Catalytic reduction of nitrate in water toward purification of real groundwater

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Abstract: We investigated purification of real groundwater polluted with NO$_3^-$ by catalytic reduction with H$_2$ over the supported Cu-Pd and Sn-Pd catalysts. While the supported Cu-Pd catalyst showed high catalytic performance in an aqueous NO$_3^-$ solution, it suffered severe deactivation in the groundwater. In contrast, Sn-Pd/Al$_2$O$_3$ showed acceptable activity and selectivity to gas products even in the groundwater. The less sensitivity for Cl$^-$ and strong adsorption of NO$_3^-$ on the Sn site over Sn-Pd/Al$_2$O$_3$ are the reasons for the high catalytic performance of Sn-Pd/Al$_2$O$_3$ in the groundwater.

Keywords: Groundwater pollution, nitrate, SnPd catalyst.

1. Introduction

Pollution of groundwater with nitrate (NO$_3^-$) is an increasing problem throughout the world. Reduction of NO$_3^-$ with H$_2$ to form N$_2$ over a solid catalyst has attracted much attention as a technology for purification of the polluted groundwater. In the catalytic reduction, formation of NH$_4^+$ (or NH$_3$) is a crucial problem. Since Cu-Pd/Al$_2$O$_3$ was reported to show activity for the reaction, many studies have been conducted to develop highly active and selective catalysts, focusing mainly on Cu-Pd bimetallic system. So far, some catalysts and catalytic reaction systems with acceptable activity and selectivity have been found. However, most studies thus far dealt with the reaction in an aqueous NO$_3^-$ solution, in other words, those did not treat real groundwater. Indeed, groundwater contains various cations, anions, and water-soluble organic matters and thus those coexisting materials may affect the catalytic performance, becoming the fatal problem for practical applications. In this study, we investigated the catalytic reduction of NO$_3^-$ over the supported Cu-Pd catalyst in real groundwater polluted with NO$_3^-$ The results showed that the catalyst was severely deactivated in the groundwater. Thus, we further investigated to clarify which coexisting materials in the groundwater caused the deactivation and then gave a solution by using Sn-Pd catalyst instead of Cu-Pd toward purification of the groundwater.

2. Experimental

Supported Cu-Pd and Sn-Pd catalysts were prepared by an incipient impregnation method. The catalytic reduction of NO$_3^-$ with H$_2$ in water was carried out in a batch reactor at 298 K. To the reaction solution (250 cm$^3$, [NO$_3^-$] = 1.0 mmol dm$^{-3}$) containing 10 mg of the catalyst, a mixture of H$_2$ (0.5 atm) and CO$_2$ (0.5 atm) was fed to start the reaction. The reaction solution was analyzed by using two ion chromatographs to determine the concentrations of NO$_3^-$, NO$_2^-$, and NH$_4^+$. In this research, two kinds of reaction solutions were employed. One was an aqueous NO$_3^-$ solution (NO$_3^-$-aq) prepared from distilled water and KNO$_3$. The other was real groundwater obtained from a well in Hokkaido (G-water). G-water contained NO$_3^-$ as well as Cl$^-$ (1.0 mmol dm$^{-3}$), SO$_4^{2-}$ (0.5 mmol dm$^{-3}$), SiO$_2$ (0.3 mmol dm$^{-3}$), Na$^+$ (1.0 mmol dm$^{-3}$), K$^+$ (0.1 mmol dm$^{-3}$), Mg$^{2+}$ (1.0 mmol dm$^{-3}$), Ca$^{2+}$ (0.5 mmol dm$^{-3}$), and water-soluble organic matters (1.2 ppm). For some experiments, the catalytic performance was evaluated with a gas-liquid continuous flow reactor.

