Electronic Supplementary Material (ESI) for Catalysis Science & Technology.


# Formic acid generating *in-situ* $H_2$ and $CO_2$ for nitrite reduction in aqueous phase

## Supporting information

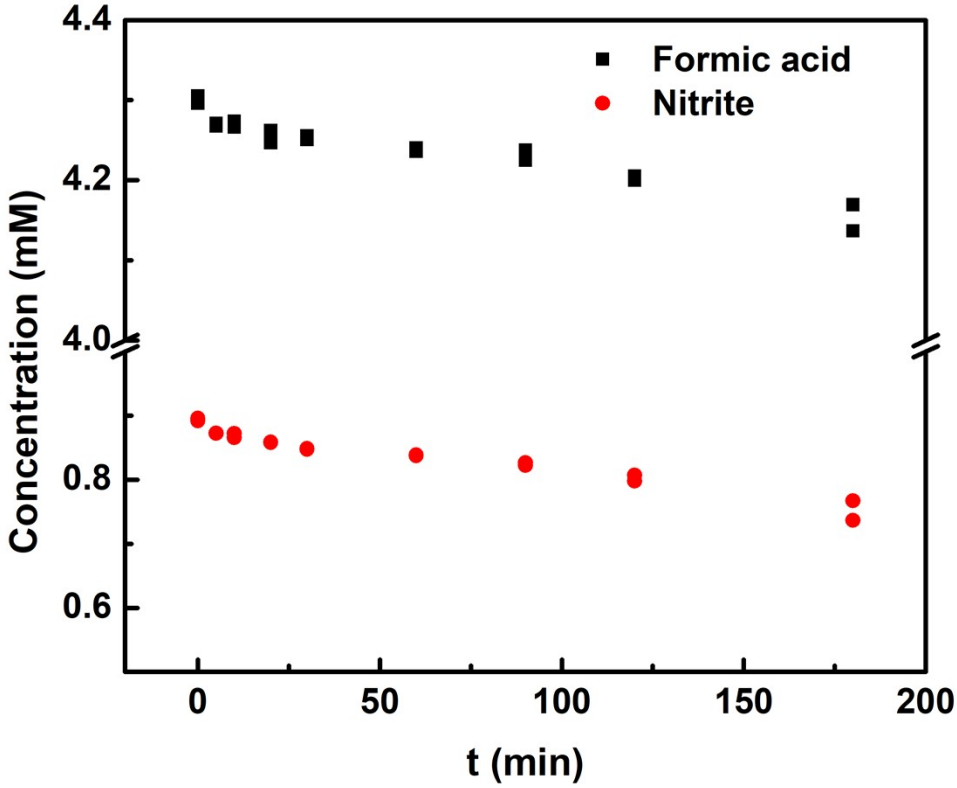


Figure S1. Concentration profile of formic-acid, nitrite under inert-flow-through mode at pH 5 condition 100 mg 0.9 wt% catalyst, 5 mM formic-acid solution, 1 mM nitrite).

