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Obstruction by CO of the decomposition of methanol on Pt nanoclusters on a thin film of Al_2O_3/NiAl(1 0 0)

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ABSTRACT

Obstructed decomposition of methanol by CO on Pt nanoclusters deposited from the vapor onto thin-film Al_2O_3/NiAl(1 0 0) was studied with various surface probe techniques. The Pt clusters had mean diameter about 2.3 nm and height about 0.4 nm, and grew with phase fcc and primarily in the (1 1 1) orientation. CO adsorbed molecularly on the Pt clusters to saturate the sites atop Pt, and methanol was subsequently adsorbed for the reactions. The probability of dehydrogenation of methanol co-adsorbed with CO on the clusters was about half that of methanol not so co-adsorbed; CO molecules produced from dehydrogenated methanol adsorbed in a conformation with the C—O bond nearly parallel to the surface. In contrast, the CO obstructed less effectively the scission of the C—O bond of methanol: the probability of that scission was decreased only 20–30%. CO with atomic hydrogen produced from dehydrogenated methanol on the clusters exhibited a comparable obstructive effect, even though the produced CO occupied only the reactive sites on the clusters. The comparison indicates also that the inactive sites of the clusters comprise primarily terrace Pt.

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1. Introduction

The catalyzed decomposition of methanol (CH_3OH) on platinum (Pt) has been investigated extensively because the key reaction is applied in direct methanol fuel cells (DMFC), which offer a prospect of efficient conversion of methanol to electricity [1–5]. The performance of DMFC is, however, degraded by CO-like reaction intermediates. To improve the performance, understanding the effect of reactive sites blocked by CO is essential. Model systems, such as Pt single crystals or supported Pt films, have been applied to achieve an understanding of the reaction mechanism at an atomic level [6–23], but the poisoning effect [15] and the contrast between real Pt catalysts and single-crystal model systems remain poorly understood. To gain insight into the poisoning effect with a realistic model system, we investigated the effect of CO on the decomposition of methanol on oxide-supported Pt nanoclusters.

The Pt nanoclusters were grown by vapor deposition of Pt onto a thin film of Al_2O_3/NiAl(1 0 0) at 300 K under ultrahigh vacuum (UHV) conditions. The morphologies and structures of the Pt clusters had been previously characterized with a scanning tunneling microscope (STM), reflection high-energy electron diffraction (RHEED), infrared reflection absorption spectroscopy (IRAS) and temperature-programmed desorption (TPD). The Pt clusters had mean diameter about 2.3 nm and stature near 0.4 nm [24–27], and grew with phase fcc and primarily in the (1 1 1) orientation (denoted as Pt(1 1 1) clusters) [26,27]. These Pt clusters had a mean lattice parameter about 4.2 Å, expanded about 7% with respect to bulk Pt [26,27]. The IRAS and TPD spectra of CO as a probe showed that CO adsorbed preferentially on atop Pt sites and that the surface of the Pt clusters consisted of both low-coordinated and terrace Pt sites [27]. As the intensities of the infrared spectral lines of CO increased linearly proportional to those of the corresponding CO TPD spectra, the infrared intensity served as a measure of the number of surface sites [27].

The obstructive effect of CO was explored on exposing the Pt clusters first to CO to saturate the Pt atop sites and then to methanol for the reactions. These processes were monitored with TPD and IRAS, and compared to those from pristine Pt clusters. Our previous studies on pristine Pt clusters showed that 60–70% of the adsorbed monolayer methanol decomposed and reacted through either dehydrogenation to CO or scission of the C—O bond [27]. The dehydrogenation was dominant and on average, one CO was produced per surface Pt site for a monolayer of methanol on Pt clusters; the scission of the C—O bond occurred primarily in methanol itself and the intermediate methyl preferentially formed methane