3. Results and discussion

We began by evaluating the catalytic performance of Cu-Pd/active carbon in G-water [1]. As Fig. 1 shows, whereas the catalyst exhibited high activity and extremely high selectivity to gas products including N$_2$ and N$_2$O in NO$_3^-$-aq, did not work well in G-water, showing pronounced decline in the catalytic performance. The catalyst deactivation was somewhat reduced when G-water was treated by oxidation with
ozone to decompose the water-soluble organic matters (G-water-Ox), the catalytic performance was still low. To investigate influence of the ionic materials in G-water on the catalytic performance, an aqueous NO$_3^-$ solution containing each ion found in the groundwater was prepared and the catalytic performance was evaluated in the solutions. It was found that anions especially Cl$^-$ had great impact on the catalyst deactivation (Fig. 1), while cations had little influence on the catalytic performance. It is known that NO$_3^-$ was reduced to NO$_2^-$ at a metallic Cu site and this is the rate-determining step. Because Cl$^-$ and NO$_3^-$ competitively adsorbed on the metallic Cu sites over Cu-Pd/active carbon, causing the catalyst deactivation, the problem arising from Cl$^-$ was inevitable for the bimetallic Cu-Pd catalyst. Therefore, catalysts without any use of Cu was necessary for purification of the real groundwater.

We tried to develop a catalyst that exhibited high catalytic performance and was unaffected by the ionic materials in the groundwater. We finally found a bimetallic Sn-Pd supported on Al$_2$O$_3$ [2]. Catalytic results in NO$_3^-$-aq showed that the Sn/Pd ratio had a great impact on the catalytic performance and the catalyst with Sn/Pd = 0.5 was the best one in terms of activity and selectivity. Fig. 2 compares the catalytic performance of Sn-Pd/Al$_2$O$_3$ with Cu-Pd/Al$_2$O$_3$ in NO$_3^-$-aq (Fig. 2(a)) and G-water (Fig. 2(b)). Sn-Pd/Al$_2$O$_3$ was more active than Cu-Pd/Al$_2$O$_3$, while both the catalysts exhibited similar high selectivity to gas products more than 95% in NO$_3^-$-aq. For the reactions in G-water, much more reaction time to reach 100% conversion was necessary than those in NO$_3^-$-aq for both the catalysts. However, the decline in the catalytic activity in G-water for Sn-Pd/Al$_2$O$_3$ was lesser than that for Cu-Pd/Al$_2$O$_3$. The deactivation of Cu-Pd/Al$_2$O$_3$ was quite notable at the conversion over 80% due to the competitive adsorption of Cl$^-$ with NO$_3^-$ and consequently 60 h was necessary for complete decomposition of NO$_3^-$. The selectivity to gas products was also decreased in G-water, but Sn-Pd/Al$_2$O$_3$ still gave the selectivity around 90%, while that for Cu-Pd/Al$_2$O$_3$ was less than 80%. Adsorption isotherms of Cl$^-$ demonstrated that adsorption of Cl$^-$ on the Sn site was weaker than that on the Cu site. In addition, kinetic experiments suggested that adsorption of NO$_3^-$ on Sn-Pd/Al$_2$O$_3$ was stronger than that on Cu-Pd/Al$_2$O$_3$. The less sensitivity for Cl$^-$ and strong adsorption of NO$_3^-$ on the Sn site can contribute considerably to the high catalytic performance of Sn-Pd/Al$_2$O$_3$ in G-water.

**4. Conclusions**

The supported Cu-Pd catalyst suffered severe deactivation in G-water, caused mainly by water-soluble organic matters and Cl$^-$ in water. The adverse impact from the former was partly avoidable by the oxidative treatment of G-water to combust the water-soluble organic matters. Sn-Pd/Al$_2$O$_3$ was also deactivated in G-water, but the decline in the catalytic performance in G-water was lesser than that for Cu-Pd/Al$_2$O$_3$ and all NO$_3^-$ was decomposed with around 90% selectivity to gas products in 24 h under the reaction conditions. The less sensitivity for Cl$^-$ and strong adsorption of NO$_3^-$ on the Sn site over Sn-Pd/Al$_2$O$_3$ are the reasons for the high catalytic performance of Sn-Pd/Al$_2$O$_3$ in G-water. We are sure that Sn-Pd/Al$_2$O$_3$ is promising and made a great contribution for the purification of real groundwater.

**References**