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## **Water Purification by Catalytic and Photocatalytic Reactions: Nitrate-Polluted Groundwater As an Example**

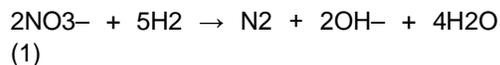
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Water quality conservation including both drinking water and wastewater is unavoidable task for us to develop sustainable society in future. The present author has no doubt that catalytic and photocatalytic sciences will play a critical role in achieving this. In this lecture, it will be shown that our research works on purification of groundwater polluted with nitrate (NO<sub>3</sub><sup>-</sup>) by catalytic and photocatalytic reactions.

Pollution of groundwater with NO<sub>3</sub><sup>-</sup> as a result of intensive agricultural activities using nitrogen fertilizers, human sewage, and industrial effluents is a serious global problem. NO<sub>3</sub><sup>-</sup> is reduced to nitrite (NO<sub>2</sub><sup>-</sup>) in the human body, which causes methemoglobinemia in infants (i.e., blue-baby syndrome) and is a possible precursor of carcinogenic nitrosamine. Thus, the World Health Organization (WHO) recommends that the concentration of NO<sub>3</sub><sup>-</sup> in drinking water should be below 0.8 mmol dm<sup>-3</sup>, which corresponds to 50 mg dm<sup>-3</sup>. Since groundwater is an important fresh water resource that is indispensable to human society, NO<sub>3</sub><sup>-</sup> needs to be removed from polluted groundwater.

Catalytic hydrogenation of NO<sub>3</sub><sup>-</sup> (Eq. 1) is an attractive technique for removing NO<sub>3</sub><sup>-</sup> from groundwater because NO<sub>3</sub><sup>-</sup> is converted into harmless nitrogen gas.



Since the discovery that Cu-Pd/Al<sub>2</sub>O<sub>3</sub> is an effective solid catalyst for the hydrogenation of NO<sub>3</sub><sup>-</sup> in water, reactions over Cu-Pd bimetallic catalysts have been studied extensively. However, most studies have dealt with the reduction of NO<sub>3</sub><sup>-</sup> in distilled water, although actual groundwater contains various cations, anions, and organic species, which must influence the catalytic performance. In fact, Cu-Pd bimetallic catalysts that showed high activity and high selectivity for the reduction of NO<sub>3</sub><sup>-</sup> in distilled water lost their high catalytic performances in real groundwater<sup>1</sup>). This was mainly due to competitive adsorption of chloride ion with NO<sub>3</sub><sup>-</sup> on Cu site on the catalysts. That made us start searching Cu-free catalysts that were resistant to chloride ion, and we finally found Sn-Pd/active carbon (Sn-Pd/AC) catalyst. In stark contrast to Cu-Pd/AC, the activity and selectivity were high

for Sn-Pd/AC even in the presence of chloride ion (Fig. 1). By using Sn-Pd/AC, we successfully purified the real groundwater polluted with  $\text{NO}_3^-$  (Fig. 2).

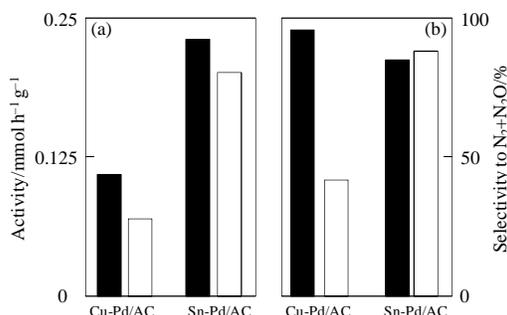


Fig. 1 Catalytic data for Cu-Pd/AC and Sn-Pd/AC in the hydrogenation of  $\text{NO}_3^-$  in distilled water (solid) and that in distilled water containing chloride ion (open). (a) Activity and (b) selectivity to harmless compounds ( $\text{N}_2$  and  $\text{N}_2\text{O}$ ).

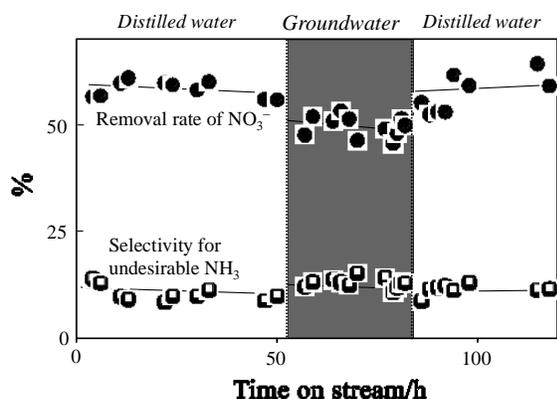


Fig. 2 Time on stream for catalytic hydrogenation of  $\text{NO}_3^-$  over Sn-Pd/AC.

