Insights into the heterogeneous Hg^0 oxidation mechanism over UIO-66 catalyst using experimental and periodic DFT method

Changsong Zhou*, Hongmin Yang
School of Energy and Mechanical Engineering, Nanjing Normal University, Nanjing 210042, China
**Corresponding author: cszhou@njnu.edu.cn*

Abstract: A large amount of mercury has been released from fossil-fuel combustion and municipal wastes processing. The heterogeneous Hg^0 oxidation over UIO-66 was studied both on bench scale text and periodic DFT method. The effect of the most relevant operational parameters were specifically studied. The experimental results showed that the UIO-66 had excellent Hg^0 removal potential. The first-principle calculations found that the UIO-66 had highly active in Hg^0 oxidation. The calculated binding energy suggested that the interaction between UIO-66 and Hg^0 was exothermic. Hg^0 oxidation processes were thermodynamically and kinetically favorable. The possible Hg^0 oxidation and desorption pathways were studied by comparing the binding energy with three different competing active sites.

Keywords: UIO-66, Hg^0 oxidation, DFT method.

1. Introduction

There is growing awareness that Hg is a dispersed toxic and persistent pollutant emitted to the environment mainly from coal-fired power plants and municipal solid waste (MSW) incinerators [1]. Zheng et al. [2] reported that the 2008 total mercury emissions in the Pearl River Delta (PRD, China) region were estimated to be 17,244 kg, of which 85% were released as Hg0. Unfortunately, however, Hg^0 is practically water insoluble and hence very difficult to capture from flue gas using the existing air pollution control devices. Accordingly, Hg^0 oxidation is considered to be the most efficient and economical method.

Both experimental and theoretical investigations indicated that some easy decomposition of small molecule additives greatly promote Hg^0 oxidation over metal-organic frameworks in flue gases. Liu et al. [3] reported that H_2S promoted the efficiency of Hg^0 removal due to the dissociation reaction of HS and thus S species generation. HBr and HCl were also selected as the oxidant for mercury oxidation by magnetic ferrite spinel to evaluate the heterogeneous reaction mechanism. However, up to date, there is still little investigation on the mechanisms of H_2O_2 decomposition and OH generation on UIO-66 structure Furthermore, the theoretical studies are very lacking for Hg^0 oxidation under the existence of gaseous H_2O_2 molecule on UIO-66 structure [4].

In this study, the experimental and DFT method was used to provide insight into the detailed OH formation from H_2O_2 decomposition and Hg^0 oxidation mechanism over UIO-66 catalyst. The effect of the most relevant operational parameters, such as adsorbent dosage, reaction temperature, O2/SO2/NO contents in simulated flue gas were studied specifically. The experimental results showed that the prepared UIO-66 had excellent Hg^0 removal potential. The binding energies, the optimized geometries, and the Mulliken charge population analysis before and after co-interaction between Hg^0 and H_2O_2/UIO-66 were investigated.

2. Experimental and Theoretical

A mercury permeation device was placed in a sealed U shaped quartz tube to introduce Hg^0 vapor to the system. A mercury concentration of 50 $\mu g\ m^{-3}$ was used in this study. The simulated flue gases, which include CO_2 (12 vol%), O_2 (6 vol%), SO_2 (0-1500 $mg\ m^{-3}$), NO (0-800 $mg\ m^{-3}$), and N_2 (balance) were provided by gas cylinders, with a total flow rate of 600-1400 mL min-1 (measured at 25 °C, 1.01×105 Pa). An online VM3000 vapor-phase mercury analyzer (Mercury Instruments, Germany) was used to detect Hg^0 outlet concentration. The stoichiometric concentration of H_2O_2 was diluted by deionized water. Vent gas was treated using activated carbon to avoid air pollution.

The calculations were performed using the Dmol3 based on PW91 functional in the GGA scheme [5]. The electron-ion interactions were described by ultrasoft pseudopotentials. The attached spin polarization correction was addressed to follow the lowest energy principle. The electronic wave functions were analyzed by plane-wave expansion method. The surface Brillouin zone integration was sampled using 2×2×2 Monkhorst-Pack k-points mesh. In order to compare the binding energies with different configurations, the binding energies were calculated as follows:

$$E_{bind} = E_{AB} - (E_A + E_B) \tag{1}$$

where E_{AB}, E_A, and E_B represent the total energies of the chosen surface with bonded species, the substrate surface, and the isolated H_2O_2 and Hg^0, respectively. The higher negative E_{bind} value is, the stronger interaction between UIO-66 and adsorbates is.

3. Results and discussion

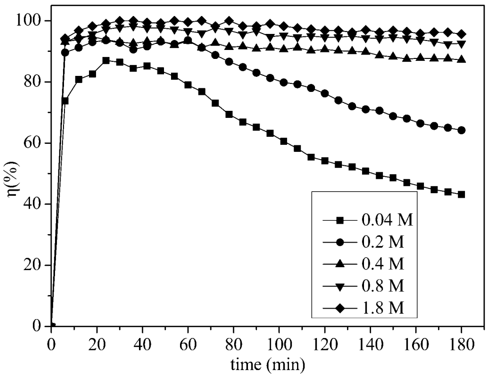

Figure 1. Hg^0 removal performance by heterogeneous H_2O_2/UIO-66 reactions (the effect of H_2O_2 concentration).

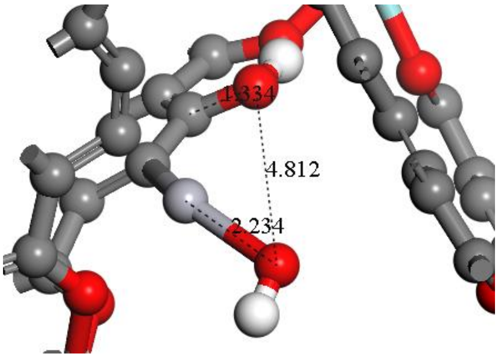

Figure 2. The optimized configuration and the geometric parameters of Hg^0 on H_2O_2/UIO-66.

4. Conclusions

The UIO-66 catalyst has the potential to act in coal combustion and refuse incineration applications as heterogeneous catalyst for Hg^0 removal. The effect of H_2O_2 concentration showed that Hg^0 removal efficiency was 91% when H_2O_2 concentration was 0.4 M. Further increasing H_2O_2 concentration to 1.8 M, Hg^0 removal efficiency slightly increased to 97%. The presence of SO_2 in the simulated flue gases had little effect on Hg^0 removal efficiency, while NO significantly improved Hg^0 removal by $Hg(NO_3)_2$ generation during the reactions. In addition, Hg^0 is chemically adsorbed on the UIO-66 structure by H_2O_2 dissociating into OH radicals. Heterogeneous Hg^0 oxidation by H_2O_2 on UIO-66 structure follows the mechanism that H_2O_2 is first dissociated on the surface and forms two OH radicals to react with Hg^0, with a relatively low energy barrier.

References

1. Pavlish JH, Sondreal EA, Mann MD, Olson ES, Galbreath KC, Laudal DL, Fuel Process Technol 2006; 82: 89−165.
2. Zheng JY, Ou JM, Mo ZW, Yin SS, Sci Total Environ 2011; 412: 214–22.
3. Liu Y, Li H, Liu J, Fuel 2016; 184: 474–80.
4. Lousada CM, Johansson AJ, Brinck T, Jonsson M, J Phys Chem 2012; 116: 9533–43.
5. Payne MC, Allan DC, Arias TA, Joannopoulos JD, Rev Mod Phys 1992; 64: 1045–97.