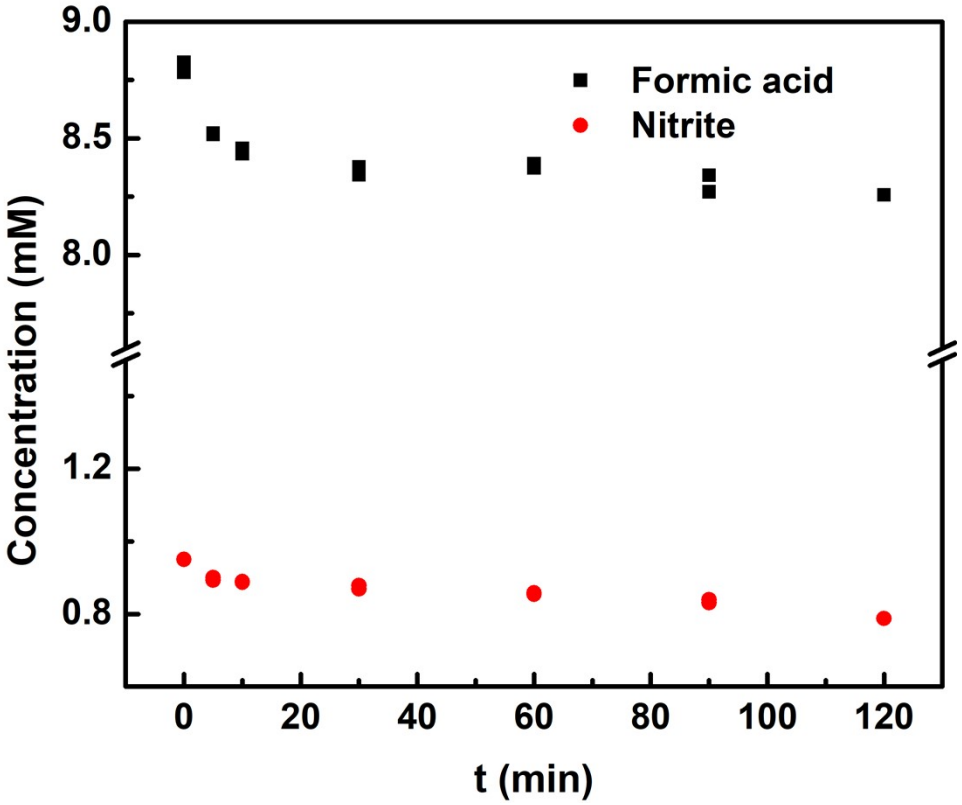


Figure S2. Concentration profile of formic-acid, nitrite under inert-flow-through mode at pH 5 condition 100 mg 0.9 wt% catalyst, 10 mM formic-acid solution, 1 mM nitrite).

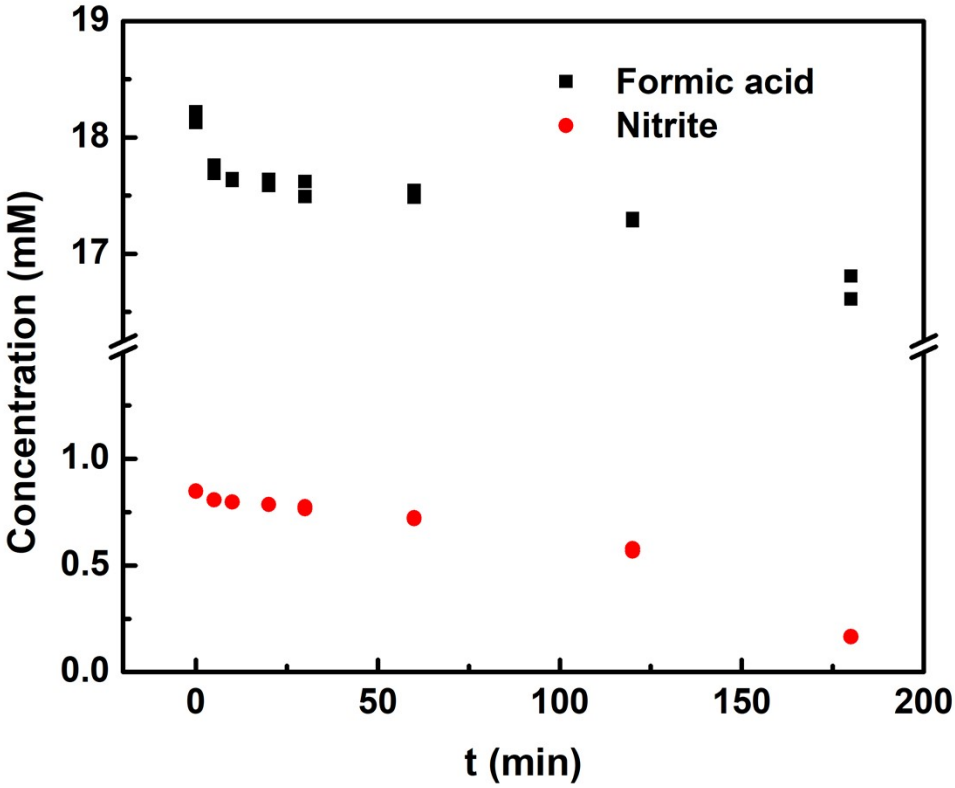


Figure S3. Concentration profile of formic-acid, nitrite under inert-flow-through mode at pH 5 condition 100 mg 0.9 wt% catalyst, 20 mM formic-acid solution, 1 mM nitrite).

