

# Thermodynamics of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> water-gas shift catalyst poisoning on yellow phosphorus off-gas

Ming Jiang<sup>1</sup>, Bo Li<sup>1</sup>, Tao Li<sup>1</sup>, Hong-pan Liu<sup>2</sup>, Fang-dong Zhan<sup>1\*</sup>, Ping Ning<sup>3</sup>

<sup>1</sup>College of Resources and Environment, Yunnan Agricultural University, Kunming 650201, China

<sup>2</sup>College of Materials and Chemical Engineering, Chongqing University of Arts and Sciences, Chongqing 402160, China

<sup>3</sup>Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China

\* Corresponding author: zfd97@ynau.edu.cn

**Abstract.** The thermodynamics of copper-based water-gas shift catalyst for yellow phosphorus off-gas have been calculated according to the thermodynamic theory of heterogeneous reaction systems. The possible chemical reactions and products were analyzed and are discussed here. The results show that AsH<sub>3</sub> and S-containing gaseous impurities (H<sub>2</sub>S, COS, CS<sub>2</sub>, and SO<sub>2</sub>) in the yellow phosphorus off-gas can preferentially lead to active CuO poisoning of the catalyst, and the poisoning products are Cu<sub>3</sub>As and Cu<sub>2</sub>S. Small amounts of PH<sub>3</sub> and P<sub>4</sub> were the main cause of the inactivation of the anti-toxic component (ZnO) and the support (Al<sub>2</sub>O<sub>3</sub>) in the catalyst. The inactive products were Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and AlPO<sub>4</sub>, respectively. If yellow phosphorus off-gas is used as the raw material gas for water-gas shift reaction, the As-, S- and P-containing gaseous impurities should be removed to avoid catalyst poisoning.

## 1. Introduction

The water-gas shift reaction (WGS)<sup>[1]</sup> is the main reaction in the production of energy fuels such as ammonia<sup>[2]</sup>, syngas<sup>[3]</sup>, and H<sub>2</sub><sup>[4]</sup>. The key to achieve the water-gas shift in the industry is to prepare highly active catalysts, which are classified into three categories: high temperature, medium temperature, and low temperature. Among them, the low temperature (150-300°C) shift catalyst<sup>[5]</sup>, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, is the most widely used and consists of the active component (Cu), an anti-toxic agent (ZnO), and a support (Al<sub>2</sub>O<sub>3</sub>). Although the catalytic activity of the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> shift catalyst is high and the activation temperature is low, the disadvantage is that the anti-toxicity is poor.

Nowadays, with the development of C1 (one carbon) chemicals technology, the direct use of CO-containing industrial off-gas as a raw material for the water-gas shift reaction has become a new approach for off-gas utilization. The yellow phosphorus production process produces a large amount of CO-rich off-gas<sup>[6]</sup>, which is a potential raw material for the water-gas shift reaction. However, the yellow phosphorus off-gas contains complex gaseous impurities (such as H<sub>2</sub>S, PH<sub>3</sub>, HF, COS, CS<sub>2</sub>, SO<sub>2</sub>, HCN, AsH<sub>3</sub>.)<sup>[7-8]</sup>, and it can not only corrode equipment of downstream purification processes, but it can also poison the shift catalyst. In this paper, FactSage7.1<sup>[9]</sup> and HSC Chemistry 6.0<sup>[10]</sup> chemical thermodynamic calculation software packages were used to study the poisoning mechanism of the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> shift catalyst by gaseous impurities when yellow phosphorus off-gas was directly used as the shift feed gas. The thermodynamics principle was used to discuss the transformation



process of poisoning products and provide references for revealing the mechanism of catalyst poisoning.

## 2. Experimental materials and methods

### 2.1 Materials

Yellow phosphorus off-gas was obtained from the Yunnan Yuxi Jianglin Group Co., Ltd. The chemical composition is shown in Table 1.

Table 1 Compositions of yellow phosphorus off-gas

Composition	Mass concentration (mg/m <sup>3</sup> )	Composition	Volume concentration (%)
H <sub>2</sub> S	15250	CO	85.5
PH <sub>3</sub>	667.5	H <sub>2</sub>	4
HF	733.5	N <sub>2</sub>	4
COS	1472.5	CO <sub>2</sub>	3.5
CS <sub>2</sub>	25	H <sub>2</sub> O	3
SO <sub>2</sub>	6	O <sub>2</sub>	0.3
HCN	553		
AsH <sub>3</sub>	47.5		
P <sub>4</sub>	493.5		

### 2.2 Methods

An Orsat gas analyzer was used to detect CO and CO<sub>2</sub>, while a gas chromatograph (SQ-206, Beijing Analysis Instrument Factory) was used to detect H<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O, and O<sub>2</sub>. A gas chromatograph (HC-6, Hubei Chemistry Research Institute) was used to detect H<sub>2</sub>S, PH<sub>3</sub>, COS, CS<sub>2</sub>, and SO<sub>2</sub>. HF and HCN were analyzed by F<sup>-</sup> and CN<sup>-</sup> ion selective electrode. The AsH<sub>3</sub> was analyzed by the silver diethyldithiocarbamate spectrophotometric method. Total phosphorus (TP) was determined by spectrophotometry. The P<sub>4</sub> was analyzed by an indirect method (P<sub>4</sub>=TP-PH<sub>3</sub>).

