Methyl Nitrite Adsorption as a Novel Route to the Surface Methoxy Intermediate

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Surface-bound methoxy species are intermediates in a variety of surface processes, ranging from heterogeneous catalysis to advanced fuel cells, yet their chemistry on many metals remains elusive because of the difficulty of cleanly preparing adsorbed layers of these species. We propose that thermal dissociation of an adsorbed precursor, methyl nitrite (CH_3ONO), can be used to produce methoxy species on reactive metal surfaces at low temperatures. On two Pt−Sn alloys, the methoxy intermediate is strongly stabilized (to 300 K) against thermal decomposition compared to Pt(111), where dissociation occurs at below 140 K, and there is a high selectivity to produce formaldehyde. These Pt−Sn alloys do not form the CO and H_2 dissociation products characteristic of methoxy chemistry on Pt(111).

Introduction

Probing the chemistry of the methoxy intermediate on transition metal surfaces is important for understanding Fischer−Tropsch and selective partial oxidation catalysis[1,2] and also advanced fuel cell technologies utilizing methanol.[3] This species has been identified and studied on a variety of metal surfaces,[4−7] yet there are many key examples where little or no information exists owing to the difficulty in preparing and trapping methoxy species. For example, methanol is reversibly adsorbed and does not thermally decompose on Pt(111) surfaces following low-temperature adsorption under ultrahigh vacuum (UHV) conditions,[8,9] except at defect sites.[6] In most past studies, preadsorbed oxygen was used as a Bronsted base to abstract a proton from methanol and produce surface-bound methoxy. This chemistry also occurs on Pt(111),[7] but of course all studies of the reactivity of methoxy prepared in this manner are dominated by the presence of large amounts of coadsorbed oxygen or hydroxyl species. While pyrolysis sources of methyl radicals can be used fairly easily to prepare surface methyl groups,[10] it is much more problematic to make clean intense beams of methoxy radicals, and so new, more general methods are needed to prepare adsorbed layers of methoxy species on reactive metal surfaces. We wish to report the results of a novel approach that utilizes the thermal decomposition of adsorbed methyl nitrite to produce surface methoxy species at low temperatures. We use this opportunity to study the reactions of this intermediate on two well-defined Pt−Sn surface alloys. Pt−Sn alloys generated interest in the past as possible electrocatalysts for methanol oxidation,[11,12] even though recent studies show that the use of these alloys inhibits[13] the rate of methanol oxidation. Our new method is an important development for surface science studies of methoxy on Pt−Sn surfaces because methanol does not decompose on these alloys under UHV conditions[9] and because it is very difficult to generate preadsorbed oxygen on the surface owing to the fact that dioxygen does not dissociatively adsorb on these surfaces.[14]

Experimental Section

Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD) studies were performed in a well-equipped stainless steel UHV chamber.[15,16] The two Pt−Sn alloy surfaces were prepared by vapor deposition of Sn onto a Pt(111) crystal and an annealing procedure that has been discussed.[17−20] The p(2 × 2) Sn/Pt(111) surface alloy has Sn as one-fourth of the surface atoms, eliminating adjacent pure-Pt 3-fold hollow sites. The ($\sqrt{3} \times \sqrt{3}$)R30° Sn/Pt(111) surface alloy has Sn as one-third of the surface atoms, eliminating all pure-Pt 3-fold hollow sites. For simplicity we will refer to these structures as the (2 × 2) and $\sqrt{3}$ alloys, respectively. Methyl nitrite was prepared from methanol, H_2O, H_2SO_4, and HSO_3ONO according to an accepted method[21] and purified by three successive distillations at −25 °C under nitrogen flow through a glass distillation column. The sample was further purified to remove noncondensable impurities at 77 K using liquid nitrogen and freeze−pump−thaw cycles. The purity was checked using both gas-phase infrared spectroscopy[22] and in-situ mass spectrometry. Gas exposures were given with the sample at a temperature below 100 K and are reported in units of langmuirs (10^{-6} Torr·s) after the measured doses were multiplied by a factor of 115 to account for the multicapillary array doser enhancement. The alloy surfaces were checked with AES and LEED following each TPD experiment to determine that no irreversible adsorbate-induced reconstruction occurred.

