Supplementary data

Enhanced denitrification of contaminated groundwater by novel bimetallic catalyst supported by kaolin-derived zeolite: Effects of natural dissolved inorganic and organic matter

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Chemicals and Materials

Sodium hydroxide (NaOH, 97.0%, Daejung Chemicals & Metals Co., Ltd., Korea) was used to synthesize zeolites from kaolin (Seoul Chemical Industry, Korea). Precursor solutions of Pd and In were prepared using palladium(II) chloride (99%, Sigma-Aldrich Inc., USA) and indium(III) chloride (98%, Sigma-Aldrich Inc., USA), respectively. The other Pd-In bimetallic catalysts supported by different materials were prepared using silicon dioxide (~99%, 0.5–10 μm, Sigma-Aldrich Inc., USA), aluminum oxide (99.5%, ≤10 μm, Sigma-Aldrich Inc., USA), and zeolite A-4 (200 mesh, Wako Pure Chemicals Corp., Japan). Pd-In bimetallic catalysts were activated using 10 mM sodium borohydride (98%, Sigma-Aldrich Inc., USA) before the reaction.

Potassium nitrate (99.0%, Duksan Pure Chemical Co., Korea), potassium nitrite (99.0%, Sigma-Aldrich Inc., USA), and ammonium chloride (98.5%, Shinyo Pure Chemicals Co., Japan) were used to prepare the stock solutions of nitrate, nitrite, and ammonia, respectively. Calcium chloride dihydrate (99.0%, Junsei Chemical Co., Ltd., Japan), sodium chloride (99.0%, Samchun Pure Chemicals Co., Korea), and sodium sulfate (99.0%, Showa Chemical Industry Co., Japan) were used for standard solutions for ion chromatography (IC). Sodium bicarbonate (99.0%, Samchun Pure Chemicals Co., Korea), sodium carbonate (99.95%, Sigma-Aldrich Inc., USA), sulfuric acid (60%, Daejung Chemicals & Metals Co., Ltd., Korea), and nitric acid/dipicolinic acid (Sigma-Aldrich Inc., USA) were used to prepare eluents for IC operation.

Characterization of ZK70 and Pd-In/ZK70

The specific surface areas of ZK70 and Pd-In/ZK70 were measured by nitrogen adsorption and desorption at −196 ℃ with a Brunauer–Emmett–Teller surface analyzer (Tristar II, Micrometrics, USA). X-ray diffraction (XRD) analysis was performed to identify the mineral

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phase using an automated diffractometer with Cu-KN radiation (DE/D8 advance, Bruker, Germany). The samples were scanned with 2θ in the range 10°–50° with a scan speed of 1° min^{-1}.

The samples for surface characterization of Pd-In/ZK70 after reduction of $NO_3^-{}_{GW}$ (reaction time = 180 min) were prepared as follows: after finishing the reaction, stirring and H_2 and CO_2 supplies were stopped and Ar purging was started to prevent a possible oxidation of the catalyst by air. The solution was then sealed and transferred to the anaerobic chamber to minimize the surface oxidation of the catalyst. The used Pd-In/ZK70 catalyst was vacuum-filtered using a mixed cellulose ester membrane filter (0.2 μm, Advantech, Japan). The collected catalyst was rinsed with DDIW, 50% deaerated ethanol, and 100% deaerated ethanol sequentially. All washed samples were dispersed in deaerated ethanol to prevent further oxidation before the analyses.

The morphological characteristics of kaolin, ZK70, and Pd-In/ZK70 were investigated using field emission scanning electron microscopy (FE-SEM) (SU8010, Hitachi, Japan), field-emission transmission electron microscopy (FE-TEM) (JEM-F200, JEOL Ltd, Japan), and Cs-TEM (JEM-ARM200F, JEOL Ltd, Japan) equipped with energy-dispersive X-ray spectroscopy (EDX). The elemental dispersion of Pd, In, Si, Al, and O on the surface of ZK70 and Pd-In/Zk70 was identified by FE-TEM/EDX. The suspensions of ZK70, fresh Pd-In/ZK70, and used Pd-In/ZK70 were diluted with deaerated ethanol and sonicated for 10 min to completely disperse the particles. The droplets of the diluted samples were put on a 200 mesh copper TEM grid and dried in the anaerobic chamber. Samples were analyzed by FE-TEM at 200 kV.

