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## Electric Supplementary Information (ESI)

**Drastic change in selectivity caused by addition of oxygen to the hydrogen stream for the  
hydrogenation of nitrite in water over a supported platinum catalyst**

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Table S1 Physical properties of Al<sub>2</sub>O<sub>3</sub>-supported catalysts

| Catalyst <sup>a</sup>             | S <sub>BET</sub> <sup>b</sup> /m <sup>2</sup> g <sup>-1</sup> | Particle size /nm |                 |
|-----------------------------------|---------------------------------------------------------------|-------------------|-----------------|
|                                   |                                                               | TEM <sup>c</sup>  | CO <sup>d</sup> |
| Pt/Al <sub>2</sub> O <sub>3</sub> | 101                                                           | 2.4 ± 0.5         | 4.1             |
| Pd/Al <sub>2</sub> O <sub>3</sub> | 112                                                           | 2.8 ± 0.7         | 4.0             |
| Ir/Al <sub>2</sub> O <sub>3</sub> | 113                                                           | 1.7 ± 0.6         | 2.3             |
| Ru/Al <sub>2</sub> O <sub>3</sub> | 117                                                           | 3.1 ± 0.7         | 3.3             |
| Rh/Al <sub>2</sub> O <sub>3</sub> | 98                                                            | 3.3 ± 0.9         | 3.9             |

<sup>a</sup> Loading amount of metal was 0.3 mmol g<sup>-1</sup>.

<sup>b</sup> Specific surface areas were calculated from the N<sub>2</sub> adsorption isotherm taken at 77 K to BET (Brunauer–Emmett–Teller) theory.

<sup>c</sup> Particle size estimated from TEM images, which are given in Fig. S1.

<sup>d</sup> Particle size estimated from CO-pulse titration at 323 K.