Results and Discussion

Figure 1 shows TPD spectra following the adsorption and reaction of methyl nitrite on the (2 × 2) alloy surface. Chemisorption of methyl nitrite is partially reversible (30%), and some methyl nitrite desorbs molecularly at 267 K. (The low-temperature peak near 140 K arises from desorption of physisorbed species condensed on top of the chemisorbed monolayer.) NO and two important products of surface reaction, formaldehyde and methanol, also desorb in TPD. The NO yield indicates that 70% of the chemisorbed methyl nitrite undergoes facile dissociation to form coadsorbed NO and methoxy. Formaldehyde was identified by recording TPD spectra for cracking fragments at m/e = 30, 28, and 12, and it desorbs from this surface in a broad peak at 280 K that is rate-limited by the dissociation of methoxy species on the surface. This conclusion is based on a previous study showing desorption of formalde-

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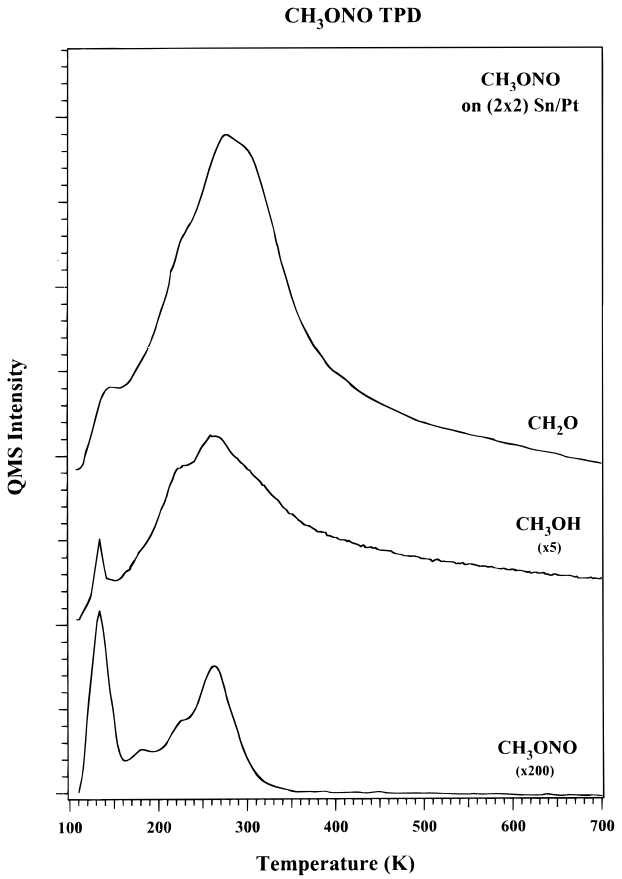

Figure 1. TPD spectra of several products following the adsorption of methyl nitrite (CH_3ONO) on the (2 × 2) Sn/Pt(111) surface alloy at 100 K for an exposure slightly larger than monolayer coverage.

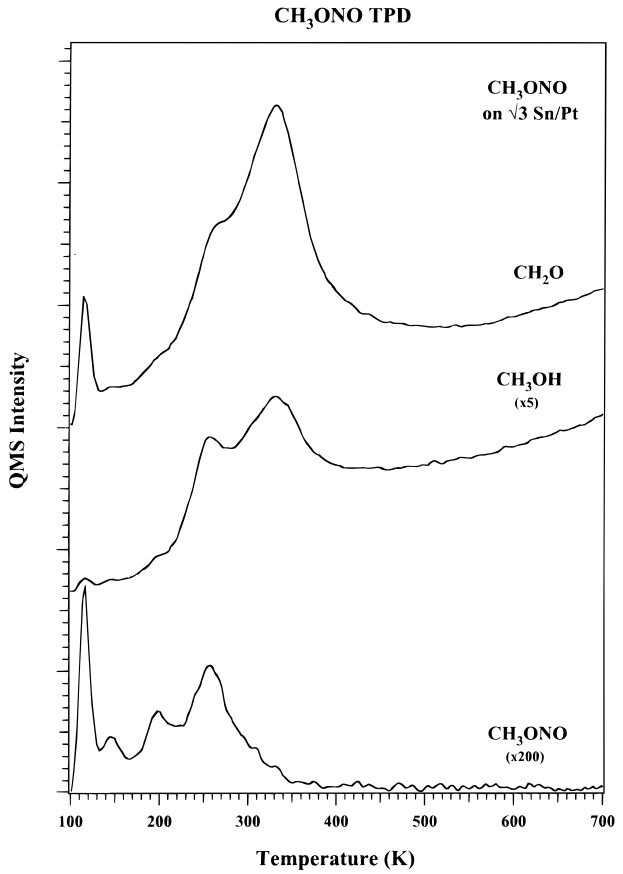

Figure 2. TPD spectra of the main desorption products following the adsorption of methyl nitrite (CH_3ONO) on the $\sqrt{3}$ Sn/Pt(111) surface alloy at 100 K for an exposure slightly larger than monolayer coverage.

