

## Direct Selective Oxygen-Assisted Acylation of Amines Driven by Metallic Silver

### Surfaces: Dimethylamine with Formaldehyde

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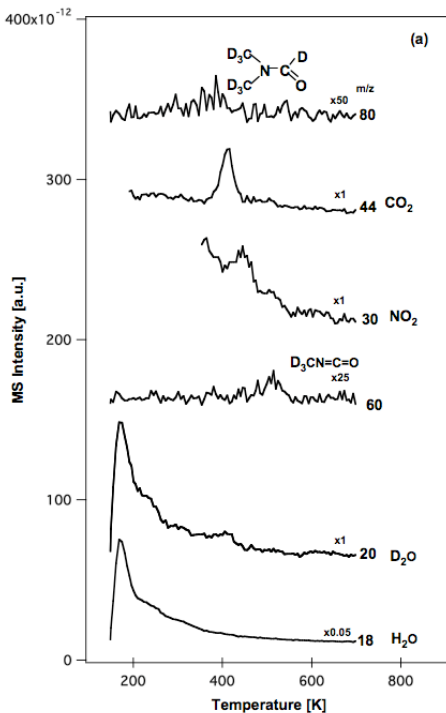
#### Experimental

Temperature programmed reactions (TPR) on Ag(111) and Ag(110) were performed separately in two ultra-high vacuum (UHV) systems, both equipped with Pfeiffer quadrupole mass spectrometer (Prisma QMS 200), low energy electron diffraction (LEED) optics, and X-ray photoelectron spectroscope (XPS). The Ag(111) and (110) surfaces were cleaned by cycles of Ar<sup>+</sup> sputtering at room temperature followed by repeated exposures to NO<sub>2</sub> at 500 K to remove any impurities by oxidation and annealing in vacuum at 900 K for 5 min until no impurity was detected by XPS, and a sharp (1×1) LEED pattern was observed. The chemisorbed atomic oxygen on both surfaces was prepared by dosing NO<sub>2</sub> (Matheson Tri-Gas, 99.5%) at 500 K to obtain the desired oxygen coverages. One monolayer (ML) is defined as one O atom per surface Ag atom. Dimethylamine (Sigma-Aldrich, 99%) and d<sub>6</sub>-dimethylamine (Cambridge Isotope Laboratories, 99%) were dosed through a 5 mm diameter tube pointing to the sample positioned about 30 mm from the end of the tube. Formaldehyde (d<sub>0</sub>- and d<sub>2</sub>-) was dosed through a capillary doser *via* paraformaldehyde, in which the glass tube holding the sample was immersed in a hot-water bath, and the whole dosing system was heated to ~ 50 °C to achieve a higher vapor pressure in the gas line during dosing. During the TPR experiments, the samples were biased at -100 V in order to avoid possible electron-induced reactions. The reaction products were identified by quantitative mass spectrometry using fragmentation patterns obtained from authentic samples.

**Table S1.** N, N-dimethylformamide, formed in the reactions of dimethylamine and formaldehyde on the oxygen-covered Ag(111) and (110) surfaces, was identified by quantitative comparison of the mass fragmentation pattern of the product appearing near 270 K to that measured for condensed neat sample desorbed from the clean surface. The other products in the reactions (CO<sub>2</sub>, NO<sub>2</sub> and H<sub>2</sub>O) were identified on the basis of their corresponding fragmentation patterns in the NIST database.

m/z	Product at 270 K	Multilayer of N, N-dimethylformamide condensed on clean surfaces at 120 K
73	45	45
72	4	4
45	9	11
44	100	100
42	69	69

**Figure S1** Reaction of  $d_6$ -dimethylamine (DMA) with  $d_1$ -formate on O/Ag(111) at 140 K.  $d_1$ -Formate ( $D\text{COO}_{\text{ads}}$ ) was formed on the surface by reacting  $d_2$ -formaldehyde on a 0.4 ML O-covered Ag(111) at 140K and annealing to 325K for ten minutes to eliminate water and unreacted formaldehyde. By careful control of the dosage of formaldehyde, formate coadsorbed with atomic oxygen was achieved. This surface was then cooled to 140K and  $d_6$ -dimethylamine was dosed in order to induce formation of a mixture of coadsorbed  $(\text{CD}_3)_2\text{N}$  and DMA. With subsequent heating the coupling product,  $d_7$ -N,N-dimethylformamide ( $(\text{CD}_3)_2\text{NC}(\text{D})=\text{O}$ ,  $m/z$  80) is not observed in significant quantity.



**Figure S2** Oxidation of dimethylamine on 0.1 ML O-covered Ag(110) at 150 K. In addition to H<sub>2</sub>O, CO<sub>2</sub> and NO<sub>2</sub> are produced at 410 K, as well as a small amount of isocyanate is produced at 510 K. The shaded areas under m/z 44 and 46 spectra are attributed to the fragments of unreacted dimethylamine, according to its fragmentation pattern.