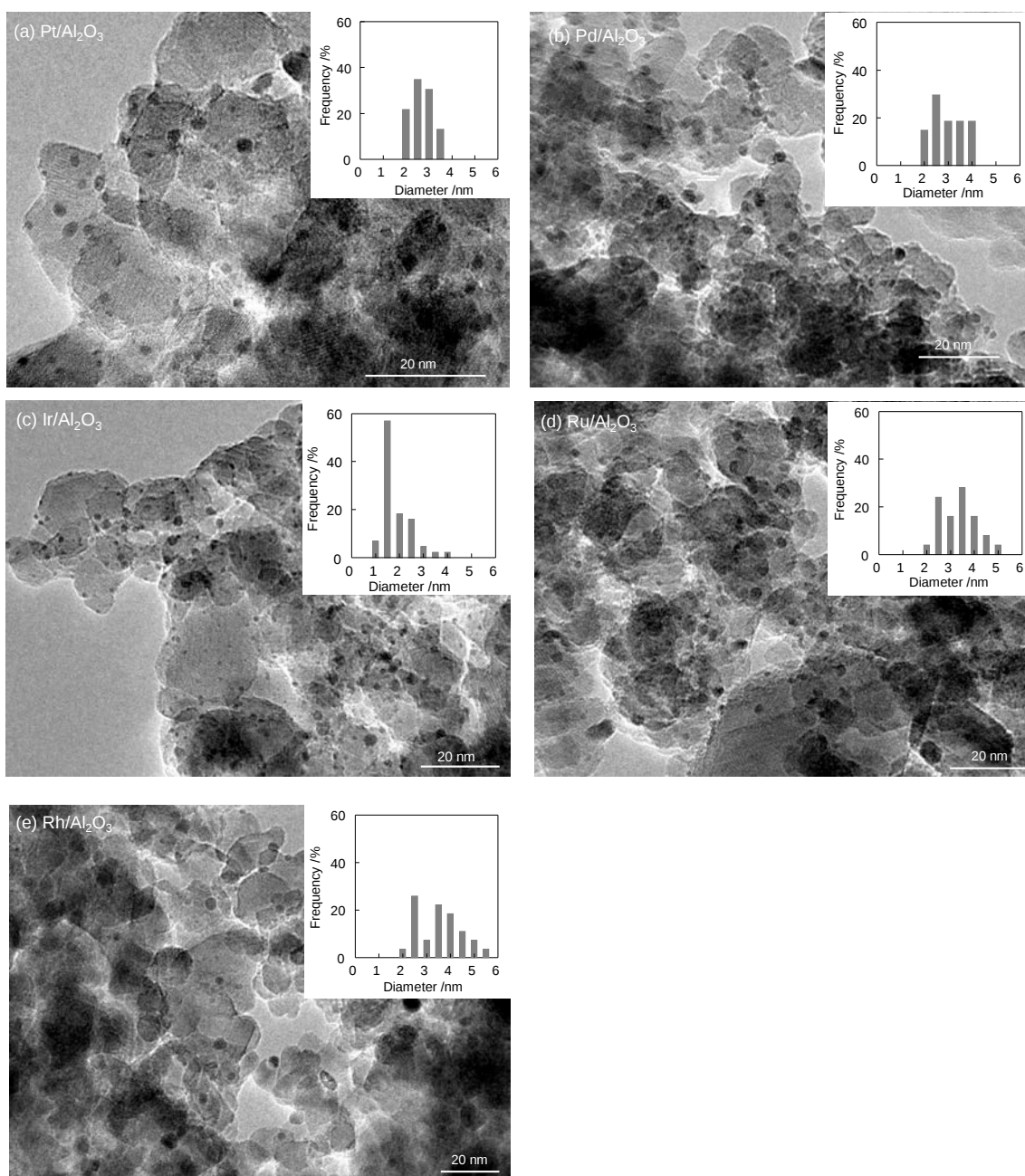


Figure S1 TEM images of (a)  $\text{Pt}/\text{Al}_2\text{O}_3$ , (b)  $\text{Pd}/\text{Al}_2\text{O}_3$ , (c)  $\text{Ir}/\text{Al}_2\text{O}_3$ , (d)  $\text{Ru}/\text{Al}_2\text{O}_3$ , and (e)  $\text{Rh}/\text{Al}_2\text{O}_3$ . Inset: distributions of metal particle sizes.

