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Surface-Mediated NH and N Addition to Styrene on Ag(110)

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Silver-based catalysts are renowned for their importance for highly selective epoxidation of ethylene, producing ethylene oxide with a selectivity $\geq$90%.[1,2] Equally impressive selectivities are found for the conversion of methanol to formaldehyde by metallic silver.[3] Because incremental improvements in selectivity are important for the economics of ethylene oxide production, tremendous effort has been devoted to elucidating the mechanism of oxygen addition to olefins by silver catalysts.[4−8] However, except for recent studies with gold,[9] the heterogeneously catalyzed addition of nitrogen (NH_x, $x = 0-2$) to unsaturated hydrocarbons has not been studied, despite the fact that the products of these reactions are important chemical intermediates.[10−12] Adsorbed NH, being isoelectronic with O, at least to first order, may possibly react with olefins in a fashion similar to adsorbed O on silver surfaces.

Here we report the investigation of the reaction of adsorbed NH and N with styrene on Ag(110). Previous studies have shown that the N−H bond in ammonia can be activated by chemisorbed oxygen on Ag[13] and Cu,[14] leading to the formation of adsorbed NH. In this study, both NH and N species were synthesized on Ag(110) by reacting ammonia with chemisorbed oxygen under well-controlled conditions. The reaction of styrene with these species yields benzonitrile and an NH addition product, provisionally identified as 2-phenylaziridine, as well as HCN and NH_3. The production of aziridine, a three-membered heterocycle and the nitrogenous analogue of epoxide, is potentially an important catalytic reaction and is of considerable interest in synthetic chemistry.[11,12]

All studies were carried out in a stainless steel ultrahigh vacuum chamber with the base pressure of $\sim 1 \times 10^{-10}$ Torr. The Ag(110) sample was cleaned by cycles of Ar^+ sputtering at room temperature (1 keV, 10 μA) followed by radiative heating in vacuum at 750 K for 5 min until no impurities were detected by Auger electron spectroscopy (AES). Then the crystal was annealed at 700 K for 10 min to give a sharp (1 × 1) low-energy electron diffraction (LEED) pattern. Mass signals were collected using a multiplexed UTI 100C quadrupole mass spectrometer with an emission current of 2 mA and using a heating rate of ~5 K/s.

Oxygen activation on the Ag(110) was performed by exposure to O_2 at 170 K. Thermal desorption showed peaks of O_2 at 210 and 575 K (data not shown). On the basis of previous work, the peak at 210 K is ascribed to desorption of chemisorbed O_2, while the peak at 575 K is due to recombination of atomic oxygen.[15] Disproportionation of hydroxyl groups yields H_2O at 340 K[16] which are most probably produced by reaction of surface oxygen with background H_2O.

The surface covered with NH and N is prepared following exposure of O-covered Ag(110) ($\theta_o \sim 0.2$ ML) to NH_3 at 3×10^{-10} Torr for 5 min at a surface temperature of 340 K. At this reaction temperature, water formed from the reaction of NH_3 and atomic oxygen readily desorbs from the surface. In temperature-programmed reaction spectra (Figure 1), only N_2 and NH_3 were detected. N_2 is evolved in an asymmetric peak at 490 K, consistent with previous studies.[13] NH_3 is evolved in a broad peak in the temperature range of 370−520 K. There is no residual oxygen or hydroxyl adsorbed on the surface after exposure of the O-covered surface to ammonia under these conditions, based on the fact that there is no detectable water or O_2 evolution. No other O-containing products—NO, N_2O, or NO_2—were detected. The N_2 desorption is attributed to nitrogen atom recombination.[13] We assign the formation of NH_3 to the disproportionation of surface NH species. The desorption of physisorbed NH_3 and reactions of NH_2 can be excluded, as it has been reported that only NH and N remain on the surface above 330 K.[13] N atoms can be produced in the disproportionation reaction of NH with the total reaction expressed as $3\ NH \rightarrow NH_3 + 2\ N$. However, N formed from this reaction accounts for only ~30% of the total amount of N shown in Figure 1, as estimated from the integrated areas of m/z 17 and 28, correcting for the relative mass spectrometric sensitivities for ammonia and nitrogen. We conclude, therefore, that NH and N species are both formed on a Ag(110) surface with this procedure, although their coverage is not known.

