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Exploring Nitrogen Reduction Pathways on MoS_2 Surfaces via by Online Electrochemical Mass Spectrometry

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Electrochemical nitrogen reduction to ammonia under ambient conditions has emerged as a promising alternative to the traditional Haber-Bosch process, [1; 2; 3] due to its potential for reducing CO_2 emissions. This green energy conversion process, which utilizes N_2 and H_2O, reduces pollutant emissions and reliance on petroleum, contributing to a more sustainable energy framework. [4; 5] However, the nitrogen reduction reaction (NRR) presents considerable challenges due to the high stability of N_2 and the limited availability of active, efficient catalysts. In this study, we explore the NRR in 1.0 mol L^{-1} NaOH using MoS_2 electrodes, with online electrochemical mass spectrometry (OLEMS) employed to identify gaseous products. The physical characterization of the electrocatalyst was performed using energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and transmission electron microscopy (TEM). Figure 1 displays chronoamperometry (CA) results and CA-MS signals for various volatile species as a function of the applied potential: m/z 30 ($N_2H_2^+$), 29 (N_2H^+), 28 (N_2^+), and 2 (H_2^+). Results for the NRR are shown in red, while measurements in the absence of nitrogen (i.e., in helium) are depicted in blue. OLEMS results notably reveal the presence of N_2H^+ and $N_2H_2^+$ species as intermediates in the NRR, with N_2 consumption beginning at -0.4 V vs. RHE and the onset of NH_3 production around -0.5 V vs. RHE. Notably, no $N_2H_3^+$ or $N_2H_4^+$ species were detected. Measurements conducted under a helium atmosphere (in the absence of nitrogen) revealed no detectable formation of the monitored species in the mass signals. The N_2 molecule adsorbs onto the catalyst surface, proceeding through two protonation steps to form N_2H and N_2H_2 intermediates at potentials below -0.4 V, with N_2H_2 identified as the primary intermediate leading to ammonia production. For the first time, this study uses OLEMS to successfully identify key intermediates in the NRR, correlating NH_3 formation with N_2 consumption as a function of applied potential, offering critical insights into the reaction pathway for ammonia synthesis.

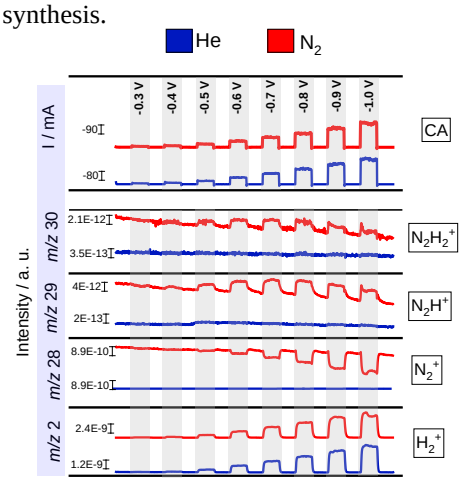

Figure 1. OLEMS mass signal results for MoS_2. CA-MS in 1.0 mol L-1 NaOH electrolyte. In the blue and red lines correspond to He and N_2, respectively.

References

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