Cerium Ferrite Composites: A New Frontier in Electrochemical Reduction of Nitrates to Ammonia

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In pursuit of sustainable ammonia synthesis and nitrate remediation, the electrochemical reduction of nitrate to ammonia (eNO_3RR) was explored as an alternative to the carbon-intensive Haber-Bosch process (HBP). The conventional HBP emits 1.6 to 2.0 tons of CO_2 per ton of ammonia,[1] whereas eNO_3RR, primarily when powered by renewable energy, offers a potential reduction in emissions and energy consumption. However, due to its complex reaction mechanism, eNO_3RR is hindered by challenges in catalytic activity and product selectivity. Addressing these challenges, we synthesized $CeO_2/CeFeO_3$ composites using a microwave polyol method with varying Ce:Fe atomic ratios and conducted comprehensive characterizations and kinetic investigations. Our electrochemical analysis indicated that pure CeO_2 catalysts provide a high ammonia yield rate of 4040.5 μg/h/cm^2. However, this catalyst exhibits lower Faradaic Efficiencies (FE) of 50.6% at -0.45 V vs. RHE 0.1 M KOH electrolyte containing 0.1 M NO_3^-. Significant improvement in the FE was observed with the formation of the $CeFeO_3$ phase in the $CeO_2/CeFeO_3$ composite catalyst. The maximum FE of 88.1% was observed in catalysts containing 75% $CeFeO_3$ with an ammonia yield rate of 3223.9 μg/h/cm^2. Furthermore, only 3.1% of the FE contributed to parasitic hydrogen evolution, with the remainder being distributed to 8.0% hydroxylamine and 0.8% nitrite, both intermediates in the ammonia synthesis pathway. This composite catalyst-maintained stability over 25 cycles of one-hour chronoamperometric electrolysis at -0.45 V (a total of 25 hours) of eNO_3RR, with electrolyte exchange in each cycle. The improved catalytic performance is attributed to the intrinsic perovskite structure of $CeFeO_3$, which utilizes oxygen vacancies[2] for oxygen exchange with the NO_x intermediates. This study highlights the potential of rare earth orthoferrites, particularly cerium ferrite composites, to facilitate eNO_3RR. These materials present a promising avenue for sustainable ammonia production and environmental remediation, showcasing a viable alternative to traditional methods.

Keywords: Sustainable Ammonia Synthesis, Cerium Ferrite Composites ($CeO_2/CeFeO_3$), Efficiency and Selectivity, Environmental Remediation

References:

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