hyde at 250 K following formaldehyde adsorption on Pt(111)[23] and our observations that alloying Sn into the Pt(111) surface reduced the adsorption energy for all adsorbed molecules studied to date.[9,15,24−26] Along with this dehydrogenation product, methanol is formed from the hydrogenation of surface methoxy and desorbs in a broad TPD peak at 270 K. This temperature is coincident with the primary desorption peak of methyl nitrite, but it is easy to show that this feature arises primarily from a methanol reaction product and not simply from a cracking fraction of methyl nitrite by subtracting an appropriately scaled (using the multilayer peak) methyl nitrite TPD spectrum from the methanol curve. CH_3OH desorbs at 186 K following CH_3OH adsorption on the (2 × 2) Sn/Pt(111) surface alloy,[9] and so methanol desorption in Figure 1 is reaction rate-limited. NO desorption following NO adsorption on the (2 × 2) alloy[27] occurs in a peak at 240 K. This is the same temperature observed for NO evolution from methyl nitrite decomposition on the (2 × 2) alloy.[26] Thus, 240 K is an upper limit on the temperature for methoxy formation from methyl nitrite decomposition. However, the O−NO bond must break at lower temperatures because the (2 × 2) alloy is more reactive than the $\sqrt{3}$ alloy (where NO is evolved from methyl nitrite decomposition at 217 K, vida infra) but less reactive than Pt(111) where methyl nitrite decomposition occurs below 140 K.[28] In stark contrast to Pt(111),[28] thermal decomposition of methoxy on the (2 × 2) surface alloy does not produce any H_2 or CO in TPD.

TPD spectra following the adsorption of methyl nitrite on the $\sqrt{3}$ Sn/Pt(111) surface alloy are presented in Figure 2. The chemistry of methyl nitrite on this surface is similar to that on the (2 × 2) alloy—methoxy is formed from the dissociation of methyl nitrite at below 220 K and undergoes both dehydrogenation and hydrogenation to form formaldehyde and methanol, respectively, upon further heating in TPD. In addition, desorption of about 40% of the chemisorbed methyl nitrite layer occurs in several CH_3ONO TPD peaks up to 255 K. NO formed from methyl nitrite decomposition on this surface desorbs in a TPD peak at 220 K, which is identical to that following NO adsorption on the $\sqrt{3}$ surface,[27] and this establishes an upper limit for the methoxy formation temperature since this NO peak is desorption rate-limited. The formaldehyde produced from methoxy decomposition desorbs mainly in a peak at 330 K (the shoulder at 260 K results from cracking of CH_3ONO). Methanol desorption also occurs primarily in a peak at 330 K, showing a shoulder at 260 K because of cracking of CH_3ONO. The desorption of both formaldehyde and methanol are reaction rate-limited by the decomposition of methoxy, and the higher temperature evolution of these two products on this alloy illustrates the effect of surface Sn to increase the thermal stability of methoxy intermediates.

The utilization of methyl nitrite as an adsorbed precursor for the preparation of methoxy intermediates on such surfaces is based on the well-known gas-phase chemistry of methyl nitrite and the existence of a weak O−NO bond (42 kcal/mol).[29] This bond is dramatically weakened in adsorbed methyl nitrite on reactive metal surfaces owing to the surface stabilization of the adsorbed NO and methoxy products of decomposition. Our observations reported here and those on Pt(111)[27] of thermal activation of methyl nitrite at low temperatures to produce NO and coadsorbed methoxy are consistent with this picture, and methyl nitrite should be useful for a number of reactive metal surfaces as an adsorbed precursor for methoxy. The novel use

of methyl nitrite in this regard here enabled us for the first time to characterize the chemistry of methoxy species on oxygen-free Pt(111) and the influence of alloyed Sn on the chemistry of methoxy intermediates on well-defined Pt−Sn alloys. The Pt(111) surface is very reactive toward methoxy, decomposing it below 160 K,[28] with a barrier below 9.5 kcal/mol. Rehydrogenation of surface methoxy is not a strongly activated process on Pt(111) (<11 kcal/mol), and a small, low-temperature methanol evolution was observed in our TPD studies. However, the main pathway for methoxy on Pt(111) is complete dehydrogenation, forming CO and H_2 desorption products. On the two Pt−Sn alloys studied here, methoxy species are thermally stable to much higher temperatures than on Pt(111), i.e., 280−330 K, with a barrier to methoxy decomposition of 15−16 kcal/mol, and these alloys show a hugh difference in selectivity for the products of methoxy decomposition compared to Pt(111). Dehydrogenation of methoxy on the alloys yields formaldehyde and adsorbed hydrogen that efficiently hydrogenates methoxy to form methanol. Both formaldehyde and methanol are reversibly adsorbed under these conditions, and no evolution of CO or H_2 occurs. Our results also provide a lower limit on the barrier to formaldehyde decomposition of 15−16 kcal/mol to form either formyl species or CO on these two alloys. The decreased reactivity of the $\sqrt{3}$ alloy compared to the (2×2) alloy observed for methoxy reactions owing to the increase in the surface Sn concentration and removal of all of the pure-Pt 3-fold sites is consistent with the general picture of Pt−Sn chemistry that we are developing.[25]

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