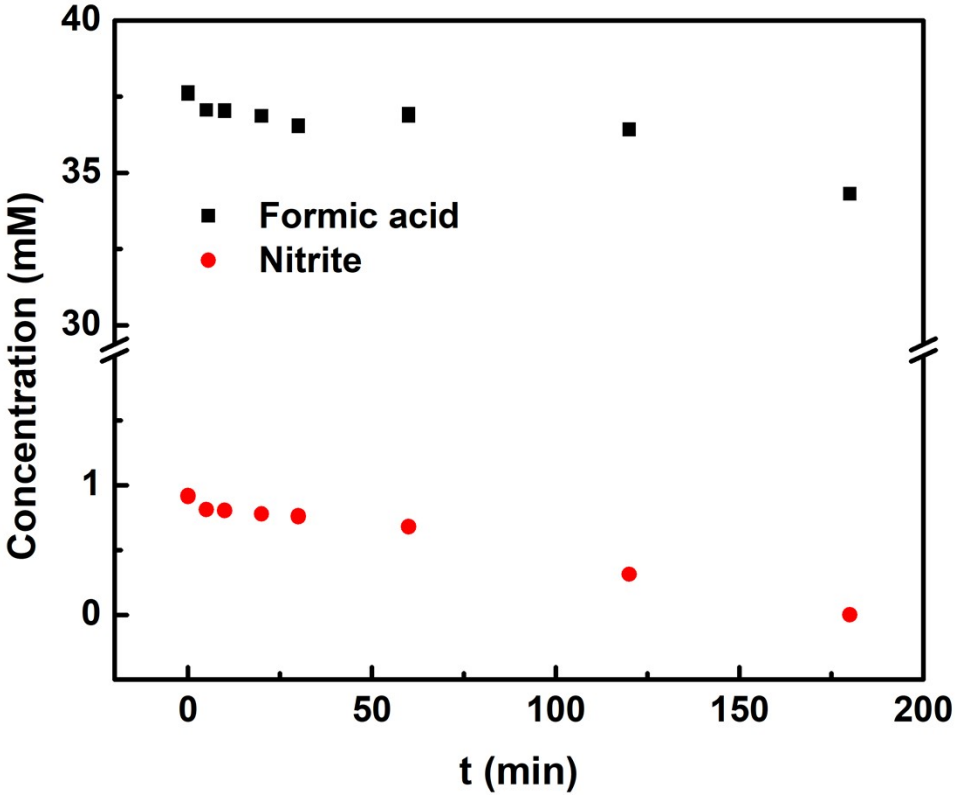


Figure S4. Concentration profile of formic-acid, nitrite under inert-flow-through mode at pH 5 condition 100 mg 0.9 wt% catalyst, 40 mM formic-acid solution, 1 mM nitrite).