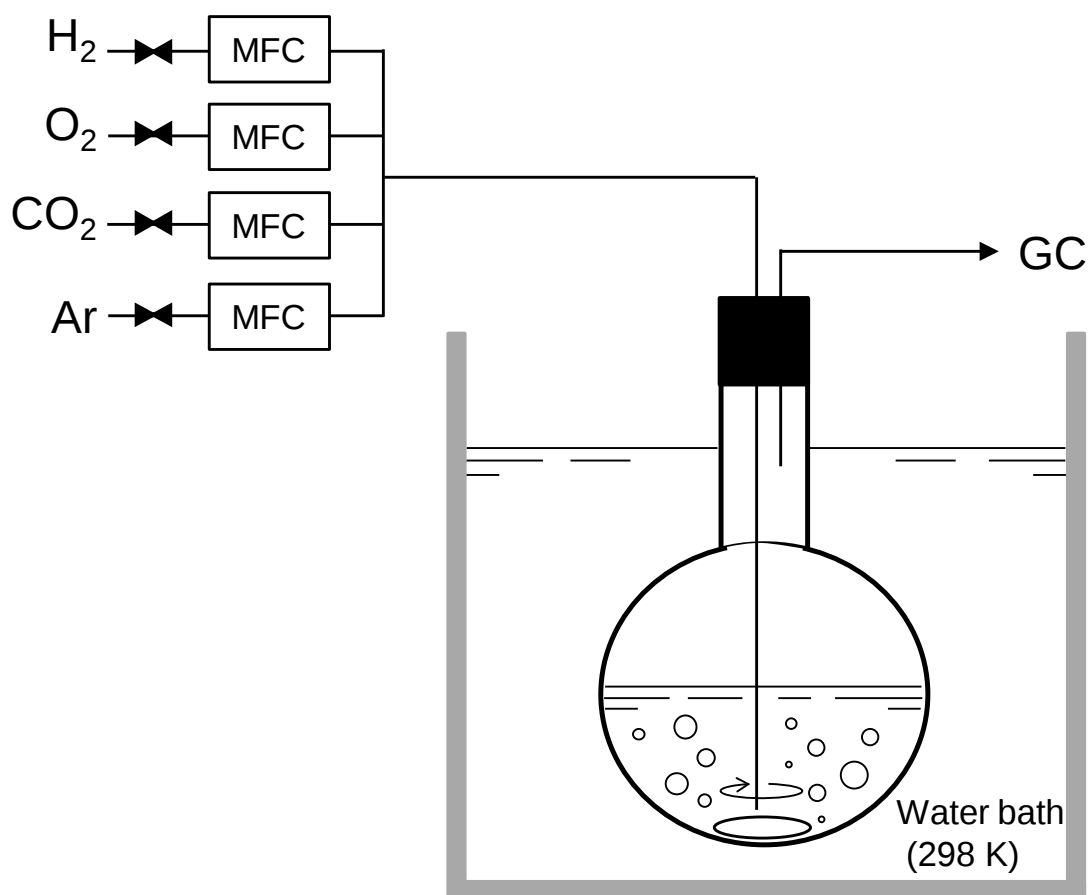


Figure S2 Schematic illustration of the catalytic reaction system. \*Because of the high risk of  $\text{H}_2$ - $\text{O}_2$  mixture for explosion, catalytic reaction experiments should be performed meticulously.

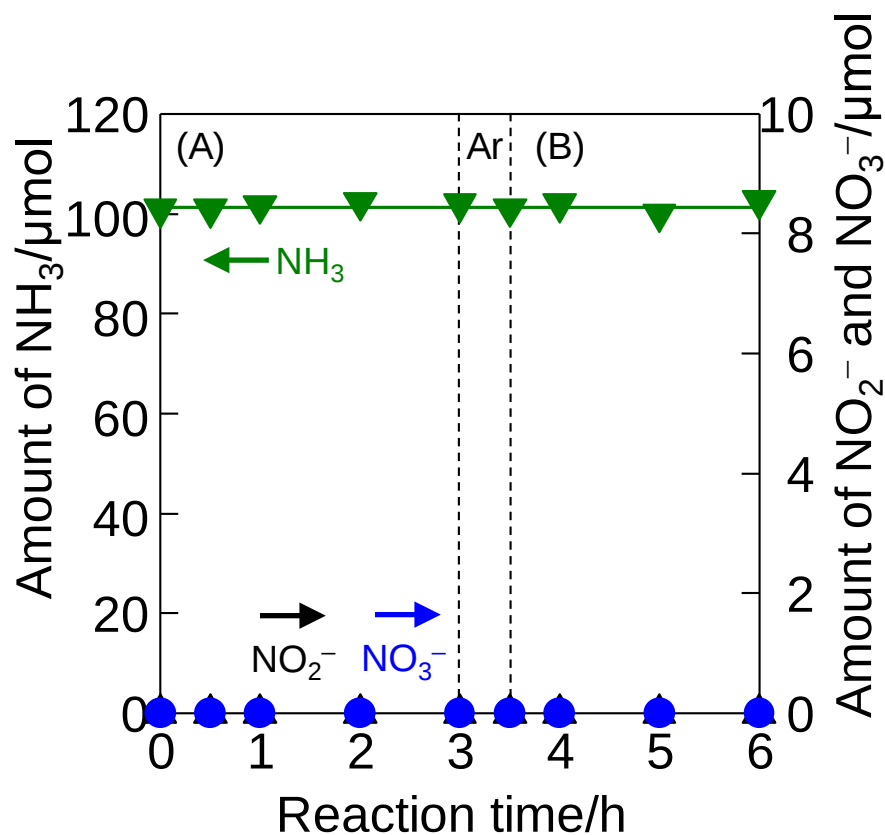


Figure S3 Time courses for the amounts of NH<sub>3</sub>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> in the solution during the oxidation of NH<sub>3</sub> with O<sub>2</sub> over Pt/Al<sub>2</sub>O<sub>3</sub> (A) in the presence and (B) absence of H<sub>2</sub>. Reaction conditions: concentration of NH<sub>3</sub>, 1.0 mmol dm<sup>-3</sup>; volume of reaction solution, 100 cm<sup>3</sup>; source of ammonium ion, NH<sub>4</sub>Cl; total pressure, 1.0 atm; gas composition, (A) H<sub>2</sub>:O<sub>2</sub>:CO<sub>2</sub>:Ar = 2:1:3:4 and (B) O<sub>2</sub>:CO<sub>2</sub>:Ar = 1:3:6; gas flow rate, 100 cm<sup>3</sup> min<sup>-1</sup>; and reaction temperature, 298 K.

