The Nature of the Surface Species Formed on Au/TiO$_2$ during the Reaction of H$_2$ and O$_2$: An Inelastic Neutron Scattering Study
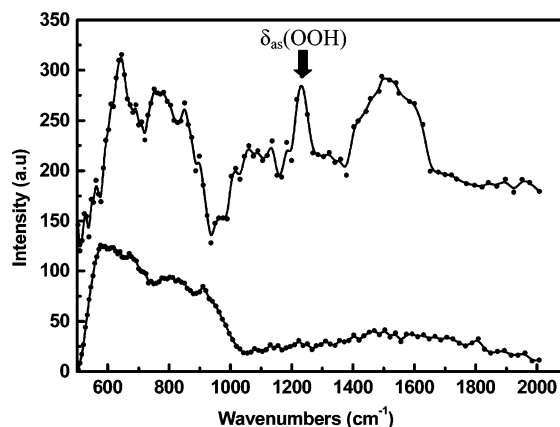
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While gold has historically been viewed as an unreactive, noble metal, recent studies have shown that supported nanosized, Au catalysts exhibit high catalytic activity for a variety of reactions.[1−5] One of the most technologically interesting of these reactions is the vapor phase epoxidation of propylene.[6] Since the conventional manufacturing methods for the synthesis of propylene oxide (an important chemical feedstock) involve multiple-step processes using either chlorohydrin or hydroperoxide as an oxidant,[7] its synthesis directly from molecular oxygen has long been sought. Recent studies have shown that nanosized Au clusters can effectively catalyze the direct vapor-phase conversion of propylene to propylene oxide using molecular oxygen and hydrogen.[3] Unfortunately little mechanistic information related to this highly complex reaction is available. An important goal in defining the mechanistic pathway of any reaction is to determine the nature of the surface species/ intermediates present under reaction conditions. It has been postulated in the literature[8,9] (but never demonstrated) that on nanosized Au clusters hydrogen and oxygen react to form one or more hydrogen peroxide/surface hydroperoxy species, which then further react with propylene to form propylene oxide.[3] The primary objective of this study was to spectroscopically identify the nature of the surface species formed during the H$_2$−O$_2$ reaction and thereby gain insights into the propylene epoxidation mechanism. Also, Landon[10a] et al., have recently shown that hydrogen peroxide can be directly synthesized from H$_2$/O$_2$ using a Au catalyst. Since the direct vapor-phase hydrogen peroxide synthesis from H$_2$ and O$_2$ is also an industrially important reaction, the reaction studied herein is also of obvious interest for understanding this process. Vibrational spectroscopy by inelastic neutron scattering (INS) is used to provide the first direct spectroscopic evidence for the formation of a hydroperoxy species during the vapor-phase H$_2$−O$_2$ reaction on nanosized Au catalysts.

The highly dispersed Au catalyst was synthesized by the deposition−precipitation (DP) of Au(OH)$_3$ onto TiO$_2$ (Degussa P-25) at pH = 7 using an aqueous solution of HAuCl$_4$. The precursor was washed several times, dried, and calcined at 673 K for 3 h. By using this synthetic method small Au clusters with uniform dispersion were obtained. The cluster size distribution was measured using a STEM (JEOL 2100), and the average cluster size was determined to be approximately 1.8 nm. Prior to reaction the catalysts were reduced in flowing hydrogen (30% in helium) at 773 K (defined as high-temperature reduction, HTR) for 4 h followed by calcination in flowing oxygen at 673 K (defined as low-temperature calcination, LTC) for 0.5 h. This pretreatment was

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Figure 1. (Top) INS spectrum of Au/TiO$_2$ reacted with H$_2$ and O$_2$ at 523 K for 4 h in flowing H$_2$:O$_2$:He (1:1:7). (Bottom) INS spectrum of water at 523 K adsorbed on Au/TiO$_2$ for comparison.

employed to obtain highly dispersed nano-Au particles.[10b] The reactor was then cooled to room temperature.