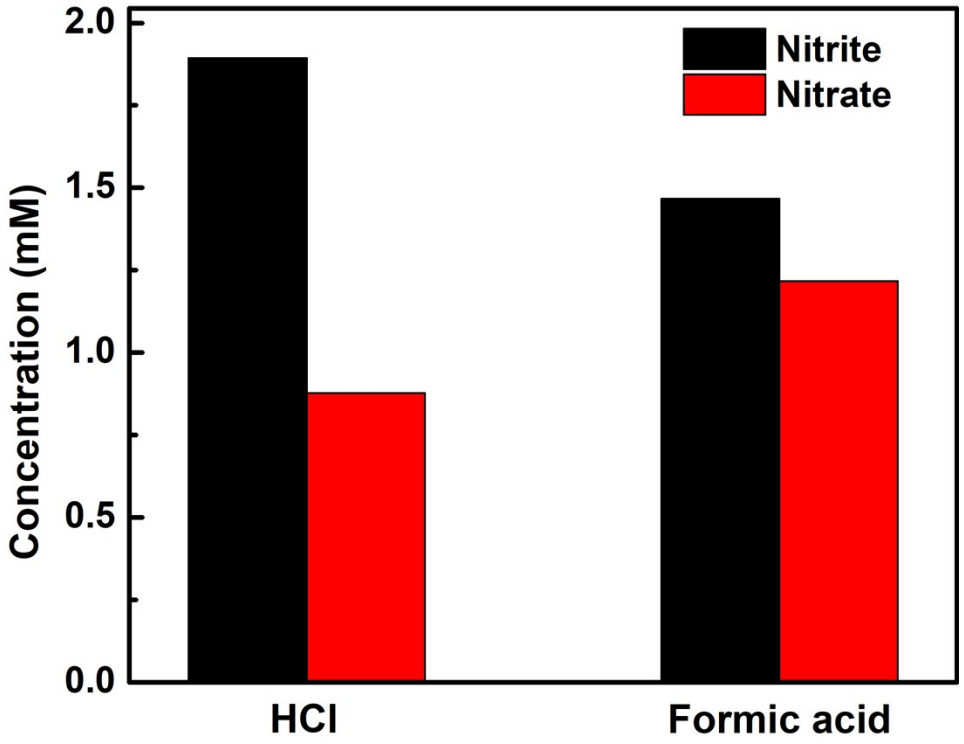


Figure S5. HCl (left bar), formic-acid (pH=3) (right bar) reacts with nitrite forming nitrate under ambient-batch mode, respectively (10 mM formic-acid, 10 mM HCl, 3 mM nitrite).

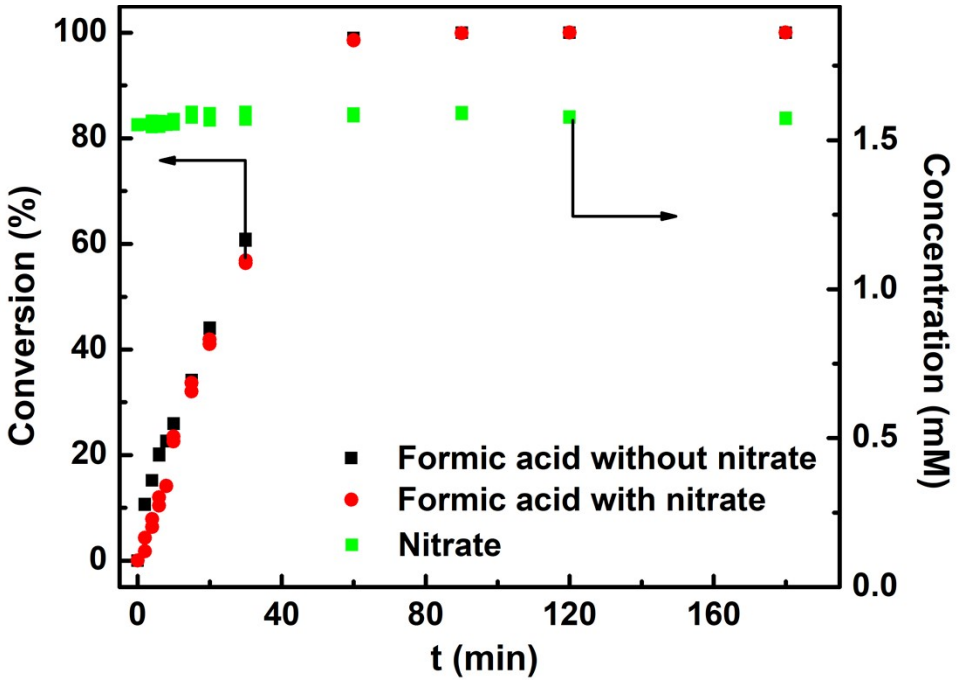


Figure S6. Formic-acid decomposition (pH = 3) experiments was performed under ambient-batch mode in presence of 0 mM and 1.5 mM nitrate, respectively,