The oxidation states of Pd and In on the surface of 1.25% Pd-0.25% In/ZK70 before activation, after activation with $NaBH_4$, and after reduction of NO_3^- in groundwater were investigated by XPS (K-Alpha, Thermo Scientific, USA) with Al Kα X-ray (1486.7 eV)
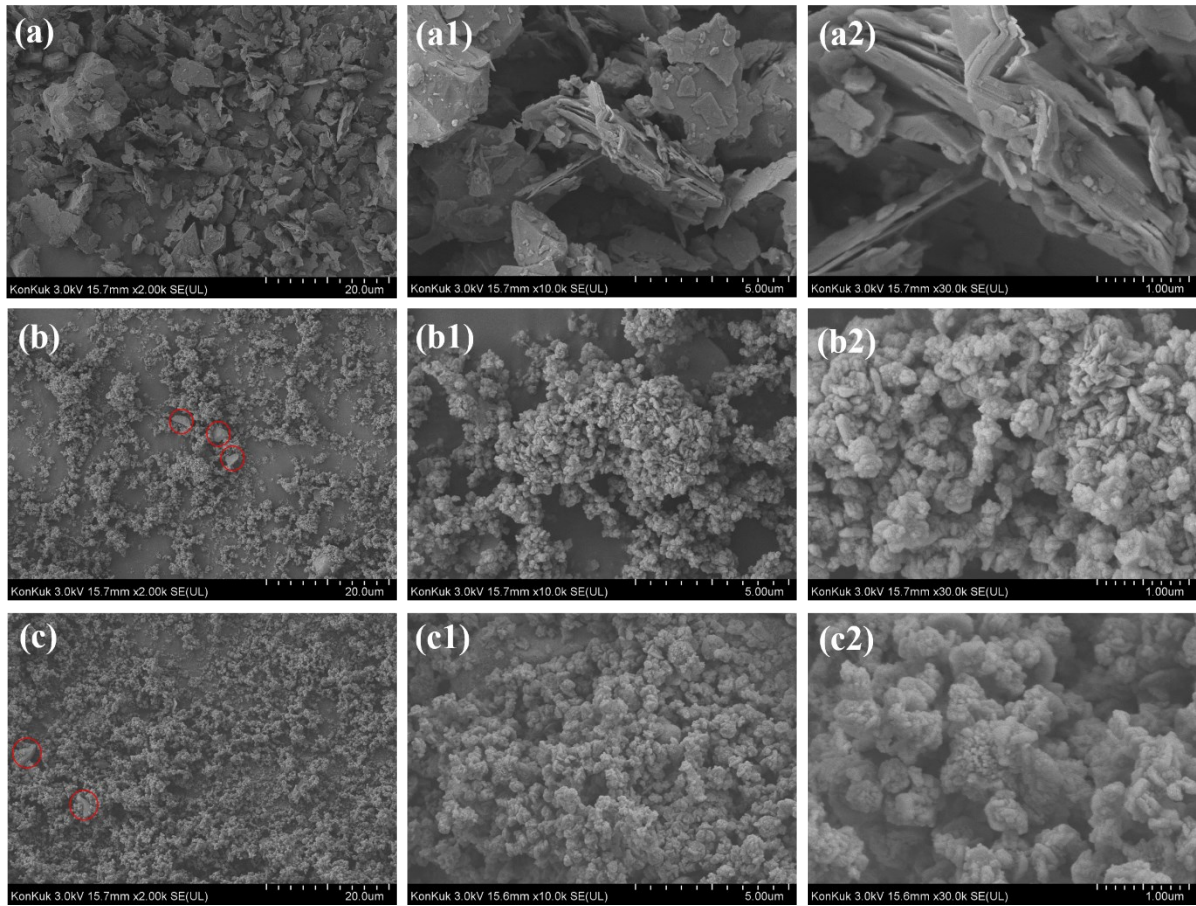
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radiation at a source power of 75 W. The C 1s peak at 285 eV was used as a reference. The narrow-scan spectra in the ranges 460–439 and 350–330 eV were obtained to identify the oxidation states of In and Pd species on the Pd-In/ZK70 surface, respectively.

ZK70, 1.25% Pd/ZK70, 0.25% In/ZK70, and 1.25% Pd-0.25% In/ZK70 were introduced into a conventional flow system for the TPR analysis (AutoChemII2920, Micromeritics Instrument Corp., USA) and examined in the temperature range of 50–1000 °C with ramping of 20°C /min. A stream of 10% H_2/Ar was passed through the system bed at a flow rate of 10 cm^3/min.

