Catalytic reduction of nitrate in water toward purification of real groundwater

Jun Hirayama,[a] **Yi Wang**,[b] **Ryoichi Otomo**[a], **Yuichi Kamiya**,[a],*
[a]*Faculty of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan*
[b]*Graduate School of Environmental Science, Hokkaido University, Sapporo 060-0810, Japan*
**Yuichi Kamiya: kamiya@ees.hokudai.ac.jp*

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_2O_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_2O_3 are the reasons for the high catalytic performance of Sn-Pd/Al_2O_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_2O_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_x^{n-} (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_2O 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.

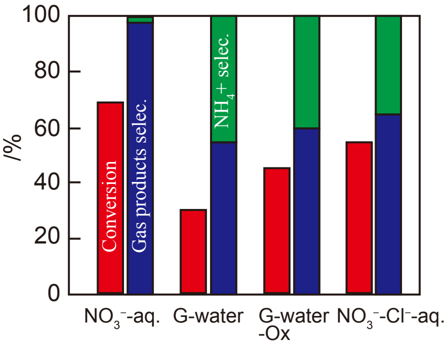

Fig. 1 Catalytic results for Cu-Pd/active carbon. The reaction was carried out at 298 K by using a gas-liquid continuous flow reactor. NO_3^--aq: aqueous NO_3^- solution; G-water: groundwater; G-water-Ox: ground -water treated by oxidation with ozone; and NO_3^--Cl^--aq: aqueous NO_3^- solution added with Cl^-.

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_2O_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_2O_3 with Cu-Pd/Al_2O_3 in **NO_3^--aq** (Fig. 2(a)) and **G-water** (Fig. 2(b)). Sn-Pd/Al_2O_3 was more active than Cu-Pd/Al_2O_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_2O_3 was lesser than that for Cu-Pd/Al_2O_3. The deactivation of Cu-Pd/Al_2O_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_2O_3 still gave the selectivity around 90%, while that for Cu-Pd/Al_2O_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_2O_3 was stronger than that on Cu-Pd/Al_2O_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_2O_3 in **G-water**.

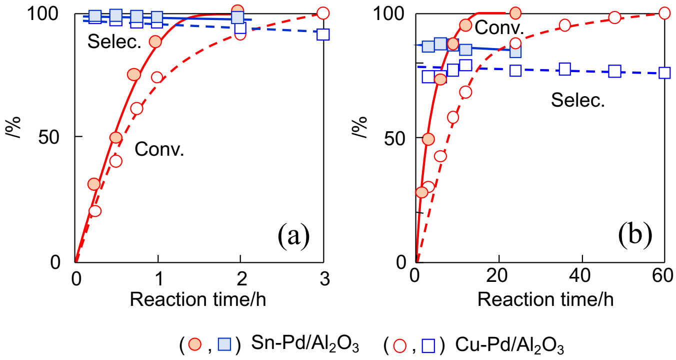

Fig. 2 Comparison of the catalytic performances of Sn-Pd/Al_2O_3 with Cu-Pd/Al_2O_3 in (a) **NO_3^--aq** and (b) **G-water**.

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_2O_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_2O_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_2O_3 are the reasons for the high catalytic performance of Sn-Pd/Al_2O_3 in **G-water**. We are sure that Sn-Pd/Al_2O_3 is promising and made a great contribution for the purification of real groundwater.

References

1. Y. Wang, Y. Sakamoto, Y. Kamiya, Appl. Catal. A, 361 (2009) 123; 2. J. Hirayama, Y. Kamiya, ACS Catal. 4 (2014) 2207.