Simultaneous removal of formaldehyde and benzene by a novel catalytic cycling process

Yu Wang, Chuan Shi*
Key laboratory of Industrial Ecology and Environmental Engineering (MOE), Dalian University of Technology, Dalian, People’s Republic of China Republic of China
chuanshi@dlut.edu.cn

Introduction

Herein, we propose a new approach which combines HCHO oxidation with a C₆H₆ “storage–oxidation” process, as depicted in Figure 1. The catalysts work under cyclic conditions of room temperature and an elevated temperature. At room temperature, HCHO is oxidized to CO₂ and H₂O, while C₆H₆ simultaneously stored on the catalyst. When the catalyst reaches its saturation point for C₆H₆ storage, it is regenerated in situ by heating. During this phase, the activity of the catalyst increases with elevation of the temperature, the stored C₆H₆ is completely oxidized into CO₂ and H₂O, resulting in regeneration of the catalyst. The regenerated catalyst can then be used for a new cycle.

One of the key issues is to find an appropriate catalyst which possesses not only good tolerance to humidity conditions (resistance to water adsorption in humid air), as well as adequate C₆H₆ adsorption capacity and good catalytic performance for HCHO oxidation (at room temperature), but also good activity for oxidation of the adsorbed C₆H₆ into CO₂ and H₂O (at elevated temperature). Thus, HZSM5 possessing a high Si/Al ratio (SiO₂/Al₂O₃ = 200), which is expected to be better resistance to water adsorption in humid air, and high surface area (ca. 350 m²·g⁻¹) was selected for this study. The 10-ring, elliptical character of the channels renders ZSM-5 accessible for diffusion of C₆H₆ (kinetic diameter of 5.8 Å). Noble metals of Pt, Pd and Ag are loaded on the zeolite, acting as active sites for HCHO and C₆H₆ oxidation.

Materials and Methods

The M/HZ (M = Pt, Pd, Ag) catalysts with nominal metal loading of 0.5 wt% were prepared via a conventional incipient wetness impregnation method using aqueous chloroplatinic acid, palladium nitrate and silver nitrate solutions, and H-ZSM-5 (SiO₂/Al₂O₃ = 200, Nankai University, China). The impregnated samples were aged overnight at room temperature, then dried at 120 °C for 6 h without washing the samples before drying, and calcined at 500 °C for 4 h in air.

Results and Discussion

Remarkably high HCHO conversions of 100% and 98% were obtained over Pt/HZ and Pd/HZ, respectively (Figure 2A); Pt/HZ was the most active catalyst, with 100% conversion achievable at about 190 °C, while 100% conversion was achieved at 270 °C for Pd/HZ. In contrast, the maximum conversion over Ag/HZ was only 50%, obtained at 486 °C. (Figure 2B) It was observed that the metal-loaded HZ catalysts showed a much larger storage capacity than the HZ support. The remarkable improvement of storage capacity for C₆H₆ on the metal-loaded HZ catalysts can be attributed to benzene adsorption on the metals by π-complexation. (Figure 2C)

The cycling experiments involving “HCHO oxidation” and “C₆H₆ storage-oxidation” were performed using Pt/HZ for 12 consecutive cycles (Figure 3). In the first cycle, during the three hours of storage (feed gas: 70 ppm HCHO + 10 ppm C₆H₆/21% O₂/1.56% H₂O/N₂, GHSV = 36,000 h⁻¹), no HCHO slip was detected. Instead, 70 ppm of CO₂ was detected in the effluent gas, which corresponds to the complete oxidation of HCHO into CO₂ and H₂O. Meanwhile, no C₆H₆ release was observed except towards the end of the storage phase. During the oxidation period (21% O₂/N₂, GHSV = 36,000 h⁻¹, heating rate: 10 °C/min), the temperature was increased to promote catalytic oxidation of the stored C₆H₆ to CO₂ and H₂O, resulting in the observation of a sharp CO₂ peak at 200 °C which corresponded to the oxidation of stored C₆H₆ (as observed in Fig. 6B). This occurred without the production of secondary pollutants as evidenced by the absence of CO in the effluent stream. The carbon balance was 97.7%.

Figure 1. Schematic diagram for the proposed HCHO and C₆H₆ removal process.
Figure 2 Complete oxidation of HCHO (A) and benzene (B) to CO₂ and C₆H₆ storage capacity (C) over HZ, Pt/HZ, Pd/HZ and Ag/HZ catalysts.
Figure 3 C₆H₆, HCHO, and CO₂ concentrations during twelve consecutive cycling process over Pt/HZ catalyst.

Significance

- Simultaneous removal of HCHO and C₆H₆ by a catalytic cycling process is reported.
- This approach exhibits extremely low energy cost without secondary pollution.
- Pt/HZ catalyst exhibits excellent activity and stability during 12 consecutive cycles.

References