The cumulative H_2 uptake, metal dispersion, metallic surface area, active particle diameter, cubic crystallite size, and active metal sites of 1.25% Pd/ZK70 and 1.25% Pd-0.25% In/ZK70 were obtained by H_2 pulse chemisorption using an AutoChemII2920 (Micromeritics Instrument Corp., USA). X% Pd/ZK70 and X% Pd-X% In/ZK70 were outgassed under vacuum, followed by reduction under the flow of 10% H_2/Ar for 2 h at 350 °C, followed by flushing with Ar for 1 h and cooling to 30 ºC. The pulse chemisorption test was conducted at 30 °C by pulsing the 10% H_2/Ar.
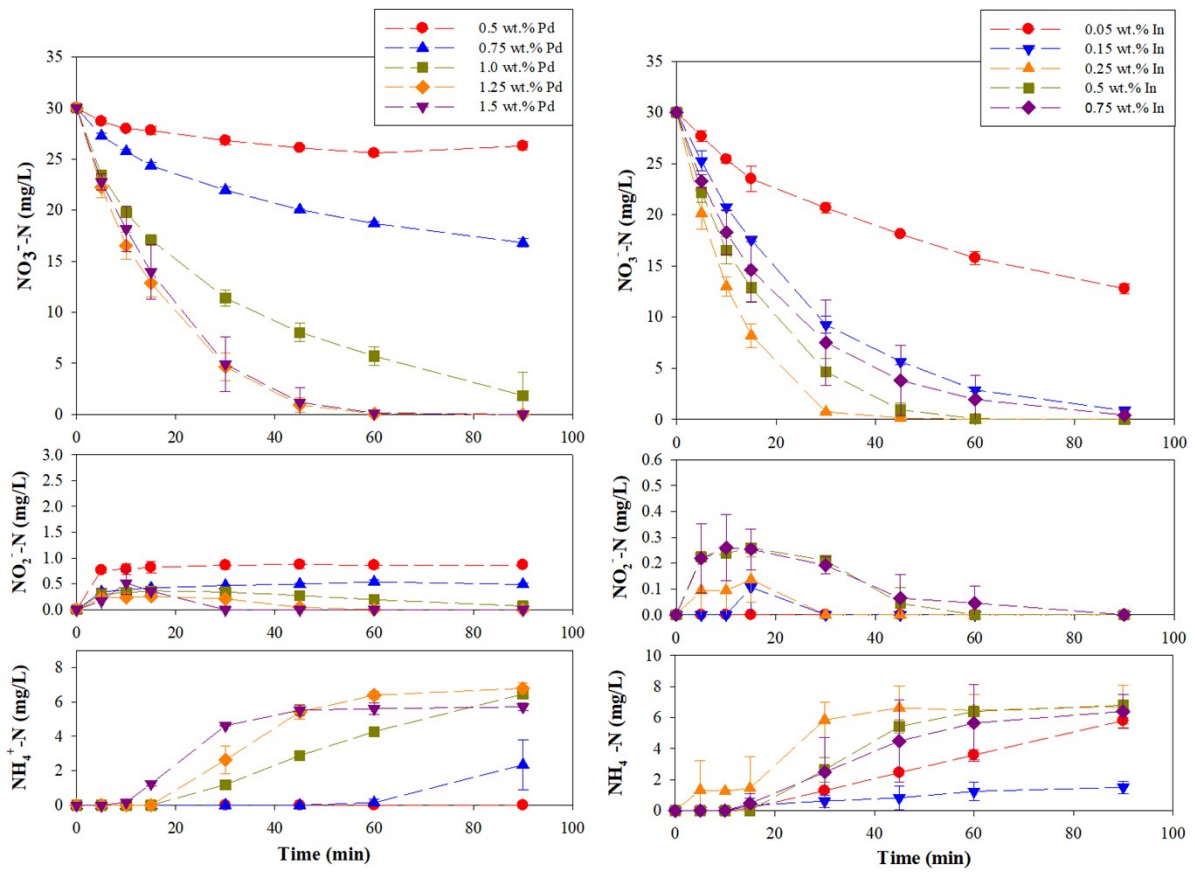
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Figure S1. FE-SEM images of (a, a1, and a2) kaolin, (b, b1, and b2) ZK70, and (c, c1, and c2) 1.25 wt% Pd-0.25 wt% In/ZK70.

