger electron spectroscopy and XPS. The reoxidized $TiO_2$ surface was prepared by exposing the crystal to a pressure of $5 \times 10^{-8}$ Torr of oxygen via a directed dosing tube for 10 min at 900 K and then heated to 500 K. The surfaces were exposed to a saturation dose of methanethiol at 100 K via a directed dosing tube using exposures that resulted in a base pressure rise of $1.2 \times 10^{-10}$ Torr for 15 s. In all TPD experiments, the surface was exposed to a saturation dose of methanethiol at 100 K and heated in front of the mass spectrometer at a rate of 2 K/s; the sample was biased at $-100$ V to avoid damage from electrons coming from the mass spectrometer ionizer.

High resolution XPS experiments were carried out at the U7a beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory in an ultrahigh vacuum chamber that has been described in detail elsewhere [48–50]. Data for the S(2p) region was collected at a beam energy of 250 eV at a step size of 0.04 eV and dwell time of 1 s. The absolute binding energies were calibrated by setting the energy corresponding to the rise in the valence band edge to zero.

Fitting of the S(2p) region was carried out with a shareware program called XPSPEAK41, which used a Shirley background and Gaussian–Lorentzian peakshapes. The energy separation of the S($2p_{3/2}$) and S($p_{1/2}$) peaks was fixed at 1.2 eV, and the two doublet peaks were also assumed to have identical values for FWHM. The

FWHM values were 0.7–0.8 eV for atomic sulfur, 0.8–1.0 eV for methyl thiolate and 1.0–1.2 eV for methanethiol.

In the first chamber, Ni was deposited using a homemade evaporator, in which a pure Ni wire was heated to evaporation temperatures by passing current through tungsten wire wrapped around the Ni. In the second chamber and U7a endstation, Ni was deposited with an Oxford Applied Research evaporator (EGCO4) via electron bombardment of a pure Ni rod. Ni depositions were carried out at a rate of 0.25 ML/min at room temperature, and coverage was monitored with a quartz crystal microbalance. One monolayer is defined as the packing density of the Ni(1 1 1) surface ($1.613 \times 10^{15}$ atoms/cm$^2$). Before all TPD and XPS studies, the Ni surfaces were flashed to 500 K to remove any CO that adsorbed during the deposition process. This 500 K flash did not change the morphology or activity of the Ni clusters, as shown by STM, XPS and TPD experiments.

For the STM studies, tips were prepared by electrochemical etching of 0.38 mm diameter tungsten wire, and images were collected with a tunneling current of 0.1 nA and sample bias of +2.0 V. Average cluster heights reported here are based on measurements from a set of at least 20 clusters. LEIS experiments were carried out with 1.0 keV $He^+$ ions. An Al K$\alpha$ anode was used for the XPS studies, and the angle between the detector and the sample was 70° off normal to enhance surface sensitivity. XPS and LEIS spectra were collected with a 0.2 s dwell time and a step size of 0.02 eV and 0.5 eV, respectively.

## 3. Results

### 3.1. Scanning tunneling microscopy studies

STM images of the various Ni surfaces studied here are shown in Fig. 1 as a function of coverage and annealing temperature. We report only height as a measure of cluster size because the diameters of the clusters are known to be overestimated by a factor of ~2 due to tip convolution effects [51], and furthermore the clusters formed at higher coverage do not have regular shapes with distinct diameters. At the lowest coverage of 0.1 ML, three-dimensional clusters are formed with an average height of 6.9 ± 1.7 Å following room temperature deposition (Fig. 1a). Although many of the clusters are found at step edges, nucleation also occurs on the terraces. The deposition of 1 ML of Ni produces clusters with an average height of 16 ± 2 Å (Fig. 1b). When the coverage is increased to 2.5 ML, the average cluster height increases to 18 ± 2 Å, and there is also a significant increase in the width of the features, which no longer have distinct circular footprints due to cluster coalescence that produces more irregular shapes (Fig. 1c). At 5 ML, the average feature height further increases to 20 ± 3 Å, and the clusters are much more irregular in both the size and shape due to extensive cluster coalescence; this surface begins to resemble a Ni film rather than individual clusters (Fig. 1d). When the 1 ML Ni clusters are heated to 850 K, an increase in average cluster height to 20 ± 3 Å is accompanied by a decrease in cluster density. Heating the 2.5 ML Ni clusters to 850 K does not preserve the identity of individual clusters. Instead, large features with heights of 27 ± 4 Å coexist with smaller, partially coalesced clusters so that the surface has the appearance of large particles supported on a rough film. After heating the 5 ML Ni clusters to 850 K, there is a substantial increase in both the height (43 ± 8 Å) and diameter of the clusters (Fig. 1e).

### 3.2. Temperature programmed desorption studies

#### 3.2.1. On TiO₂(1 1 0)

The reaction of methanethiol was initially carried out on titania and oxidized titania in order to understand potential reactivity on the support surface itself. On both the oxidized (Fig. 2, bottom) and