

## High Efficient Fenton-Like Catalysts for Free Radical Generation in Degradation of Organic Contaminants

Yiyi Sheng, Yang Sun, Jing Xu\*, Yi-Fan Han\*

*1*State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China; *2* Research Center of Heterogeneous Catalysis and Engineering Sciences, School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, China

\*Corresponding author: xujing@ecust.edu.cn; yifanhan@ecust.edu.cn

### Highlights

- High activity for the production of hydroxyl radical ( $\bullet\text{OH}$ ) by  $\text{H}_2\text{O}_2$  decomposition
- The relationship of catalyst structure and performance was established
- High performance of as-prepared catalysts for degradation of organic compounds

### 1. Introduction

The Fenton reaction has been proved to be a powerful approach for the treatment of refractory organic pollutants with the generation of hydroxyl radicals ( $\bullet\text{OH}$ ), which are the most powerful oxidant in nature ( $E^0 = 2.80 \text{ V/NHE}$ ) except for fluorine. Nevertheless, the application of this technique is often limited by low pH value (2.5-4.0) and will yield a large amount of iron-containing sludge. To overcome these drawbacks, the heterogeneous Fenton-like reaction is becoming a promising alternative which substitutes solid catalysts for  $\text{Fe}^{2+}$ . In this work, a series of heterogeneous Fenton-like catalysts with outstanding performance, such as  $\text{FeOCl}$ ,  $\text{Au/C}$  and  $\text{Cu/Al}_2\text{O}_3$ , were investigated in the degradation of refractory organic contaminants.

### 2. Methods

Multiple characterization techniques such as, X-ray diffraction (XRD), UV-vis diffuse reflectance (UV-vis DRS) and transmission electron microscope (TEM), electron paramagnetic resonance (EPR) were used to investigate the structure, morphology and electronic state of active species of the as-synthesized catalysts.

### 3. Results and discussion

The relationship of catalyst structure and performance for as-prepared catalysts has been established by using multi-techniques, such as XRD, HRTEM, XPS and EPR. An iron oxychloride ( $\text{FeOCl}$ ) catalyst was developed for oxidative degradation of persistent organic compounds in aqueous solutions. Exceptionally high activity for the production of hydroxyl radical ( $\bullet\text{OH}$ ) by  $\text{H}_2\text{O}_2$  decomposition was achieved, being 2-4 orders of magnitudes greater than that over other Fe-based heterogeneous catalysts. The unique structural configuration of iron atoms and the reducible electronic properties of  $\text{FeOCl}$  are responsible for the excellent activity.

Solid iron-based catalysts have showed comparable catalytic performance to the conventional Fenton catalyst ( $\text{Fe}^{2+}$ ); however, the leaching of iron generally leads to a significant deactivation. Therefore, the development of novel heterogeneous Fenton system with enhanced stability is strongly desired. In the following study, the design and utilization of a new Fenton system consisting of the Au/styrene based activated carbon catalyst and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) for the degradation of BPA was described. TEM, XRD and XPS results showed that the negatively charged Au nanoparticles were evenly distributed in a range 3.9-6.4 nm dominated with (110) facet. The generation of  $\bullet\text{OH}$  over Au catalysts through the decomposition of  $\text{H}_2\text{O}_2$  was evidenced using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) trapped electron paramagnetic resonance (EPR). The experimental results suggested that the conversion of BPA was affected by several factors such as the loading amount of Au, pH value, reaction temperature and the initial concentration of  $\text{H}_2\text{O}_2$ . In an optimum experiment, BPA could be degraded from 110 to 10 ppm within 12 h.

The active sites was envisaged to be negatively charged Au atoms at the interface between Au particles and carbon support, the carbon surface is enriched with dangling carbon atoms as evidenced by the O<sub>2</sub>-temperature programmed desorption (TPD) technique. A mechanism including the redox between Au<sup>δ-</sup> ↔ Au<sup>0</sup> during the decomposition of H<sub>2</sub>O<sub>2</sub> method for the degradation of bisphenol A (BPA) in aqueous solution is highly desired.

Due to high generation rate of •OH and a broader pH working range, Cu-embedded mesoporous alumina was developed and showed excellent activity and durability for the degradation of refractory compounds. The origin of active sites for the generation of hydroxyl radicals (•OH) were thoroughly studied using multi techniques. Cu, as the only active element, could be penetrated into the bulk of alumina and some Cu atoms were embedded into the framework. The dynamic structure of surface Cu species (the variety of Cu<sup>+</sup>/Cu<sup>2+</sup> ratio) during the reaction were determined as well. Furthermore, the structure plasticity of catalyst has proved by optimizing preparation and reaction conditions. A 98.53 % degradation of RhB was recorded within 30 min, following a pseudo-first-order reaction rate expression. ESR spectra and •OH scavenging experiments have confirmed that •OH is the main reactive oxidant for the elimination of RhB. By the surface-enhanced Raman spectroscopy and gas chromatography-mass spectrometer results, plausible pathways of RhB degradation were elaborated.

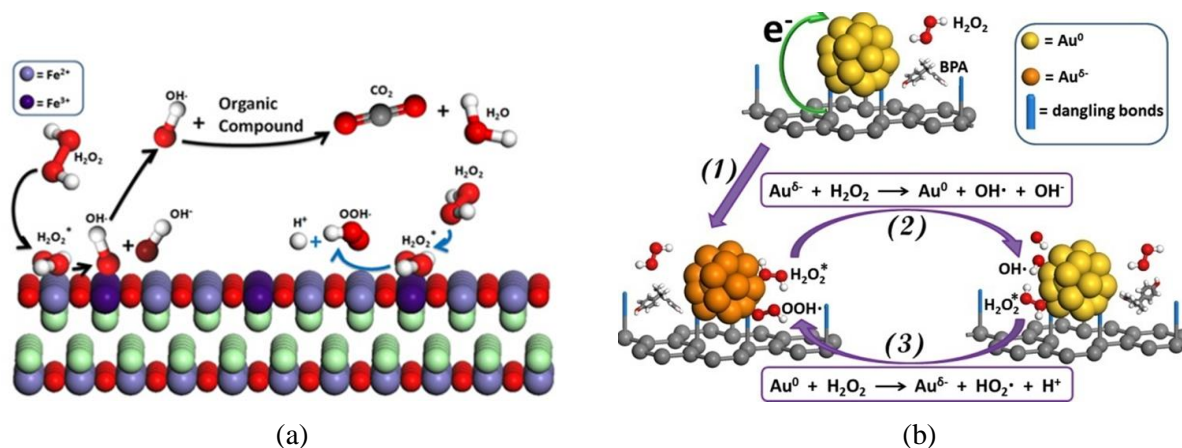


Figure 1. Plausible reaction mechanism for the generation of •OH in the FeOCl (a) and Au-Fenton (b) system

#### 4. Conclusions

Oxidative degradation using hydroxyl radicals (•OH) is an efficient approach for the remedy of toxic organic compounds. With the combination of the characterization results and the performance test, the relationship between the structure of solid Fenton catalyst and the •OH generation efficiency was systematically studied. This study paves the way toward the rational design of relevant catalysts for applications, such as wastewater treatment, soil remediation, and other emerging environmental problems.

#### References

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#### Keywords

Fenton-like catalyst; generation of •OH; kinetics; degradation of organic contaminants