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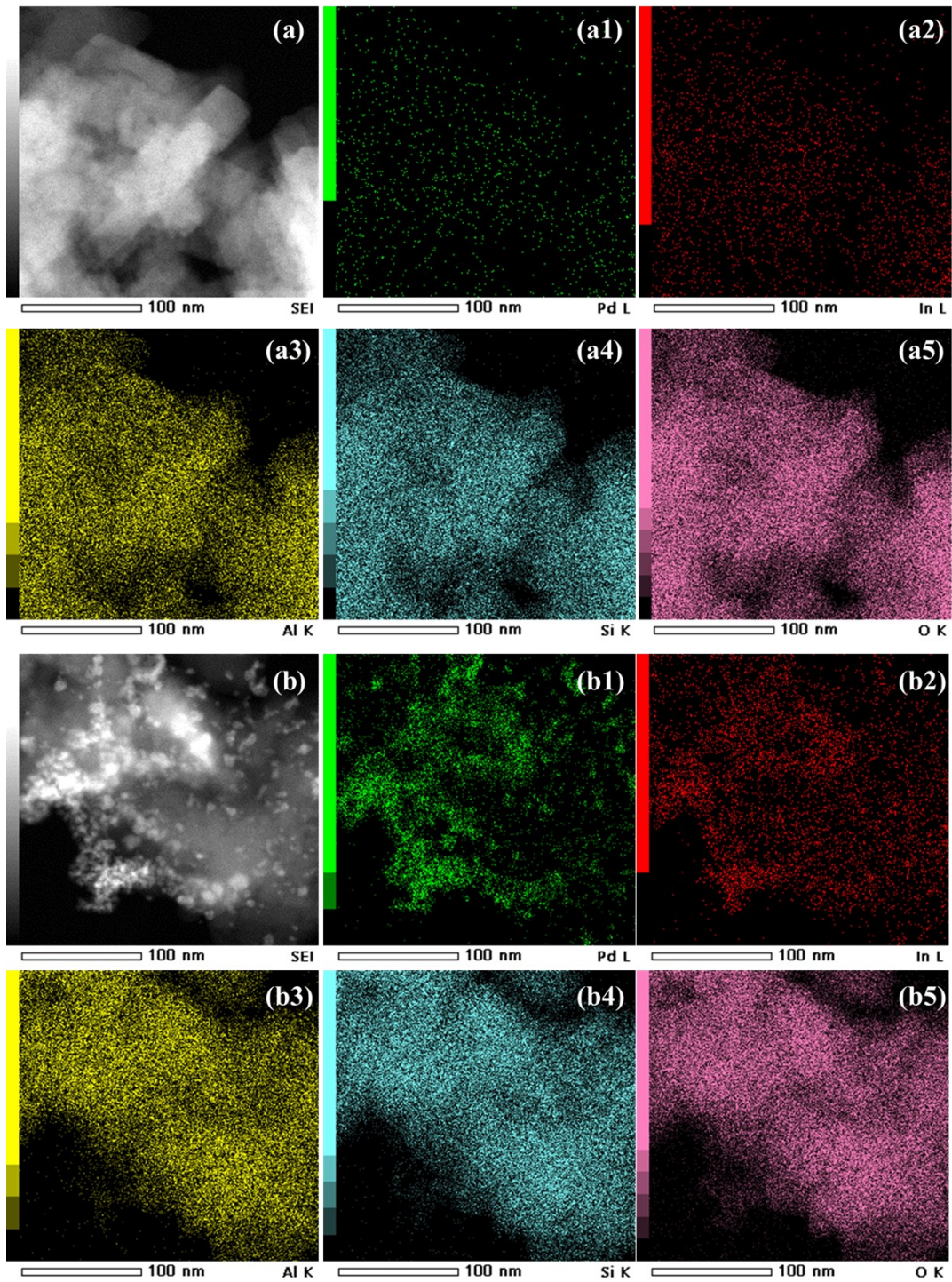
Figure S2. FE-TEM/EDS results of (a) ZK70 and (b) 1.25 wt% Pd-0.25 w.% In/ZK70 after activation; EDS electron mapping of (a1 and b1) Pd, (a2 and b2) In, (a3 and b3) Al, (a4 and b4) Si, and (a5 and b5) O.