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on combining with atomic H from the dehydrogenation [27]. The present experiments on the CO-saturated Pt clusters show that the quantity of monolayer methanol adsorbed was comparable to that on pristine clusters; the methanol decomposed primarily through dehydrogenation to CO and secondarily through scission of the C—O bond, as on pristine clusters. The probability of dehydrogenation was decreased about half, and the produced CO adsorbed with a tilted C—O bond; the scission of the C—O bond was less hindered — the probability was decreased by only 20–30%. The obstructive effect is evidently weaker than that on a Pt(1 0 0) single crystal [15], for which the probability of dehydrogenation decreased more than 80%. The obstructive effect of the intermediates from the decomposed methanol, primarily CO and atomic hydrogen, was investigated for comparison; we found a similar effect, and also that the inactive sites of the clusters consist primarily of terrace Pt.

2. Experimental

Our experiments were performed in UHV chambers with a base pressure 4×10^{-10} Torr. A NiAl(1 0 0) sample (MaTeck GmbH) was polished to a roughness less than 30 nm and an orientation accuracy better than 0.1°. To obtain a clean surface, the sample underwent alternative cycles of sputtering and subsequent annealing before each experiment. The cleanliness of the sample was monitored with Auger electron spectroscopy, low-energy electron diffraction and STM. An ultra-thin θ-Al_2O_3 film was formed on oxidation of a NiAl(1 0 0) alloy surface at 1000 K; the formation of Al_2O_3 thin films is described elsewhere [28–31]. To achieve a homogeneous crystalline Al_2O_3 surface with no NiAl facets [31,32], we refrained from protracted post-oxidation annealing of the oxide films. The content of amorphous oxide surface was negligible [31] and the grown θ-Al_2O_3 thin film had thickness 0.5–1.0 nm [28,31]. The sample was then quenched to 300 K for vapor deposition of Pt from an ultra-pure Pt rod heated by electron bombardment in a commercial evaporator (Omicron EFM 3). The rate of deposition of Pt was fixed about 0.1 ML/min, calculated according to the coverage prepared at 300 K [24–26]. The coverage was estimated from the volume of the Pt clusters observed with STM; 1 ML corresponds to density 1.5×10^{15} atoms/cm^2 of fcc Pt(1 1 1) surface atoms. After the deposition, the sample was cooled to the desired adsorption temperature (100 K, unless specified). Methanol gas and CO were dosed by a doser pointing to the sample, with a background pressure 2–5 $\times 10^{-9}$ Torr. The methanol and methanol-d_4 (Merck, purity 99.8%) was additionally purified by repeated freeze-pump-thaw cycles. We report methanol exposures in Langmuir units: 1 L = 10^{-6} Torr s.