### 2.3 Simulation calculation

The calculation parameters are as follows: (1) the reaction time was 5000 min, the gas flow rate was 200 mL/min, the space velocity was 1500 h<sup>-1</sup>, the volume of the shift feed gas was 1 m<sup>3</sup>, and the mass of the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst was 8.69 g (Cu:ZnO:Al<sub>2</sub>O<sub>3</sub> = 33% : 43% : 6.4%); (2) the input reactant is calculated according to the formula of water-gas shift feed gas in Table 2; (3) the calculated temperature was maintained in the range of 170-260°C, and the step length was 10°C; (4) the pressure was 101.325 kPa.

Table 2 Compositions of raw material in the water gas shift reaction

Composition	Mass (g)	Composition	Mass (g)
H <sub>2</sub> S	15.25	CO	979.1
PH <sub>3</sub>	0.67	H <sub>2</sub>	3.27
HF	0.73	N <sub>2</sub>	45.81
COS	1.47	CO <sub>2</sub>	62.98
CS <sub>2</sub>	0.03	H <sub>2</sub> O	2669.76
SO <sub>2</sub>	0.006	O <sub>2</sub>	3.93
HCN	0.55	Cu	2.87
AsH <sub>3</sub>	0.05	ZnO	3.74
P <sub>4</sub>	0.49	Al <sub>2</sub> O <sub>3</sub>	0.56

## 3. Results and discussion

### 3.1 Transformation of Cu in yellow phosphorus off-gas

The phase transformations of active Cu in yellow phosphorous off-gas at different temperatures are

shown in Figure 1. In the water-gas shift temperature range of 170-230°C, the Cu poisoning product in the catalyst always exists in the form of Cu<sub>2</sub>S. The calculation result showed that S-containing gaseous impurities (H<sub>2</sub>S, COS, CS<sub>2</sub> and SO<sub>2</sub>) in the yellow phosphorus off-gas at this temperature may react with Cu. Spontaneous reactions calculated by HSC Chemistry 6.0 are shown in equations (1)-(4). Reaction (3) is the most spontaneous, indicating that CS<sub>2</sub> can preferentially inactivate Cu. At 240°C, solid phase Cu<sub>3</sub>As begins to appear in the system, and the content of Cu<sub>3</sub>As is always stable in the temperature range of 240-260°C. This result indicates that the gas-solid reaction occurred between AsH<sub>3</sub> and Cu in the off-gas, and the product Cu<sub>3</sub>As was the main cause of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> shift catalyst poisoning. The calculation result agrees well with a previously-reported study<sup>[11]</sup>, and the reaction can be described by equation (5).

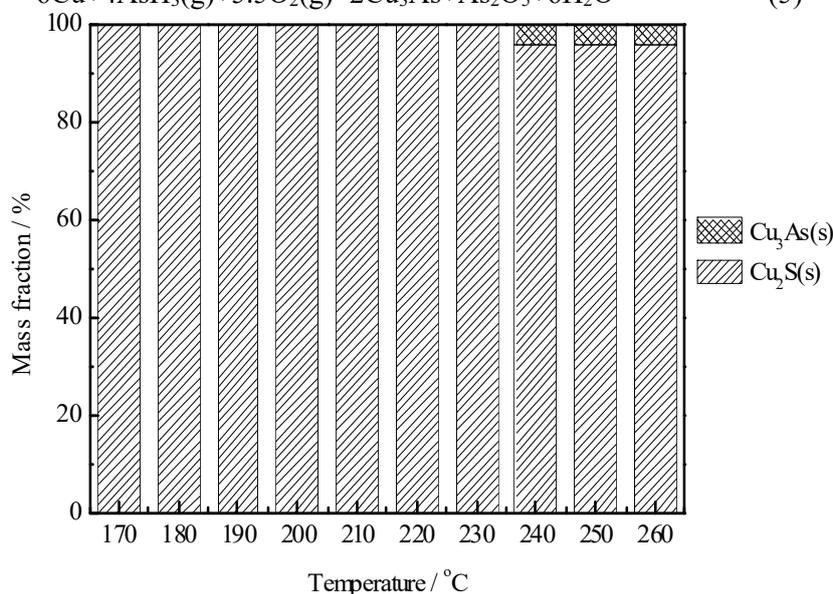
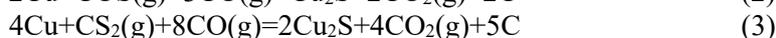
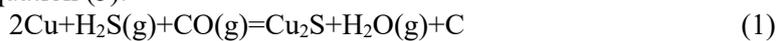


Fig.1 The transformation of Cu at different temperature in yellow phosphorous off-gas

### 3.2 Transformation of ZnO in yellow phosphorus off-gas

Figure 2 depicts the phase transformation of ZnO in yellow phosphorus off-gas at different temperatures. Zn in the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> shift catalyst exists as solid-phase ZnS (19.9%) and Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (80.1%) in the entire temperature range from 170 to 260°C. The result indicates that the S-containing gaseous impurities (H<sub>2</sub>S, COS, CS<sub>2</sub>, and SO<sub>2</sub>) and P-containing gaseous impurities (PH<sub>3</sub> and P<sub>4</sub>) in the yellow phosphorus off-gas are most likely to react with ZnO. Using ZnO as the sacrificial agent appears to reduce the poisoning effect of gaseous impurities on the active Cu in the catalyst.