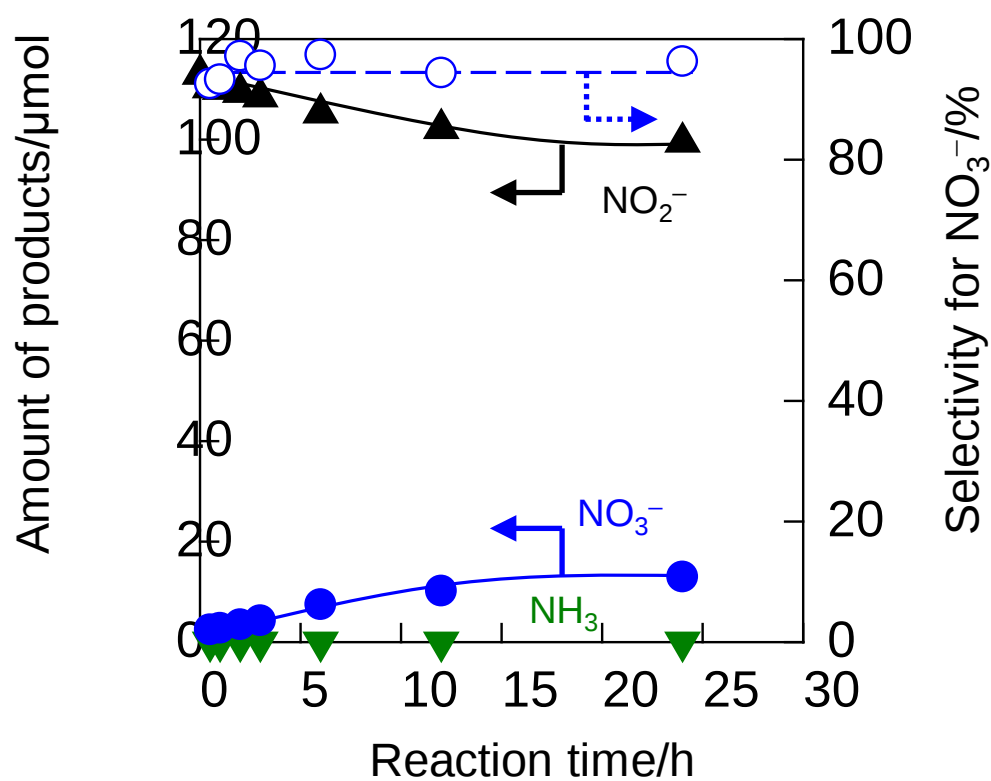
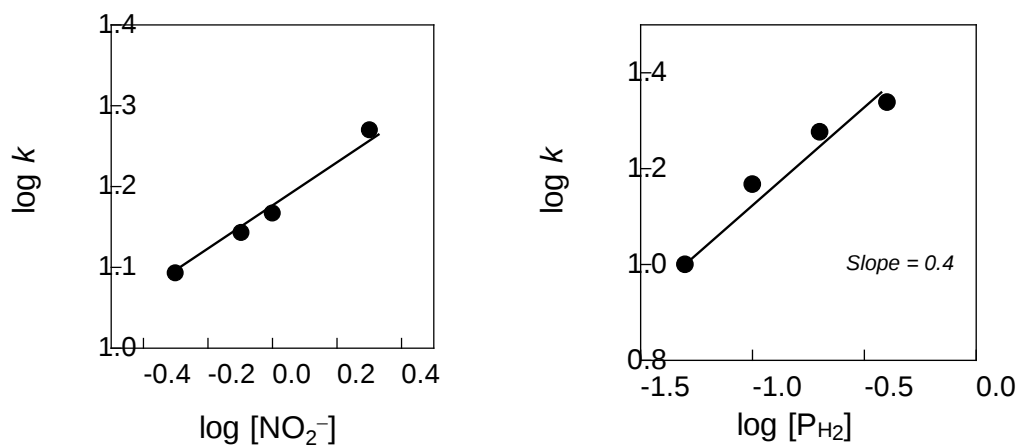