In the investigations described so far, hydrogen gas was of course necessary. However, the supply of hydrogen gas is a serious issue for practical applications because this is not readily available in most homes and businesses and hydrogen gas is hard to deal with. It is well known that photocatalysts, like  $\text{Pt}/\text{TiO}_2$ , readily generate hydrogen gas in water along with consuming sacrificial compounds, like ethanol and glucose, under UV irradiation. Thus, we thought that a combination of  $\text{Pt}/\text{TiO}_2$  and supported Sn-Pd catalyst

showed promise for the removal of  $\text{NO}_3^-$  from groundwater without  $\text{H}_2$  gas (Fig. 3)<sup>2</sup>.

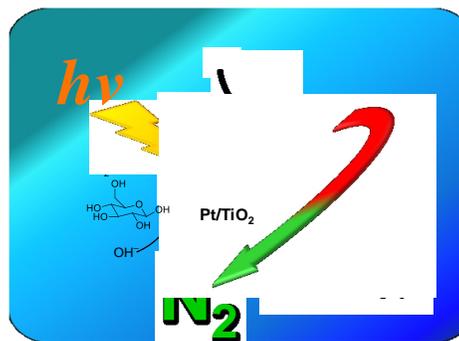


Fig. 3 Schematic image of the combined photocatalytic reaction system that we propose for groundwater

As Table 1 summarizes, sole  $\text{Pt}/\text{TiO}_2$  and sole  $\text{Sn}_2\text{-Pd}/\text{Al}_2\text{O}_3$  (Entry 2) were inactive or less active for conversion reaction of  $\text{NO}_3^-$  even under UV irradiation (Entry 1). In contrast, when  $\text{Pt}/\text{TiO}_2$  and  $\text{Sn-Pd}/\text{Al}_2\text{O}_3$  were simultaneously present in the reaction solution (Entry 3), the high  $\text{NO}_3^-$  conversion (39%) was obtained. At that time, formation of undesirable  $\text{NH}_4^+$  was suppressed at low level (selectivity for  $\text{NH}_4^+ = 10\%$ ) and toxic  $\text{NO}_2^-$  was not formed at all.  $\text{NO}_3^-$  was converted with time with low selectivity for  $\text{NH}_4^+$  only when UV light was irradiated and reached to a complete conversion after 24 h. When the reaction was carried out without ethanol, no conversion reaction of  $\text{NO}_3^-$  took place even in the presence of both catalysts (Entry 4). The present photocatalytic system that  $\text{Pt}/\text{TiO}_2$  and  $\text{Sn}_2\text{-Pd}/\text{Al}_2\text{O}_3$  existed simultaneously in the reaction solution was compared to  $\text{TiO}_2$  modified with  $\text{Sn}_2\text{-Pd}$  bimetal. As Table 1 demonstrates, our system was more active and selective for desirable gas formation than  $\text{Sn}_2\text{-Pd}/\text{TiO}_2$  (Entry 6) and  $\text{Sn}_2\text{-Pd}/\text{Pt}/\text{TiO}_2$  (Entry 7).

Table 1 Photocatalytic reduction of nitrate in water in the presence of various catalyst

Entry	Catalyst	Conv. /%	Selectivity/%		
			NO <sub>2</sub> <sup>-</sup>	NH <sub>3</sub>	gas
1	Pt/TiO <sub>2</sub>	0	---	---	---
2	(Sn <sub>2</sub> -Pd)/Al <sub>2</sub> O <sub>3</sub>	2	0	31	69
3	Pt/TiO <sub>2</sub> <sup>a</sup> + (Sn <sub>2</sub> -Pd)/Al <sub>2</sub> O <sub>3</sub>	3	0	10	90
4	Pt/TiO <sub>2</sub> <sup>a</sup> + (Sn <sub>2</sub> -Pd)/Al <sub>2</sub> O <sub>3</sub> w/o ethanol <sup>a</sup>	0	---	---	---
5	Pt/TiO <sub>2</sub> <sup>a</sup> + (Sn <sub>2</sub> -Pd)/active carbon	0	---	---	---
6	(Sn <sub>2</sub> -Pd)/TiO <sub>2</sub>	19	0	23	77
7	(Sn <sub>2</sub> -Pd)/Pt/TiO <sub>2</sub>	23	0	24	76

<sup>a</sup>Photocatalytic reduction of NO<sub>3</sub><sup>-</sup> was conducted in the absence of ethanol.

Finally we applied the combined photocatalytic reaction system to purification of real groundwater. Some problems arose for purification of the real groundwater, but NO<sub>3</sub><sup>-</sup> (1.0 mmol dm<sup>-3</sup>) in the real groundwater completely and selectively decomposed to N<sub>2</sub> (yield 83%) after 120 h under UV irradiation over our photocatalytic reaction system in

combination with photooxidative pretreatment of the groundwater over Pt/TiO<sub>2</sub> to decompose organic compounds.

#### References

- [1] *Chem. Lett.* 33 (2004) 908–909; *Chem. Lett.* 34 (2005) 1510; *Chem. Lett.* 36 (2007) 994–995; *Appl. Catal. A* 361 (2009) 123–129.  
 [2] *Catal. Commun.* 20 (2012) 99–102; *Appl. Catal. B.* 144 (2014) 721–729; *ACS Catalysis* (in press).