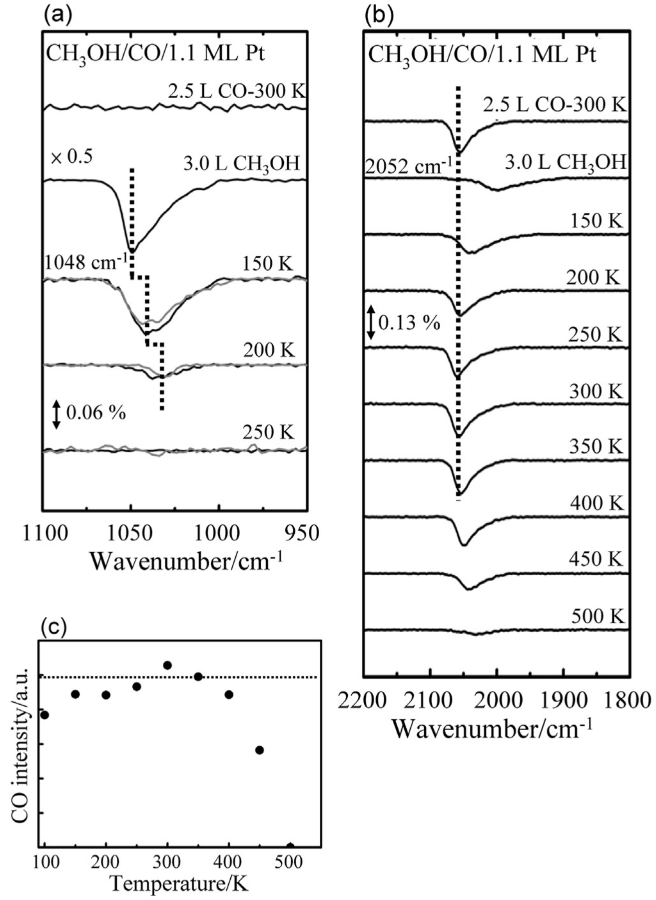

Fig. 1. (a) IRAS spectra of C—O stretching mode of methanol for 1.1 ML Pt clusters on Al_2O_3/NiAl(1 0 0) first exposed to 2.5 L CO at 100 K and annealed to 300 K, and subsequently exposed to 3.0 L CH_3OH and annealed stepwise to selected temperatures; (b) shows the corresponding CO IRAS spectra and (c) plots the integrated intensity of the CO IRAS spectrum as a function of temperature. The gray lines in (a) are for comparison, from 1.1 ML Pt clusters/Al_2O_3/NiAl(1 0 0) exposed to 3.0 L CH_3OH at 100 K and annealed to selected temperatures as indicated. The dotted line in (c) indicates the integrated intensity of CO IRAS spectrum from 1.1 ML Pt clusters/Al_2O_3/NiAl(1 0 0) exposed to 2.5 L CO at 100 K and annealed to 300 K.

STM images (recorded with a RHK UHV 300 unit), constant-current topographies, were obtained at 90 K with a sample bias voltage typically 2.8–3.2 V and a tunneling current 0.1–0.2 nA. The STM tip consisted of an electrochemically etched tungsten wire. TPD spectra were taken by ramping the sample at 3 K/s and monitoring the various masses on a quadruple mass spectrometer (Hiden), which was shielded and placed close (about 2 mm) to the sample. IRAS spectra were collected using a Fourier transform infrared spectrometer (FTLA 2000) with external optics aligned for an incident angle 75° from the sample normal, and a liquid nitrogen-cooled HgCdTe detector. The IRAS spectra are presented as a ratio of data of sample and oxide surface (or Pt clusters) measured at the same surface temperature (100 K), and are typically the average of 256 scans at resolution 4 cm^{-1}.

3. Results and discussion

3.1. Obstruction by molecularly adsorbed CO

To ensure the same features as those in previous work (described above) [24–27] were retained, we examined the structural and morphological features of Pt clusters on a thin film of Al_2O_3/NiAl(1 0 0) with STM, RHEED and IRAS. To assess the obstructive effect of CO on methanol decomposition on the Pt clusters, we saturated the surface of the Pt clusters with CO and then adsorbed methanol for subsequent reactions. The saturation with CO was performed on exposing the clusters to 2.5 L CO at 100 K and annealing the sample to 300 K; this annealing induced no CO desorption but CO molecules became adsorbed in an optimal conformation [27]. Fig. 1(a) shows IRAS spectra of the C—O stretching mode for methanol on CO-saturated 1.1 ML Pt clusters (denoted as Pt$_{\text{-CO}}$ clusters) annealed to selected temperatures (black lines). The exposure of 3.0 L methanol is sufficient to develop an entire monolayer of methanol on either the thin film Al_2O_3/NiAl(1 0 0) or the Pt clusters. The top line for only CO adsorbed on the sample exhibited no signal in this regime; on adsorbing methanol at 100 K, a broad and asymmetric line appeared, with maximum at 1048 cm^{-1}, due to multilayer methanol, and an extension to about 1020 cm^{-1}, attributed to monolayer methanol. This feature resembles those for methanol on Pt, Au clusters and a thin film of Al_2O_3/NiAl(1 0 0) [27,33]. The signals at 1020–1030 cm^{-1} were not simply assigned to methoxy or other intermediates, because

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