

**Thermal Activation of *t*-Butyl Nitrite on Pt(111):
t-Butoxy Dehydrogenation and Oxametallacycle Formation**

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Abstract

The adsorption and thermal reactions of *t*-butyl nitrite, $t\text{-C}_4\text{H}_9\text{ONO}$, on Pt(111) are reported. $t\text{-C}_4\text{H}_9\text{ONO}$ is a good source for *t*-butoxy, $t\text{-C}_4\text{H}_9\text{O}$, on surfaces because of the weak (171.1 kJ/mole) RO–NO bond. $t\text{-C}_4\text{H}_9\text{O}$ is the simplest alcohol which lacks of more reactive $\alpha\text{-C-H}$ bonds, and therefore the surface chemistry is of interest. $t\text{-C}_4\text{H}_9\text{O}$ is also a good candidate source for oxametallacycle species when it dehydrogenates on surfaces.

This study shows the facile dissociation of $t\text{-C}_4\text{H}_9\text{O-NO}$ bond upon adsorption at 115 K. During heating to 200 K, some $t\text{-C}_4\text{H}_9\text{O}$ dehydrogenates at the β -carbon to form an oxametallacycle species that dehydrogenates further upon heating to 300 K. The vibrational modes of the oxametallacycle was acquired by HREELS at 250 K, and was compared with the density functional theory (DFT) calculation results of several candidate oxametallacycle species. Based on the comparison, the oxametallacycle is identified as a 4-membered ring species with only one Pt atom participating. The desorption products are $t\text{-C}_4\text{H}_9\text{OH}$, H_2 , and NO. Three $t\text{-C}_4\text{H}_9\text{OH}$ desorption peaks indicate different hydrogenation mechanisms, which are hydrogenation of both $t\text{-C}_4\text{H}_9\text{O}$ and oxametallacycle. The competition between hydrogenation and dehydrogenation results in variations of $t\text{-C}_4\text{H}_9\text{OH}$ desorption peak distributions as a function of initial coverage. Finally, a reaction path potential energy diagram was constructed.