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Figure S3. (a) The effect of Pd loading on $NO_3^-{}_{aq}$ reduction by X wt.% Pd-0.5 wt% In/ZK70 (X= 0.5, 0.75, 1.0, 1.25, 1.5). (b) The effect of In loading on NO_3^- reduction by 1.25 wt% Pd-X wt% In/ZK70 (X = 0.05, 0.15, 0.25, 0.5, 0.75).
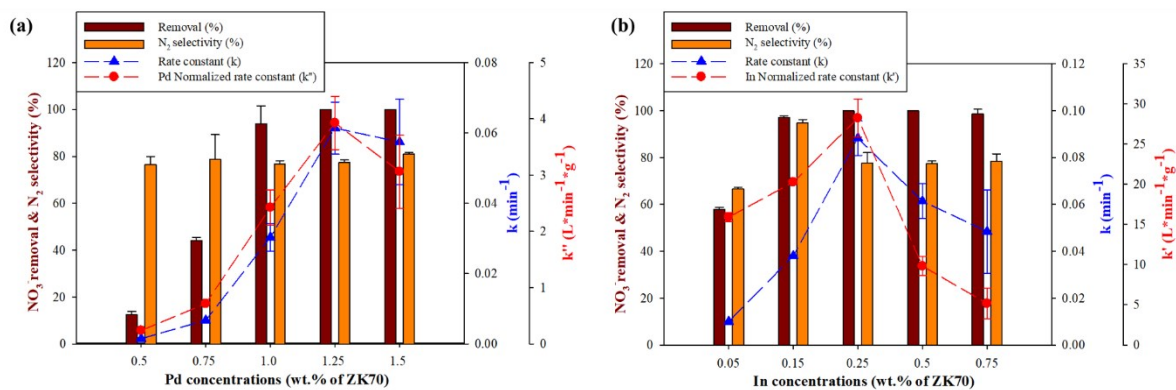
Figure S4. (a) $NO_3^-{}_{aq}$ removal, N_2 selectivity, rate constant (k), and Pd normalized rate constant (k'') of X wt% Pd-0.5 wt% In/ZK70 (X= 0.5, 0.75, 1.0, 1.25, 1.5). (b) $NO_3^-{}_{aq}$ removal, N_2 selectivity, rate constant (k), and In normalized rate constant (k') of 1.25 wt% Pd-X wt% In/ZK70 (X = 0.05, 0.15, 0.25, 0.5, 0.75).
