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Dimerization of 1,3-Butadiene on Highly Characterized Hydroxylated Surfaces of Ultrathin Films of γ - Al_2O_3

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We describe here the dimerization of 1,3-butadiene to form 4-vinyl-cyclohexene on highly ordered hydroxylated ultrathin films of γ - Al_2O_3 . High surface area, powdered γ - Al_2O_3 is widely used as a catalyst and catalyst support. In addition, there is interest in the chemistry of Al_2O_3 particulates which exist in the troposphere. In contrast to the less reactive and more stable α - Al_2O_3 , which is available in macroscopic single crystal form, γ - Al_2O_3 is usually only available in powdered form. Thus, it has been difficult to study the details of the surface chemistry of this chemically important phase of Al_2O_3 using the powerful methods of modern surface sensitive spectroscopy. There are many examples of careful surface science studies of thin films of Al_2O_3 grown on aluminum and other metal substrates.^{1–7} Surface science techniques have also been used to characterize the reactive sites and the chemistry on powdered samples.^{8–15} Recently, Libuda et al.¹⁶ and Gassmann et al.¹⁷ have shown that ultrathin films of highly ordered γ - Al_2O_3 can be grown on substrates of NiAl(110) and NiAl(100). Using their methods, essentially single crystalline films of γ - Al_2O_3 can be prepared which are 10–15 Å in thickness. Such ultrathin films are sufficiently thin to allow characterization by conventional surface electron spectroscopies and electron diffraction without complications due to charging which occur when working with bulk samples of such electrically insulating materials.

We have extended the methods of Libuda et al.¹⁶ and Gassmann et al.¹⁷ to prepare not only highly characterized surfaces of γ - Al_2O_3 , but also to prepare hydroxylated γ - Al_2O_3 ultrathin films. These films can be characterized by low energy electron diffraction (LEED) for structure, Auger electron spectroscopy (AES) for elemental composition, and high-resolution electron energy loss spectroscopy (HREELS) for vibrational spectra. We report here the use of laser desorption Fourier transform mass

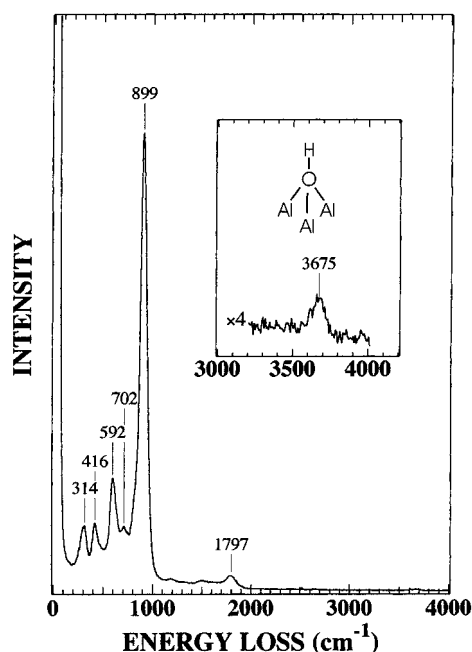


Figure 1. HREELS vibrational spectrum of a hydroxylated γ - Al_2O_3 ultrathin film which was grown on a NiAl(100) surface by a 100 L exposure of H_2O to the surface as it was held at 900 K. The inset shows a blow-up of the O–H stretching region of the spectrum.

spectrometry (LD-FTMS) to study the chemistry of 1,3-butadiene adsorbed on these ultrathin films of non-hydroxylated and hydroxylated γ - Al_2O_3 . To our knowledge, this is the first demonstration of the generation of highly characterized hydroxyl species on structurally characterized ultrathin films of γ - Al_2O_3 and the first observation of the dramatic differences in surface chemistry which can be caused by surface hydroxyls on these ultrathin films. 1,3-Butadiene has recently been added to the California Air Toxics list as the cause of increases in leukemia and certain types of cancers which can result from chronic exposure.^{18,19} The chemistry of 1,3-butadiene on the surfaces of Al_2O_3 particulates, which are known to exist in the troposphere, is one piece of the development of a complete picture of the eventual fate of butadiene which is emitted by industrial sources.

Figure 1 shows the vibrational spectrum (HREELS) of a γ - Al_2O_3 ultrathin film with a hydroxylated surface which was grown on a NiAl(100) substrate. This spectrum was obtained with an LK 2000 HREELS spectrometer in an ion-pumped ultrahigh vacuum chamber with a base pressure of 1×10^{-10} Torr. The vibrational modes at 899, 702, 592, and 416 cm^{-1} are the γ - Al_2O_3 phonons. The mode at 1797 cm^{-1} , and the low intensity modes at ~ 1500 cm^{-1} and ~ 1100 cm^{-1} are combination modes of the phonons. The narrow widths of the phonon peaks are limited by the spectrometer resolution in these experiments and are indicative of the highly ordered nature of the oxide film. The mode at 3675 cm^{-1} shown in the inset of Figure 1 is the OH stretching mode of the surface hydroxyl groups. This mode is extremely narrow when compared to the corresponding OH stretching mode seen for hydroxyl groups on Al_2O_3 powdered samples.¹³ The OH stretching mode frequency which we observe is characteristic of isolated OH groups on the surface which are bonded to three Al sites.²⁰ Identical spectra can be obtained by

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either growing the oxide film with water as the oxidant or growing the film by oxidizing the NiAl(100) surface by O₂ exposure followed by water exposure at room temperature. We also have characterized the films with Auger electron spectroscopy. The ratio of the O (505 eV) to Ni (848 eV) Auger peaks is typically ~3:1. In our experiments, we have shown by CO exposure experiments that the films are free of pinholes. Details of the growth and characterization of the hydroxylated γ -Al₂O₃ films is the subject of a full length paper in preparation.²¹

