An STM investigation on the CO_2 activation and conversion on Au/MgO(001) ultrathin film

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Finding a way to react CO_2 back into useful chemicals and fuels would represent a major breakthrough in fighting climate change [1,2]. In previous research [3], we have shown that a layered system consisting of single-layer Au nanoislands on an ultrathin Ag(001)-supported epitaxial MgO film can catalyze the activation of CO_2 to oxalate $(CO_2)^{2-}$ — a stable intermediate for many chemicals and synthetic fuels —even below room temperature. However, the active site for the reaction, as well as the role of the islands and of the substrate, have yet to be pinpointed.

In this work, we investigate this system with STM before and after exposure to reaction condition [3], with the aim of observing the reaction product on the surface. Our experiments have indeed identified an adsorbate species with a characteristic asymmetric appearance, shown in Figure 1a, which was only observed in presence of single-layer thickness Au islands after exposure to CO_2 at 200-300 K.

Most surprising, however, was that this species was not located beside the Au islands, despite them being fundamental for the reaction. As the adsorbate species is not mobile on the surface, this indicates that the CO_2 to oxalate reaction is not a simple process occurring on or around the islands, as we expected: instead, it suggests that a more complex process takes place, with an electron first tunnelling through the MgO tunnel barrier into the gold, and then diffusing over MgO into a CO_2 molecule.

This was confirmed by our measurements on a physisorbed CO_2 layer on the MgO/Ag(001) epitaxial layer, where the application of localized voltage pulses induced charge-activated desorption and dissociation [4] across several tens of nm, as shown in Figure 1b-c.

These results provide important insight on this promising catalyst, highlighting the importance of the combined role of the Au islands and the MgO substrate in the CO_2 activation and reaction.

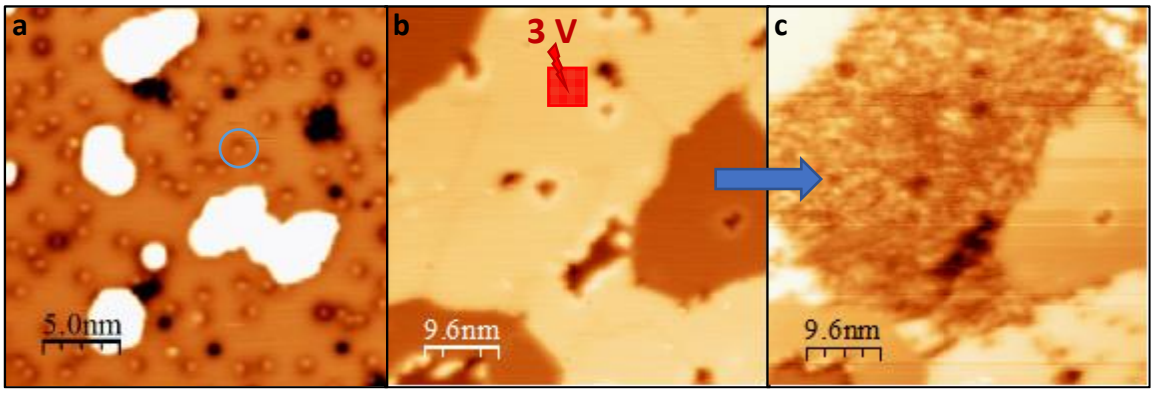

Fig. 1. a: Image of Au/MgO/Ag(001) after CO_2 exposure. One molecule of the reaction product is highlighted. b: Appearance of CO_2 on MgO/Ag(001) before and c: after a voltage pulse applied in the highlighted region in b.

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