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Promotion of the Electrocatalytic Reduction of Nitrate

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Citation

Yang, J. (2012, October 24). *Promotion of the Electrocatalytic Reduction of Nitrate*. Retrieved from <https://hdl.handle.net/1887/22045>

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Issue Date: 2013-10-24

Summary

Nitrate reduction is a very important step in the nitrogen cycle. Among many methods dealing with nitrate, the electrocatalytic reduction of nitrate is a promising one, not only in fundamental research but also from an applied point-of-view, since both selectivity and activity can be obtained by controlling the electrode potential, surface condition and chemical nature of electrode and solution composition.

Platinum is widely applied in the research of electrocatalysis but it is a relatively poor catalyst for nitrate reduction. Thus, it is necessary to modify the Pt electrode with a foreign metal to obtain a considerable activity for nitrate reduction. This thesis aims to understand the mechanism of this promotion and how the product selectivity is influenced. In Chapter 2, nitrate reduction has been investigated on Sn-modified polycrystalline Pt electrode in perchloric acid with two typical coverages of Sn species. The selectivity for volatile products as measured by online electrochemical mass spectrometry (OLEMS) is found to be dependent on the Sn coverage on Pt surface. At high Sn coverage, NO is the main product, whereas N₂O is the dominant product at relatively low Sn coverage. This observation suggests the important catalytic effect of pristine Pt in the PtSn ensemble for nitrate reduction. The electrochemical formation of N₂ from N₂O reduction has been investigated on polycrystalline Pt electrode with different coverages of Sn species, showing that electrochemical formation of N₂ is related to the N₂O reduction on pristine Pt sites. It is suggested that the main effect of Sn modification of the Pt surface is to enhance the rate determining step of nitrate reduction to nitrite. Moreover, homogeneous chemical reactions of non-volatile products, such as nitrite (NO₂⁻), ammonium (NH₄⁺) and hydroxylammonium (HONH₃⁺), which are intermediates in the nitrate reduction, also contribute to the formation of N₂O and N₂ in solution. The product distribution from these chemical reactions is strongly dependent on the pH of the environment. Therefore, the long term chemical contribution to N₂ formation in solution must be considered during the constant potential electrolysis, since it is favored when the pH increases locally near the electrode surface as a result of nitrate reduction.

Since Sn shows a strong catalytic enhancement on nitrate reduction on Pt, the other elements surrounding Sn in the periodic table are investigated in Chapter 3. The anion effect and the formation of volatile products have been studied as well to compare the catalytic trends among the p-block metals for nitrate reduction on Pt. Of them, Cd, In and Sn show a promoting effect on nitrate reduction and N_2O is the dominant product for Cd and In; Ga shows a limited enhancement on nitrate reduction on Pt; Tl shows a special promoting effect on nitrate reduction in sulfuric acid rather than perchloric acid, which points to a role of removing inhibitor from Pt surface; Pb shows a weak formation of N_2O ; As, Sb and Bi only inhibit nitrate reduction on polycrystalline Pt electrode and there is no evidence for the formation of volatile products. Sn is the most active modifier to enhance nitrate reduction of all p-block metals that have been studied. Density Functional Theory calculations show that on both Sn and In modified Pt(111) surface, a more negative energy of nitrate adsorption is found compared with the pristine Pt(111) surface. Especially on Sn-Pt(111) system, hydroxide state of Sn species gives the lowest adsorption energy for nitrate. As a result, the first step of nitrate reduction to nitrite, which is the rate determining step on Pt for the whole nitrate reduction, is facilitated by Sn in the hydroxylated state.

To demonstrate the formation of nonvolatile products, such as nitrite, ammonia and hydroxylamine, nitrate reduction on Sn modified polycrystalline Pt electrode in perchloric acid has been studied by combining ion chromatography and voltammetry, which can reveal the potential dependence of nonvolatile products (Chapter 4). On a Pt electrode, formation of ammonia is observed as the only product from nitrate reduction, since no volatile products have been measured by OLEMS. After the Pt surface is modified by Sn species, a specific selectivity to hydroxylamine formation is found in addition to ammonia formation. Also, the formation of nitrite can be detected, which is not observed on a pristine Pt electrode. This supports the suggestion that the rate determining step of nitrate reduction to nitrite is enhanced by Sn. The selectivity to form hydroxylamine also suggests a third role that Sn could play, namely to steer the hydrogenation of NO_{ads} on Pt sites without breaking the N-O bond.

In nitrate reduction, solution pH is an important factor that has a significant influence on the reduction activity. To have a basic understanding of the role of pH in nitrate reduction, two noble metals, Pt and Rh, are used to investigate the pH effect on nitrate reduction in a wide pH range (Chapter 5). On Pt, nitrate reduction

is slow and only observed in acidic solution up to pH=4. The peak current density decreases as the solution pH increases in the pH range investigated. On Rh, a higher activity of nitrate reduction is observed in acidic solution, whereas within a wide pH range from 5 to 13 a certain constant reduction activity is still maintained. The trend that the peak current density decreases as solution pH increases in the acidic pH range on both Pt and Rh electrode suggests a mechanism in which the HNO_3 molecule is the active species that is reduced on Pt and Rh electrodes. Since the concentration of HNO_3 is determined by solution pH, there is no nitrate reduction on Pt when solution pH is above 5. However, Rh additionally shows a special ability to reduce NO_3^- directly so that nitrate reduction can still be achieved even in solution of higher pH.