Figure S4 Time courses for the amounts of NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>3</sub>, and selectivity for NO<sub>3</sub><sup>-</sup> for the oxidation of NO<sub>2</sub><sup>-</sup> with O<sub>2</sub> in water over Pt/Al<sub>2</sub>O<sub>3</sub> in the absence of H<sub>2</sub>. Reaction conditions: concentration of NO<sub>2</sub><sup>-</sup>, 1.0 mmol dm<sup>-3</sup>; volume of reaction solution, 100 cm<sup>3</sup>; total pressure, 1.0 atm; source of NO<sub>2</sub><sup>-</sup>, KNO<sub>2</sub>; gas composition, O<sub>2</sub>:CO<sub>2</sub>:Ar = 2:3:5; gas flow rate, 100 cm<sup>3</sup> min<sup>-1</sup>; and reaction temperature, 298 K.

(a)



(b)

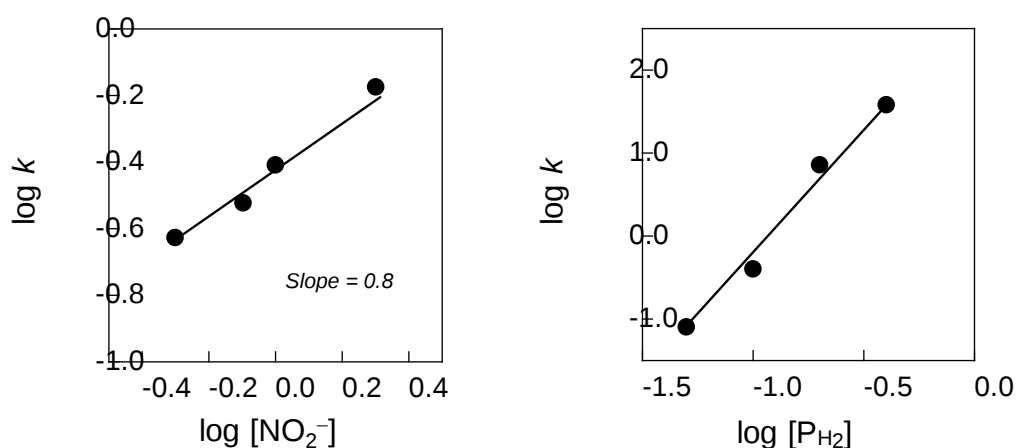


Figure S5 Log-log plots for  $\text{NO}_2^-$  decomposition rates in the catalytic hydrogenation of  $\text{NO}_2^-$  over  $\text{Pt}/\text{Al}_2\text{O}_3$  in the (a) absence and (b) presence of  $\text{O}_2$ . Reaction conditions: reactant  $\text{NO}_2^-$  (from  $\text{KNO}_2$ ),  $0.5\text{--}2.0\text{ mmol dm}^{-3}$ ; reaction volume,  $250\text{ cm}^3$ ; partial pressure of  $\text{H}_2$ ,  $P_{\text{H}_2} = 0.1\text{--}0.4\text{ atm}$ ; and gas flow rate,  $30\text{ cm}^3\text{ min}^{-1}$ . For the reaction in the absence of  $\text{O}_2$ ,  $P_{\text{H}_2}$  was fixed at  $0.1\text{ atm}$ . On the other hand, concentration of  $\text{NO}_2^-$  and partial pressure of  $\text{O}_2$  were fixed at  $1.0\text{ mmol dm}^{-3}$  and  $0.1\text{ atm}$ , respectively.