We have used LD-FTMS to follow the adsorption and chemistry of 1,3-butadiene on both non-hydroxylated and hydroxylated γ -Al₂O₃ ultrathin films. In a typical LD-FTMS experiment, butadiene is adsorbed on the surface of the ultrathin film at a sample temperature of 140 K. The molecular composition of the surface is then probed by irradiating a small spot on the sample surface with a pulsed laser (KrF excimer laser, 248 nm, 20 ns pulse width) which results in a rapid temperature jump at the surface sufficient to cause molecular desorption. The laser-induced temperature jump is sufficiently rapid that intact molecular desorption is favored over thermally activated surface reactions.²² The desorbed neutral molecules are then ionized by electron ionization (70 eV) and detected by standard methods of Fourier transform mass spectrometry.²³ Figure 2 shows the LD-FTMS spectra obtained from an 800 L dosage of 1,3-butadiene exposed to the non-hydroxylated γ -Al₂O₃ (Figure 2a) and hydroxylated γ -Al₂O₃ (Figure 2b) surfaces. The spectrum obtained from the non-hydroxylated surface is characteristic of the electron impact ionization mass spectrum of butadiene.²⁴ The spectrum obtained from 1,3-butadiene adsorbed on the hydroxylated γ -Al₂O₃ surface shows additional mass peaks at 66, 67, 79, and 80 amu. These peaks are highly characteristic of 4-vinylcyclohexene (the dimer of 1,3-butadiene). In particular, in the EI mass spectrum of 4-vinylcyclohexene, the parent mass peak at mass 108, is expected to be quite small, and substantial peaks at masses 66, 67, 79, and 80 are expected as we observed. The peak at mass 66 is particularly uncommon for small hydrocarbons and is highly characteristic of the electron beam fragmentation of 4-vinylcyclohexene.²⁴ The EI fragmentation pattern even allows us to distinguish 4-vinylcyclohexene from other mass 108 isomers. Cyclooctadiene, for example, has an EI fragmentation pattern which produces a substantial parent mass peak at mass 108, and the mass 67 peak is substantially larger than the mass 66 peak in contrast to our observations. The spectrum in Figure 2b also shows a somewhat larger mass 44 peak than the spectrum in Figure 2a, which is not attributable to the 4-vinylcyclohexene. We assign this to CO₂ since we and others²⁵ have observed that the Al₂O₃ ultrathin films have a substantial affinity for CO₂. Thus, the spectrum which we observed (Figure 2b) is characteristic of a mixture of 1,3-butadiene and 4-vinylcyclohexene on the surface.

The dimerization of 1,3-butadiene to form 4-vinylcyclohexene is well-known and could be occurring via either a proton-initiated cationic polymerization or by a Diels–Alder dimerization which is activated by interaction of one of the butadiene molecules with

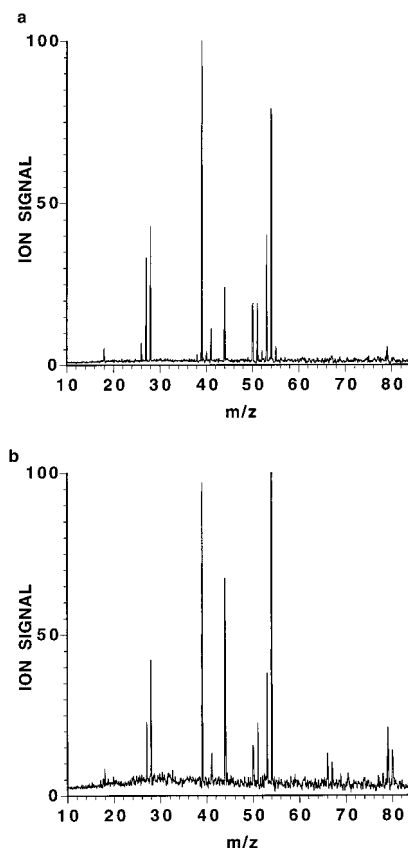


Figure 2. (a) LD-FTMS spectrum following adsorption of 1,3-butadiene on a non-hydroxylated ultrathin film of γ -Al₂O₃ on a NiAl(100) substrate held at 140 K. (b) LD-FTMS spectrum following adsorption of 1,3-butadiene on a hydroxylated ultrathin film of γ -Al₂O₃ on a NiAl(100) substrate held at 140 K. The additional peaks in this spectrum at $m/z = 66, 67, 79, 80$ are characteristic of 4-vinylcyclohexene, the dimer of 1,3-butadiene.

the acidic surface OH groups. At the present time, we favor the Diels–Alder mechanism in this case for two reasons. First, we would expect the possibility of a number of products from a cationic polymerization, whereas the Diels–Alder dimerization should give a single product which is most consistent with our experimental results. Second, we have carried out experiments utilizing surfaces with deuterated hydroxyl groups and did not see any incorporation of the deuterium into the product molecule, consistent with the Diels–Alder mechanism.

We show here for the first time that modern surface spectroscopies can be used to follow chemistry on highly characterized surfaces of both non-hydroxylated γ -Al₂O₃ and hydroxylated γ -Al₂O₃. We have used the LD-FTMS technique to show that the hydroxylated γ -Al₂O₃ surface is active for the dimerization of 1,3-butadiene, most likely via a Diels–Alder mechanism in which the surface OH helps activate one of the butadienes as a dienophile. In contrast, the dimerization reaction does not occur when 1,3-butadiene is exposed to the non-hydroxylated γ -Al₂O₃ surface.

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