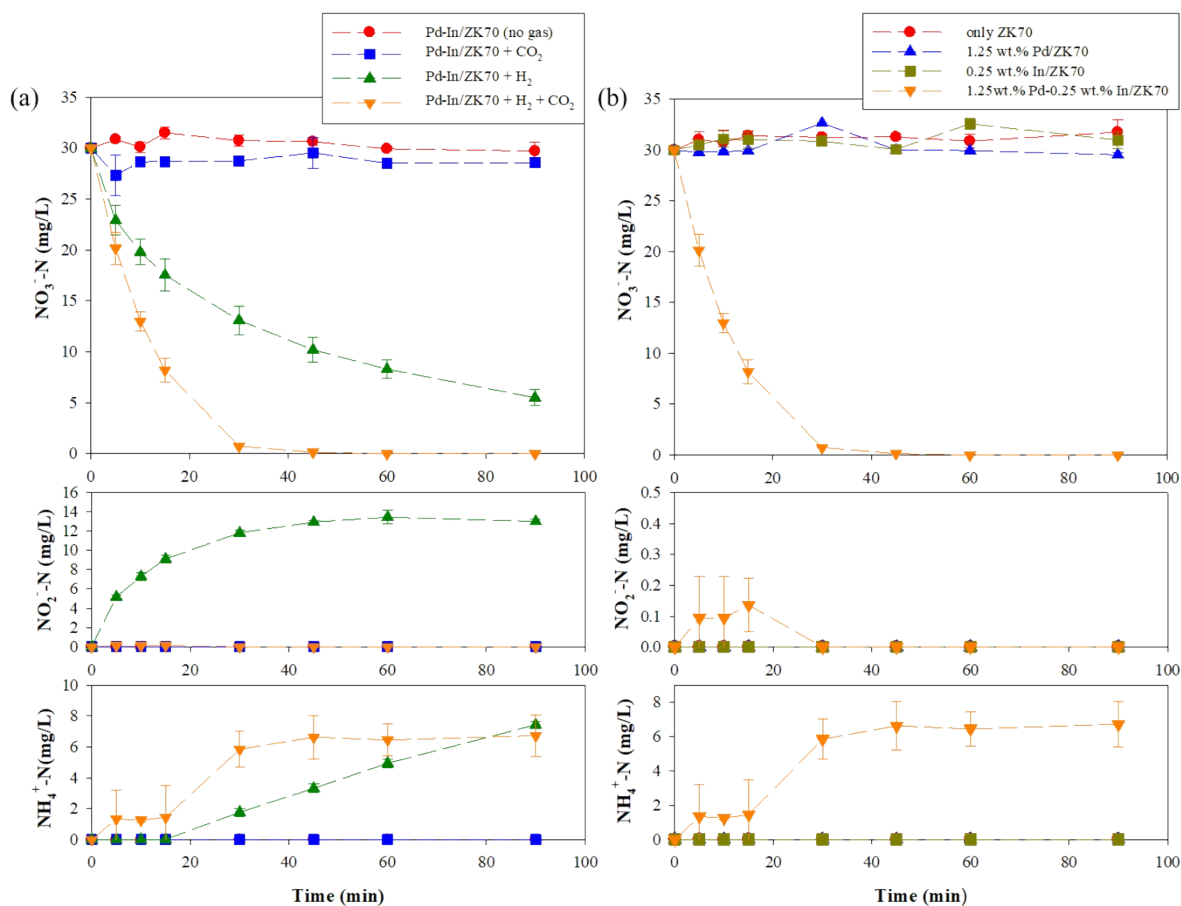
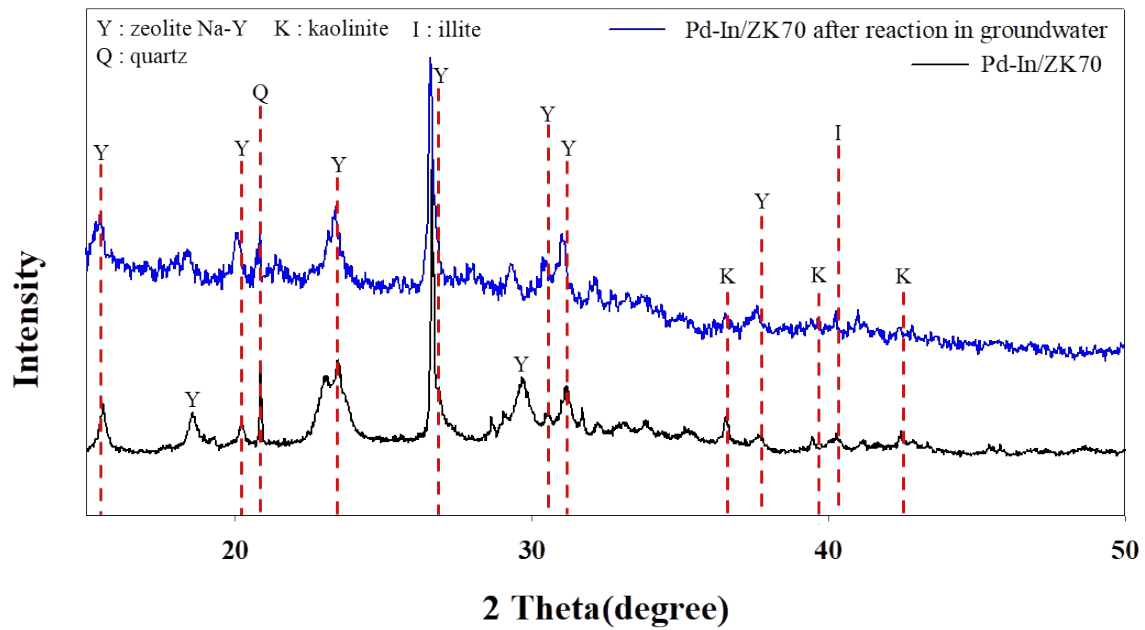**Figure S5.** (a) The concentrations of $NO_3^-_{aq}$, NO_2^-, and NH_4^+ as a function of reaction time during the catalytic reduction of $NO_3^-_{aq}$ by Pd-In/ZK70 (1.25 g/L, Pd = 1.25 wt%, In = 0.25 wt%) catalysts with only H_2, only CO_2, and both H_2 and CO_2, and without both H_2 and CO_2; H_2 flow rate = 45 cm³/min, CO_2 flow rate = 40 cm³/min. Reaction time was 90 min. (b) The concentrations of $NO_3^-_{aq}$, NO_2^-, and NH_4^+ as a function