For the INS experiments, the catalyst was first treated by carrying out the reaction in a stainless steel reactor at 423 K for 4 h in flowing H$_2$:O$_2$:He (1:1:7). Following this, H$_2$ and O$_2$ gases were stopped and cooled under flowing He for 15 min; the reactor was quenched in a liquid nitrogen bath and mounted while cold onto a closed-cycle refrigerator. Background spectra were collected independently for a sample pretreated by HTR and LTC. Reference spectra of water adsorbed directly onto the Au/TiO$_2$ catalyst were also collected under identical conditions. All INS spectra were collected on the filter difference spectrometer (FDS) at the Lujan Center of the Los Alamos Neutron Science Center at Los Alamos National Laboratory.[11]

Figure 1 shows the INS spectrum (T = 20 K) of Au/TiO$_2$ quenched after reaction with H$_2$, O$_2$, and He. (The INS spectrum of the bare catalyst has been subtracted.) The features in Figure 1 can be assigned to water, a hydroperoxy radical either bound to the surface or complexed with water and/or hydrogen peroxide itself. Vibrational frequencies have been reported for the free hydroperoxy radical[12] and for the hydroperoxy−water complex.[13] The hydroperoxy radical and its complex with water have also been treated theoretically in ab initio studies,[14−15] while INS spectra of adsorbed water molecules have been observed on various surfaces including oxides.[16] Peak positions from the INS spectra are listed in Table 1 along with vibrational frequencies of the relevant species reported in the literature.

The relatively sharp band at 1230 cm^{-1} is attributed to the δ_{as}-(OOH) mode of the hydrogen peroxide species. This mode is assigned at 1266 cm^{-1} in the gas phase and at 1274 cm^{-1} in an Ar

Table 1. Comparison of the Observed INS Vibrational Frequencies (cm^{-1}) With Those of Water, Hydrogen Peroxide, the Hydroperoxo−Water Complex (Calculation) and the Hydroperoxo Radical (Calculation and Experiment)

assignment	INS	H_2O_2		$HO_2 \cdots H_2O$	HO_2	HO_2
	(this work)	(gas)	(inAr) 17	(calcd) 15	(calcd) 14	(matrix) 13
torsion	215	314		101		
water librations	630					
$\delta(HO \cdots H)$	690			679		
water librations	770					
	835					
$\nu(OO)$ (H_2O_2)	900	864	867			
$\nu(OO)$ (HO_2)	1065			1183	1120	1098
$\delta_a(OOH)$	1230	1266	1274			
$\delta_s(OOH)(H_2O_2)$	1440	1394	1345			
$\delta(OOH)$ (HO_2)	1505			1556		1392
$\delta(HOH)$	1610			1625	1479	

a Note: the average frequencies (for four different calculations) are from ref 14.

matrix.[17] The broad, structured band between 500 and 900 cm^{-1} is very typical of the librations (twist, wag, rock) of bound or adsorbed water molecules. This spectral region also contains a component of the $\nu(OO)$ mode of the hydrogen peroxide molecule (observed at 864 cm^{-1} in the gas phase). The INS intensity associated with $\nu(OO)$ would, however, be expected to be relatively weak because of the small displacement of H's in this mode. A deformation of a water−hydroperoxy hydrogen-bonded complex is also predicted at 679 cm^{-1} by Aloisio and Francisco.[15] Close inspection of this part of the INS spectrum does indeed suggest that at least five different peaks may be identified and are tentatively assigned according to Table 1. A comprehensive computational study would, however, be required to relate each of the particular frequencies to the various librational modes of the water molecule, especially since more than one type of water may be present after the reaction.

The broad, structured band above 1400 cm^{-1} extends far beyond the highest frequency (other than $\nu(OH)$, of course) of hydrogen peroxide, the $\delta_{as}(OOH)$ mode, found at 1345 cm^{-1} in an Ar matrix, and at 1394 cm^{-1} in the gas phase. Complexes of the hydroperoxy radical with water[13,15] show the $\delta_{as}(OOH)$ mode blue-shifted into the region 1450−1600 cm^{-1}. The water deformation mode, $\delta(HOH)$, at approximately 1640 cm^{-1} is not strongly affected by complexation[15] with HOO. In fact, the INS spectrum in this region from adsorbed water molecules (not complexed with OOH) is well-known to give rise to a very broad band extending from 1000 cm^{-1} due to overtones and combinations as well as to the $\delta(HOH)$ mode

itself. This band is also evident in Figure 1 as the broad background in the spectral range above ~1000 cm^{-1}. We are left therefore with assigning the features in the INS spectrum between 1525 and 1600 cm^{-1} to a hydroperoxy species complexed to water, or possibly bound to the surface as indicated in Table 1.

The INS spectra resulting from reaction of H_2 and O_2 over supported Au nanoclusters therefore provides evidence for the formation of hydrogen peroxide and a hydroperoxo radical. The latter is likely to form a hydrogen-bonded complex with water or bind directly to the oxide surface. In addition, water molecules bound to the surface are also clearly in evidence. It is well-known that hydrogen peroxide, once formed on a catalyst surface, rapidly decomposes to water unless an acid or surface protons are present to stabilize it. Thus, the hydroperoxy species identified here is likely either bound to Au or complexed with water that is also formed in this reaction.

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