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# Adsorption behaviors of a 2D covalent organic framework toward Pd(II) in acid solution \*Hao WU<sup>1</sup> and Seong-Yun KIM<sup>1</sup> <sup>1</sup>Tohoku Univ.

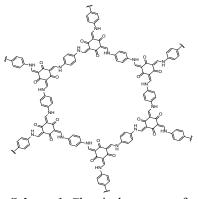
A 2D covalent organic framework (COF TpPa-1) was synthesized by reversible Schiff base reaction and the following irreversible enol-keto tautomerism. The adsorption behaviors of COF TpPa-1 toward palladium (Pd(II)) in acid solutions (hydrochloric acid, nitric acid) were investigated under the effect of contact time, concentration of acid etc. The adsorbed species on COF TpPa-1 were further clarified by X-ray photoelectron spectroscopy (XPS). **Keywords:** covalent organic framework, adsorption, palladium, X-ray photoelectron spectroscopy

## 1. Introduction

COF TpPa-1 is reported to be prepared by a combination of reversible and irreversible reactions using 1,3,5triformylphloroglucinol (Tp) with *p*-phenylenediamine (Pa-1). The first reversible Schiff base reaction facilitates to the formation of a crystalline framework. Exceptional resistance towards acid treatment could be realized through enhancing its chemical stability by the following irreversible enol-to-keto tautomerization. In this study, the adsorption performances of the prepared COF TpPa-1 toward Pd(II) were evaluated under the effect of contact time, acid concentration, and adsorption capacity in acid solutions.

## 2. Experimental

The chemical structure of COF TpPa-1 is depicted as shown in **Scheme 1** and its synthesis was conducted using a method previously reported<sup>[1]</sup>. Subsequently, certain amount of COF TpPa-1 was weighed in a 9 mL vial bottle with a screw cap and 3 mL of the prepared working solution was added. The concentration of the tested metal ions before and after adsorption were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimazu ICPS-7510).



Scheme 1. Chemical structure of COF TpPa-1

#### 3. Conclusion

In nitric acid solution, the 2D COF TpPa-1 prepared in this study exhibited enormously high adsorption ability toward Pd(II) without the interference of rare earth metals and slight co-adsorption of Mo(VI) and Zr(IV). And the adsorption performance of COF TpPa-1 was independent with the variation of nitric acid concentration. Moreover, the adsorbed species on COF TpPa-1 was considered as Pd(NO<sub>3</sub>)<sub>2</sub> by XPS analysis.

On the other hand, in hydrochloric acid solution, it demonstrated that the adsorption process of COF TpPa-1 was dependent on contact time, chloride concentration, and initial metal concentrations, exhibiting a faster adsorption speed and higher adsorption quantity toward Pd(II). COF TpPa-1 also exhibited an excellent affinity toward Pd(II) than other competing metal ions. The adsorption mechanism was temporarily assumed as adsorption of chloridometalates by XPS analysis.

#### References

[1] Sharath Kandambeth et al., J. Am. Chem. Soc. 2012, 134, 19524–19527.