The C_8H_9N (m/z 119, Chart 1), benzonitrile (C_6H_5CN, m/z 103), hydrogen cyanide (HCN, m/z 27), and ammonia (NH_3, m/z 17) are produced following exposure of NH- and N-covered Ag(110) discussed above to styrene, as shown in Figure 2. The desorption of unreacted styrene (C_8H_8, m/z 104) occurs with a broad peak centered at 330 K. Benzonitrile is observed as a high temperature shoulder on the m/z 103 mass fragment of styrene, confirmed by subtracting the contribution from styrene fragmentation (shaded area). Separate experiments (not shown) with higher concentrations of adsorbed N reveal a distinct peak for m/z 103 at 402 K, in agreement with this conclusion. NH_3 desorbs near 400 K, as expected. HCN is produced in peaks at 400 and 490 K. There is also residual C and N after reaction, based on the fact that CO_2 and NO are produced after exposure of the surface to O_2 and heating after the temperature-programmed reaction data are obtained. We estimate that the equivalent of 0.04 ML of N and 0.07 ML of C remain on the surface after reaction.

The product formed at 450 K shows mass fragments with m/z at 119, 118, and 91; m/z 119 is the highest mass observed for this product. The stoichiometry of this product was determined to be C_8H_9N from the parent ion (m/z 119), and it is provisionally identified as 2-phenylaziridine by its cracking fraction. Loss of one hydrogen atom results in the most intense fragment (m/z 118). The second most intense fragment (m/z 91) of 2-phenylaziridine can be assigned as $C_6H_5CH_2$, which is also a fragment of its oxygen-containing analogue, styrene epoxide, due to the structural similarity between aziridine and epoxide (Chart 1). The formation of its isomers, indoline, 4-aminostyrene, and *N*-phenylaziridine, can be excluded by quantitatively comparing their fragmentation patterns

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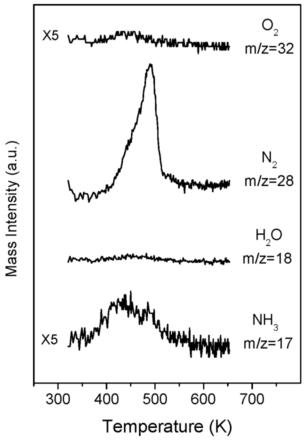


Figure 1. Temperature-programmed reaction spectra after exposure of O-covered Ag(110) to ~0.1 L of ammonia at 340 K. It shows the desorption of NH_3 (*m*/*z* 17) and N_2 (*m*/*z* 28). No residual O_2 due to recombination of adsorbed O (*m*/*z* 32) is observed. The heating rate was ~5 K/s.

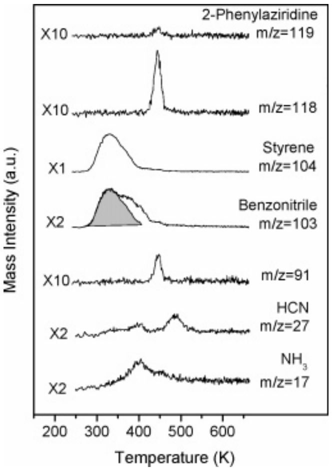
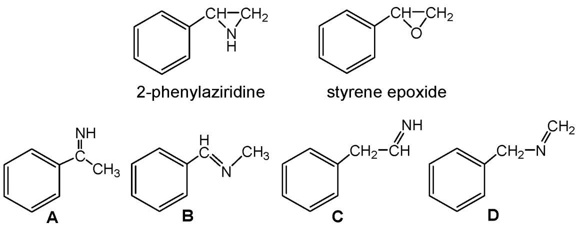


Figure 2. Temperature-programmed reaction spectra of styrene (*m*/*z* 104) on Ag(110) predeposited with NH and N. It shows the formation of a product assigned as 2-phenylaziridine (*m*/*z* 91, 118, 119), benzonitrile (*m*/*z* 103), HCN (*m*/*z* 27), and NH_3 (*m*/*z* 17). The shaded area represents contribution from fragmentation of styrene. Styrene was dosed on the surface at 275 K. The heating rate was ~5 K/s.

Chart 1. 2-Phenylaziridine is a Nitrogenous Analogue of Styrene Epoxide, and Its Isomers of Imine Are Shown



with those observed here (Table S1, Supporting Information). The production of imines $C_6H_5C({=}NH)(CH_3)$ and $C_6H_5CH{=}NCH_3$ (Chart 1, A and B) can be readily excluded based on the intense fragment at *m*/*z* 91 ($C_6H_5CH_2$). Unfortunately, the formation of another two imines, C and D in Chart 1, cannot be entirely ruled out because the aziridine might isomerize to the imine upon ionization.[17]

To further assist with the identification of the products from styrene reaction with NH and N on Ag(110), isotopically labeled $^{15}NH_3$ was used to produce adsorbed ^{15}NH and ^{15}N on the surface. Subsequent reaction with styrene yields the same products, namely, $C_8H_9{}^{15}N$ (*m*/*z* 120), $C_6H_5C^{15}N$ (*m*/*z* 104), $HC^{15}N$ (*m*/*z* 28), and $^{15}NH_3$ (*m*/*z* 18). The identification of the N-containing products is confirmed by the shift of +1 in the masses of key ions. Specifically, the parent ion of C_8H_9N shifts from *m*/*z* 119 to 120, and the most intense fragment shifts from *m*/*z* 118 to 119. The fragment *m*/*z* 91 does not shift, verifying its assignment as $C_6H_5CH_2$, excluding *N*-phenylaziridine as a product (Table S1).