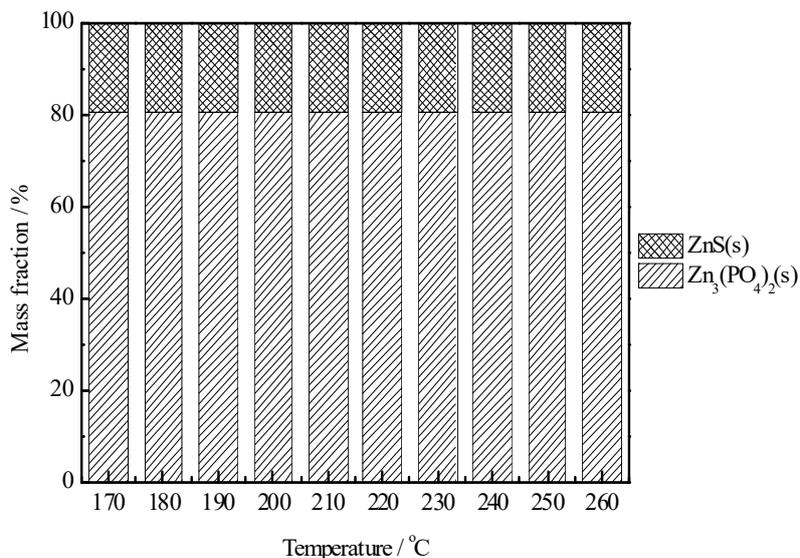


Fig.2 The transformation of ZnO at different temperature in yellow phosphorous off-gas

### 3.3 Transformation of Al<sub>2</sub>O<sub>3</sub> in yellow phosphorus off-gas

Al<sub>2</sub>O<sub>3</sub> is responsible for the thermal stability and mechanical strength of the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> low-temperature shift catalyst. The phase transformation of Al<sub>2</sub>O<sub>3</sub> support in yellow phosphorous off-gas at different temperatures is shown in Figure 3. Al exists in the form of solid phase AlPO<sub>4</sub> (100%) in the temperature range of 170-260°C. This result indicates that the P-containing gaseous impurities (PH<sub>3</sub>, P<sub>4</sub>) in the off-gas are most likely to react with Al<sub>2</sub>O<sub>3</sub>, and the thermodynamic competitiveness is the strongest. The production of the poisoning product AlPO<sub>4</sub> appears to be the main reason for the deactivation of the catalyst support.

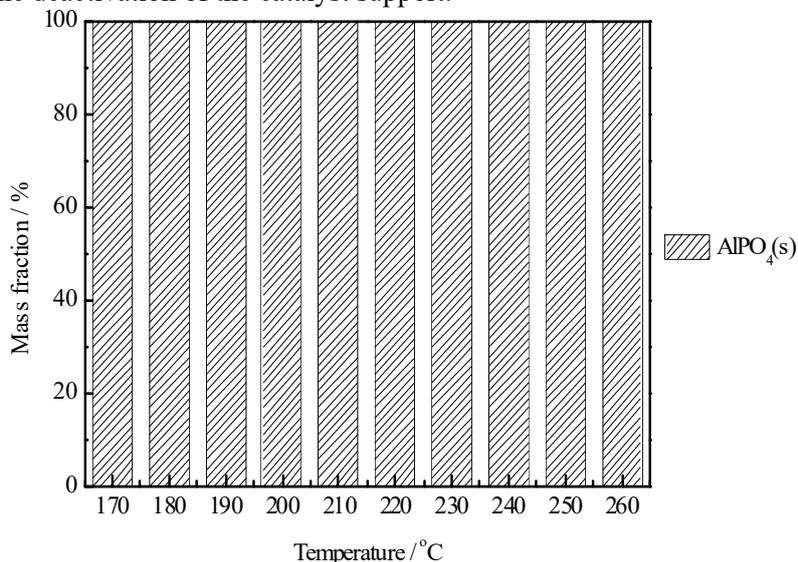


Fig.3 The transformation of Al<sub>2</sub>O<sub>3</sub> at different temperature in yellow phosphorous off-gas

## 4. Conclusion

When yellow phosphorus off-gas was used as the water-gas shift reaction feed gas, the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> shift catalyst showed poor anti-toxicity to the gas phase impurities in the off-gas. Gas phase CS<sub>2</sub>, AsH<sub>3</sub>, PH<sub>3</sub>, and P<sub>4</sub> played very important roles in catalyst deactivation. Solid phase Cu<sub>2</sub>S, Cu<sub>3</sub>As, ZnS, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and AlPO<sub>4</sub> were shown to be the main poisoning products.

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