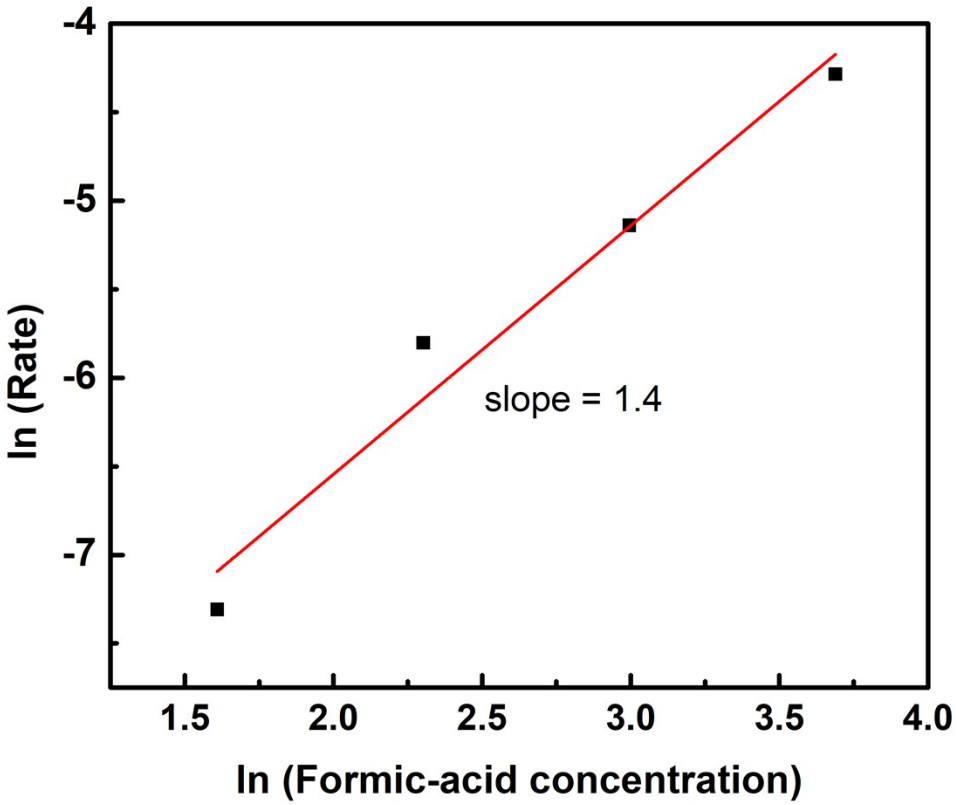


Figure S7. Effect of the initial formic-acid concentration on the formic-acid decomposition rate.

## 1. Calculation the nitrite reduction rate in batch and ATR experiments

### 1.1. Batch experiment

The reaction rate was estimated based on a the batch experiment at pH 5 (1 mM nitrite, 20 mM formic-acid, 100 mg catalyst, 50 ml/min He flow through). As shown in Table 4, nitrite conversion after 2 hours is 33 %, resulting in an averaged rate:

$$average\ rate = \frac{converted\ nitrite}{reaction\ time} = \frac{1\ mM * 0.33 * 0.3\ L}{120\ min} = 8.25 * 10^{-7}\ mol/min$$

Amount of surface Pd (mol) is calculated based on the dispersion by:

$$n_{Pd} = \frac{mass\ of\ catalyst * loading\ of\ Pd * dispersion\ of\ Pd}{molecular\ weight\ of\ Pd} = \frac{100\ mg * 0}{106.42} = 10^{-6}\ mol$$

Apparent TOF is calculated by:

$$apparent\ TOF = \frac{average\ rate}{n_{Pd}} = \frac{8.25 * 10^{-7} mol/min}{4.7 * 10^{-6}\ mol} = 0.18\ min^{-1}$$

**1.2. ATR experiment**

The ATR reaction rate is estimated based on the results shown Figure 6b, observing disappearance of the free nitrite peak within 38 min. The reaction volume is the volume of the ATR cell, estimated as 0.4 mL based on the dimension of the cell. The average reaction rate is estimated according:

$$average\ rate = \frac{nitrite\ concentration\ in\ the\ ATR\ cell}{reaction\ time} = \frac{10\ mM * 0.4\ mL}{38\ min} = 1 * 10^{-}$$

Amount of the surface Pd (mol) based on the dispersion of Pd is calculated by:

$$n_{Pd} = \frac{mass\ of\ catalyst * loading\ of\ Pd * dispersion\ of\ Pd}{molecular\ weight\ of\ Pd} = \frac{5\ mg * 0.0}{106.42\ g/mol}$$

Apparent TOF is calculated by:

$$apparent\ TOF = \frac{average\ rate}{n_{Pd}} = \frac{1 * 10^{-7} mol/min}{5.1 * 10^{-7} mol} = 0.19\ min^{-1}$$

Therefore the rate observed in both experiments are remarkably similar.