As the analogue to epoxide, we suggest that NH attacks the ene group to induce cycloaddition to form aziridine. The surface NH species is isoelectronic with O, having two unpaired electrons, though the electron distribution around the nitrogen and oxygen differs in detail. Thus, we propose that the formation of aziridine is the result of cycloaddition of NH to the C=C bond, although it is possible that the aziridine isomerizes to imines C or D (Chart 1). Further, we propose that N is responsible for the production of benzonitrile and HCN, where the breaking of the C=C bond is necessary. Two processes might contribute to NH_3 evolution: (1) the disproportionation reaction of NH groups and/or (2) NH and/or N reaction with styrene or reactive intermediates. The NH_3 peaks in Figure 2 are narrower and evolve at lower temperatures compared to those arising from the disproportionation reaction of NH (Figure 1), indicating different rate-limiting steps for the two processes. Therefore, process (2) most probably involves reaction of styrene with NH and N, reminiscent of hydrogen abstraction of hydrocarbons on oxygen-covered Ag surfaces to form water.[8,18]

In conclusion, the Ag(110) surface-mediated reaction of styrene with NH and N yields 2-phenylaziridine and benzonitrile, with additional products HCN and NH_3. While the aziridines might isomerize, we propose that cycloaddition of adsorbed NH to the carbon−carbon double bond occurs, in analogy to oxygen addition to form epoxide. Here, the successful demonstration of the functionalization of styrene with NH and N on silver using O_2 and NH_3 to generate the reactive intermediate, NH, suggests that Ag-based heterogeneous catalysts may be useful for analogous functionalization of olefins.

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Supporting Information Available: Estimation of the equivalent coverage of C and N on the surface after reaction, and analysis of fragmentation patterns of the product C_8H_9N. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Jørgensen, K. A. *Chem. Rev.* **1989**, *89*, 431.
(2) Park, D. W.; Ghazali, S.; Gau, G. *Appl. Catal.* **1983**, *6*, 175.
(3) Bao, X.; Deng, J.; Zhai, R.; Wang, D.; Guo, X. *Catal. Lett.* **1990**, *4*, 25.
(4) Backx, C.; De Groot, C. P. M.; Biloen, P. *Surf. Sci.* **1981**, *104*, 300.
(5) Campbell, C. T.; Parrett, M. T. *Surf. Sci.* **1984**, *139*, 396.
(6) Tan, S. A.; Grant, R. B.; Lambert, R. M. *J. Catal.* **1987**, *104*, 156.
(7) van Santen, R. A.; Kuipers, H. P. C. E. *Adv. Catal.* **1987**, *35*, 265.
(8) Roberts, J. T.; Madix, R. J. *J. Am. Chem. Soc.* **1988**, *110*, 8540.
(9) Deng, X.; Baker, T. A.; Friend, C. M. Submitted for publication.
(10) Tanner, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 599.
(11) Sweeney, J. B. *Chem. Soc. Rev.* **2002**, *31*, 247.
(12) Müller, P.; Fruit, C. *Chem. Rev.* **2003**, *103*, 2905.
(13) Thornburg, D. M.; Madix, R. J. *Surf. Sci.* **1989**, *220*, 268.
(14) Afsin, B.; Davies, P. R.; Pashusky, A.; Roberts, M. W.; Vincent, D. *Surf. Sci.* **1993**, *284*, 109.
(15) Barteau, M. A.; Madix, R. J. *Surf. Sci.* **1980**, *97*, 101.
(16) Stuve, E. M.; Madix, R. J.; Sexton, B. A. *Surf. Sci.* **1981**, *111*, 11.
(17) Hammerum, S.; Henriksen, J.; Henriksen, T.; Sølling, T. I. *Int. J. Mass Spectrom.* **2000**, *195/196*, 495.
(18) Lambert, R. M.; Williams, F. J.; Cropley, R. L.; Palermo, A. *J. Mol. Catal. A* **2005**, *228*, 27.

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