of reaction time during the catalytic reduction of NO_3^- on only ZK70, Pd/ZK70 (Pd = 1.25 wt%), In/ZK70 (In = 0.25 wt%) and Pd-In/ZK70 (Pd = 1.25 wt%, In = 0.25 wt%). Catalyst loading: 1.25 g/L.
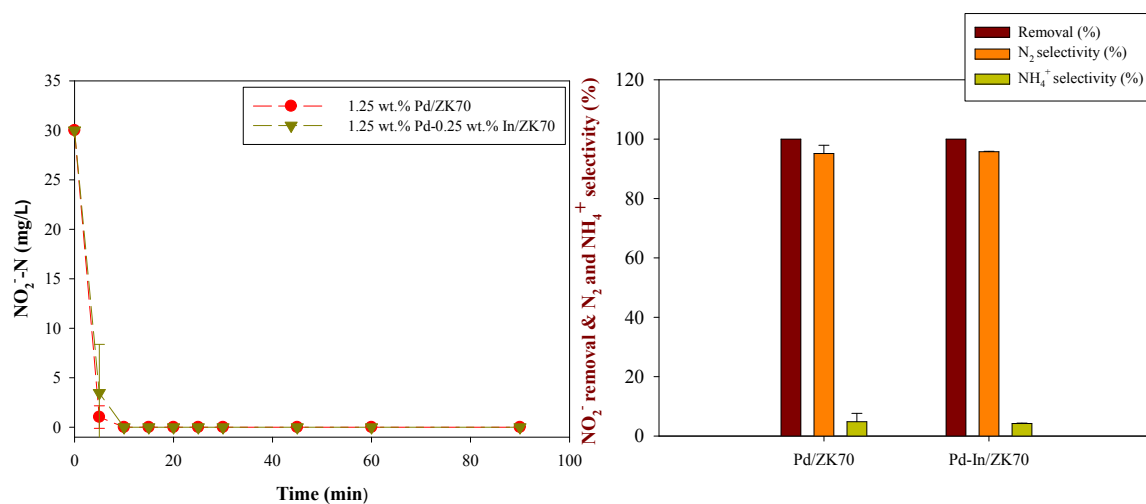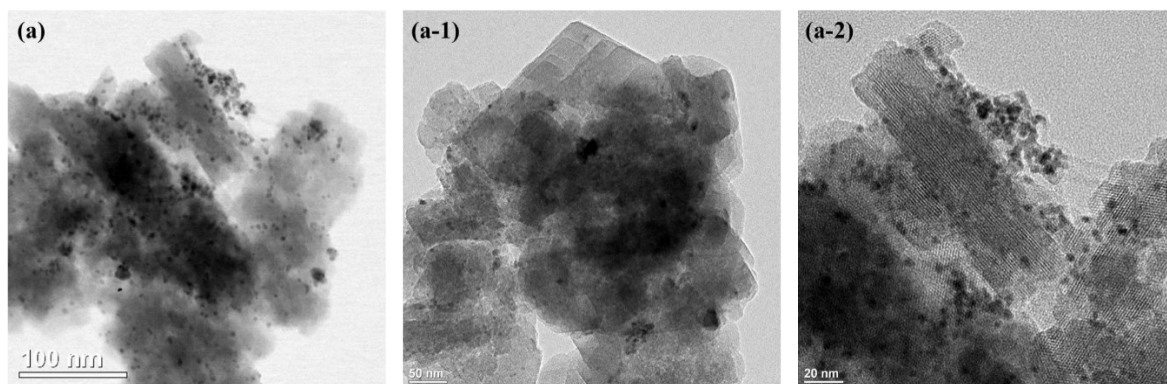
Figure S6. (a) The removal kinetics of NO_2^- by 1.25 wt% Pd/ZK70 and 1.25 wt% Pd-0.25 wt% In/ZK70, (b) NO_2^- removal and byproduct selectivity of 1.25 wt% Pd/ZK70 and 1.25 wt% Pd-0.25 wt% In/ZK70.
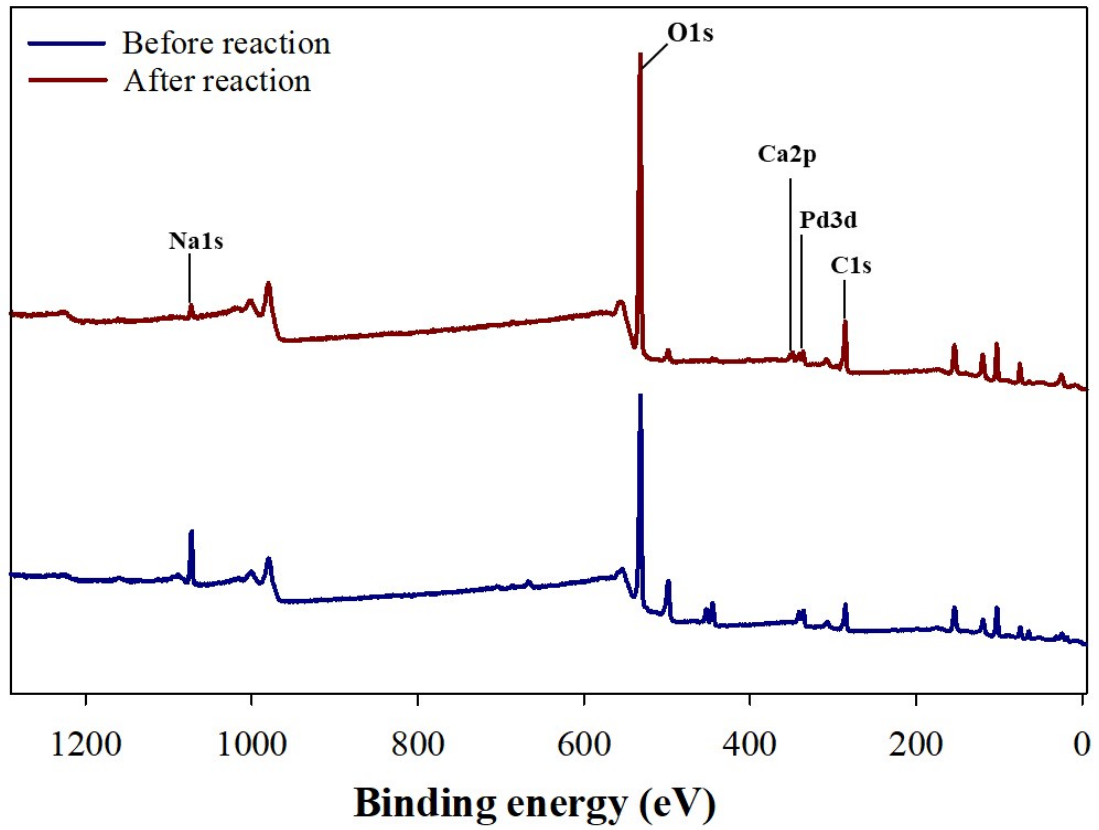
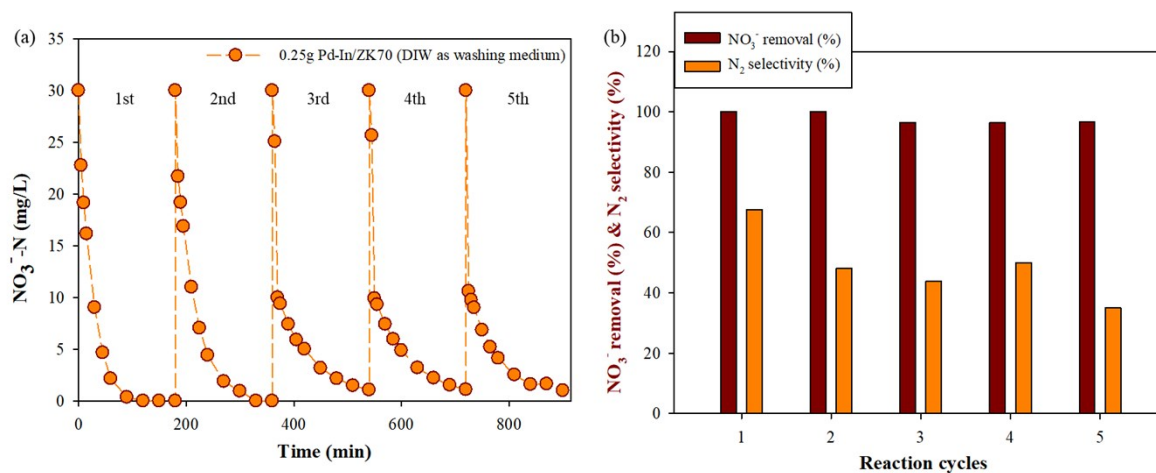**Figure S7.** XRD spectra of Pd-In/ZK70 before reaction, and after reaction in groundwater (Pd = 1.25 wt%, In = 0.25 wt%).

Figure S8. TEM images of Pd-In/ZK70 after reaction in real groundwater (Pd = 1.25 wt%, In = 0.25 wt%).

Figure S9. Survey scan of XPS for the sample of 1.25 wt% Pd-0.25 wt% In/ZK70 before and

after reaction of $NO_3^-{}_{GW}$ reduction.

Figure S10. (a) Kinetics of NO_3^- reduction by 0.25g of 1.25 wt% Pd- 0.25 wt% In/ZK70 during five recycling test in groundwater without regeneration and reactivation process. (b) N_2 selectivity and NO_3^- removal by 0.25g of 1.25 wt.% Pd- 0.25 wt.% In/ZK70 on repeated five recycling test.